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Fluorescence Turn-on Enantioselective Recognition of both Chiral Acidic Compounds and α-Amino Acids by a Chiral Tetraphenylethylene Macrocycle Amine

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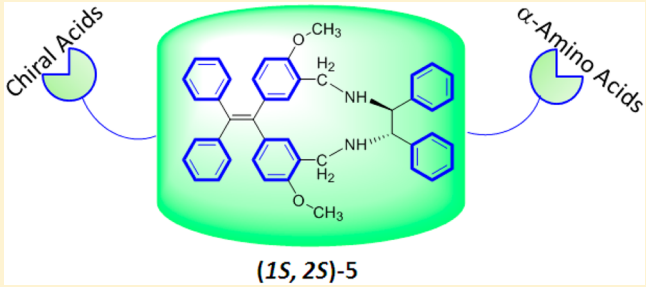
Supporting Information

ABSTRACT: New chiral tetraphenylethylene (TPE) macrocycles bearing optically pure amine groups were synthesized and found to have a discriminating ability between the two enantiomers of not only chiral acidic compounds but also α-amino acids by enantioselective aggregation and aggregation-induced emission (AIE) effects. NMR spectra, including 2D-NOESY, disclosed that the host−guest interaction of the macrocycle receptor played a key role in addition to the acid−base interactions.



INTRODUCTION

Chiral recognition is an important process in the natural world; it plays a vital role in asymmetric synthesis, chiral drug separation, organic three-dimensional structure theory, and the chiral origin of life. However, distinguishing the two chiral enantiomers is still a challenge. The various techniques that have been applied to the discrimination and analysis of enantiomers include high-performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR), UV/vis, circular dichroism (CD), and fluorescence spectroscopy.[1] Among them, chiral recognition through fluorescence changes has attracted keen interest because it can provide time-efficient, accurate, and sensitive enantiomer determination of chiral compounds.[2,3] The enantioselective recognition of chiral amines, acids, or modified amino acids has been actively investigated by fluorescence spectroscopy,[4] because of the importance of this class of compounds in biological processes as well as in organic synthesis. However, the selective detection of unprotected α-amino acids by a fluorescence strategy is still a challenging assignment 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.[5] Rare examples of chiral detection of α-amino acids by a fluorescent probe have been reported.[6]

Recently, a new class of aggregation-induced emission (AIE) compounds, which are nonemissive in solution but emit strong fluorescence upon aggregation, has attracted intense attention because of their great potential for applications as optoelectronic materials and fluorescence sensors.[7] In 2009, Pu and Hou reported enantioselective precipitation and solid-state fluorescence enhancement when α-hydroxycarboxylic acids were mixed with a 1,1′-bi-2-naphtholamine receptor, although the receptor was not an AIE molecule.[5c] In 2014, Tang and Wong reported a chiral AIE molecule containing a silole luminogenic unit with chiral recognition of acids by a mechanism of complexation-induced circularly polarized luminescence (CPL) in the solid thin film state.[8] Previously, some chiral AIE carboxylic acids or amines were demonstrated by our group to have exceptionally high enantioselectivity and sensitivity for some chiral amines or acids.[9] To make the chiral AIE receptors applicable to wider chiral analytes, chiral macrocycle receptors based on AIE effect were synthesized,[10] with the hope that the additional cavity of the macrocycle could also play a role in interactions with the analytes. Here, we report the synthesis of AIE macrocycles bearing an optically pure diphenyldiaminoethylene group that display enantiomer discrimination not only for chiral acidic compounds but also for unprotected α-amino acids.

RESULTS AND DISCUSSION

By the formylation of the starting material dimethoxyltetraphenylethylene (**1**)[9b] with urotropine in trifluoroacetic acid (TFA), the key intermediate TPE dialdehyde **2** was prepared (Scheme 1). The reduction of **2** with $NaBH_4$ gave the TPE dialcohol **3**, followed by chlorination with thionyl chloride to afford the TPE dichloride **4**[10b] in 85% yields. Finally, the reaction of (1*S*,2*S*) - or (1*R*,2*R*)-1,2-diphenyl-1,2-diaminoethane with TPE dichloride **4** gave the chiral TPE macrocycles (1*S*,2*S*)-**5** and (1*R*,2*R*)-**6**. The macrocycles were characterized by NMR spectra, MS, IR, and optical rotation.

