Supporting Information

Chiral Adaptive Recognition with Sequence Specificity of Aromatic Dipeptides in Aqueous Solution by an Achiral Cage

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1. General Experimental Details.

Starting materials were purchased from commercial suppliers were used without further purification. NMR spectra were recorded on a spectrometer operating at 400 MHz spectra on Bruker ascend spectrometer and JEOL 600 spectrometer. UV/vis spectra were done on Agilent Cary-100 spectrometer. Fluorescence spectra were performed by using a Horiba Fluorolog-3 spectrometer. Isothermal titration calorimetry (ITC) was carried out using a VP-ITC (Malvern) at 25 ˚C, and computer fitting of the data were performed using the VP-ITC analyze software. The Circular dichroism (CD) spectra were recorded on a J-1500 spectropolarimeter, using a 1 cm quartz cuvette. Circularly polarized luminescence (CPL) spectra were measured on JASCO CPL-300 spectrophotometers. X-ray diffraction data collection of the compounds were recorded by Bruker D8 Venture photon II diffractometer.

X-ray data of 1 and 1⊃(*L*-PhePhe)$_2$

Table S1. Crystal Data for ***PM*-1**, ***PP/MM*-1** and **1⊃(*L*-PhePhe)$_2$**

Parameters	***PM*-1**	***PP*/*MM*-1**	**1⊃(*L*-PhePhe)$_2$**
Empirical formula	$C_{244}H_{352}Cl_8N_8O_{48}$	C_{124} H_{96} Cl_8 N_8	$C_{160}H_{134}Br_6N_{12}O_6$
Formula weight	4448.92	1981.68	2800.24
Temperature (K)	100(2)	90	173(2)
Wavelength (Å)	1.34138	1.34138	1.34139
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C12/m1*	*I222*	*C2*
a, (Å)	28.8074(18)	18.7340(7)	39.987(3)
b, (Å)	21.7271(18)	21.4715(8)	16.180(2)
c, (Å)	19.0790(19)	66.271(3)	29.951(4)
α, (°)	90	90	90
β, (°)	131.248(6)	90	121.416(4)
γ, (°)	90	90	90

V (Å^3)	8978.4(14)	26657.3(18)	16537(3)
Z	2	6	4
ρ_{calcd} (g/cm^3)	1.646	0.741	1.125
μ (mm^{-1})	1.283	0.930	1.421
F(000)	4784	6192	5744
Crystal size (mm^3)	0.09×0.04×0.03	0.22×0.20×0.18	0.22×0.20×0.18
θ range for data collection (°)	2.506 to 50.494	1.882 to 52.998	1.950 to 55.315
Limiting indices	-33 ≤ h ≤ 33 -24 ≤ k ≤ 24 -20 ≤ l ≤ 21	-20 ≤ h ≤ 22 -25 ≤ k ≤ 21 -78 ≤ l ≤ 78	-47 ≤ h ≤ 48 -19 ≤ k ≤ 19 -36 ≤ l ≤ 36
Reflections collected	9883	9857	9979
Data/restraints/parameters	7226/12/337	23569/1485/899	31270/25/1657
Goodness-of-fit	1.079	1.279	1.034
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0909,0.2798	0.1160, 0.3104	0.0420, 0.1160
$R1$, $wR2$ (all data)	0.1030, 0.2885	0.1362, 0.3424	0.0440, 0.1169
Largest diff. peak and hole, e Å^{-3}	0.359 and -0.345	1.187 and -0.412	0.741 and -0.676
CCDC	2100784	2100668	2155590

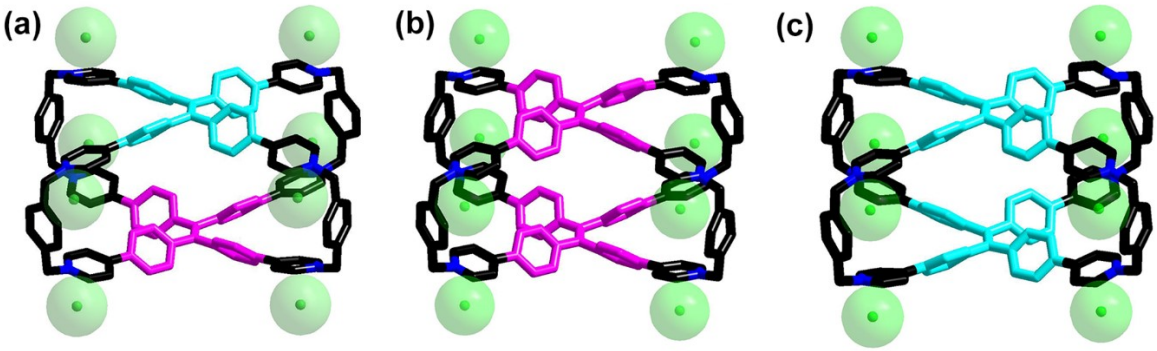

Figure S1. X-ray structures of (a) *PM*-**1**, (b) *MM*-**1**, and (c) *PP*-**1**.

2. Recognition of Amino Acids

2.1 UV-vis and circular dichroism experiments

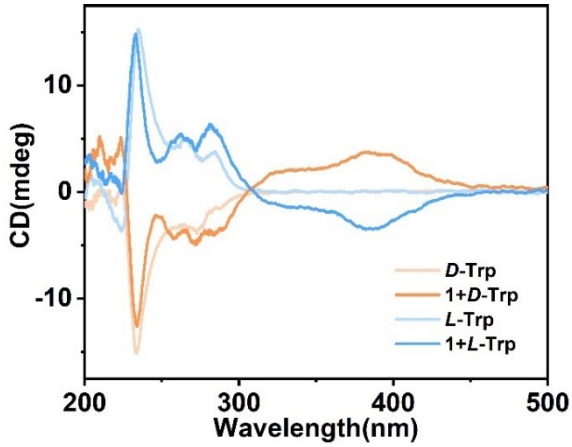

Figure S2. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Trp in phosphate buffer (10 mM, pH = 7.4).

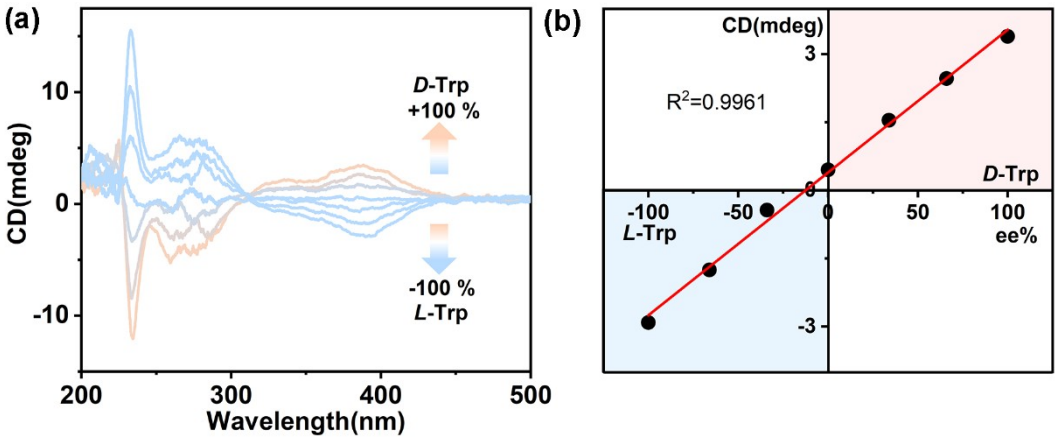

Figure S3. a) CD spectra of **1** (0.10 mM) in the presence of *D*/*L*-Trp (3.0 mM) with *ee* ranging from -100% to +100%. b) The calibration curve obtained for the CD signals (390 nm) upon varying *ee* values of *D*/*L*-Trp.

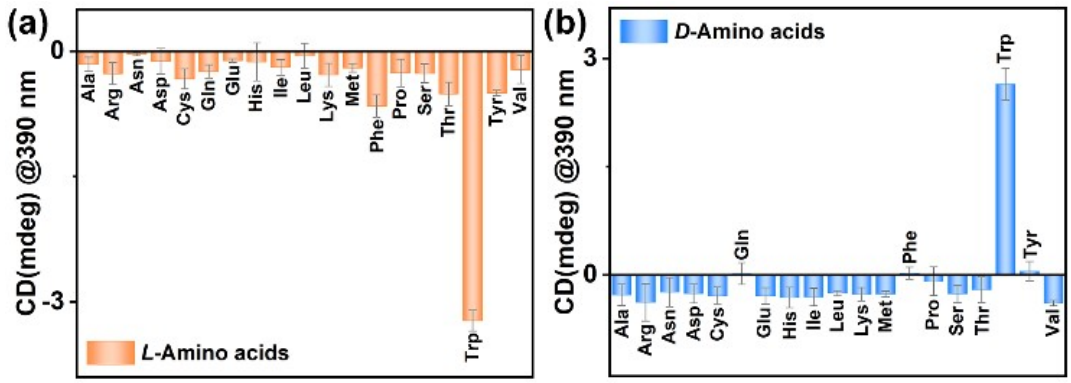

Figure S4. CD intensities of **1** (0.10 mM) with (a) *D*- and *(b) L*-amino acids (30.0 equiv) in phosphate buffer (10 mM sodium phosphate, pH = 7.4). Error bars are standard deviations based on three times of independent measurements.

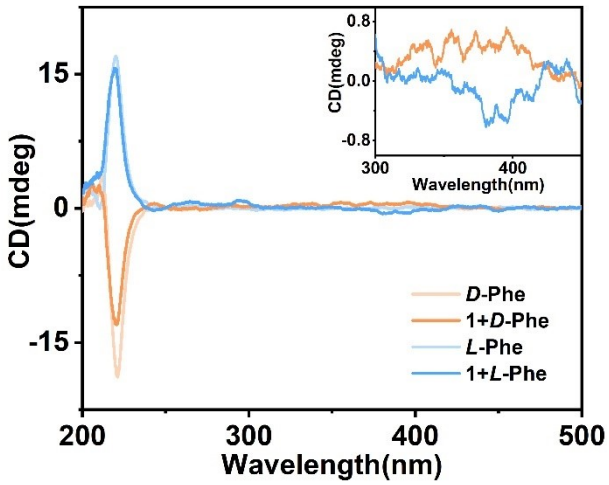

Figure S5. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Phe in phosphate buffer (10 mM, pH = 7.4)

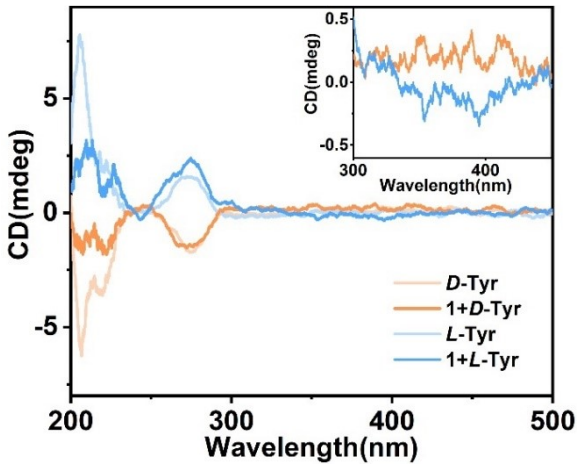

Figure S6. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Tyr in phosphate buffer (10 mM, pH = 7.4).

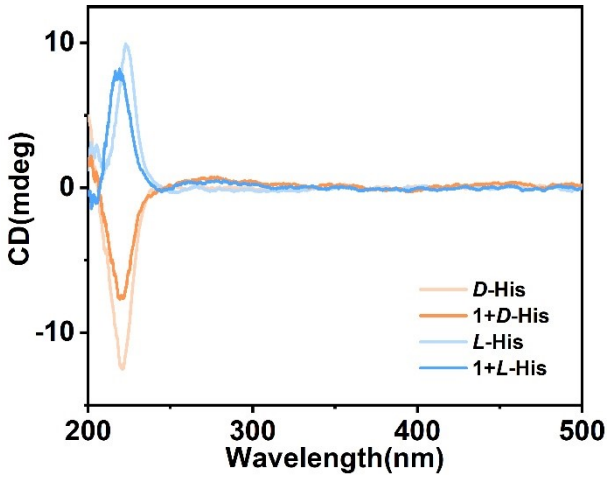

Figure S7. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-His in phosphate buffer (10 mM, pH = 7.4).

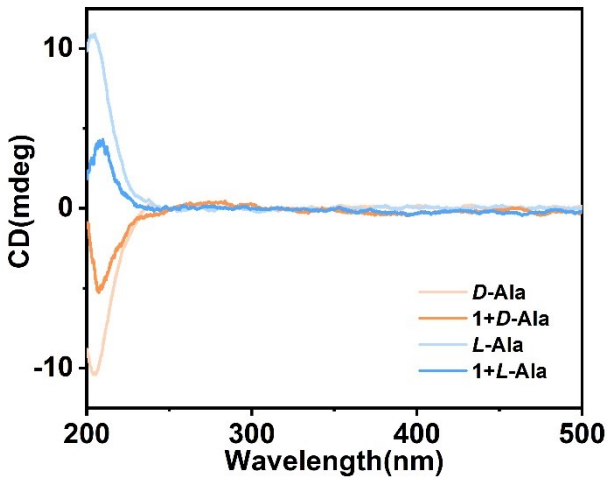

Figure S8. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Ala in phosphate buffer (10 mM, pH = 7.4).

