Supplementary Information for

Zn(II)-Promoted Dramatic Enhancement in the Enantioselective Fluorescent Recognition of Functional Chiral Amines by a Chiral Aldehyde

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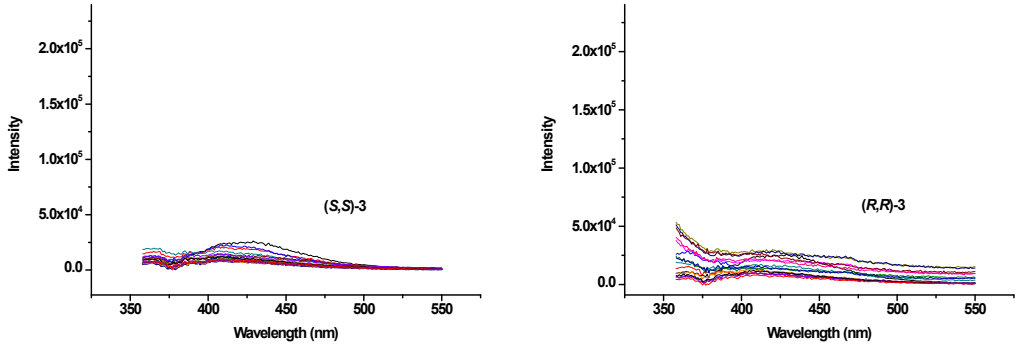
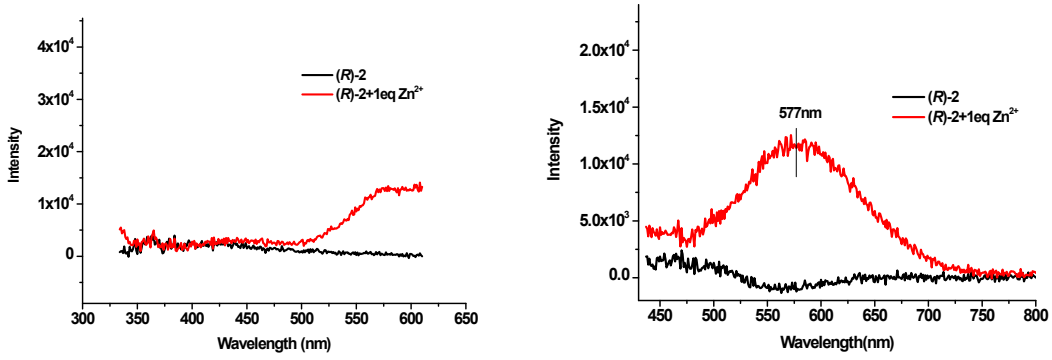
Supplementary Fluorescence Spectra, TOF Mass Spectra and NMR Titration Plots

Figure S1. Fluorescent spectra of (*R*)-**2** (2.0×10^{-5} M) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 equiv (*S,S*)-**3** (a) and (*R,R*)-**3** (b). (Solvent: methanol/1% CH_2Cl_2. λ_{exc} = 338 nm, slit = 5/5 nm.).



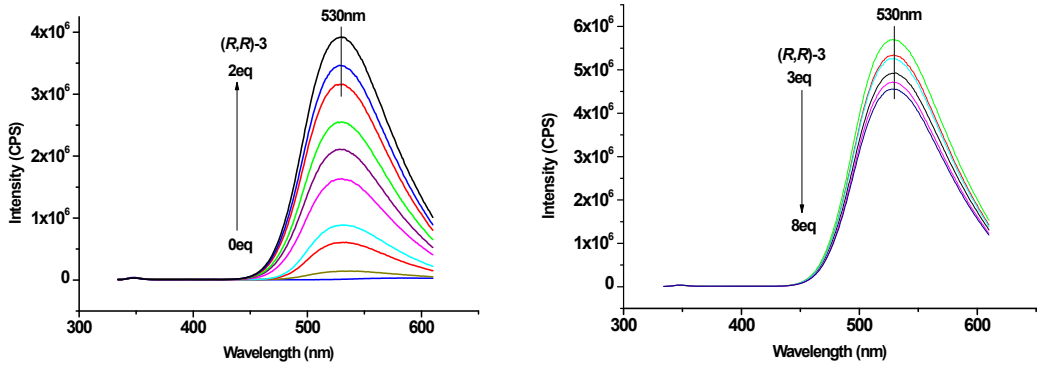
(a) (b)

Figure S2. Fluorescent spectra of (*R*)-**2** (2.0×10^{-5} M) in the presence of 1equiv $Zn(OAc)_2 \cdot 2H_2O$ Solvent: methanol/1% CH_2Cl_2. λ_{exc} = 314 nm or 417nm, slit = 5/5 nm.).

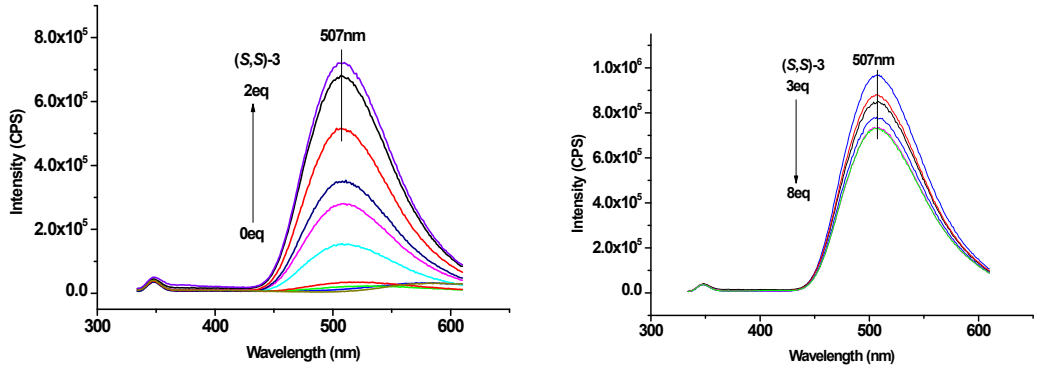


(a) λ_{exc} = 314 nm (b) λ_{exc} = 417 nm

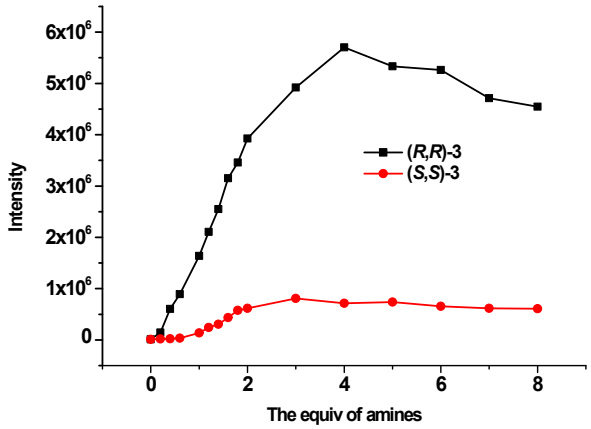
Figure S3. Fluorescent spectra of (*S*)-**2**+Zn^{2+}(1equiv) (2.0×10^{-5} M) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*R,R*)-**3** (a) and (*S,S*)-**3** (b). Fluorescent intensity at 530 nm versus the equiv of the amines (c). (Solvent: methanol/1% CH_2Cl_2. λ_{exc} = 314 nm, slit = 5/5 nm.).