As expected, the dilute solution of (1*S*,2*S*)-**5** or (1*R*,2*R*)-**6** in $CHCl_3$ or THF had almost no fluorescence. But when the nonsolvent water was gradually added into the solution of the macrocycles in THF until a turbid appeared, the resultant suspension started to emit fluorescence. After that, with the rising

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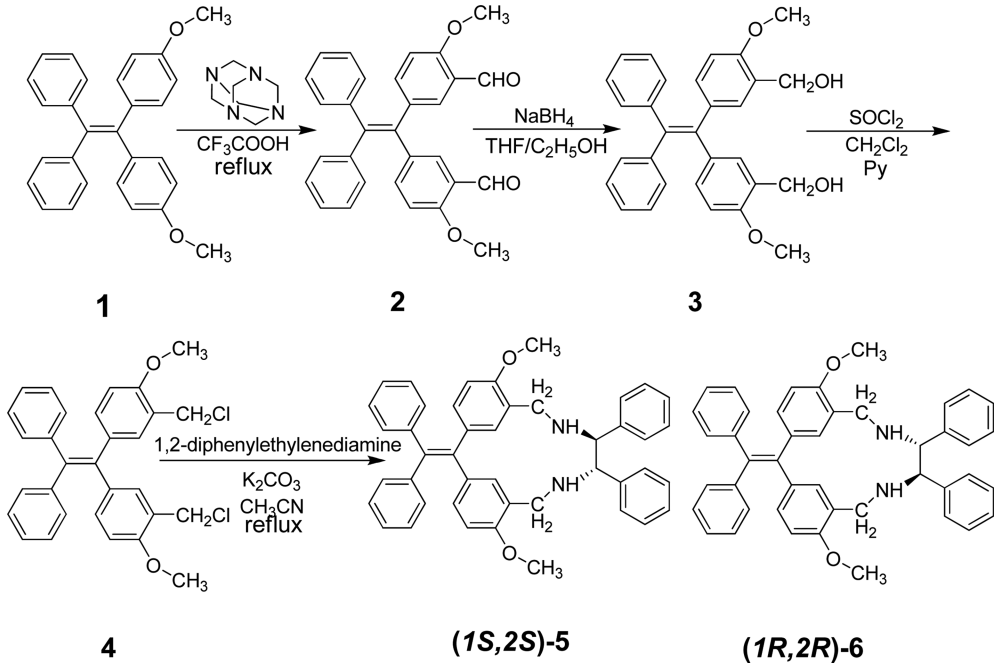
Scheme 1. Synthesis of Chiral TPE Macrocycles (1*S*,2*S*)-5 and (1*R*,2*R*)-6



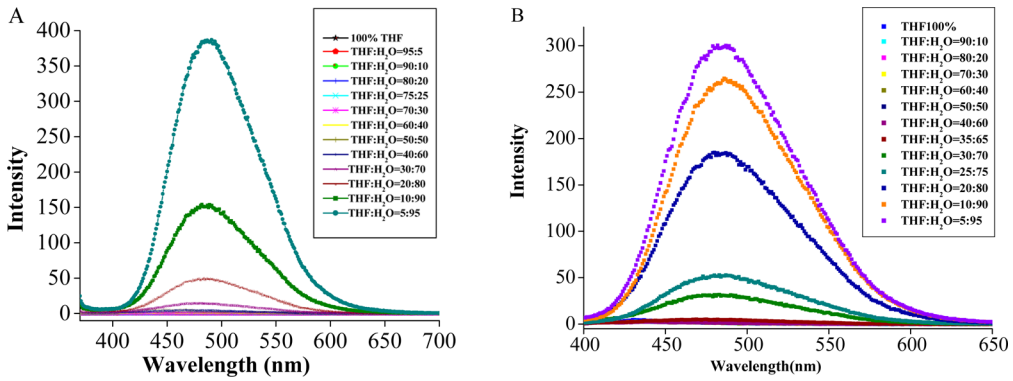


Figure 1. (A) Changes in the fluorescence spectra of (1*S*,2*S*)-**5** (2.0×10^{-3} M) with increasing water in THF; (B) Changes in the fluorescence spectra of (*1R, 2R*)-**6** (2.0×10^{-3} M) with increasing water in THF. λ_{ex} = 365 nm, ex/em slits =5/5 nm.