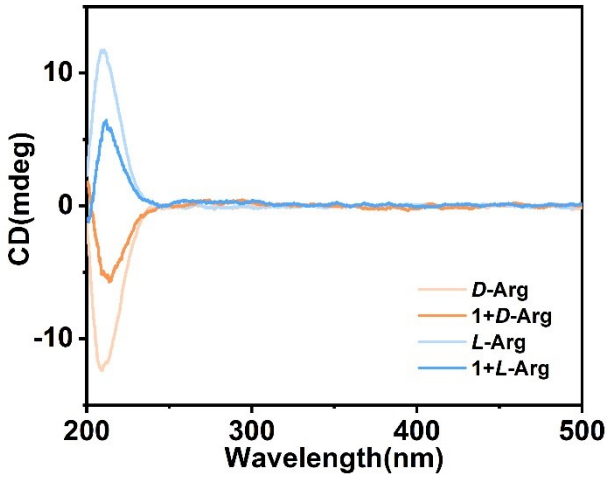

Figure S9. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Arg in phosphate buffer (10 mM, pH = 7.4).

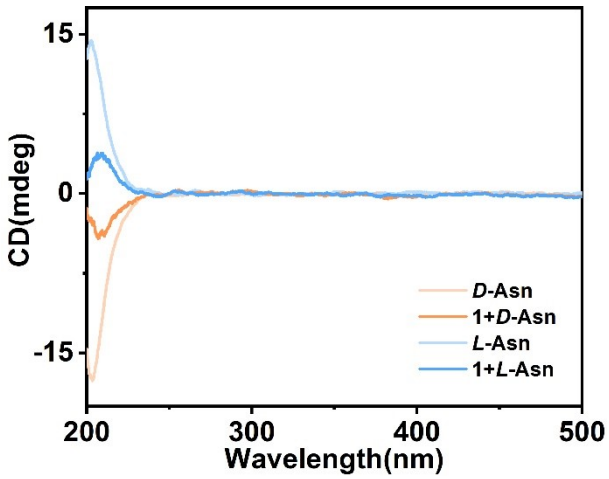

Figure S10. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Asn in phosphate buffer (10 mM, pH = 7.4).

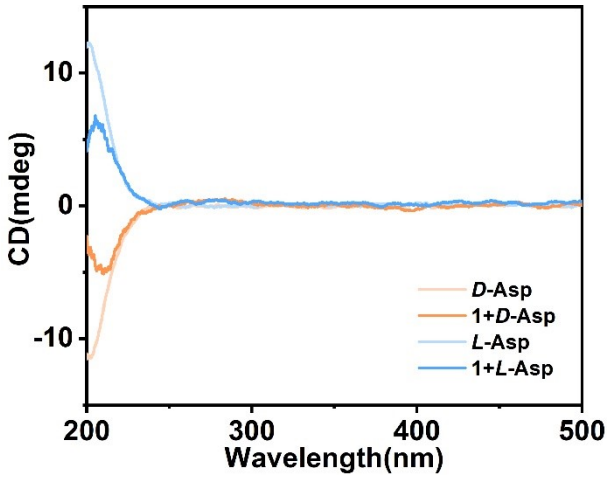

Figure S11. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Asp in phosphate buffer (10 mM, pH = 7.4).

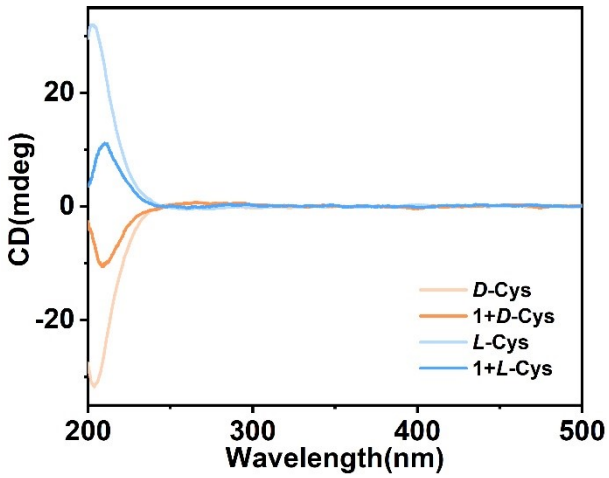

Figure S12. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Cys in phosphate buffer (10 mM, pH = 7.4).

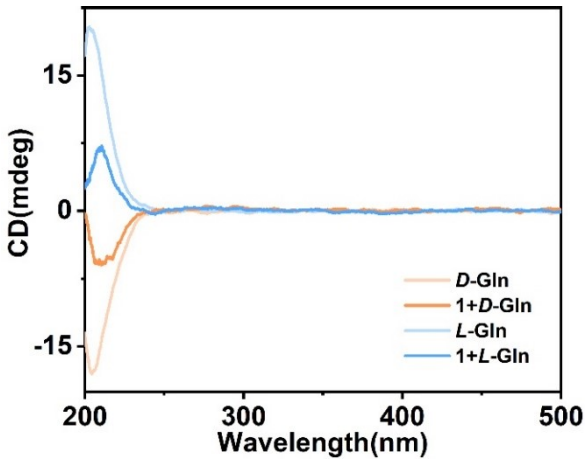

Figure S13. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Gln in phosphate buffer (10 mM, pH = 7.4).

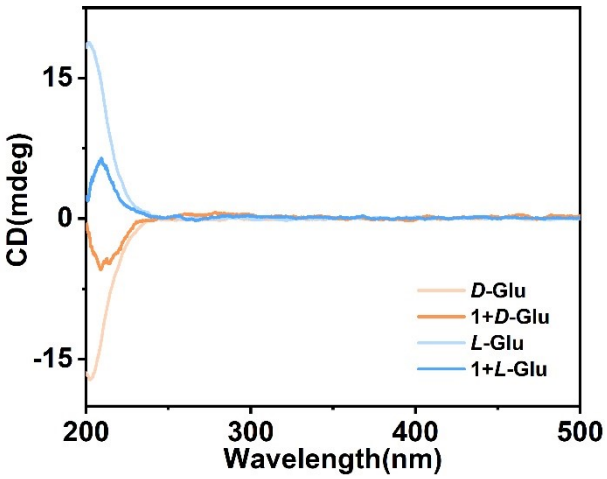

Figure S14. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Glu in phosphate buffer (10 mM, pH = 7.4).

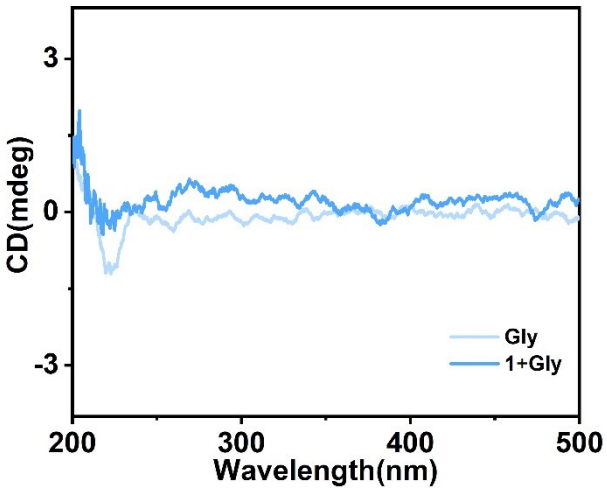

Figure S15. CD spectra of **1** (0.10 mM) with 30.0 equiv of Gly in phosphate buffer (10 mM, pH = 7.4).

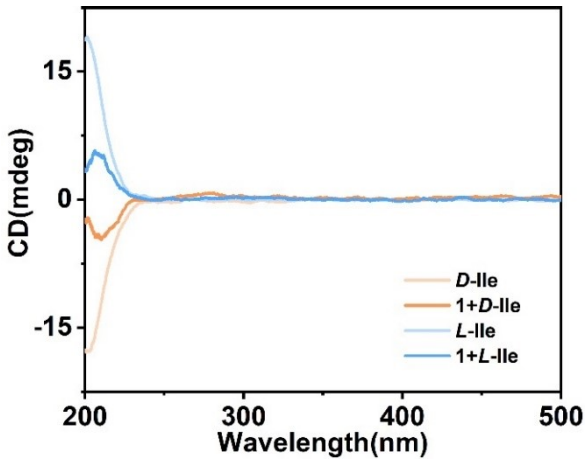

Figure S16. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Ile in phosphate buffer (10 mM, pH = 7.4).

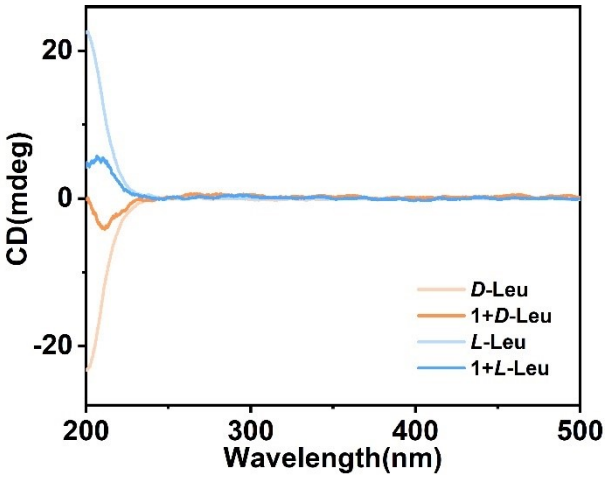

Figure S17. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Leu in phosphate buffer (10 mM, pH = 7.4).

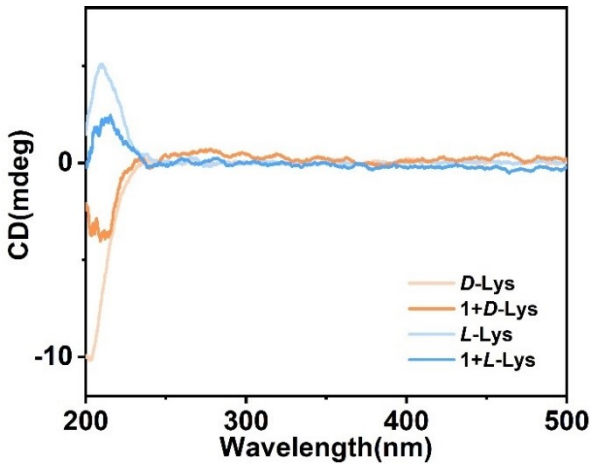

Figure S18. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Lys in phosphate buffer (10 mM, pH = 7.4).

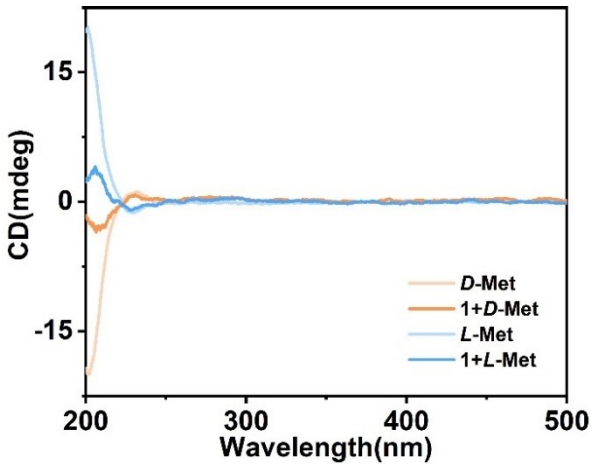

Figure S19. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Met in phosphate buffer (10 mM, pH = 7.4).

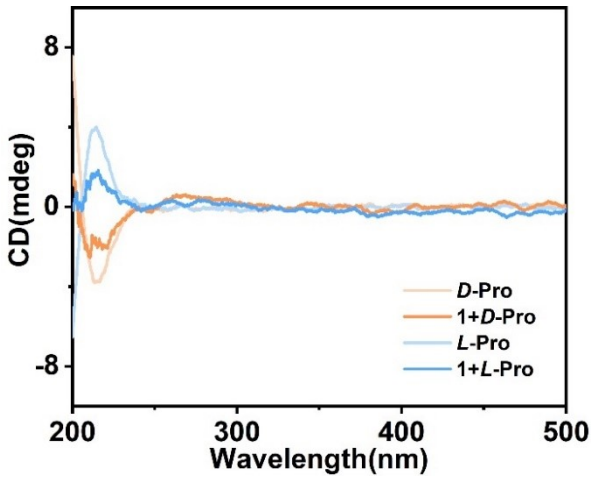

Figure S20. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Pro in phosphate buffer (10 mM, pH = 7.4).

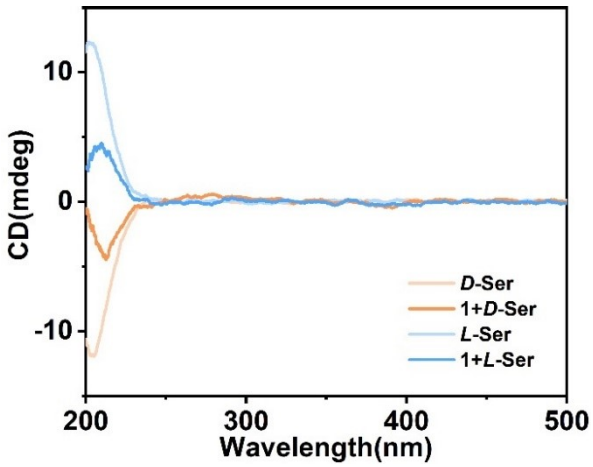

Figure S21. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Ser in phosphate buffer (10 mM, pH = 7.4).

