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Chiral Recognition Based on Enantioselectively Aggregation-Induced Emission

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Novel chiral AIE compounds bearing a tartaric acid group were synthesized. They selectively aggregated with one enantiomer of a number of chiral amines, such that one enantiomer led to strong fluorescence and another enantiomer showed no or only weak fluorescence. This was used for the quantitative analysis of enantiomeric composition.

Many light-emitting compounds are quenched in the solid state. This is an undesirable trait in light-emitting diodes or solid-state sensors. Recently, a number of compounds exhibiting aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) have been developed.[1−8] These compounds show great potential for applications as optoelectronic materials,[2] as highly selective and stable fluorescence sensors for proteins,[3] DNA,[4] organic vapors,[5] heparin,[6] metal ions,[7] chlorine,[8] and immuno assays,[9] and even in monitoring the layer-by-layer self-assembling process.[10]

Chiral recognition through changes in fluorescence has attracted much interest because it can provide time-efficient and sensitive enantiomer determination of chiral reagents, catalysts, natural products, and drugs.[11] However, to design and synthesize fluorescent chiral receptors is still a challenge.[11,12] Although chiral AIE compounds bearing cholesteryl groups have been evaluated as crystalline light-emitting materials,[13] work related to chiral recognition based on AIE or AIEE effects has not been reported to the best of our knowledge. Here, we report highly selective chiral

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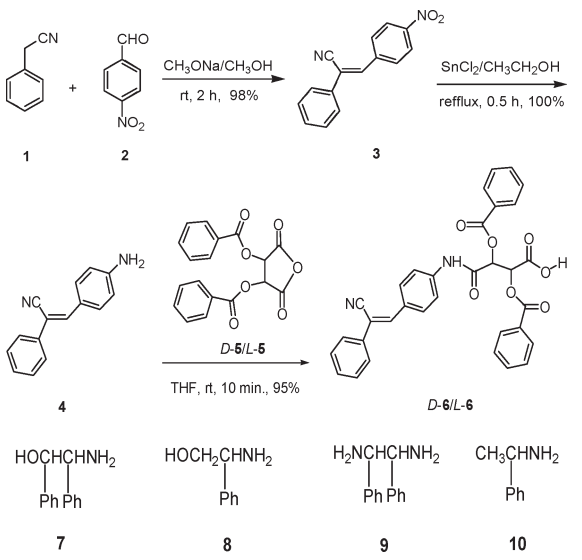
SCHEME 1. Synthesis of the Chiral AIE Compounds D-6 and L-6 and the Structures of the Chiral Amines



recognition system based on the AIE character of an organic compound.

The chiral compounds D-**6** and L-**6** bearing tartaric acid groups were synthesized in excellent yield without the use of column chromatography (Scheme 1). D-**6** and L-**6** are soluble in common organic solvents such as ethanol, THF, and chloroform but are insoluble in water, methanol, and hexane. Dilute solutions in ethanol or THF had almost no fluorescence, but as solids they displayed a strong blue emission under UV irradiation. When water was added in a solution of L-**6** in ethanol or THF, the resulting suspension also exhibited emission. Figure 1 shows that the fluorescence intensity of L-**6** did not increase very much when the volume ratio of water vs ethanol was less than 65:35. When the ratio was more than 70:30, a suspension appeared and the fluorescence intensity increased rapidly. At a ratio of 90:10, the fluorescence intensity of the resultant suspension was 1494 times larger than the solution without water. Therefore, D-**6** and L-**6** exhibit AIE.

The chiral recognition of amines **7**−**10** by receptor L-**6** was studied initially. Aggregates formed enantioselectively when L-**6** and chiral amines were mixed in the appropriate solvent (Table 1). When equal volumes of L-**6** (0.04 M in 1,2-dichloroethane) was mixed with (1*R*,2*S*)-**7** (0.04 M in 1,2-dichloroethane) or (*R*)-**10** a precipitate formed, but the solutions of L-**6** mixed with (1*S*,2*R*)-**7** or (*S*)-**10** remained clear after standing for more than 1 day at 5 °C. Under the same conditions, L-**6** mixed with (2*R*)-**8** remained clear, but L-**6** mixed with (2*S*)-**8** led to a suspension. Neither enantiomer of amine **9**, (1*R*,2*R*)-**9**, or (1*S*,2*S*)-**9** in 1,2-dichloroethane gave an aggregate with L-**6** that could be observed with the naked eye. Nevertheless, addition of *n*-hexane to the solution (*n*-hexane/1,2-dichloroethane 3:2, 0.01 M) of L-**6** with (1*R*,2*R*)-**9** led to a suspension and that of L-**6** with (1*S*,2*S*)-**9** remained clear.