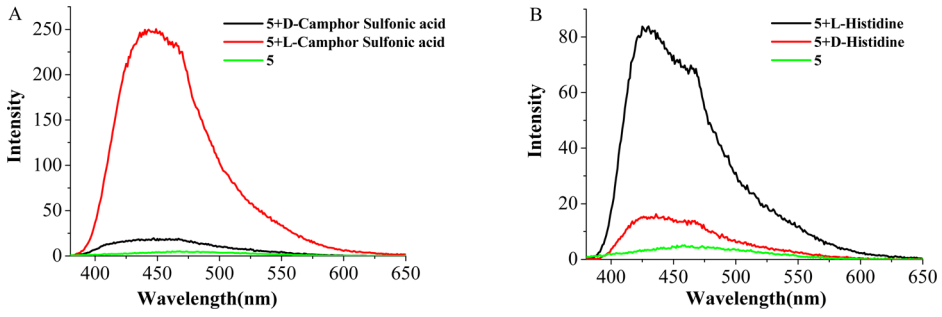


Figure 2. (A) Fluorescence spectra of a mixture of (1*S*,2*S*)-**5** and enantiomers of camphor sulfonic acid **8** in 1.4:3.3 THF/H_2O. [(1*S*,2*S*)-**5**] = [**8**] = 4.4×10^{-4} M. (B) Fluorescence spectra of a mixture of (1*S*,2*S*)-**5** and enantiomers of histidine **18** in 11.1:14 THF/H_2O. [(*1S, 2S*)-**5**] = [**18**] = 7.9×10^{-4} M. λ_{ex} = 365 nm, ex/em slits =5/10 nm.

of water fraction in THF, the fluorescence intensity of the macrocycles increased (Figure 1). At a ratio of 95:5 H_2O/THF (volume ratio, the same below), the fluorescence intensity of the resultant suspension was 400 times larger than that of the solution without water. Therefore, (*1S, 2S*)-**5** and (1*R*,2*R*)-**6** are AIE compounds. The fluorescence quantum yield of the suspension of (*1S, 2S*)-**5** and (1*R*,2*R*)-**6** in 95% water was 8.7 and 8.1%, respectively, using quinine sulfate as a reference standard. The molar absorptivities of (*1S, 2S*)-**5** and (1*R*,2*R*)-**6** in 95% water was 5.06×10^4 and 5.01×10^4 L/mol cm, respectively.

As shown in Figure 2, Figure S15−S27 (ESI) and Table 1, the selectivity and chiral recognition ability of (1*S*,2*S*)-**5** was tested

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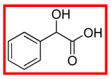
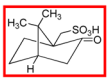
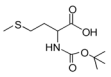
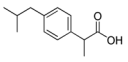
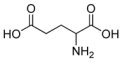
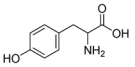
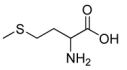
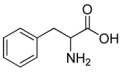
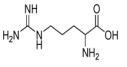
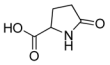
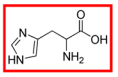
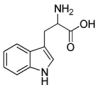
Table 1. Enantioselectivity (I_1/I_2) of (1*S*,2*S*)-5 Resulting from Two Enantiomers of Chiral Acids

Entry	Acids	I_1/I_0[a]	I_1/I_2[b]	State
7. Mandelic acid		*28.6*	*8.4*	**Pre/Sol**
8. Camphor sulfonic acid		*26.5*	*14.6*	**Pre/Sol**
9. N-Boc-methionine		*16.7*	*4.2*	**Pre/Sol**
10. Ibuprofen		*11.9*	*2.6*	**Pre/Sol**
11. Glutamic acid		*18.2*	*1.7*	**Pre/Sol**
12. Tyrosine		*15.1*	*2.3*	**Pre/Sol**
13. Methionine		*13.5*	*2.1*	**Pre/Sol**
14. Phenylalanine		*16.8*	*2.1*	**Pre/Sol**
15. Proline		*11.4*	*2.2*	**Pre/Sol**
16. Arginine		*23.1*	*1.8*	**Pre/Sol**
17. Pyroglutamic acid		*10.2*	*2.4*	**Pre/Sol**
18. Histidine		*14.2*	*5.8*	**Pre/Sol**
19. Tryptophan		*18.9*	*2.1*	**Pre/Sol**