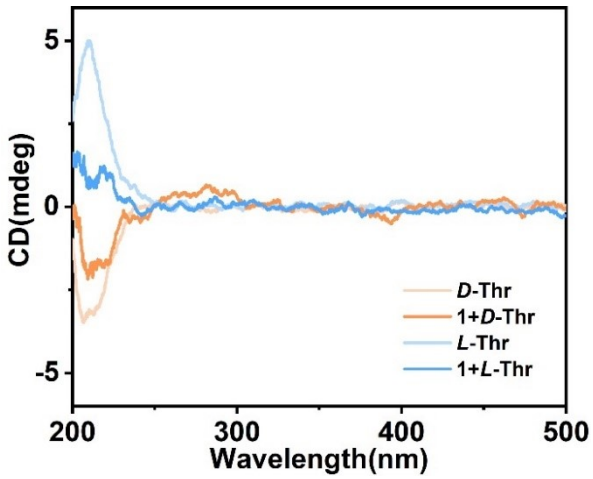

Figure S22. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Thr in phosphate buffer (10 mM, pH = 7.4).

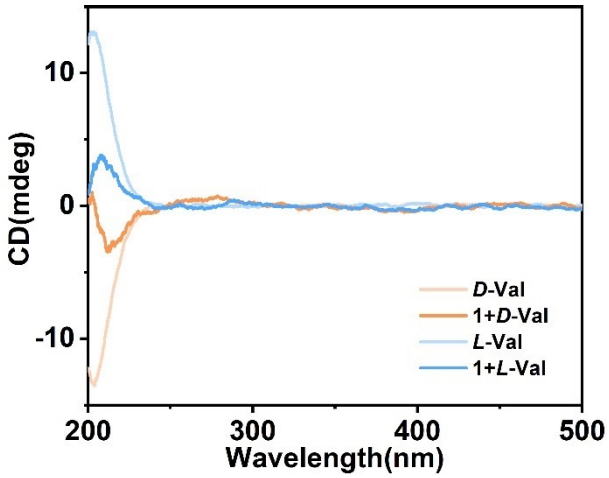

Figure S23. CD spectra of **1** (0.10 mM) with 30.0 equiv of *D*/*L*-Val in phosphate buffer (10 mM, pH = 7.4).

2.2 NMR experiments

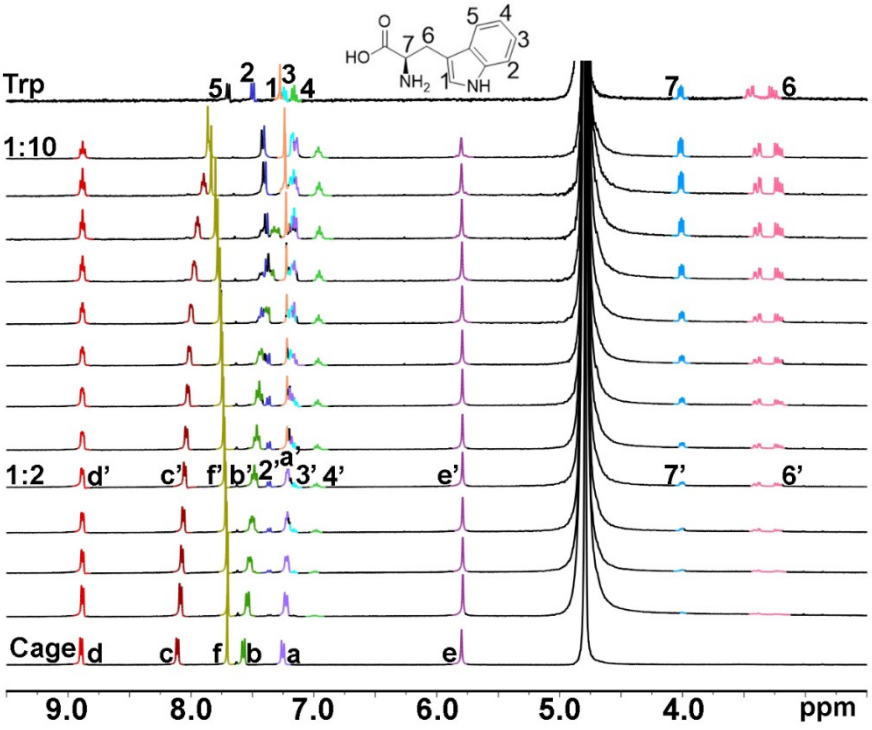

Figure S24. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Trp (0 – 10.0 equiv).

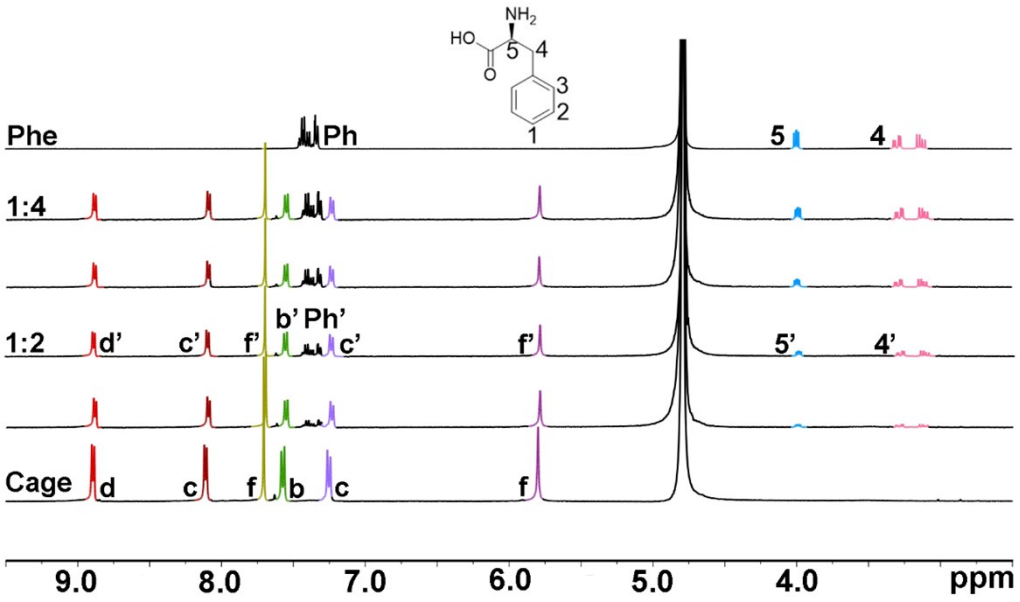

Figure S25. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Phe (0 – 4.0 equiv).

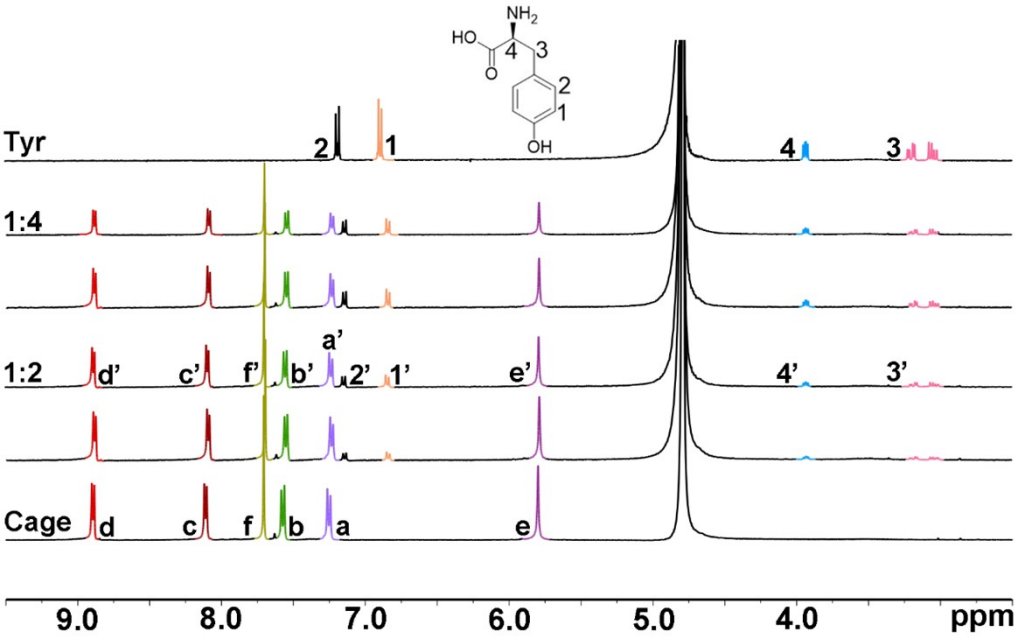

Figure S26. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Tyr (0 – 4.0 equiv).

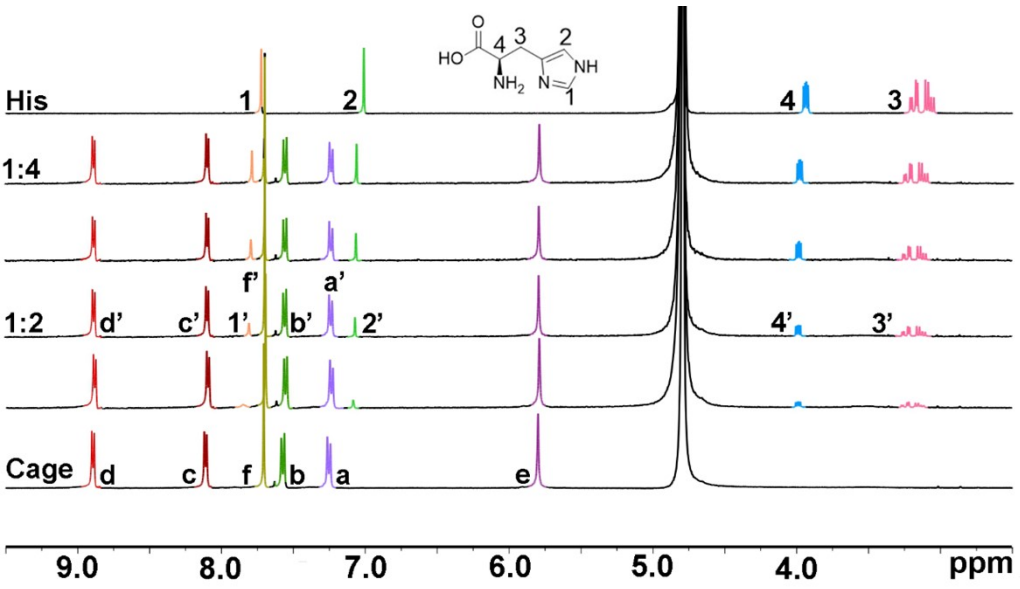

Figure S27. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-His (0 – 4.0 equiv).

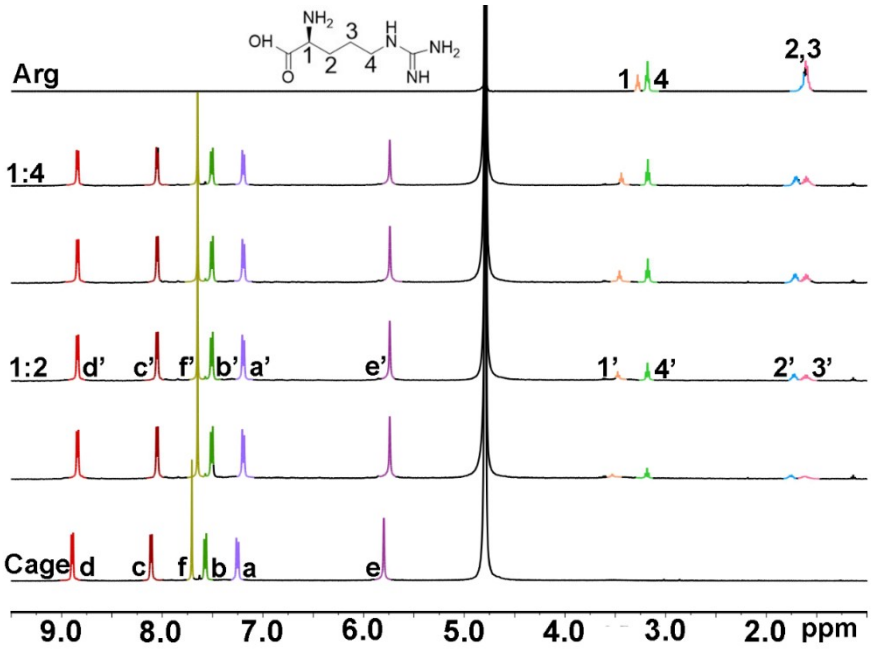

Figure S28. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Arg (0 – 4.0 equiv).

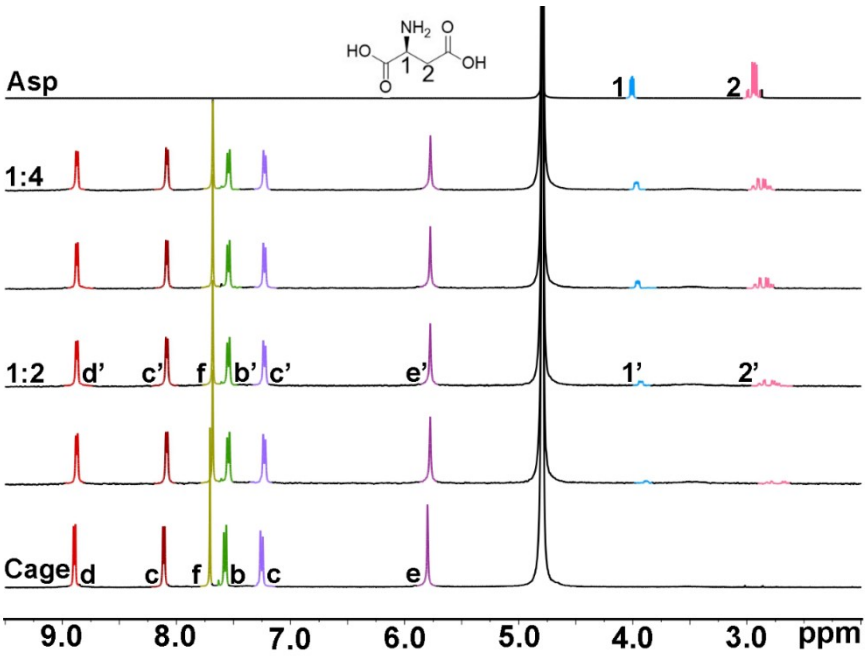

Figure S29. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Asp (0 – 4.0 equiv).