(a)

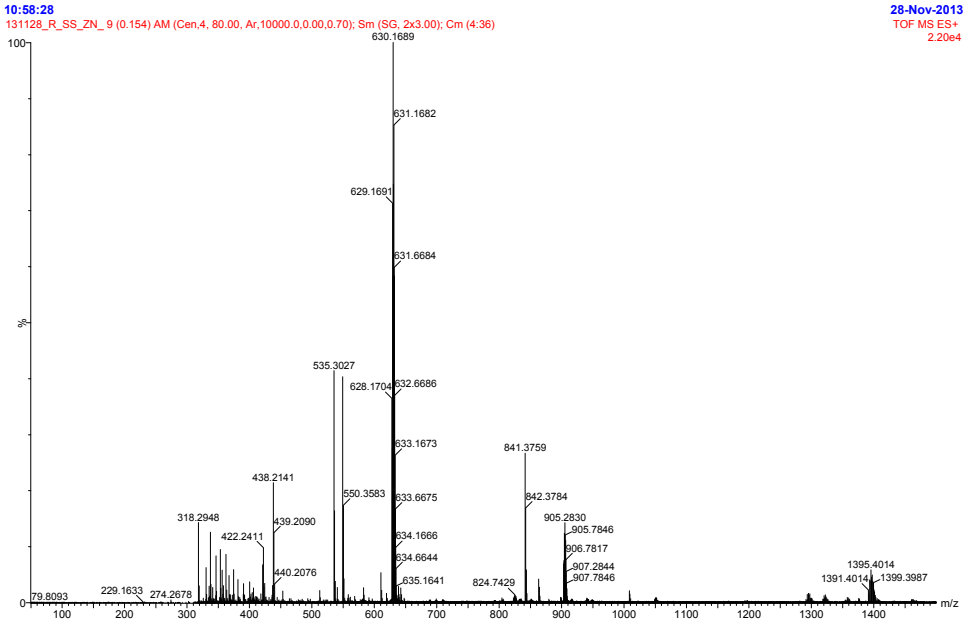


(b)

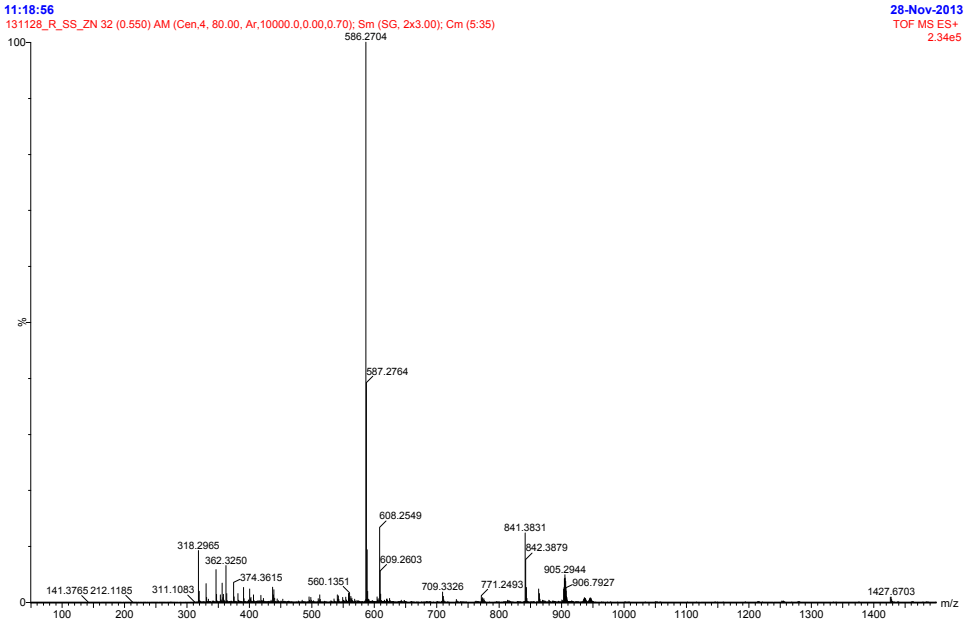


(c)

Figure S4. TOF mass spectra of (*R*)-**2**+$Zn(OAc)_2 \cdot 2H_2O$ (1 equiv) +(*S*,*S*)-**3**(2 equiv) (a) and the macrocycle **6**+ $Zn(OAc)_2 \cdot 2H_2O$ (1 equiv) (b).



(a) (*R*)-**2**+1eq $Zn(OAc)_2 \cdot 2H_2O$ +2eq (*S*,*S*)-**3**



(b) **6**+$Zn(OAc)_2 \cdot 2H_2O$ (1 equiv)

Figure S5. TOF mass spectrum of (*R*)-**2**+ $Zn(OAc)_2 \cdot 2H_2O$ (1 equiv) + (*R*,*R*)-**3**(2 equiv)

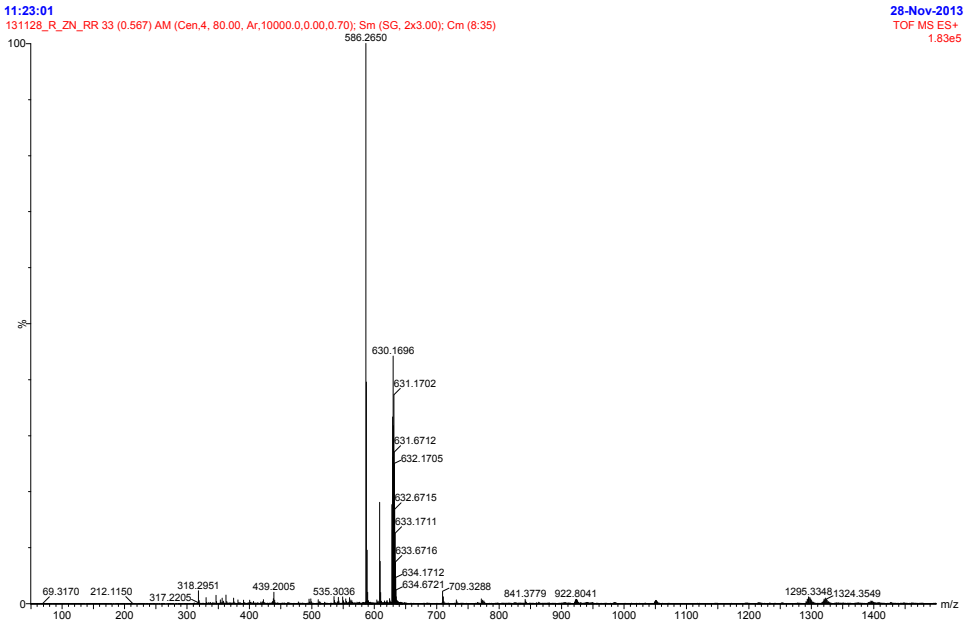


Figure S6. ^{1}HNMR titration of (*R*)-**2**+$ZnBr_2$ (1 equiv) (9.1mM) with (*S*,*S*)-**3** in $CDCl_3$: CD_3OD (2: 1) in comparison with the macrocycle **6** + $ZnBr_2$ (1 equiv) (9.1 mM). (The ^{1}HNMRspectra were taken after the solution was allowed to stand at room temperature for 4 h).

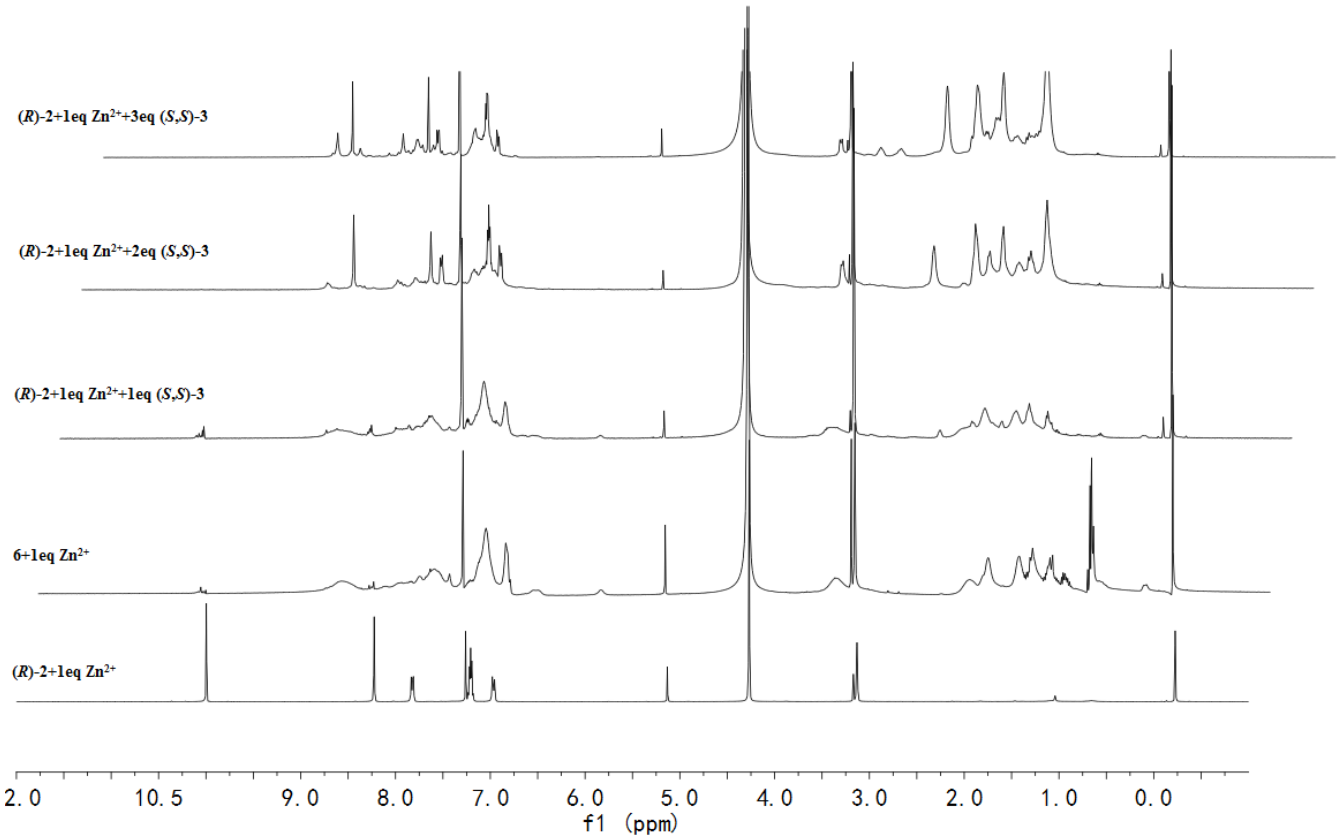


Figure S7. ^{1}HNMR titration of (*R*)-**2**+$ZnBr_2$ (1 equiv) (9.1mM) with (*R*,*R*)-**3** in $CDCl_3$: CD_3OD (2: 1). (The ^{1}HNMR spectra were taken after the solution was allowed to stand at room temperature for 4 h).