Suspensions of L-**6** and (1*S*,2*R*)-**7** produced by adding water (1.33 mL) to a mixture of the two compounds (molar ratio 1:1) in ethanol (0.4 mL) could be redissolved by adding a small amount of additional ethanol (0.26 mL). Under the same conditions, L-**6** and (1*R*,2*S*-**7**) remained in suspension. This methodology was extended to mixtures of L-**6** with (2*S*)-**8**, (1*R*,2*R*)-**9**, or (*R*)-**10**, which remained in suspension, and mixtures with (2*R*)-**8**, (1*S*,2*S*)-**9**, or (*S*)-**10** which became clear. These results are consistent with those in 1,2-dichloroethane, indicating that the interaction of L-**6** with chiral amines was unaffected by the polarity of the solvent used.

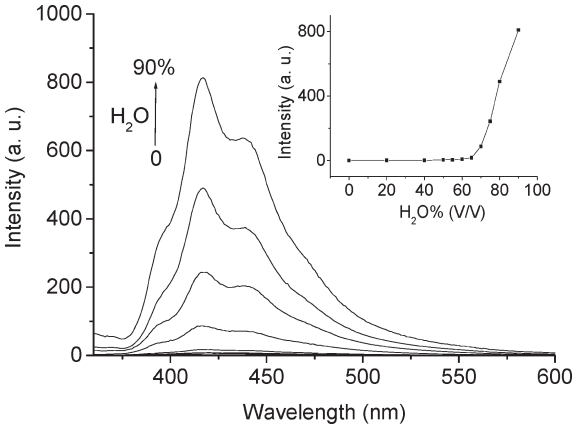


FIGURE 1. Changes in the fluorescence spectra of L-**6** (2.0×10^{-3} M) with increasing water in ethanol. $\lambda_{ex} = 320$ nm, ex/em slits = 5/5 nm. Inset: curve of fluorescence intensity vs water percentage measured at 420 nm.

TABLE 1. Interaction Results of L-6 with Chiral Amines in Solvents[a]

amine	state	amine	state
(1*S*,2*R*)-**7**	solution	(1*R*,2*R*)-**9**	suspension[b]
(1*R*,2*S*)-**7**	precipitates	(1*S*,2*S*)-**9**	solution[b]
(2*R*)-**8**	solution	(*R*)-**10**	precipitates
(2*S*)-**8**	suspension	(*S*)-**10**	solution

[a] 0.02 M L-**6** and 0.02 M amine in 1,2-dichloroethane at approximately 5 °C. [b] 0.01 M L-**6** and 0.01 M amine in a mixed solvent of *n*-hexane and 1,2-dichloroethane (volume ratio 3:2).

The enantioselective aggregation in aqueous ethanol could not only be visualized with the naked eye, but quantified by fluorescence measurements. The AIE character of **6** is shown in Figure 2A−D. A suspension of L-**6** and (1*R*,2*S*)-**7** gave a fluorescence intensity of 419, but the solution of L-**6** and (1*S*,2*R*)-**7** gave only 1.6, proving this system exhibits a high enantiomer fluorescence intensity ratio of 262 ($I_{(1R,2S)\text{-}7}/I_{(1S,2R)\text{-}7}$). For amines **8**, **9**, and **10**, the same methodology with L-**6** gave $I_{(2S)\text{-}8}/I_{(2R)\text{-}8} = 10$, $I_{(1R,2R)\text{-}9}/I_{(1S,2S)\text{-}9} = 18$, and $I_{(R)\text{-}10}/I_{(S)\text{-}10} = 17$.