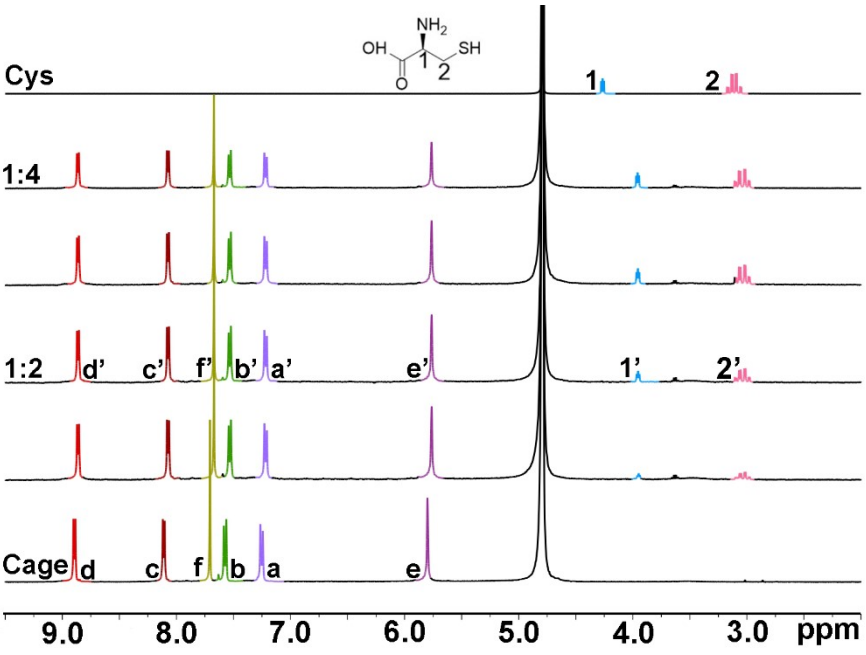

Figure S30. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Cys (0 – 4.0 equiv).

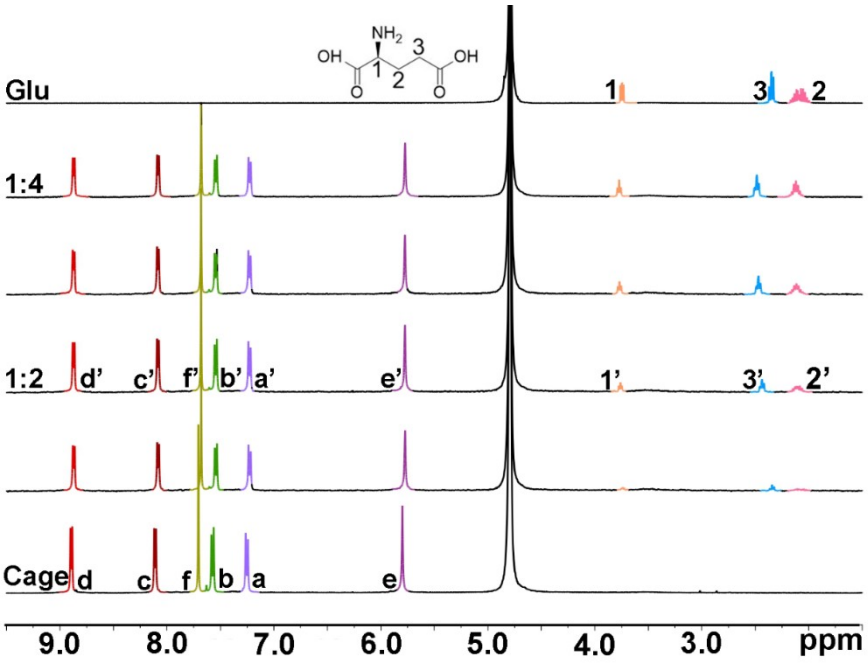

Figure S31. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Glu (0 – 4.0 equiv).

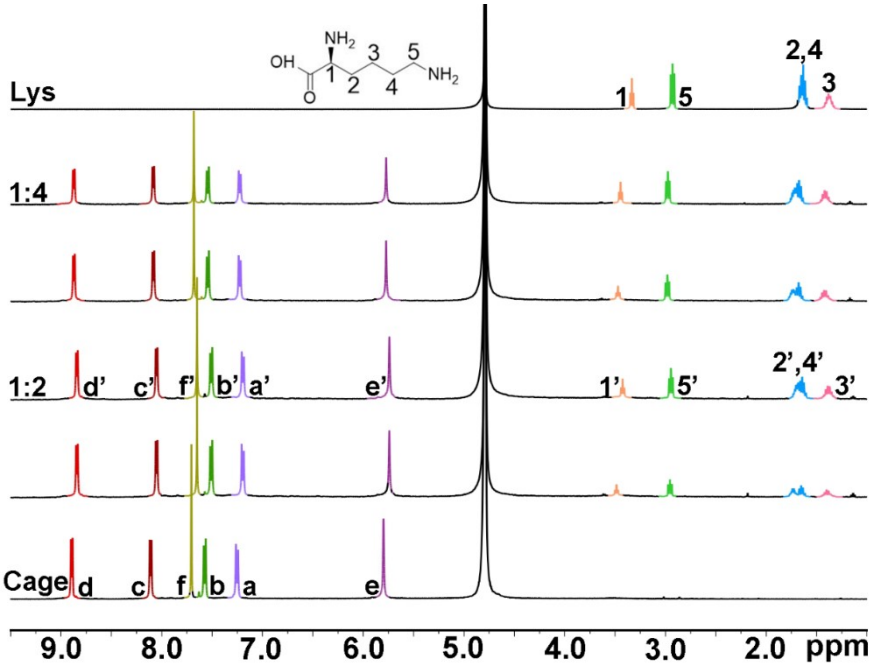

Figure S32. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Lys (0 – 4.0 equiv).

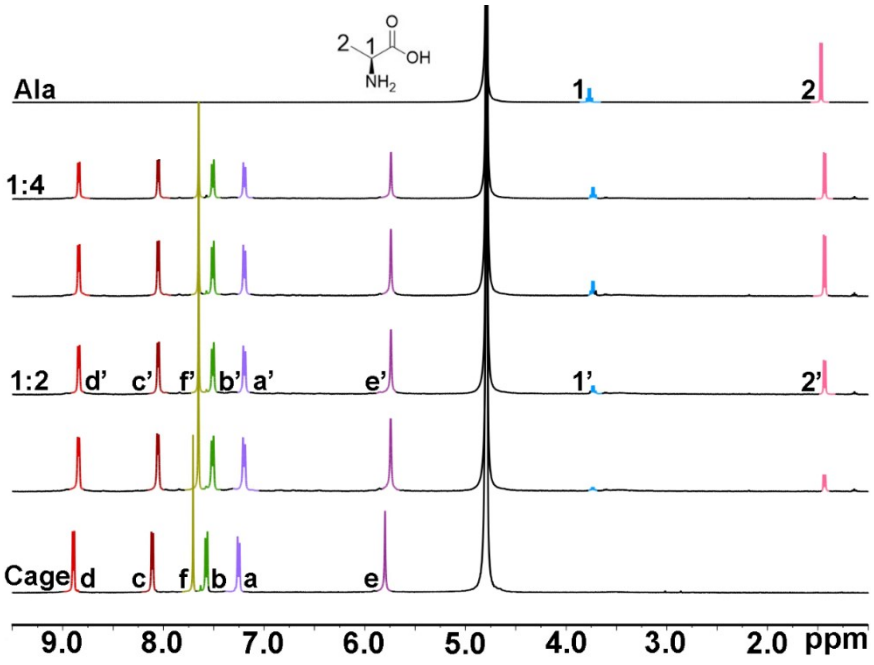

Figure S33. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Ala (0 – 4.0 equiv).

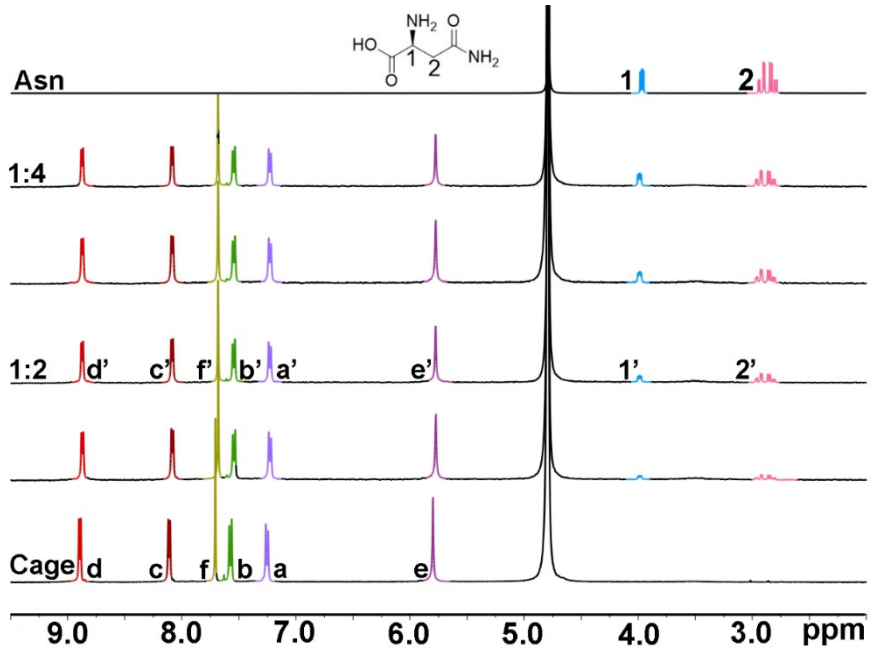

Figure S34. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Asn (0 – 4.0 equiv).

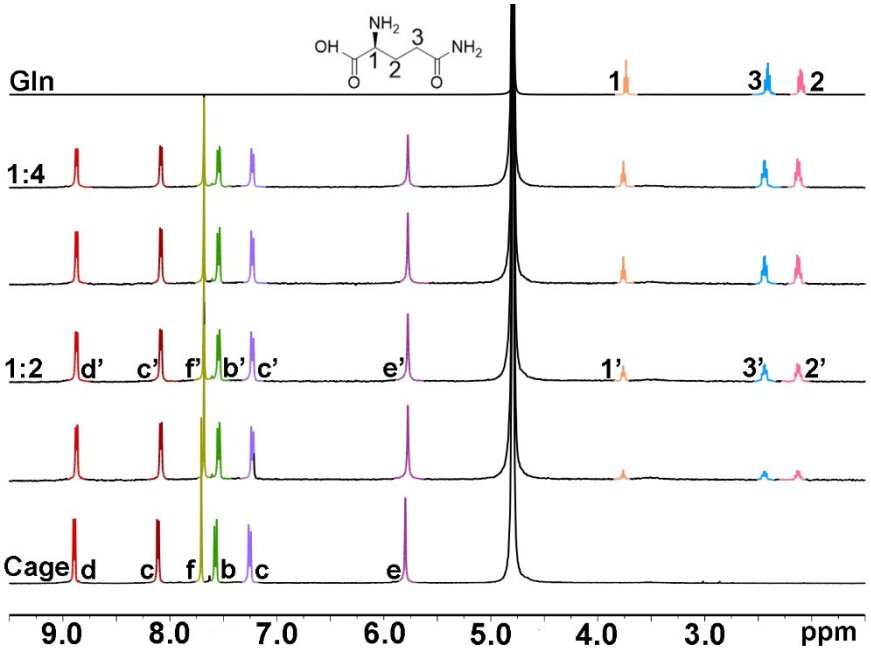

Figure S35. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Gln (0 – 4.0 equiv).

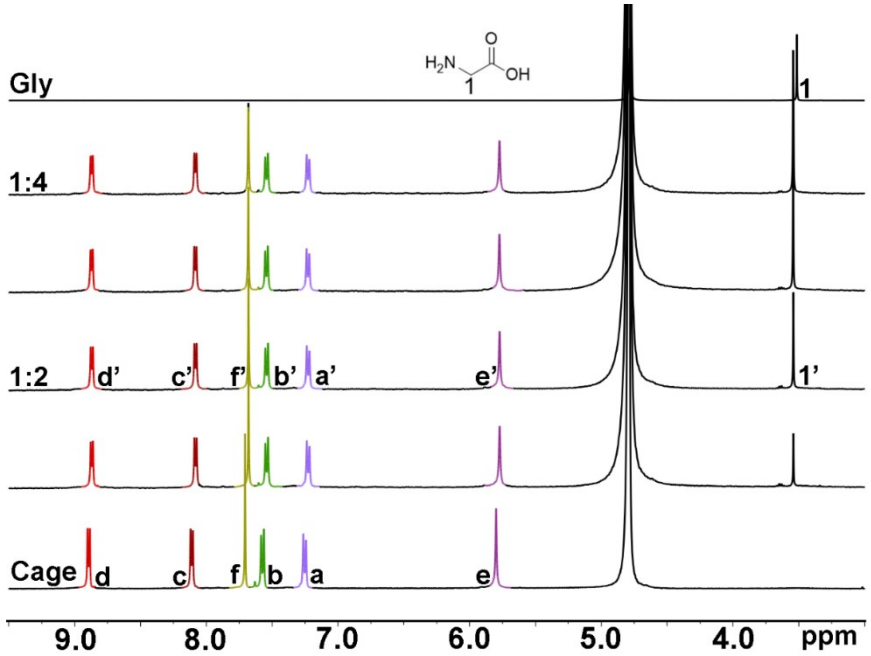

Figure S36. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with Gly (0 – 4.0 equiv).