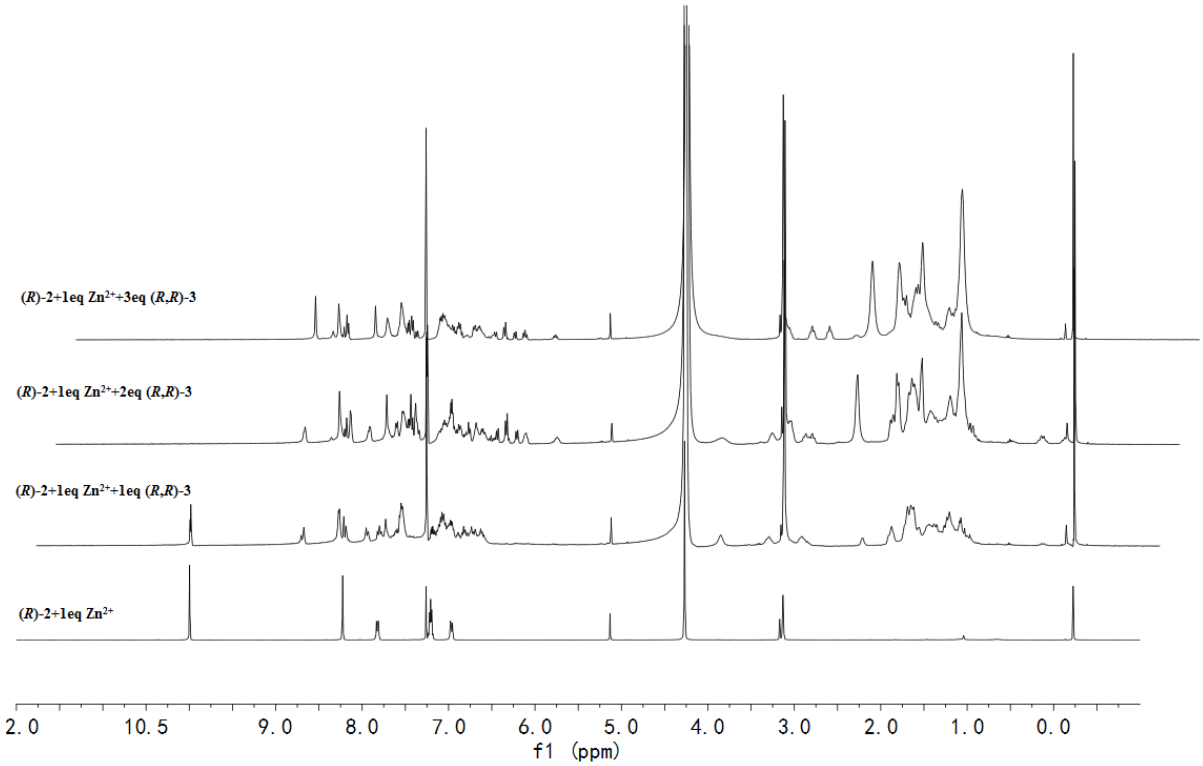


Figure S8. $I_{521}/I_{506}$for (*R*)-**2**+Zn^{2+}(1 equiv) (2.0×10^{-5} M in methanol/1% CH_2Cl_2) versus the concentration of (*S*)- and (*R*)-**9**. (λ_{exc}= 417nm, slits: 5/5nm).

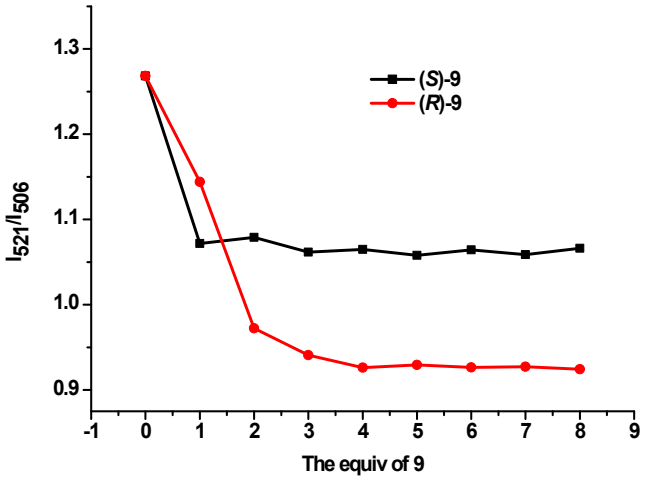
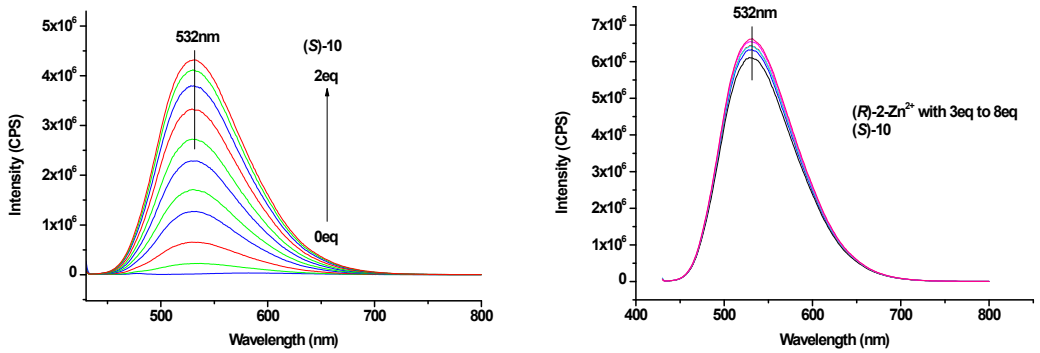
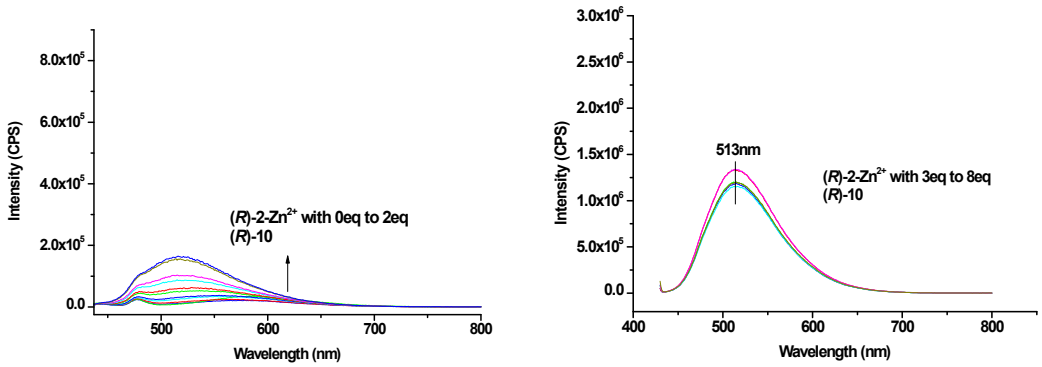


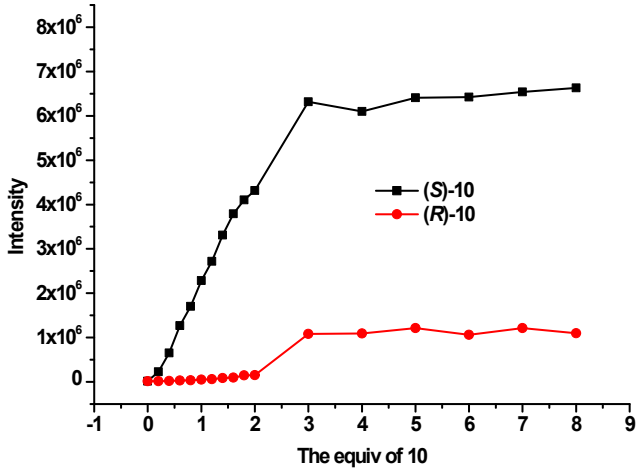
Figure S9. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1equiv) (2.0×10^{-5} M) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**10** (a) and (*R*)-**10** (b). Fluorescent intensity at 532 nm versus the equiv of **10** (c). (Solvent: methanol with 1% CH_2Cl_2. λ_{exc} = 417 nm, slit = 5/5 nm.).