To confirm that the enantioselective aggregation was the result of chiral recognition by the receptor, the same chiral amines were mixed with D-**6** under the same conditions. When D-**6** was mixed with **7**, **8**, and **9**, the expected results were observed. The mixtures with (1*S*,2*R*)-**7**, (2*R*)-**8**, or (1*S*,2*S*)-**9** formed suspensions more easily than the mixtures with (1*R*,2*S*)-**7**, (2*S*)-**8**, or (1*R*,2*R*)-**9**. And similarly, the suspensions had stronger fluorescence than the solutions (Figures S11−S13, Supporting Information). Again the fluorescence intensity ratio for the mixture of D-**6** with amine-**7** ($I_{(1S,2R)\text{-}7}/I_{(1R,2S)\text{-}7}$) was high at 1125 (Figure S11, Supporting Information). D-**6**, however, showed a preference to aggregate with (*R*)-**10** instead of the expected (*S*)-**10**. To clarify this result, a ^{1}H NMR titration (Figures S28 and S29, Supporting Information) was conducted. This revealed the binding ratio of **6** to **10** was 1:2. Contrary to the result at the ratio of 1:1, the mixture of L-**6** with (*S*)-**10** precipitated,

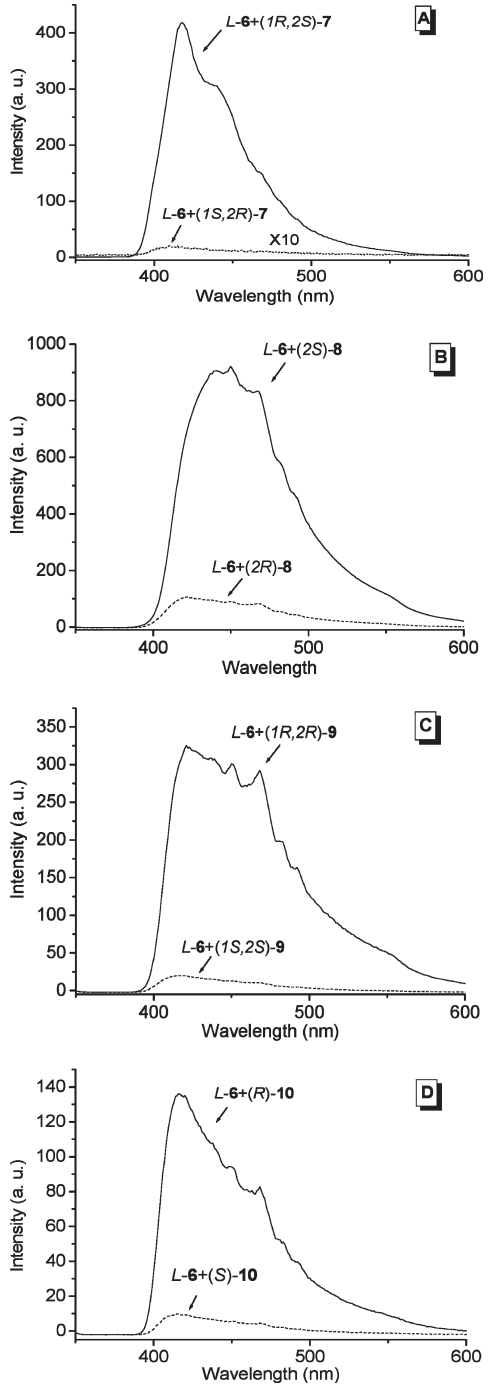


FIGURE 2. Fluorescence spectra of mixture of L-**6** and enantiomers of amines in aqueous ethanol (concentration of all compounds was 0.002 M, $\lambda_{ex} = 320$ nm, ex/em slits = 5/5 nm): (A) of L-**6** with **7** in H_2O/EtOH 2:1; (B) of L-**6** with **8** in H_2O/EtOH 2.4:1; (C) of L-**6** with **9** in H_2O/EtOH 1.5:1; (D) of L-**6** with **10** in H_2O/EtOH 1:1.

but the mixture of L-**6** with (*R*)-**10** stayed in solution. Similar results have been found when different catalyst stoichiometries have resulted in inverted enantioselectivity in Sharpless asymmetric epoxidations.[14] The enantioselective aggregation was repeated with D-**6** (Figures S14 and S15, Supporting Information) and showed that the mixture of D-**6** with (*R*)-**10** remained a suspension but D-**6** mixed with (*S*)-**10** became a solution at a ratio of 1:2. This result demonstrates that the selectivity of D-**6** and L-**6** toward the enantiomers of amine **10** is as expected when the binding ratio reaches saturation. Therefore, the interaction of chiral receptor **6** with chiral amines is indeed enantioselective.