[a] I_0 is the intensity of (*1S, 2S*)-**5** with no acids; [b] I_1/I_2 = Enantiomer 1/Enantiomer 2, Pre= Precipitates; Sol= Solution.

for a number of chiral acids and amino acids. Aggregates formed enantioselectively when (1*S*,2*S*)-**5** and chiral acids or amino acids were mixed in the appropriate solvent. When a mixture of (1*S*,2*S*) and mandelic acid (1:1 molar ratio, 0.5 mM) was dissolved in 7:13.5 THF/H_2O by heating for several minutes, the mixture of (1*S*,2*S*)-**5** and *R*-mandelic acid produced suspended precipitates, but with *S*-mandelic acid it gave a clear solution under the same condition. The suspended precipitates strongly emitted fluorescence while the solution did not. The maximal fluorescence enhancement ratio I_{Rmax}/I_0 reached 28.6 and the fluorescence intensity ratio resulted from two enantiomers of **7** was 8.4 (in Table 1). Even for a strong acid, camphor sulfonic acid **8**, (1*S*,2*S*)-**5** could also discriminate its two enantiomers with a good enantioselectivity of 14.6 and I_{Rmax}/I_0 of 26.5. Other carboxylic acids, such as N-Boc-methionine **9**, Ibuprofen **10** gave a high fluorescence intensity ratio I_{Lmax}/I_0 of 16.7 and 11.9, respectively.

In addition, chiral (1*S*,2*S*)-**5** could also discriminate the enantiomers of some α-amino acids. For example, after D- or L-histidine was added to (1*S*,2*S*)-**5** in a mixed solvent of THF and water, only a mixture of (1*S*,2*S*)-**5** and L-histidine appeared as a precipitate and

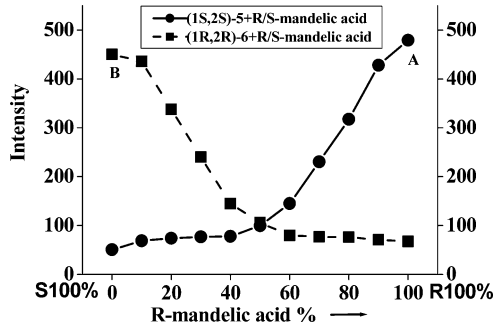


Figure 3. Change of fluorescence intensity of (1*S*,2*S*)-**5** or (1*R*,2*R*)-**6** with the enantiomeric content of **7** in 7:13.5 THF/H_2O. Conditions: [(1*S*,2*S*)-**5**] = [(1*R*,2*R*)-**6**] = [**7**] = 5.0×10^{-4} M.

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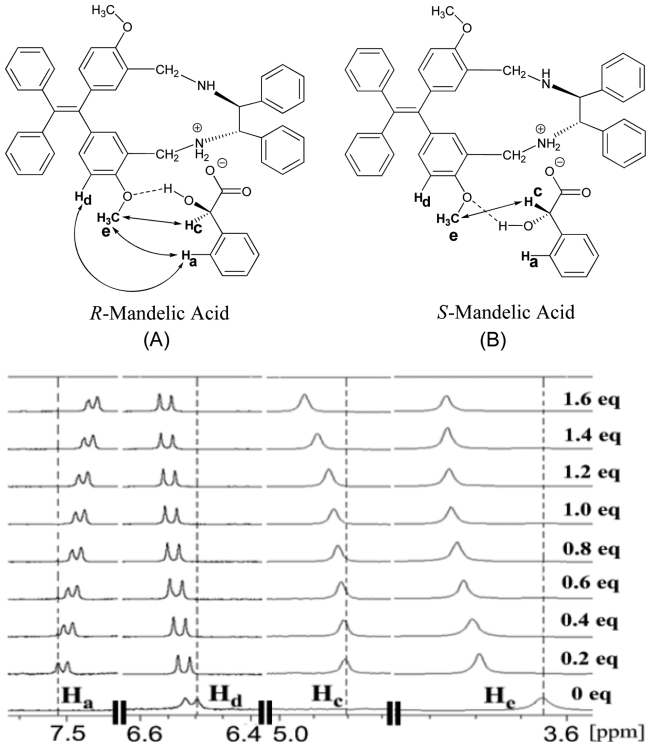