(a)

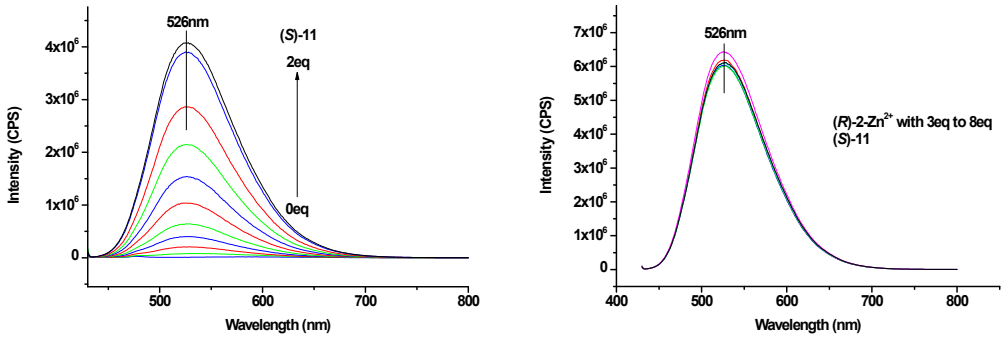


(b)

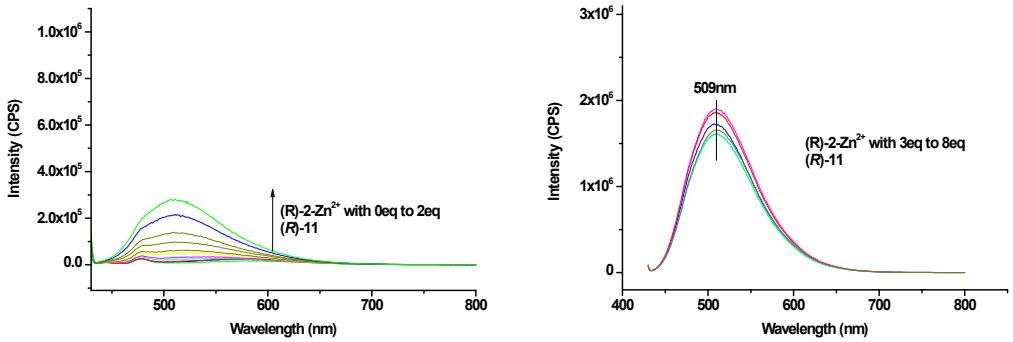


(c)

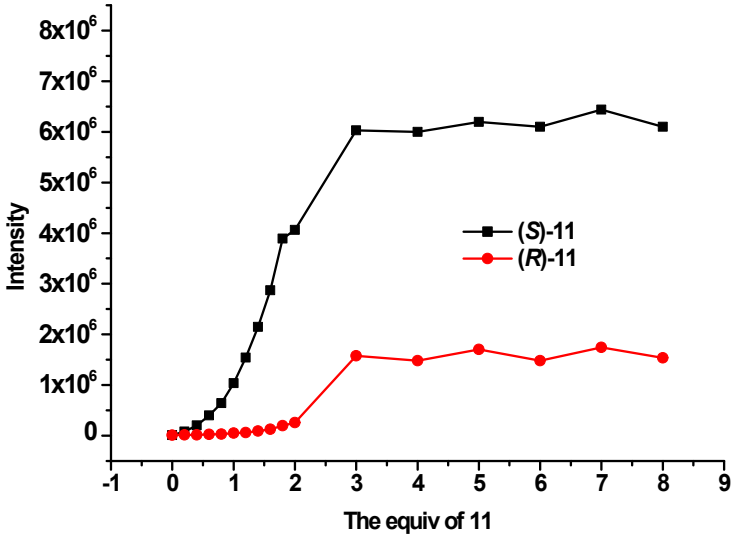
Figure S10. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1equiv) (2.0×10^{-5} M) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**11** (a) and (*R*)-**11** (b). Fluorescent intensity at 526 nm versus the equiv of **11** (c). (Solvent: methanol with 1% CH_2Cl_2. λ_{exc} = 417 nm, slit = 5/5 nm.).



(a)

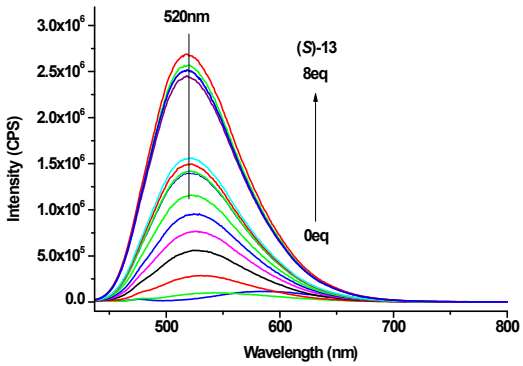


(b)

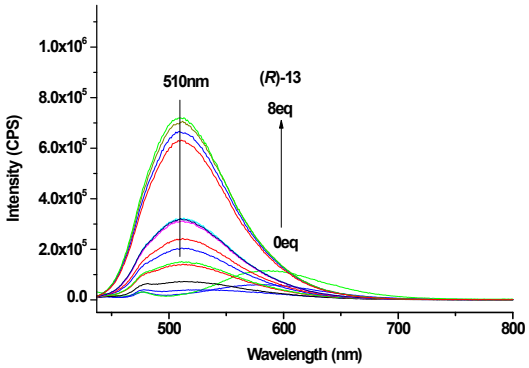


(c)

Figure S11. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1 equiv) (2.0 x 10^{-5} M in methanol/1% CH_2Cl_2 with 10 equiv Bu_4NOH) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**13** (a) and (*R*)-**13** (b). Fluorescent intensity at 520 nm versus the equiv of **13** (c). I_{520}/I_{510} versus the concentration of (*S*)- and (*R*)-**13** (d). (λ_{exc} = 417 nm, slit = 5/5 nm.).



(a)



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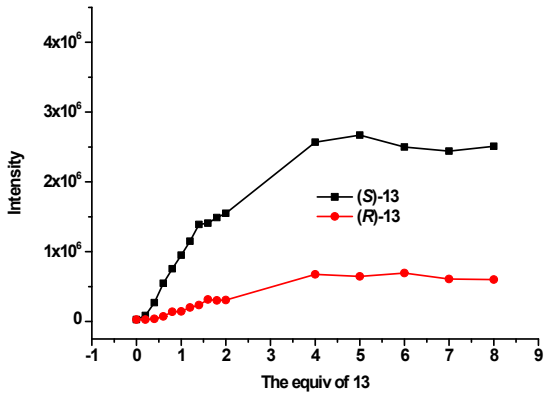
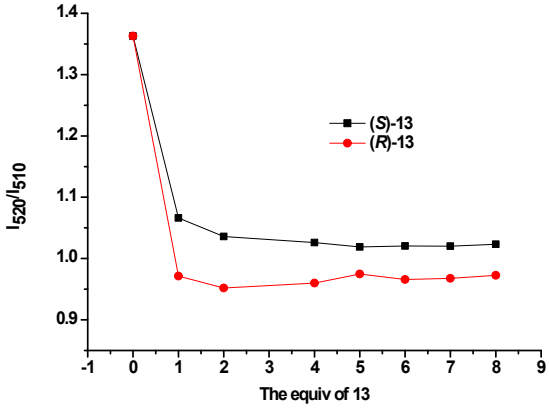
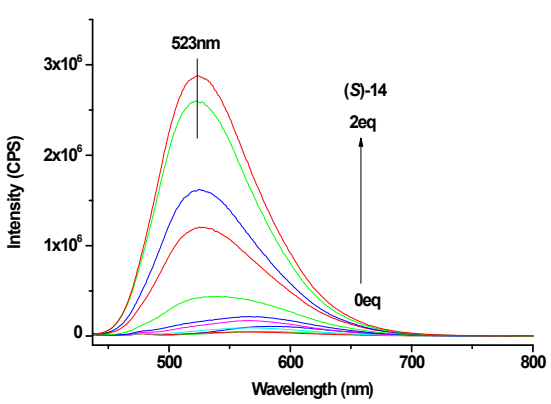