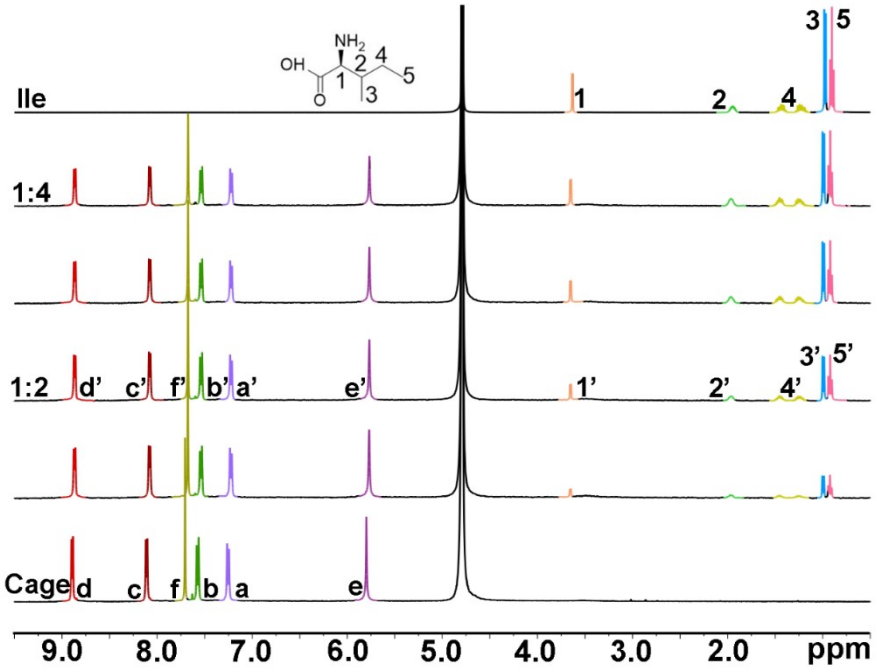

Figure S37. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Ile (0 – 4.0 equiv).

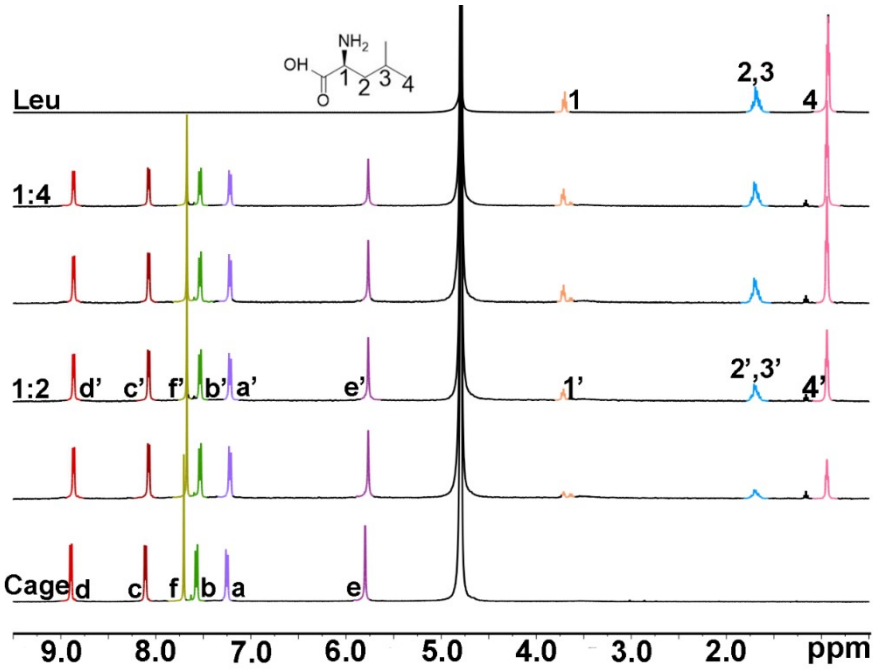

Figure S38. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Leu (0 – 4.0 equiv).

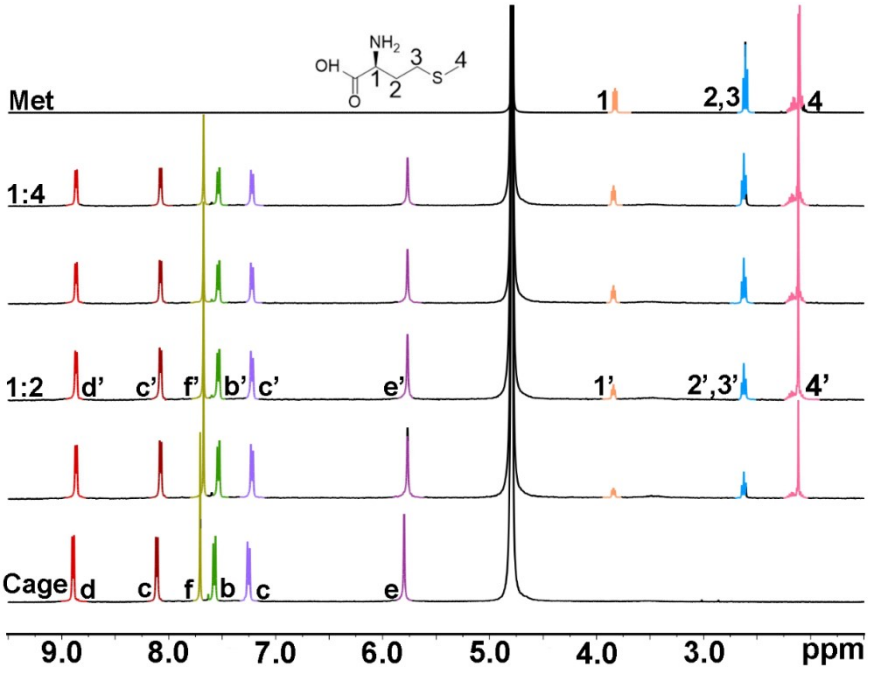

Figure S39. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Met (0 – 4.0 equiv).

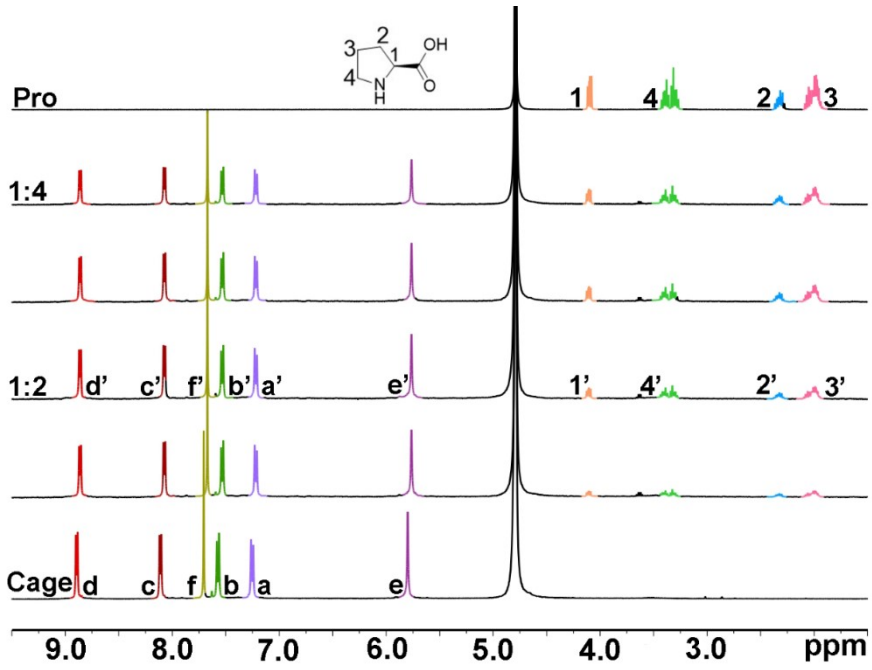

Figure S40. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Pro (0 – 4.0 equiv).

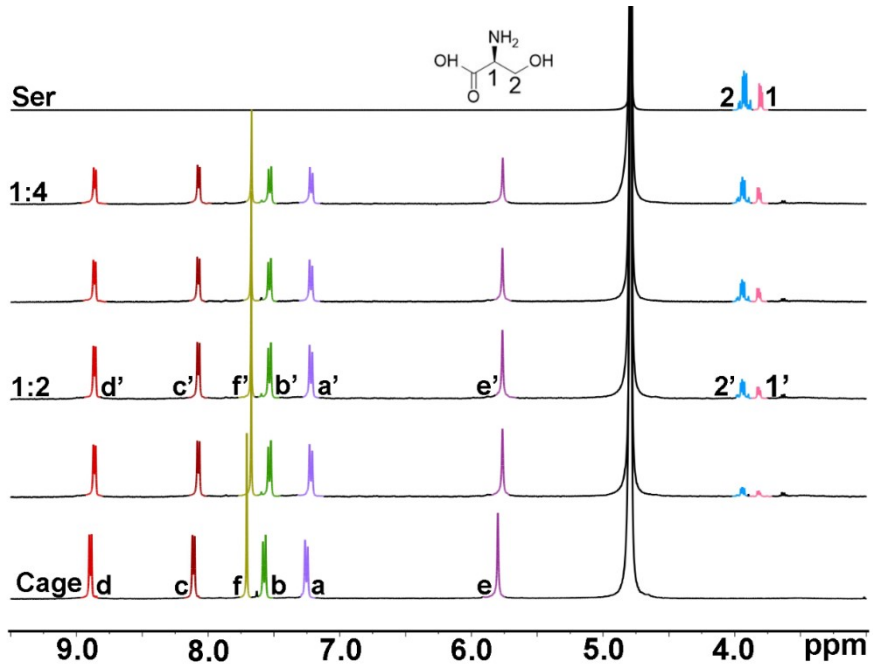

Figure S41. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Ser (0 – 4.0 equiv).

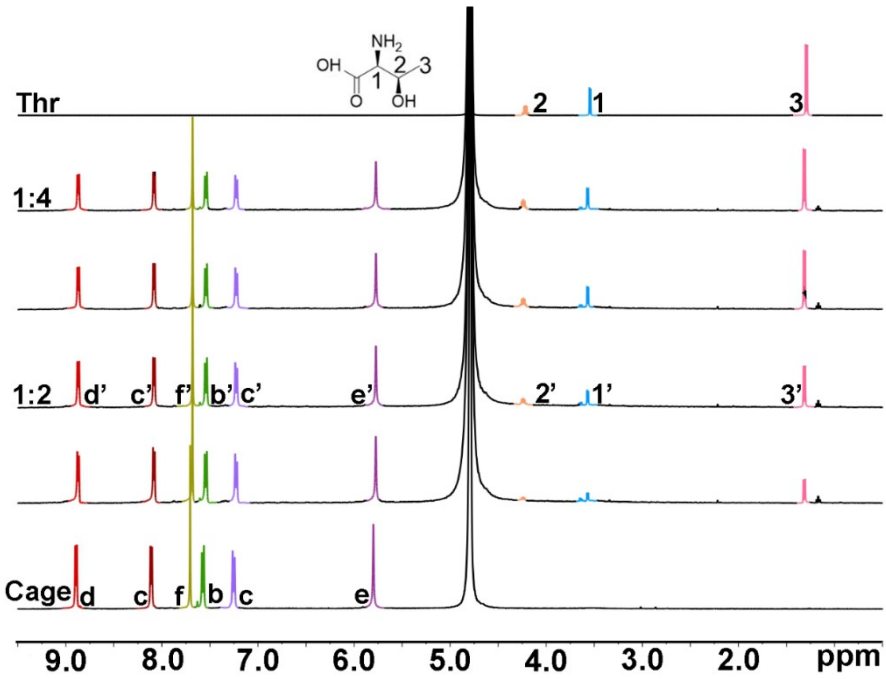

Figure S42. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Thr (0 – 4.0 equiv).

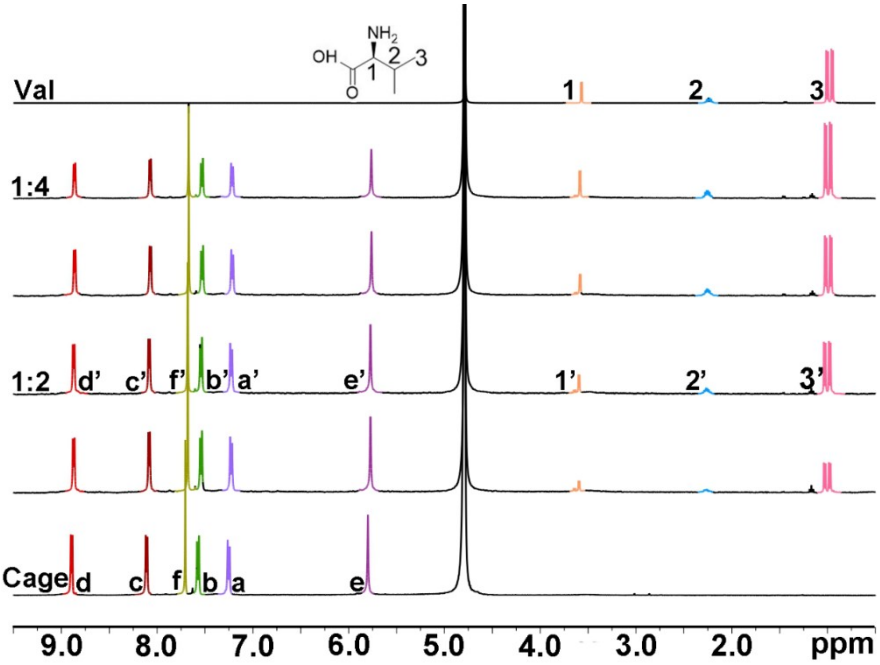

Figure S43. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-Val (0 – 4.0 equiv).