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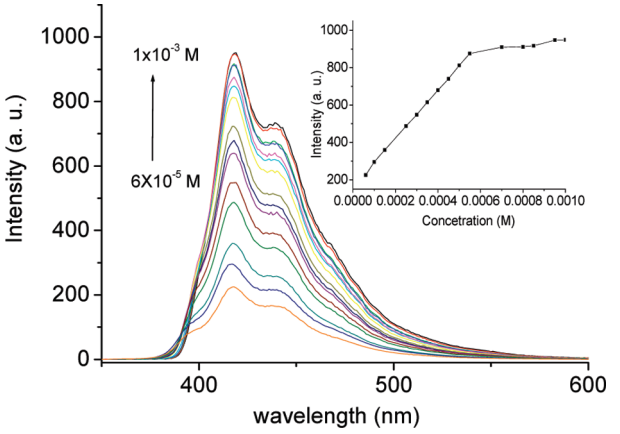

FIGURE 3. Change of fluorescence intensity of mixture of L-**6** and (1*R*,2*S*)-**7** (molar ratio 1:1) with concentrations from 6×10^{-5} to 1×10^{-3} M in H_2O/EtOH 2:1. Inset: curve of intensity vs concentration measured at 420 nm.

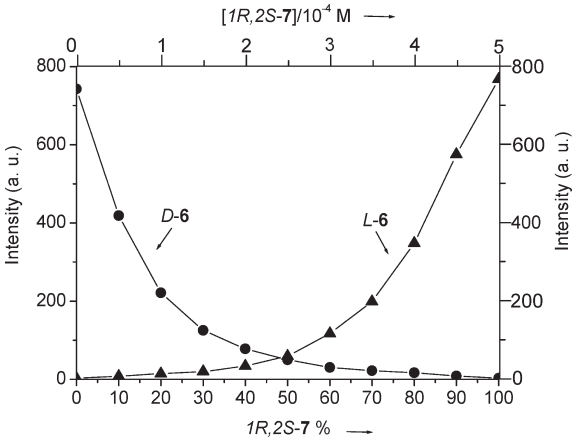

FIGURE 4. Change of fluorescence intensity of the mixture of L-**6** and **7** (molar ratio 1:1) with enantiomer content. [L-**6**] = 5×10^{-4} M. Total concentration of two enantiomers of **7** was 5×10^{-4} M in H_2O/EtOH 2:1).

In addition, the interaction of chiral receptor L-**6** with other chiral amines such as prolinamide **11**, 1,2-diaminocyclohexane **12**, and 2-aminobutanol **13** also resulted in enantioselective aggregation. The fluorescence intensity ratio of two enatiomers of these three chiral amines is $I_{D\text{-}11}/I_{L\text{-}11} = 455$, $I_{(1R,2R)\text{-}12}/I_{(1S,2S)\text{-}12} = 47$, and $I_{D\text{-}13}/I_{L\text{-}13} = 1.4$, respectively (Figures S16−S18, Supporting Information).

It was noted that the fluorescence intensity of the suspensions increased with increasing concentration of L-**6** and (1*R*,2*S*)-**7** (Figure 3). Valuably, when the concentration was less than 5.5×10^{-4} M, the fluorescence intensity increased linearly with the concentration (inset in Figure 3). This means that the fluorescence intensity of the suspension can be used to determine the enantiomer concentration. When 5.0×10^{-4} M solutions of **7** with varying enantoimeric ratios were tested with L-**6** at the same concentration

TABLE 2. Association Constant K_a (M^{-1}) of L-6 with Chiral Amines

amine	K_a	amine	K_a	amine	K_a
(1*S*,2*R*)-**7**	$(1.02 \pm 0.98) \times 10^5$	(2*R*)-**8**	$(1.43 \pm 0.18) \times 10^4$	(1*R*,2*R*)-**9**	$> 10^6$
(1*R*,2*S*)-**7**	$(8.98 \pm 0.71) \times 10^3$	(2*S*)-**8**	$(7.86 \pm 0.85) \times 10^3$	(1*S*,2*S*)-**9**	$> 10^6$

(Figure 4), the fluorescence intensity increased with increasing molar percentage of (1*R*,2*S*)-**7**. Similarly, the fluorescence intensity of the same experiment with D-**6** increased with increasing molar percentage of (1*S*,2*R*)-**7**. As a result, two standard curves were drawn from which the enantiomeric purity of chiral amine **7** could be obtained. This is very important for high-throughput analysis of enantiomer purity of chiral drugs and reagents.[12] By the same method, the enantiomer composition of other amines such as **8**−**10** could be also analyzed.