Figure 4. (top) Schematic interaction of (1*S*,2*S*)-**5** with (*R*)-7 (A) and with (*S*)-7 (B). (bottom) Changes in the ^{1}H NMR spectra of (1*S*,2*S*)-**5** with increasing (*R*)-7 in $CDCl_3$. Conditions: [(1*S*,2*S*)-**5**] = 3.0 mM. The number over the spectrum is the molar ratio of (*R*)-7 vs (1*S*,2*S*)-**5**. The double-headed arrows indicated the NOE signals existing between two hydrogen atoms.

emitted strong fluorescence but the interaction of (1*S*,2*S*)-**5** with D-histidine gave a solution which emitted almost no fluorescence (Figure 2B). The maximum fluorescence enhancement ratio I_L/I_0 reached 14.2 and the selectivity I_L/I_D reached 5.8. For other α-amino acids, including glutamic acid, tyrosine, methionine, phenylalanine, proline, arginine, pyroglutamic acid, and tryptophan, their enantiomers could also be discriminated by the chiral TPE macrocycle (1*S*,2*S*)-**5** with a good enantioselectivity.

Due to inherent chiral recognition, using the mirror receptor (1*R*,2*R*)-**6** instead of (1*S*,2*S*)-**5**, a contrasting result was obtained in the tests of enantioselective aggregation with the enantiomers of acids or amino acids. Thus, by making use of (1*S*,2*S*)-**5** and (1*R*,2*R*)-**6**, the enantiomeric composition of the chiral carboxylic acids could be quantitatively measured (Figure 3). This is very important for high-throughput analysis of the enantiomeric purity of chiral drugs and reagents.

To get a clear insight into the chiral discrimination ability of (1*S*,2*S*)-**5**, ^{1}H NMR titration was carried out and 2D NOESY spectra of mixtures of (1*S*,2*S*)-**5** with the enantiomers of (*R*/*S*)-7 were measured. ^{1}H NMR titration of (1*S*,2*S*)-**5** with (*R*)-7 or (*S*)-7 was carried in *d*-chloroform (Figures 4 and 5 and Figure S28 in the Supporting Information). When 3 mM (1*S*,2*S*)-**5** in $CDCl_3$ was mixed with 1 molar equiv of (*R*)-7, it was found that the methoxyphenyl proton (H_e) and phenyl protons (H_d) of (1*S*,2*S*)-**5** and proton H_c of (*R*)-7 exhibited downfield shifts of 0.0326, 0.0477, and 0.0266 ppm, respectively, while proton H_a of (*R*)-7 had a upfield shift of 0.0554 ppm (Figure 4). Protons H_a and H_d in the mixture of (1*S*,2*S*)-**5** with *S*-7 had the same shift direction as that observed with (*R*)-7, but the value was less. Proton H_a had an upfield shift (0.0451 ppm), and H_d showed a downfield shift (0.0441 ppm), while other protons had almost no chemical shift change. Due to the 0.01 ppm larger upfield shift of the phenyl ring of (*R*)-7, it should be included much more in the cavity of the macrocycle than that of (*S*)-7. From the Job plots of the ^{1}H NMR titration, it was found that both (*R*)-7 and (*S*)-7 formed a 1/1 complex with (1*S*,2*S*)-**5**. The association constants of the (1*S*,2*S*)-**5**−(*R*)-7 and (1*R*,2*R*)-**6**-(*S*)-7 complexes were 2.24×10^4 and 1.16×10^4 M^{-1}, respectively, demonstrating different binding forces when (*R*)-7 and (*S*)-7 interacted with (1*S*,2*S*)-**5**, respectively.

The 2D NOESY spectra of the mixture of (1*S*,2*S*)-**5** with the enantiomers of (*R*)-mandelic acid 7 showed distinct NOE signals between proton H_a of (*R*)-7 and phenyl proton H_d of (1*S*,2*S*)-**5**, H_a, and H_e (Figure S29 in the Supporting Information), indicating that the phenyl ring of the acid was close to the phenoxy group. The NOE between the α-proton H_c of (*R*)-7 and proton H_e of the methoxy group of (1*S*,2*S*)-**5** was also observed, indicating that H_c was close to the phenoxy group in the complex. For a mixture of (1*S*,2*S*)-**5** with (*S*)-7, the only NOE signal was observed between H_e and H_c, which implied a weak interaction between (1*S*,2*S*)-**5** and (*S*)-7. This result also implied that (*R*)-7 went into the cavity of the macrocycle (1*S*,2*S*)-**5** more deeply than (*S*)-7, which could restrict more intramolecular rotations and result in emission of stronger fluorescence. Therefore, in addition to the acid−base interaction, the host−guest interaction of the macrocycle receptor also played a key role in its chiral recognition.