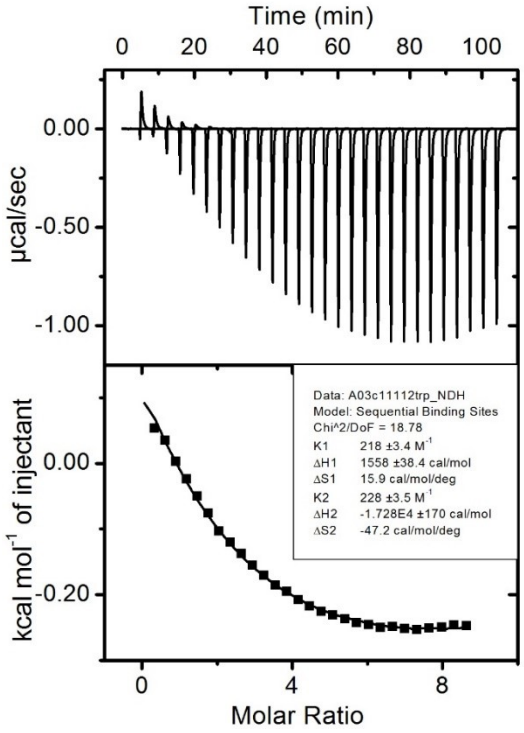

Figure S44. ITC of **1** (0.30 mM) with *L*-Trp (12.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

3. Recognition of Dipeptides

3.1 NMR, UV-vis, and ITC experiments

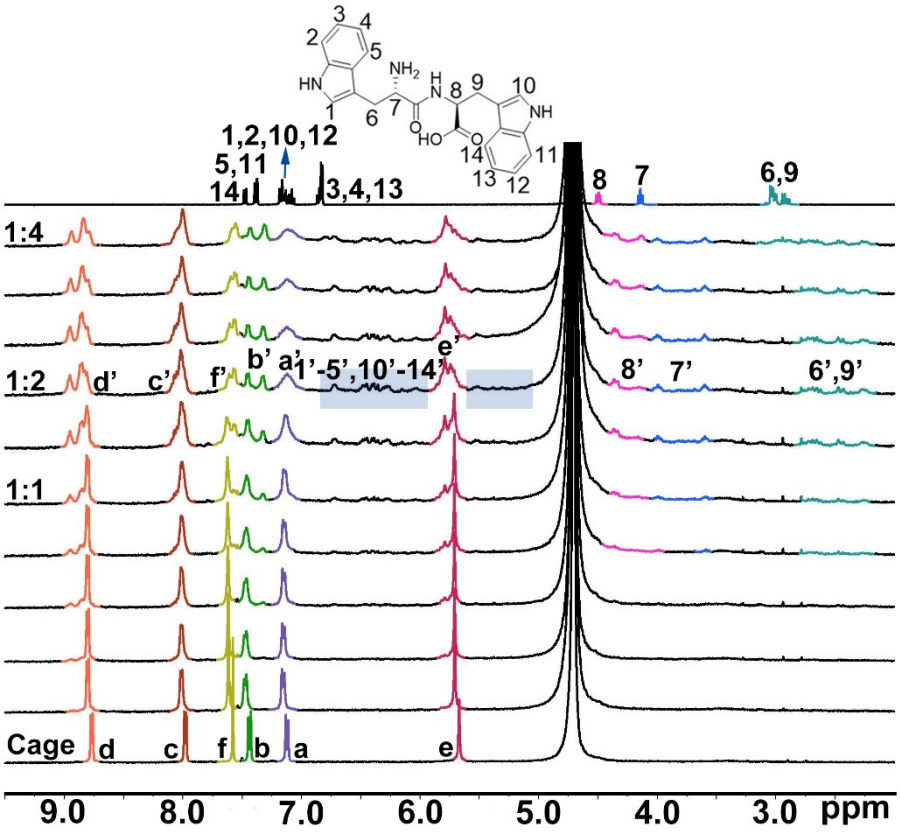

Figure S45. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-TrpTrp (0 – 4.0 equiv).

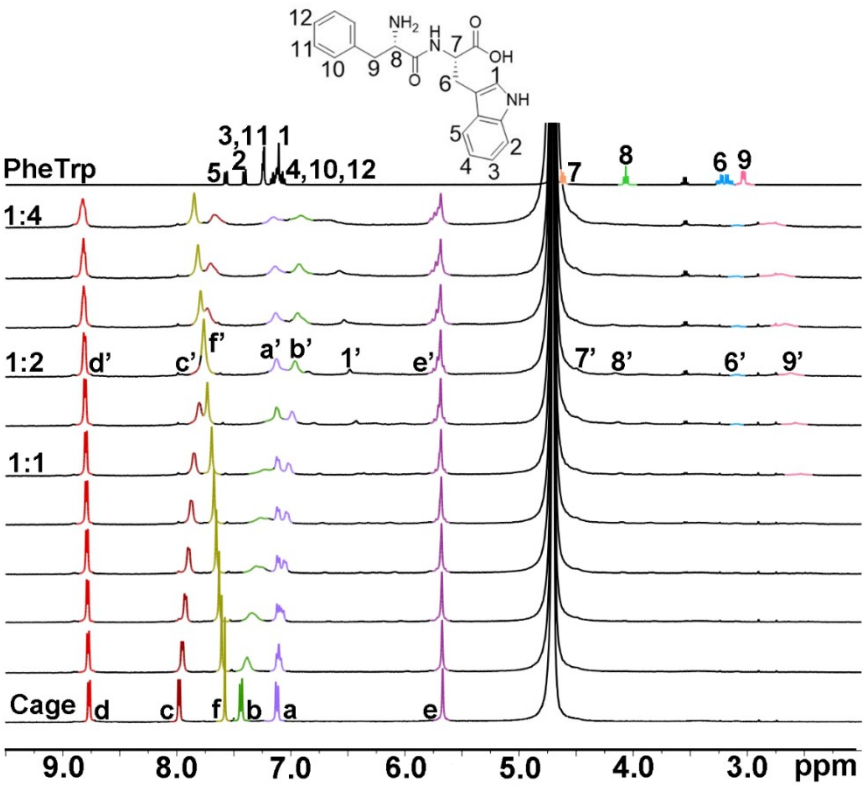

Figure S46. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-PheTrp (0 – 4.0 equiv).

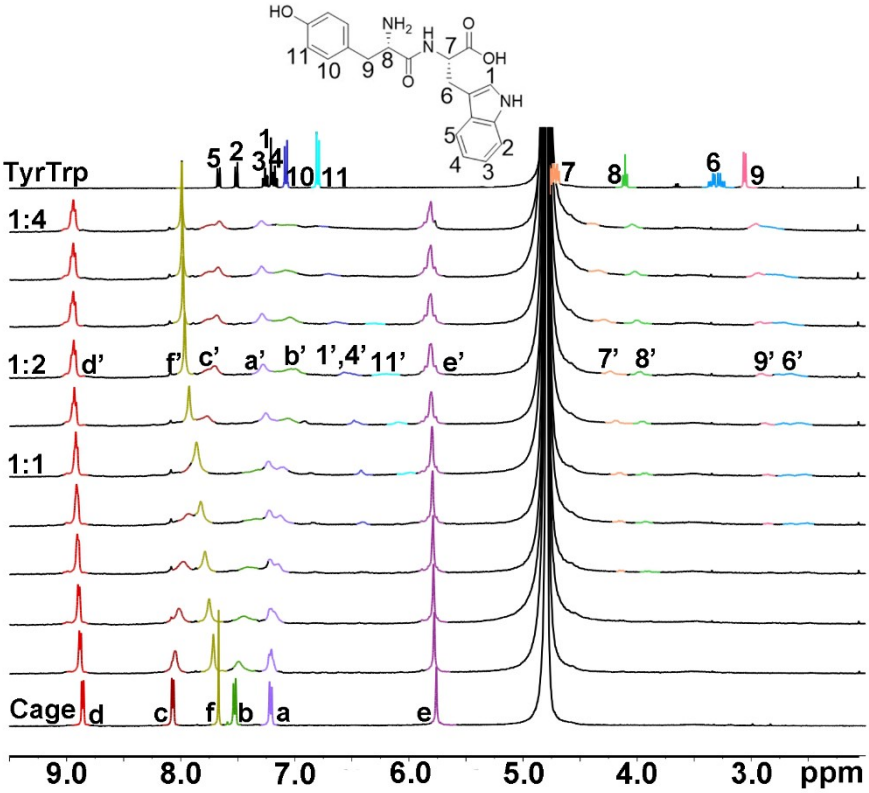

Figure S47. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-TyrTrp (0 – 4.0 equiv).

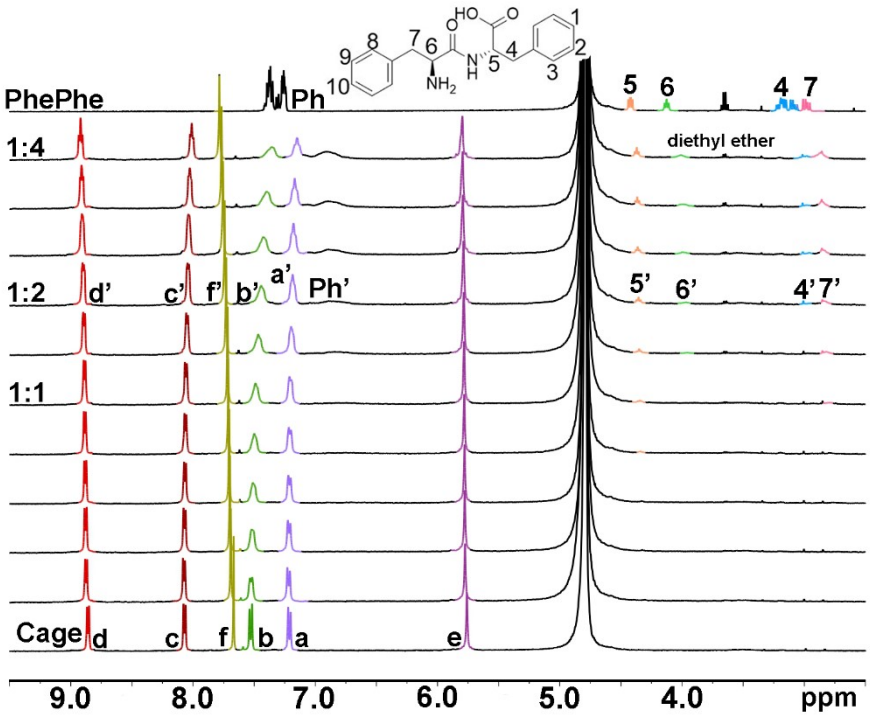

Figure S48. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-PhePhe (0 – 4.0 equiv).

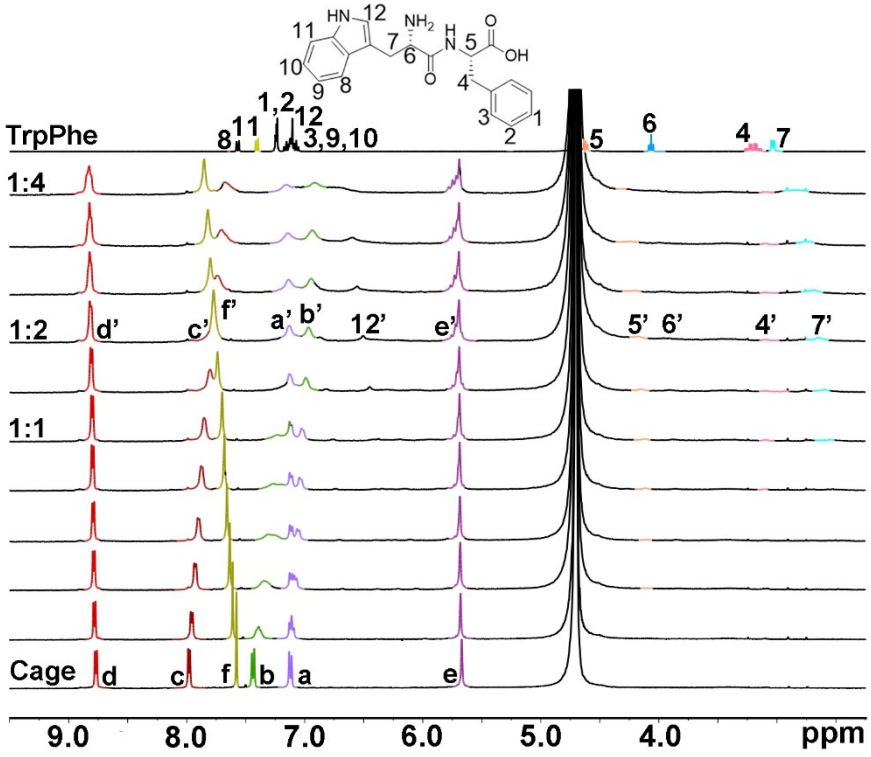

Figure S49. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-TrpPhe (0 – 4.0 equiv).