(c)

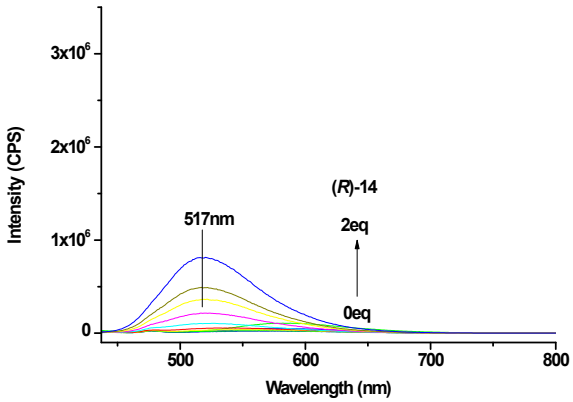


(d)

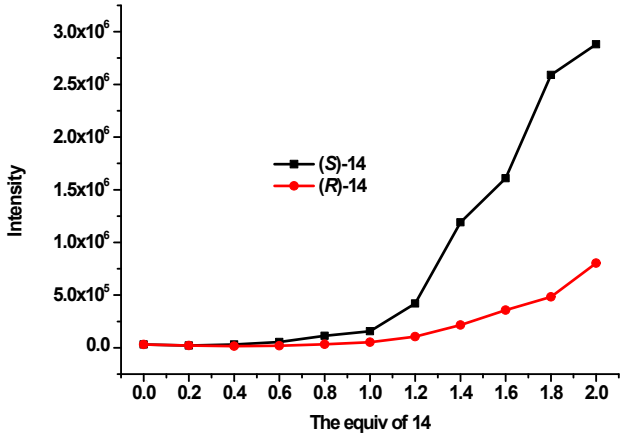
Figure S12. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1 equiv) (2.0 x 10^{-5} M in methanol/1% CH_2Cl_2 with 10 equiv Bu_4NOH) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 quiv(*S*)-**14** (a) and (*R*)-**14** (b). Fluorescent intensity at 523 nm versus the equiv of **14** (c). (λ_{exc} = 417 nm, slit = 5/5 nm.).



(a)

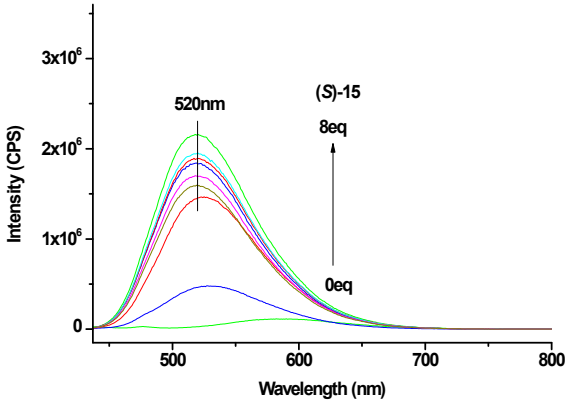


(b)

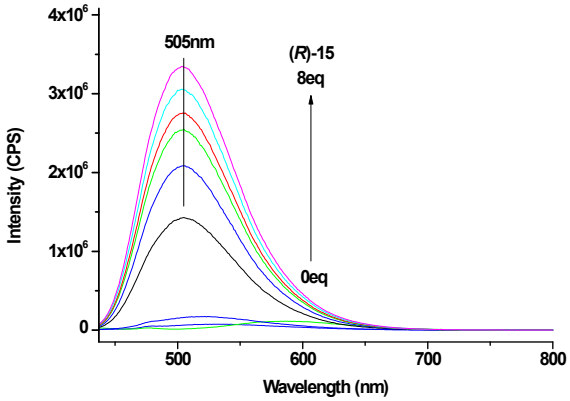


(c)

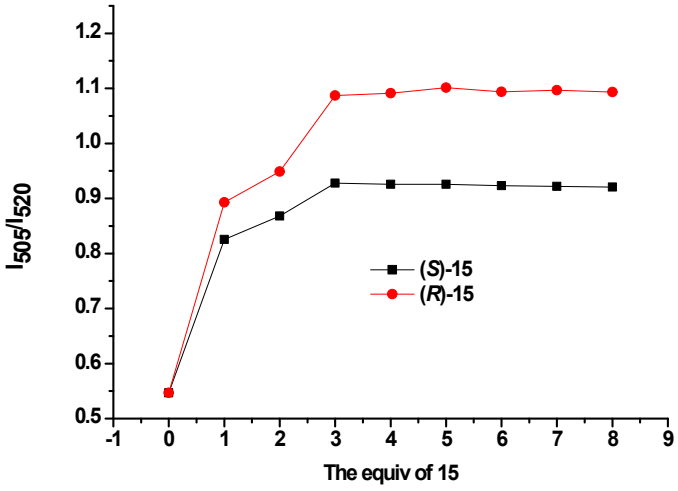
Figure S13. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1 equiv) (2.0 x 10^{-5} M in methanol/1% CH_2Cl_2 with 10 equiv Bu_4NOH) in the presence of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**15** (a) and (*R*)-**15** (b). I_{505}/I_{520}versus the concentration of **15**(c). (λ_{exc} = 417 nm, slit = 5/5 nm.).



(a)

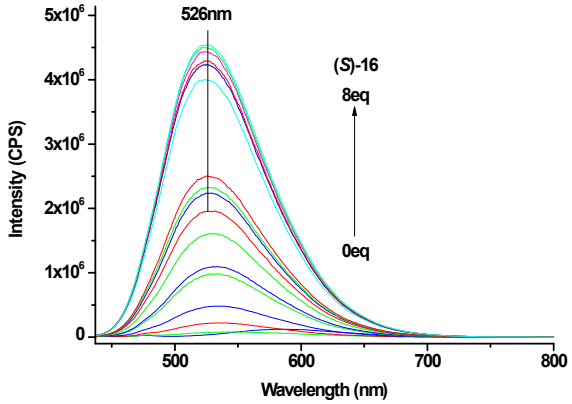


(b)

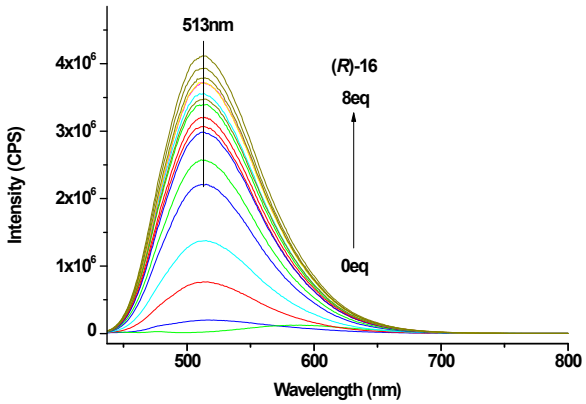


(c)

Figure S14. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1 equiv) (2.0 x 10^{-5} M in methanol/1% CH_2Cl_2 with 10 equiv Bu_4NOH) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**16** (a) and (*R*)-**16** (b). I_{526}/I_{513}versus the concentration of **16** (c). (λ_{exc} = 417 nm, slit = 5/5 nm.).