To further demonstrate the selective interaction of L-**6** with enantiomers of a chiral amine, ^{1}H NMR titrations of L-**6** with different amines were carried out in $CDCl_3$. By producing a Job plot of the amide NH resonance, it was found that L-**6** bound to **7**, **8**, and **9** in a 1:1 molar ratio. Compound **10**, however, formed at a 2:1 ratio (**10** vs L-**6**) as previously described in ethanol (Figures S19−S32, Supporting Information). The association constants for **7** and **8** were calculated by nonlinear curve fitting with relative coefficient R^2 more than 0.996 (Table 2). The association constant of L-**6** with **9** was much larger than 10^6 M^{-1} and so could not be accurately determined by ^{1}H titration.[15] The difference in the binding affinities of L-**6** with the two enantiomers of **7** and **8** indicated that L-**6** exhibited chiral recognition, and this resulted in enantioselective aggregations.

In conclusion, highly selective chiral recognition has been achieved with the combination of AIE and chirality in an organic compound for the first time. This finding provides a simple method for the synthesis of a chiral receptor and a new method for the determination of chiral excess through changes in the fluorescence with high enantioselectivity.

Experimental Section

Synthesis of Compound 6. Compound **4** (2.2 g, 0.01 mol), L-2,3-dibenzoyltartaric acid anhydride **5** (3.7 g, 0.011 mol), and dry THF (30 mL) were stirred at room temperature for 0.5 h. The resulting solution was evaporated to about 2 mL, and **6** was precipitated by addition of methanol. The resultant white solid was collected by filtration and air-dried (5.2 g, 93%). D-**6**: mp 166−168 °C; $[\alpha]^{20}_D$ +77.8 (*c* 1.0, EtOH); IR (KBr) λ 3514, 3295, 2923, 2852, 1739, 1712, 1669, 1525 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.07 (d, J = 7.6 Hz, 2H), 8.03 (d, J = 7.6 Hz, 2H), 7.93 (s, 1H), 7.91 (d, J = 8.8 Hz, 2H), 7.72 (quintet, J = 8.4 Hz, 6H), 7.59 (quintet, J = 8.0 Hz, 4H), 7.50 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 6.05, 5.98 (2d, J = 2.8 Hz, 2×1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 165.4, 165.3, 164.3, 142.7, 140.6, 134.5, 134.4, 130.6, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 129.2, 129.1, 126.1, 120.1, 118.5, 109.2, 73.4, 72.2; ESI- MS m/z calcd for $C_{33}H_{24}N_2O_7$ 560 [M], found 559.1 $[(M - 1)]^-$. Anal. Calcd for for $C_{33}H_{24}N_2O_7$: C, 70.71; H, 4.32; N, 5.00. Found: C, 70.58; H, 4.37; N, 4.95. L-**6**: mp 167−169 °C; $[\alpha]^{20}_D$ −81.5 (*c* 1.0, EtOH); IR (KBr) λ 3516, 3292, 2976, 2921, 1740, 1712, 1669, 1523 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.84 (s, 1H), 8.07 (d, J = 7.6 Hz, 2H), 8.03 (d, J = 7.6 Hz, 2H), 7.93 (s, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.76 − 7.66 (m, 6H), 7.63−7.54 (m, 4H), 7.52 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 6.04, 5.99 (2d, J = 2.8 Hz, 2×1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.9, 165.5, 165.3, 164.6, 142.7, 140.6, 134.4, 134.3, 130.6, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 129.3, 126.1, 120.1, 118.5, 109.1, 73.6, 72.4; ESI-MS m/z calcd for $C_{33}H_{24}N_2O_7$ 560 [M], found 559.1 $[(M - 1)]^-$. Anal. Calcd for for $C_{33}H_{24}N_2O_7$: C, 70.71; H, 4.32; N, 5.00. Found: C, 70.65; H, 4.35; N, 4.98.

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Supporting Information Available: Experimental details, spectra of compounds, and calculation of association constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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