As disclosed by FE-SEM and TEM, there truly existed an aggregation difference between the mixtures of (1*S*,2*S*)-**5** and the two enantiomers of the mandelic acid **7**. The mixture of (1*S*,2*S*)-**5** and (*S*)-7 in 7/13.5 THF/H_2O showed almost no aggregates with uniform morphology (Figure 6A), while the mixture of (1*S*,2*S*)-**5** and (*R*)-7 formed nanospheres which filled up the FE-SEM images (Figure 6B,C). TEM images (Figure 6D−F) disclosed that the mixture of (1*S*,2*S*)-**5** with

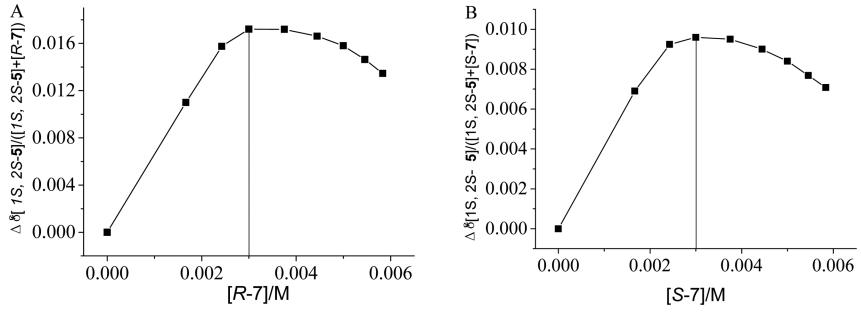

Figure 5. Job plots for ^{1}H NMR titration of (A) (1*S*,2*S*)-**5** (0.003 M) with (*R*)-7 in $CDCl_3$ and (B) (1*S*,2*S*)-**5** (0.003 M) with (*S*)-7 in $CDCl_3$.

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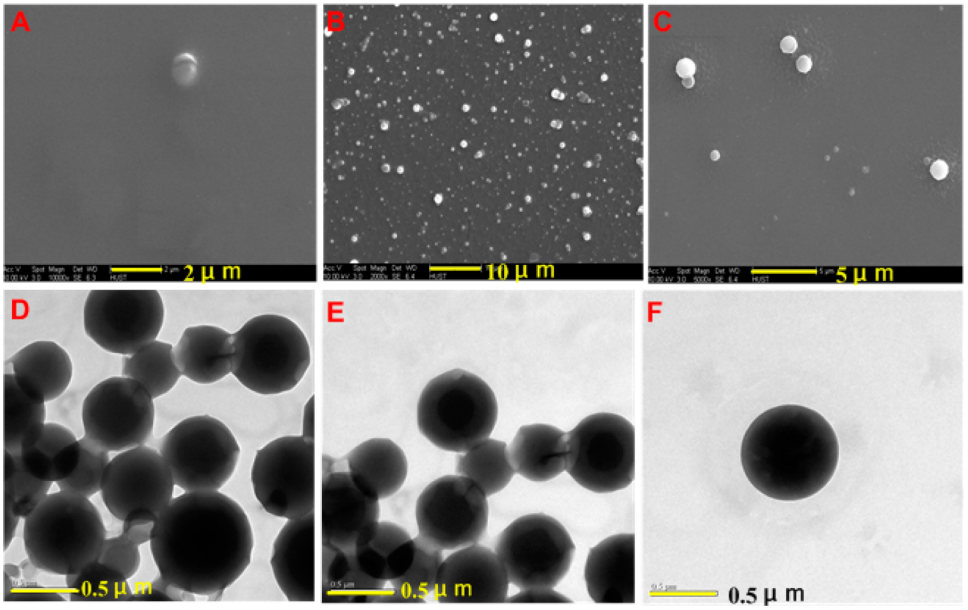

Figure 6. (A) FE-SEM image of (1*S*,2*S*)-**5** with (*S*)-**7** in 7/13.5 THF/H_2O, (B, C) FE-SEM images of (1*S*,2*S*)-**5** with (*R*)-**7**. (D−F) TEM images of (1*S*,2*S*)-**5** with (*R*)-**7** in 7/13.5 THF/H_2O. Conditions: [(1*S*,2*S*)-**5**] = [(*R*)-**7**] = [(*S*)-**7**] = 0.5 mM.