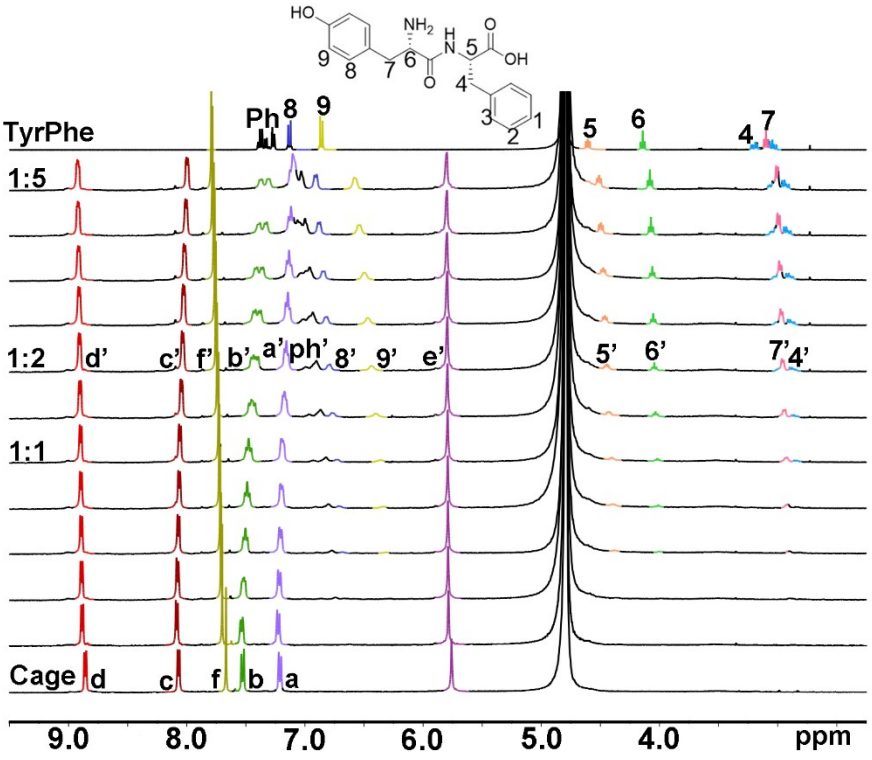

Figure S50. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-TyrPhe (0 – 5.0 equiv).

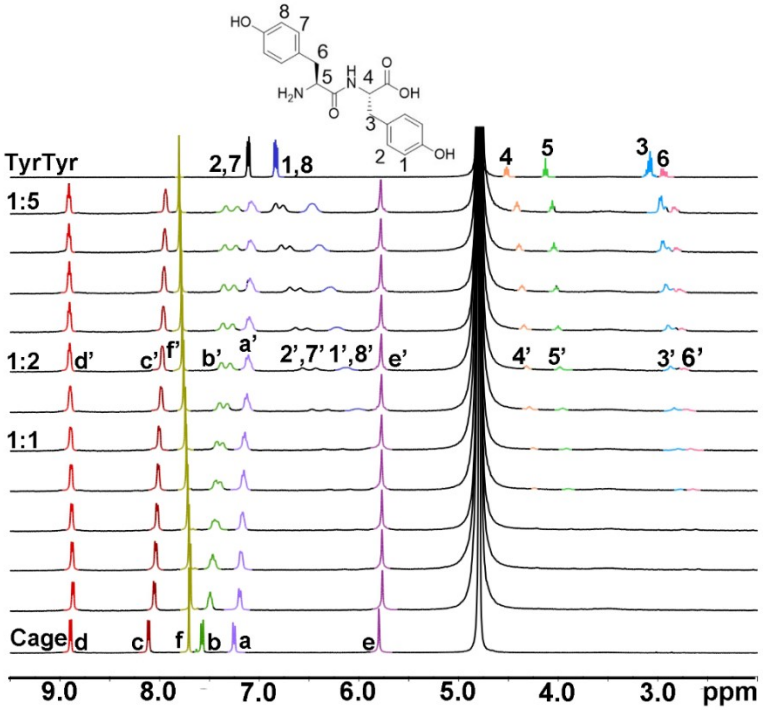

Figure S51. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-TyrTyr (0 – 5.0 equiv).

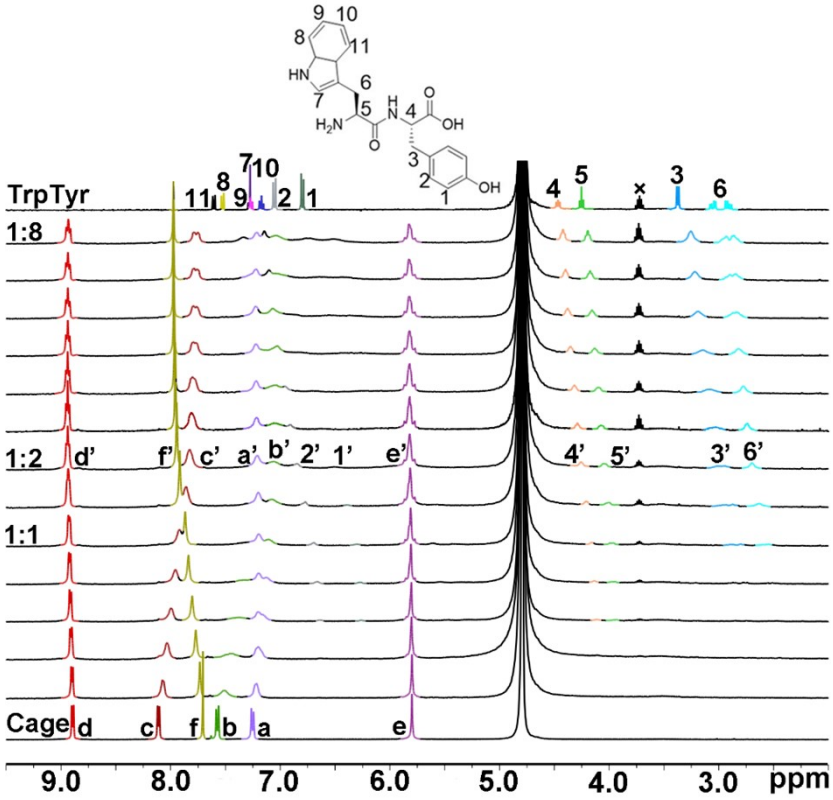

Figure S52. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-TrpTyr (0 – 8.0 equiv).

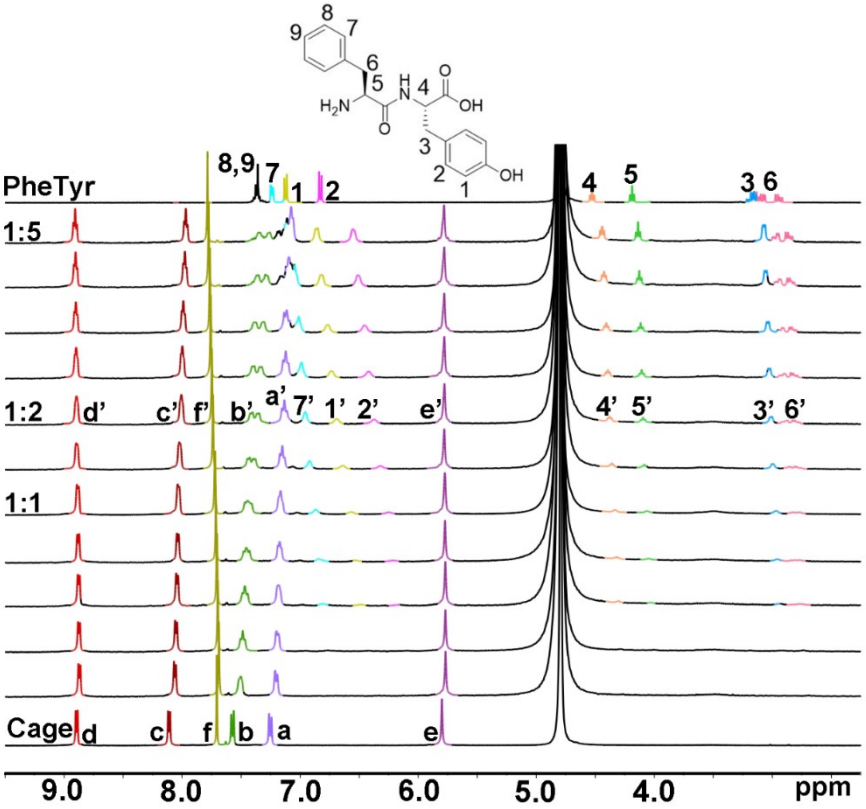

Figure S53. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with *L*-PheTyr (0 – 5.0 equiv).

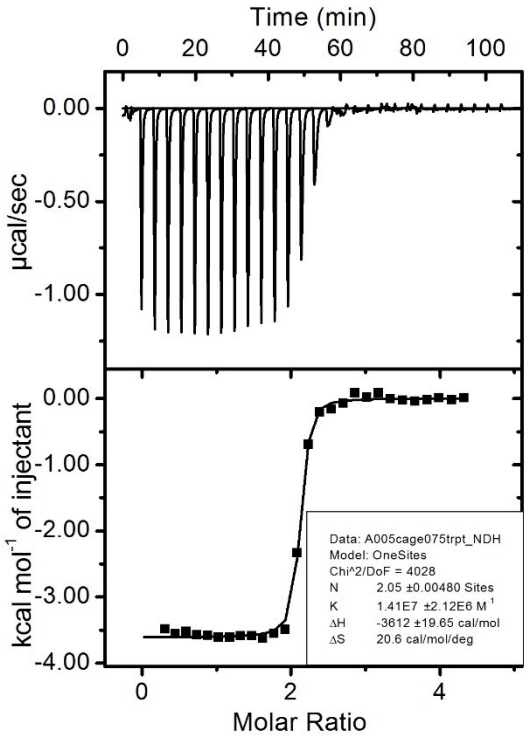

Figure S54. ITC of **1** (50 µM) with *D*-TrpTrp (1.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

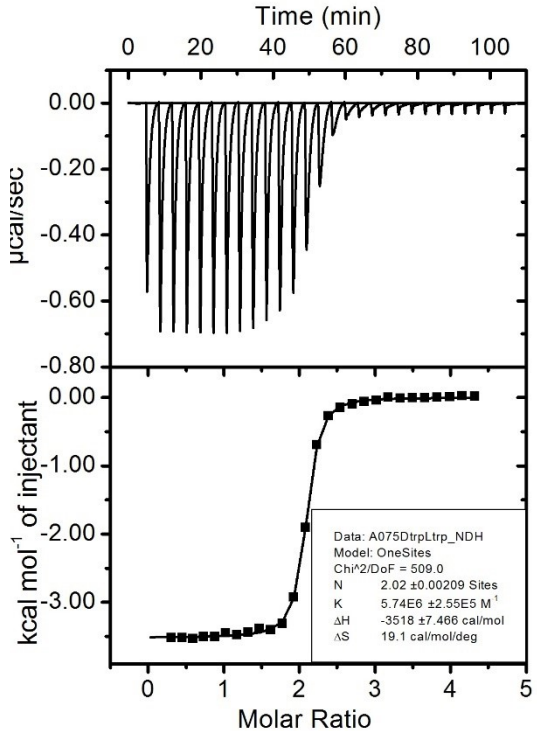

Figure S55. ITC of **1** (50 µM) with *D*-Trp-*L*-Trp (1.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

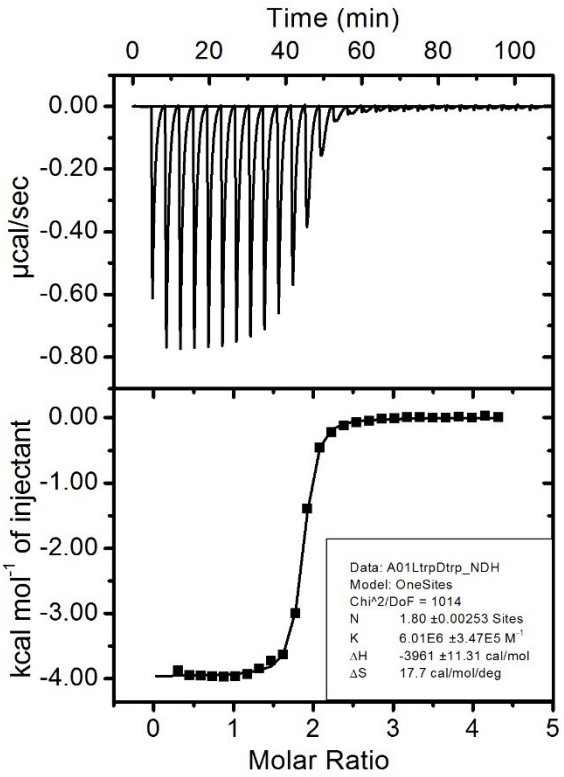

Figure S56. ITC of **1** (50 µM) with *L*-Trp-*D*-Trp (1.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

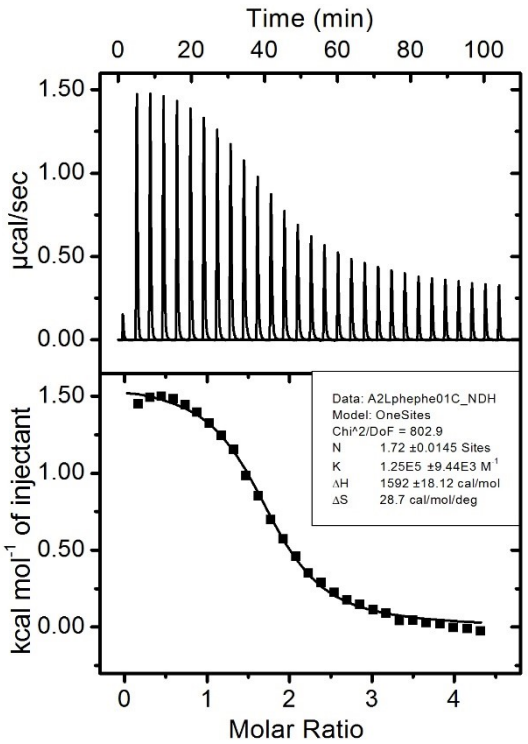

Figure S57. ITC of **1** (0.10 mM) with *L*-PhePhe (2.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