(a)



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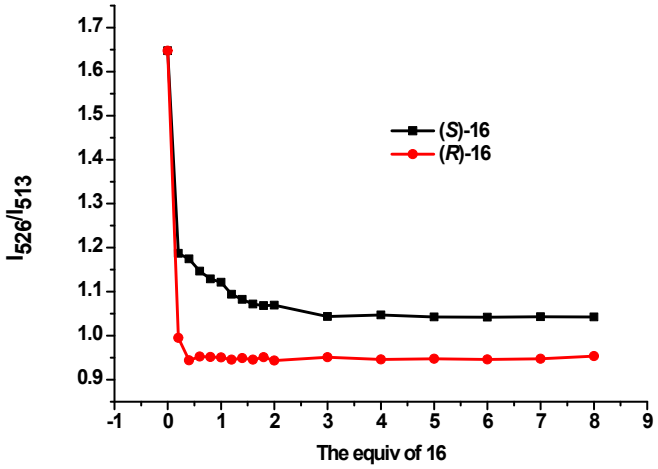
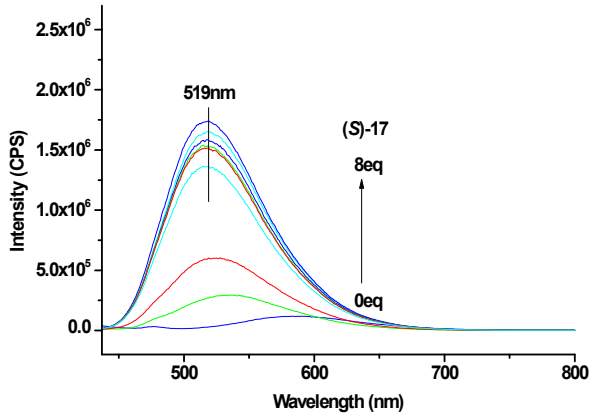
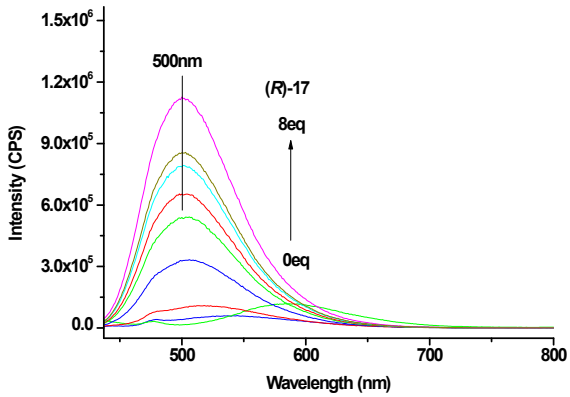


(c)

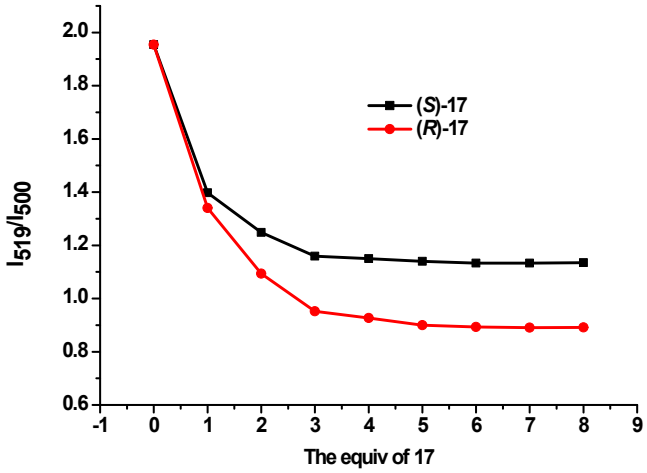
Figure S15. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1 equiv) (2.0 x 10^{-5} M in methanol/1% CH_2Cl_2 with 10 equiv Bu_4NOH) in the presence of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**17** (a) and (*R*)-**17** (b). I_{519}/I_{500}versus the concentration of **17**(c). (λ_{exc} = 417 nm, slit = 5/5 nm.).



(a)

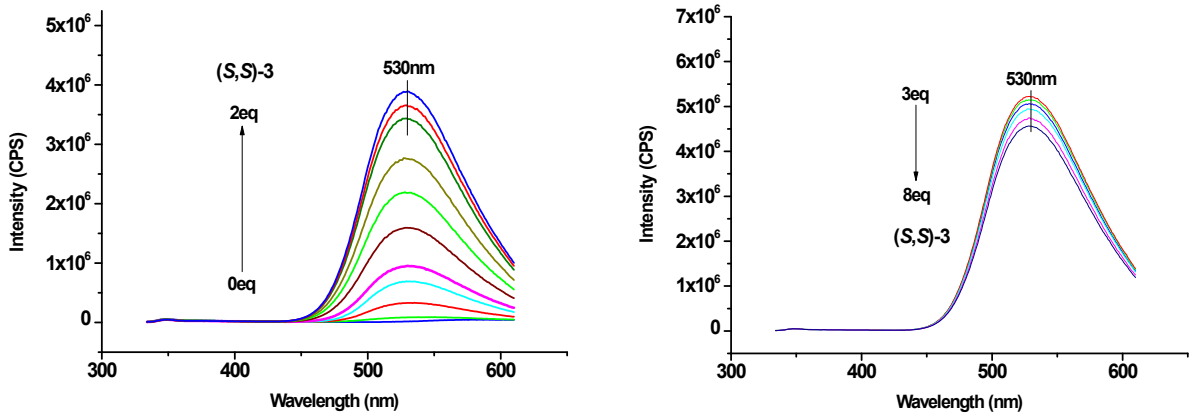


(b)

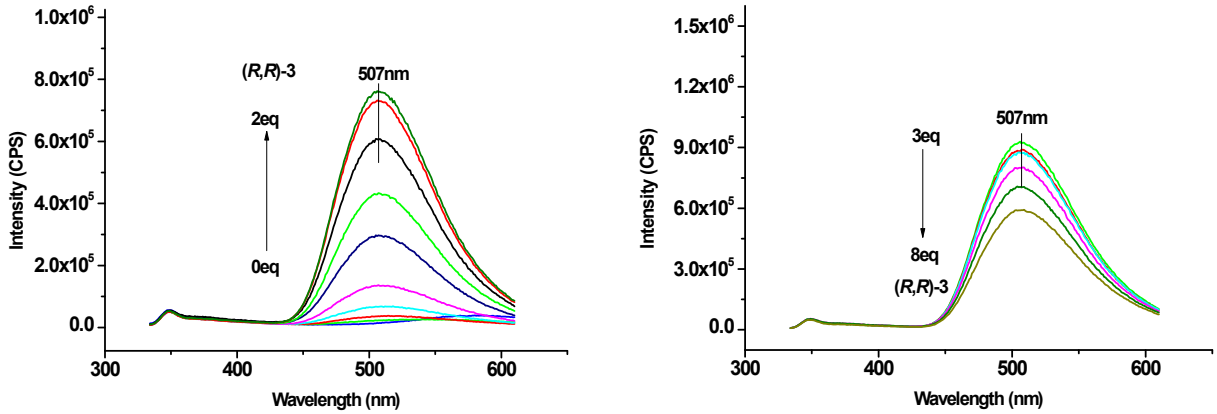


(c)

Figure S16. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1equiv) (2.0×10^{-5} M) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S,S*)-**3** (a) and (*R,R*)-**3** (b). (Solvent: methanol with 1% CH_2Cl_2. λ_{exc} = 314 nm, slit = 5/5 nm.).



(a)



(b)

Figure S17. Fluorescence spectra of (*R*)-**2** +Zn^{2+}(1 equiv) (2.0×10^{-5} M) in the presence ofthe enantiomeric mixture of *trans*-cyclohexane-1,2-diamine [from 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% to 100% (*S*,*S*)-**3**] at a total concentration of $4x10^{-5}$M. (Solvent: methanol with 1% CH_2Cl_2.λ_{exc} = 314 nm, slit = 5/5 nm.).

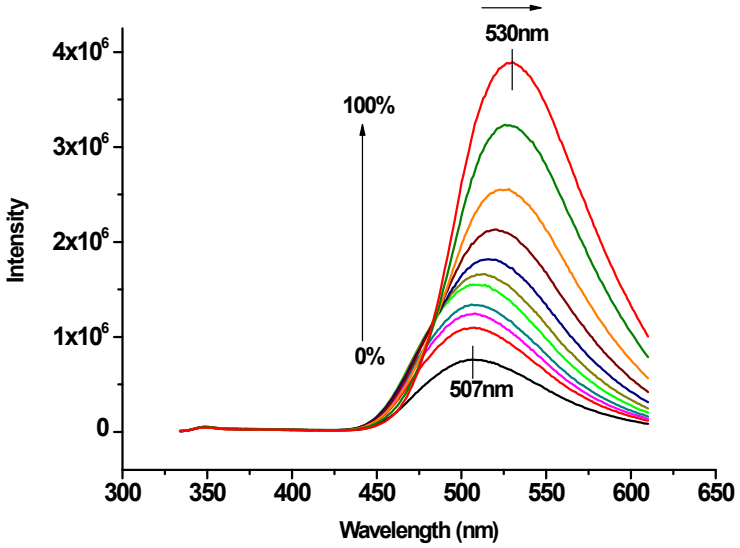


Figure S18. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1equiv) (2.0×10^{-5} M) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**9** (a) and (*R*)-**9** (b). (Solvent: methanol with 1% CH_2Cl_2. λ_{exc} = 417 nm, slit = 5/5 nm.).