(*R*)-**7** was composed of round spherical aggregates with diameters of 300−500 nm, in accordance with the FE-SEM results.

In summary, the chiral TPE macrocycles (1*S*,2*S*)-**5** and (1*R*,2*R*)-**6** bearing an optically pure amine group were synthesized and were found to discern the two enantiomers of acidic compounds as well as α-amino acids by enantioselective aggregation and AIE effects. Due to the cavity of the macrocycle and the probable host−guest interaction, not only the chiral acidic compounds but also the zwitterionic α-amino acids could be enantioselectively recognized. This result demonstrates the great potential of a chiral AIE macrocycle as a fluorescence chiral receptor.

EXPERIMENTAL SECTION

Compounds **2**−**4** were synthesized according to our previous reports.[10b]

Synthesis of 2. In a one-neck flask were placed **1** (2.5 g, 6.4 mmol), hexamethylenetetramine (17.8 g, 0.127 mol), and TFA (70 mL), and the mixture was refluxed for about 2 h until the starting material **1** disappeared (monitored by TLC). The mixture was quenched with cold water and extracted with chloroform. The organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 4/1) to yield the desired bis-formyl product **2** as a yellow solid (1.85 g, 65% yield): mp 179.5−181.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 6H), 6.73−6.71 (d, *J* = 8.8 Hz, 2H), 7.03−7.01 (m, 4H), 7.15−7.10 (m, 6H), 7.229−7.223 (d, *J* = 2.4 Hz, 1H), 7.027−7.021 (d, *J* = 2.4 Hz, 1H), 7.474−7.468 (d, *J* = 2.4 Hz, 2H), 10.326 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) 55.6, 111.1, 124.3, 126.6, 127.9, 131.2, 131.2, 135.7, 137.7, 138.8, 141.6, 143.6, 160.5, 168.5 ppm; IR (KBr film) ν_{max} 3075.0, 3006.2, 2965.0, 1665.5, 2941.0, 2886.4, 1681.0, 1601.8, 1569.6, 1493.4, 1392.2, 1260.9, 1176.9, 1024.1, 756.3, 704.3 cm^{-1}.

Synthesis of 3. In a one-neck flask were placed 5/2 THF/C_2H_5OH (70 mL), **2** (1.76 g, 3.92 mmol), and $NaBH_4$ (1.49 g, 39.2 mmol). The mixture was stirred at room temperature for about 7 h until **2** disappeared (monitored by TLC, 1/1 ethyl acetate/petroleum). After the solvent was removed by evaporation under reduced pressure, to the residue was added a saturated NH_4Cl aqueous solution and the mixture was extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4. The crude product was recrystallized with chloroform and methanol to give compound **3** as a white solid (1.60 g, 90% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.027 (s, 2H), 3.793 (s, 6H), 4.458 (s, 4H), 6.614−6.593 (d, *J* = 8.4 Hz, 2H), 6.935−6.909 (m, 4H), 7.021−7.002 (m, 4H), 7.124−7.049 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) 55.2, 61.9, 109.4, 126.1, 127.7, 128.1, 131.3, 131.9, 132.0, 135.9, 139.7, 139.7, 144.1, 156.0 ppm; IR (KBr film) ν_{max} 3415.6, 3064.7, 3024.1, 2943.2, 2929.5, 2871.4, 1603.1, 1499.2, 1440.3, 1380.7, 1292.2, 1244.6, 1027.0, 1001.0, 755.9, 698.4 cm^{-1}.

Synthesis of 4. To a chilled solution of **3** (1.71 g, 3.78 mmol) and pyridine (380 μL) in CH_2Cl_2 (30 mL) at 0 °C was added dropwise a solution of $SOCl_2$ (0.1 mL) in CH_2Cl_2 (30 mL) with stirring. The mixture was stirred at room temperature for 8 h. After removal of the solvent, toluene (20 mL) was added and the mixture was evaporated to dryness. The oily residue was extracted with CH_2Cl_2 three times, and the combined organic phases were washed with H_2O followed with brine and dried over Na_2SO_4. After the removal of the solvent, the crude product was purified by column chromatography to give **4** as a white solid (1.58 g, 85% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.811 (s, 6H), 4.421 (s, 4H), 6.621 (d, *J* = 8.4 Hz, 2H), 6.964−6.938 (dd, *J* = 2.0 Hz, *J* = 2.0 Hz, 2H), 7.019−6.987 (m, 6H), 7.109−7.074 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) 41.5, 55.5, 110.0, 124.9, 126.3, 127.8, 131.2, 133.1, 133.9, 135.8, 138.9, 140.1, 143.9, 155.9 ppm; IR (KBr film) ν_{max} 3052.2, 2994.2, 2929.4, 1606.7, 1501.4, 1442.3, 1267.2, 1111.5, 1028.4, 815.5, 769.9 cm^{-1}.

Synthesis of (1*S*,2*S*)-5. In a flask were placed **4** (700 mg, 1.43 mmol), (1*S*,2*S*)-1,2-diphenyl-1,2-diaminoethane (1.20 g, 5.72 mmol), K_2CO_3 (600 mg, 4.29 mmol), and dry acetonitrile (30 mL). The mixture was refluxed for about 4 h until **4** disappeared (monitored by TLC, 1/3 ethyl acetate/petroleum). After acetonitrile was removed by evaporation under reduced pressure, to the residue was added dichloromethane. The organic phase was washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 4/1 ethyl acetate/petroleum) to give the light yellow solid (1*S*,2*S*)-**5** (0.29 g, 32% yield): mp 168.0−171.1 °C; $[\alpha]^{22}_D$ = +655°; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.729 (s, 2H), 3.698 (s, 6H), 3.758−3.718 (d, *J* = 16 Hz, 4H), 3.882−3.844 (d, *J* = 15.2 Hz, 2H), 6.510−6.488 (d, *J* = 8.8 Hz, 2H), 6.749−6.734 (d, *J* = 6.0 Hz, 4H), 7.003−6.976 (dd, *J* = 2.4 Hz, 2.0 Hz, 2H), 7.206−7.124 (m, 19H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) 45.6, 55.2, 61.3, 109.0, 126.3, 126.9, 127.2, 127.9, 129.0, 131.6, 132.8, 134.4, 136.1, 137.3, 145.2, 156.5 ppm; IR (KBr film) ν_{max} 3053.7, 3024.0, 2926.5, 2834.2, 1600.7, 1497.3, 1459.7, 1442.2, 1244.4, 1028.7, 922.8, 818.0, 699.5 cm^{-1}; HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{44}H_{41}N_2O_2$ 629.3168, found 629.3145.

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J. Org. Chem. 2015, 80, 8096−8101

Synthesis of (1*R*,2*R*)-6. (1*R*,2*R*)-**6** was prepared by the same procedure as that for (1*S*,2*S*)-**5** as a light yellow solid (0.28 g, 31% yield): $[\alpha]^{22}_{D} = -625°$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.729 (s, 2H), 3.698 (s, 6H), 3.758−3.718 (d, J = 16 Hz, 4H), 3.882−3.844 (d, J = 15.2 Hz, 2H), 6.510−6.488 (d, J = 8.8 Hz, 2H), 6.749−6.734 (d, J = 6.0 Hz, 4H), 7.003−6.976 (dd, J = 2.4 Hz, 2.0 Hz, 2H), 7.206−7.124 (m, 19H) ppm; ^{13}C NMR ($CDCl_3$,100 MHz) 45.6, 55.2, 61.3, 109.0, 126.3, 126.9, 127.2, 127.9, 129.0, 131.6, 132.8, 134.4, 136.1, 137.3, 145.2, 156.5 ppm; IR (KBr film) ν_{max} 3054.0, 3024.0, 2921.6, 2834.6, 1597.4, 1497.2, 1453.6, 1288.6, 1244.6, 1121.4, 1029.6, 920.7, 817.5, 765.2, 700.0 cm^{-1}; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{44}H_{41}N_2O_2$ 629.3168, found 629.3116.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01194.

^{1}H and ^{13}C NMR, IR, and HRMS spectra (PDF)

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The authors declare no competing financial interest.

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