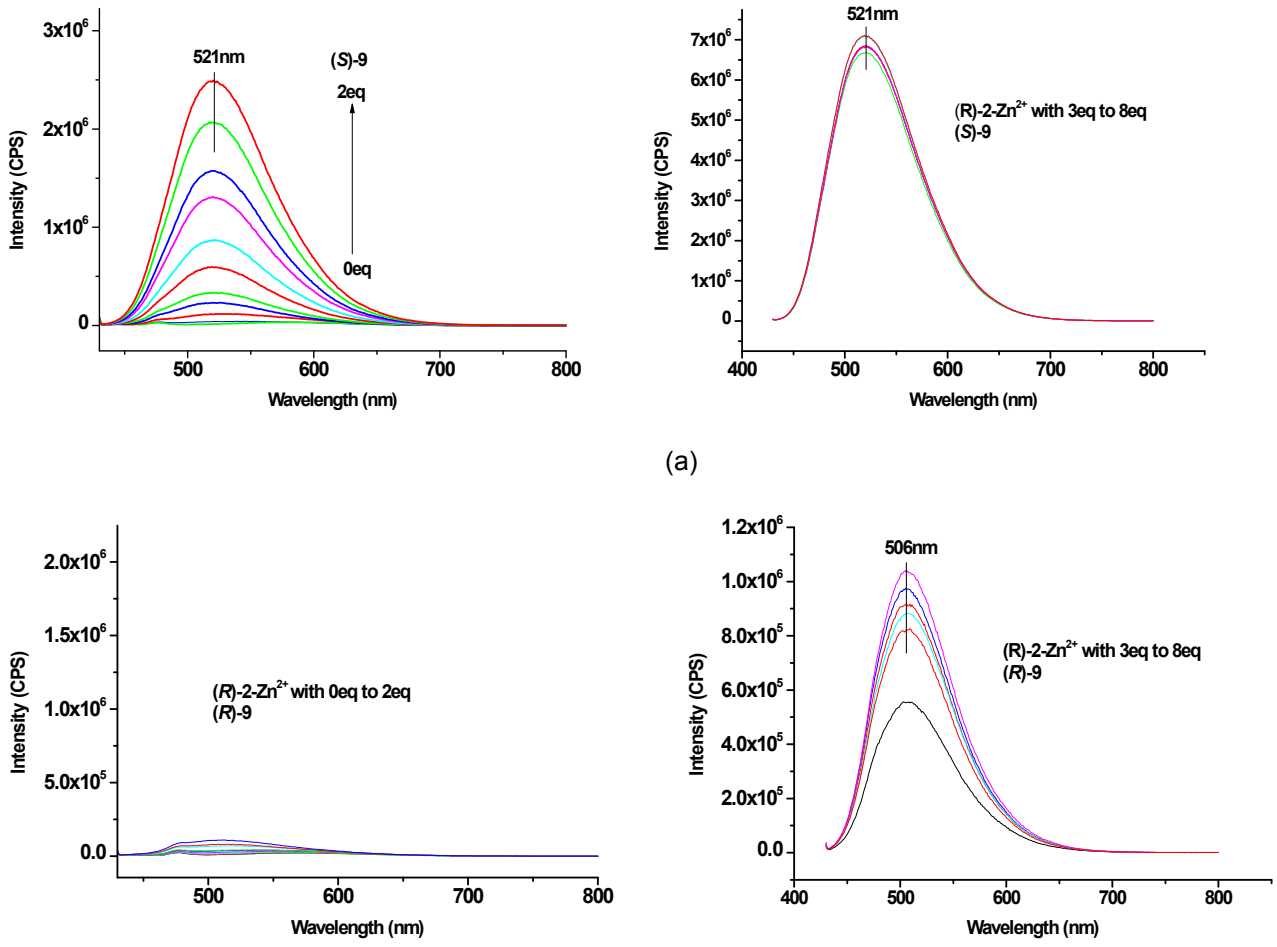
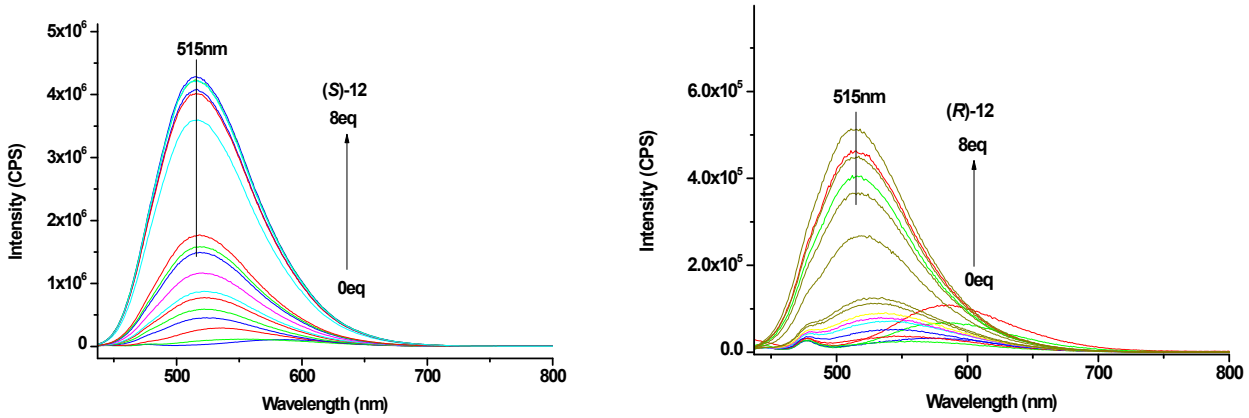


Figure S19. Fluorescent spectra of (*R*)-**2**+Zn^{2+}(1 equiv) (2.0 x 10^{-5} M in methanol/1% CH_2Cl_2 with 10 equiv Bu_4NOH) in the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 equiv (*S*)-**12** (a) and (*R*)-**12** (b). (λ_{exc} = 417 nm, slit = 5/5 nm.).



Time Dependence Fluorescence Responses

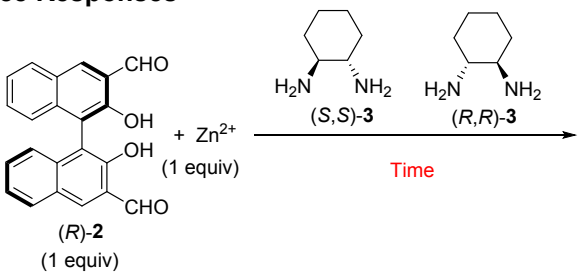
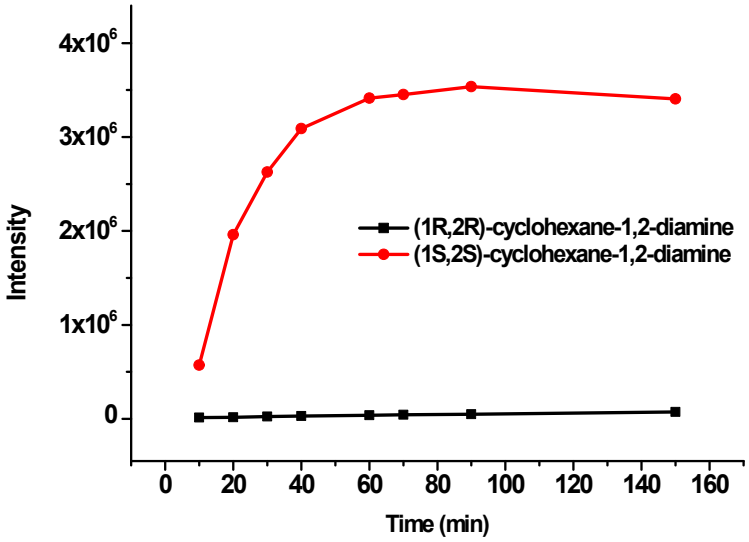


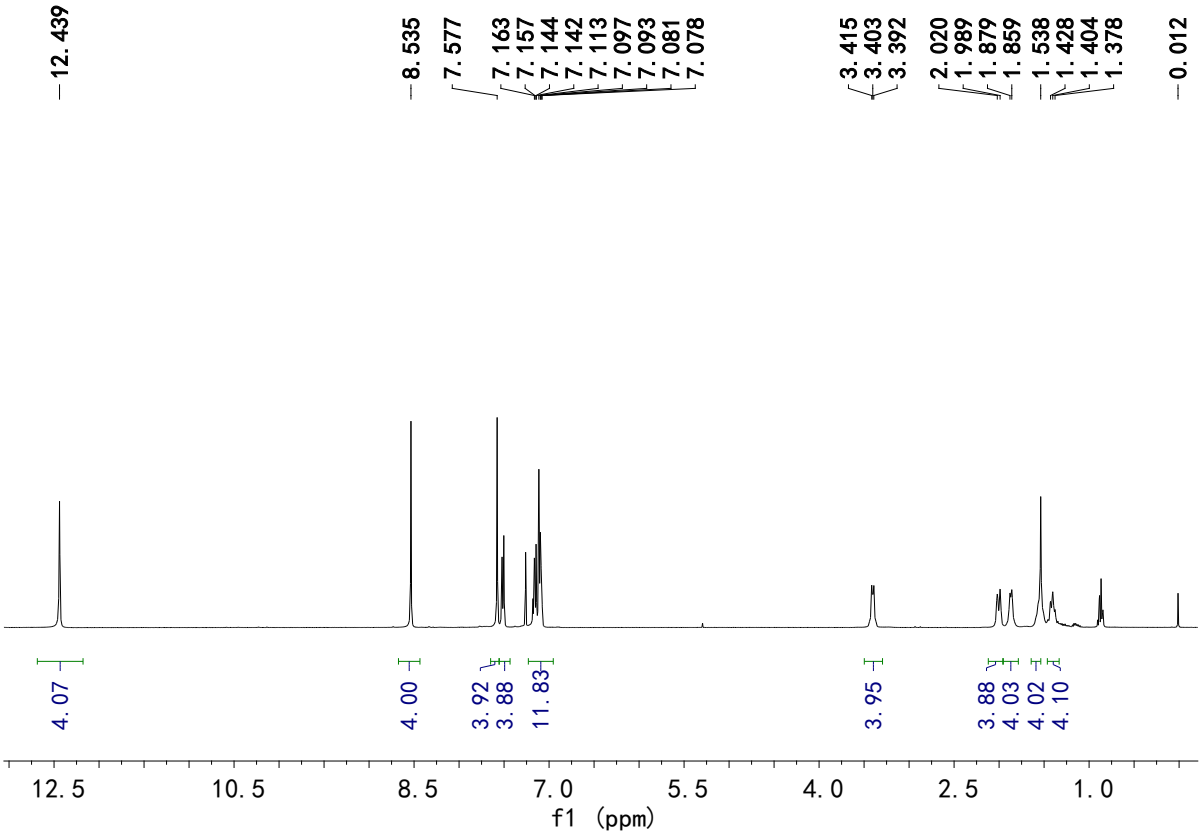
Figure S20. (*R*)-**2** (50 μL, 2x10^{-3} M in CH_2Cl_2) and Zn^{2+} (50 μL, 2x10^{-3} M in CH_3OH) were placed in a 10 mL test tube, to which was added (*R,R*)- or (*S,S*)-cyclohexane-1,2-diamine (100 μL, 1x10^{-3} M in CH_3OH). The resulting solutions were allowed to stand at room temperature for 10, 20, 30, 40, 60, 70, 90, and 150 min respectively. Then, each of the solutions was diluted to 5 mL and its fluorescent spectrum was obtained. This figure plots the fluorescent intensities at 530 nm for (*S,S*)-cyclohexane-1,2-diamine and at 507 nm for (*R,R*)-cyclohexane-1,2-diamine versus the reaction time. It shows the fluorescent intensity reached maximum and became stable after ~~50~~ 60 min of the reaction. This indicates that the fluorescent response difference for (*R*)-**2** toward (*R,R*)- and (*S,S*)-cyclohexane-1,2-diamine is due to the thermodynamics of the reactions. (λ_{exc}=314nm, slits: 5nm/5nm).



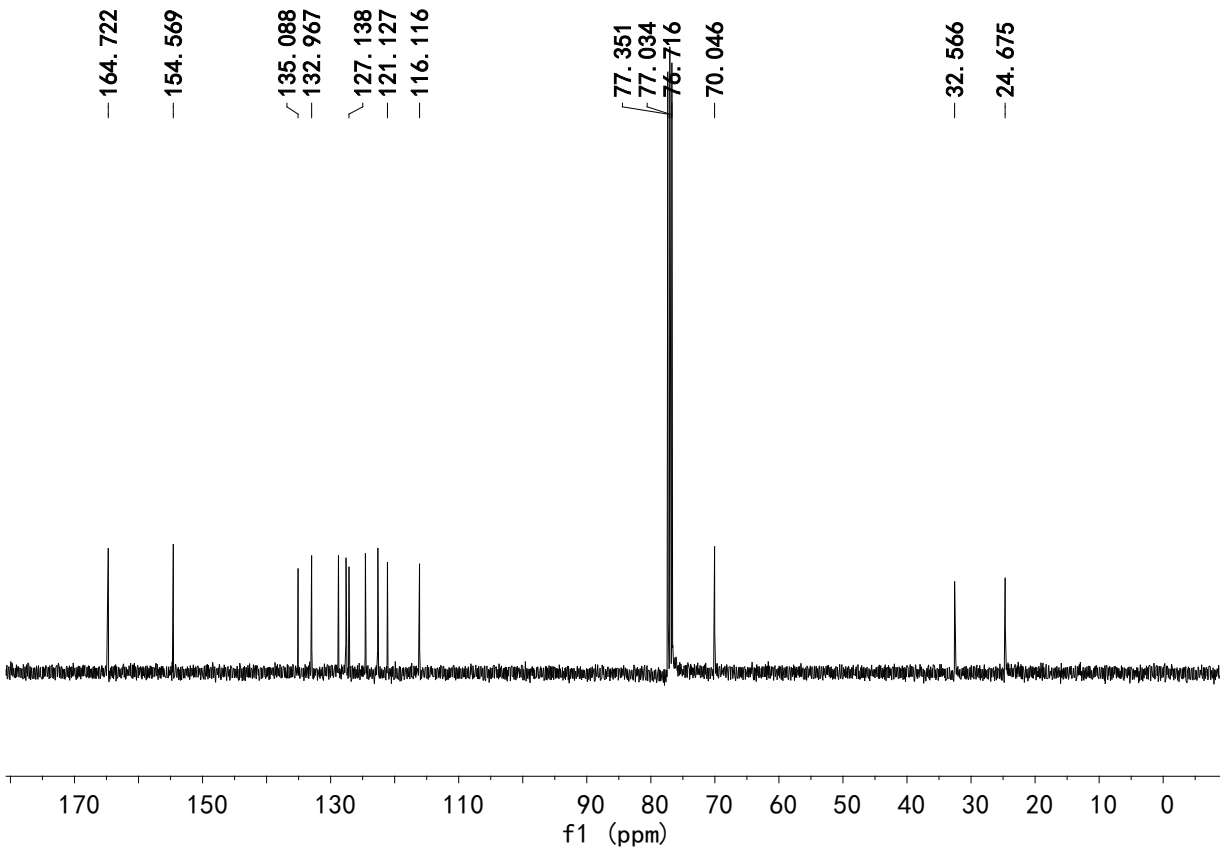
Ⅳ. Preparation and Characterization of the Macrocycle 6

Compound macrocycle **6** was synthesized by modifyingthe reported procedure.[#] Under argon, (*S,S*)-**3** (57 mg, 0.5 mmol) and (*R*)-**2** (171 mg, 0.5 mmol) were dissolved in dry methylene chloride (20 mL) and CH_3OH (5 mL). The mixture was stirred at room temperature for 2 d. After evaporation of the solvent, the crude product was dissolved in CH_2Cl_2 (3 mL), and then CH_3OH (10 mL) was added slowly to precipitate out the macrocycle **6.** The yellow solid was collected by filtration and washed with CH_3OH (5 mL). After dried under vacuum, the macrocycle **6** was obtained in 85% yield (178 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 142.44 (s, 4H), 8.54(s, 4H), 7.58 (s, 4H), 7.51 (d, *J*=8.8Hz, 4H), 7.18-7.08 (m, 12H), 3.42-3.39 (m, 4H), 2.02-1.98 (m, 4H), 1.88-1.86 (m, 4H), 1.63-1.55 (m, 4H), 1.43-1.38 (m, 4H). ^{13}CNMR ($CDCl_3$, 100 MHz) δ 164.7, 154.6, 135.1, 133.0, 128.8, 127.6, 127.1, 124.6, 122.6, 121.1, 116.1, 70.1, 32.6, 24.7. HR-MS (ES+) calcd for $C_{56}H_{49}N_4O_4$ ($M+H^+$) 841.3748 and $C_{56}H_{48}N_4O_4Na^+$($M+Na^+$) 863.3568, found 841.3756 and 863.3608. (#Reference: Li, Z. –B.; Lin, J.; Sabat, M.; Hyacinth, M.; Pu, L. *J. Org. Chem*. **2007**, *72*, 4905-4916.)

^{1}H-NMR of themacrocycle 6 ($CDCl_3$, 400 MHz)



^{13}C-NMR of the macrocycle 6 ($CDCl_3$, 100 MHz)



HRMS of the macrocycle 6