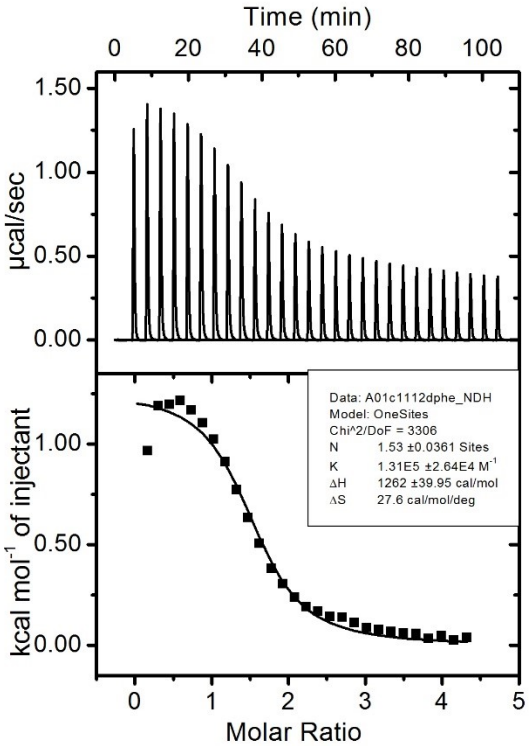

Figure S58. ITC of **1** (0.10 mM) with *D*-PhePhe (2.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

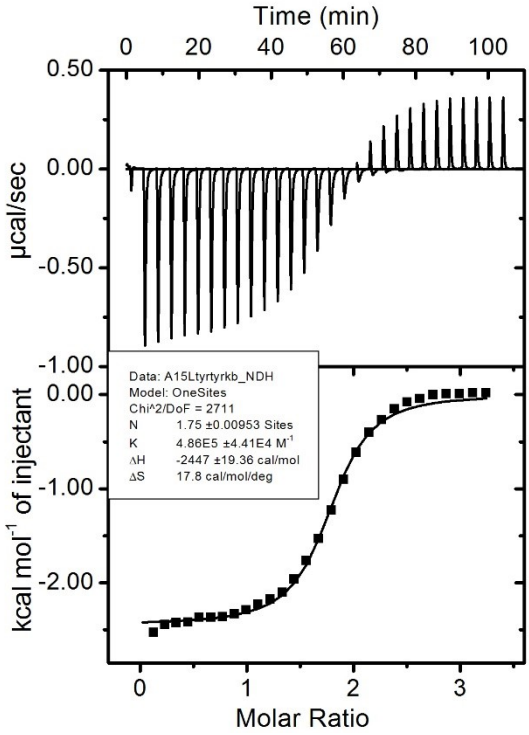

Figure S59. ITC of **1** (0.10 mM) with *L*-TyrTyr (1.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

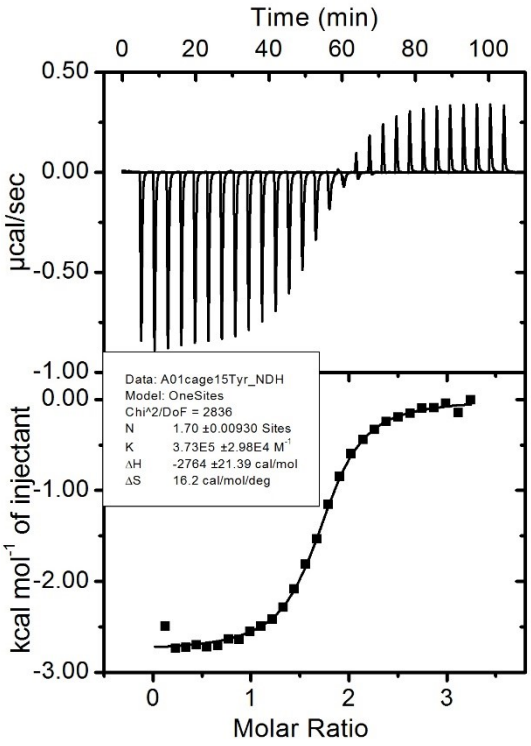

Figure S60. ITC of **1** (0.10 mM) with *D*-TyrTyr (1.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

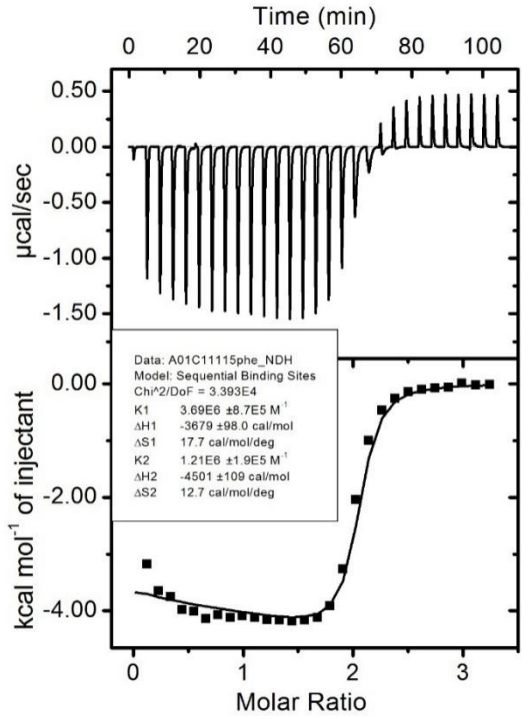

Figure S61. ITC of **1** (0.10 mM) with *L*-PheTrp (1.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

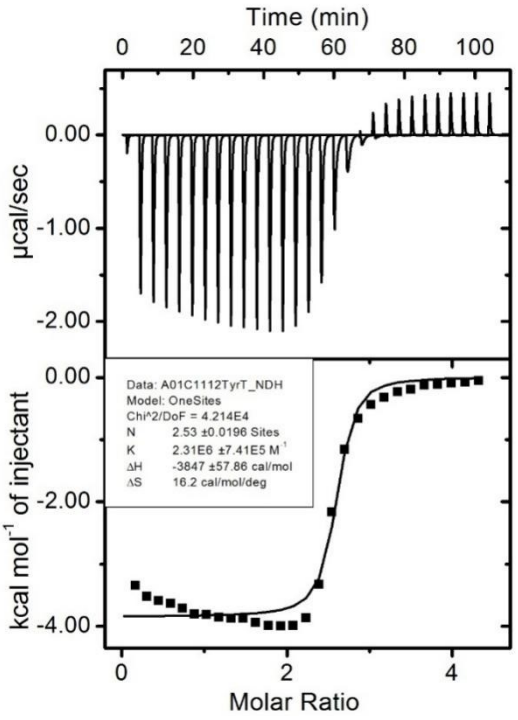

Figure S62. ITC of **1** (0.10 mM) with *L*-TyrTrp (2.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

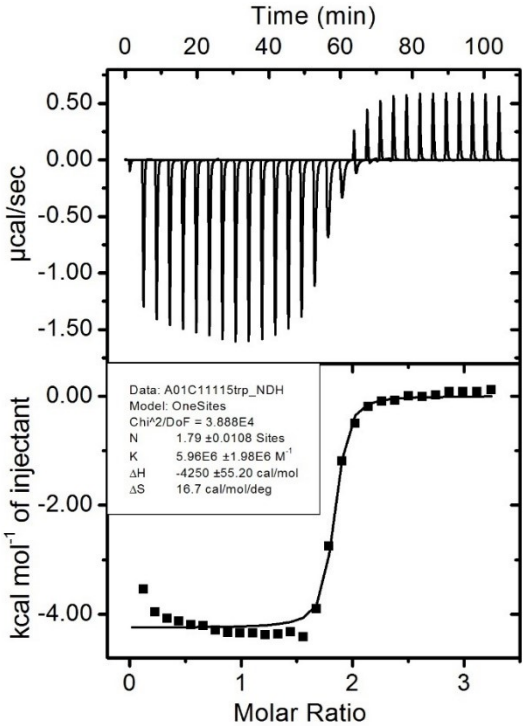

Figure S63. ITC of **1** (0.10 mM) with *L*-TrpPhe (1.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

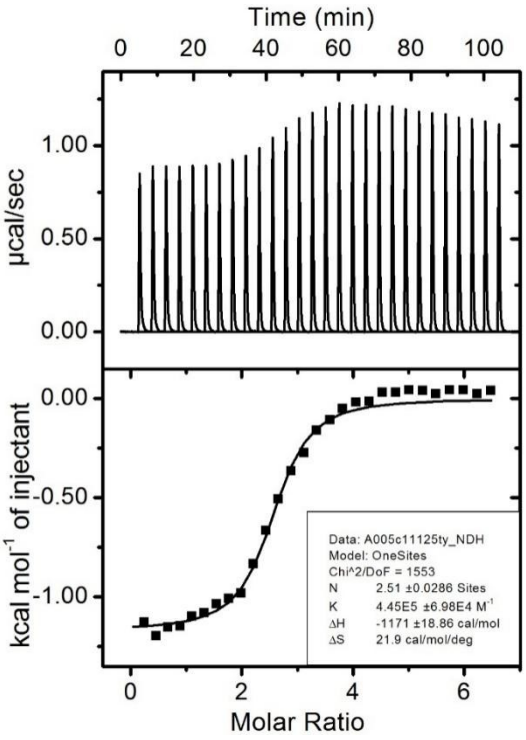

Figure S64. ITC of **1** (50 µM) with *L*-TyrPhe (1.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

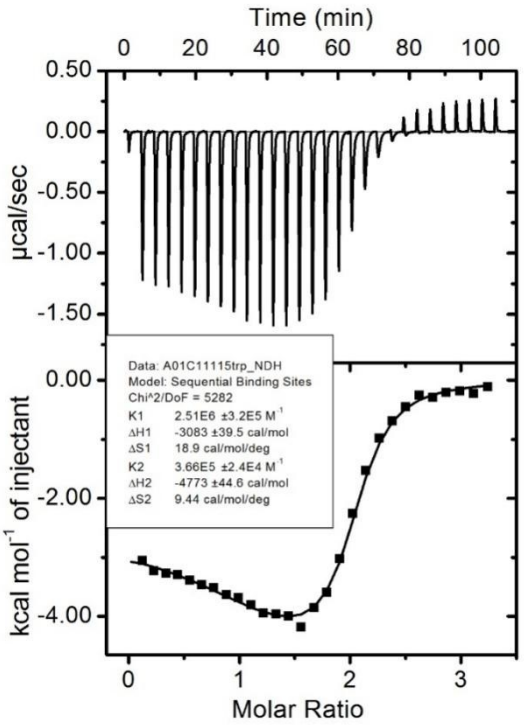

Figure S65. ITC of **1** (0.10 mM) with *L*-TrpTyr (1.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

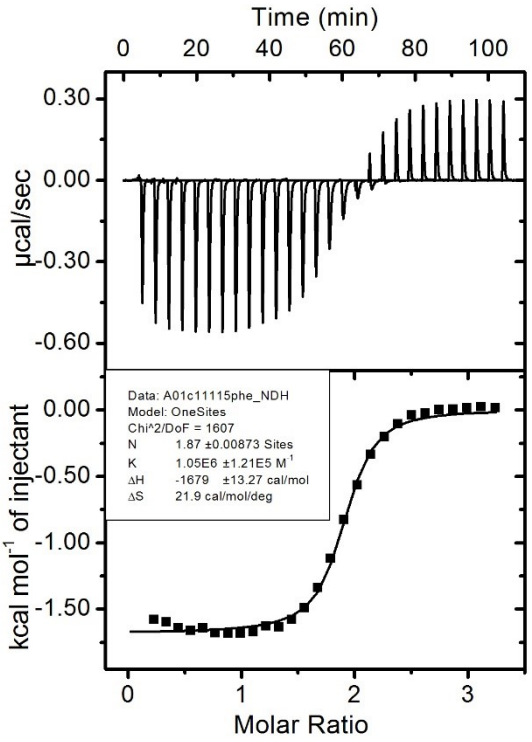

Figure S66. ITC of **1** (0.10 mM) with *L*-PheTyr (1.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

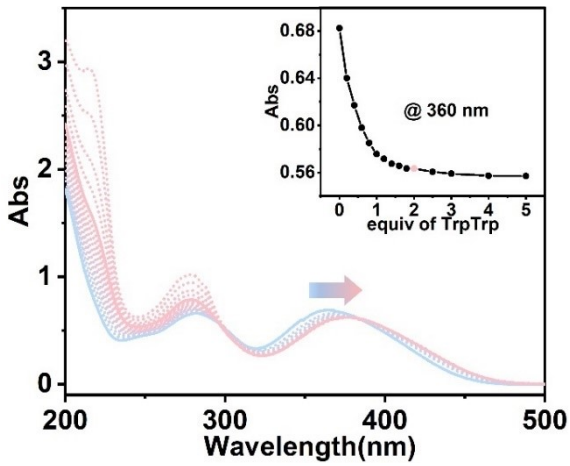

Figure S67. UV/vis titration of **1** (10 µM) with *L*-TrpTrp in water. Insert: Plots of Abs vs the equiv of *L*-TrpTrp.

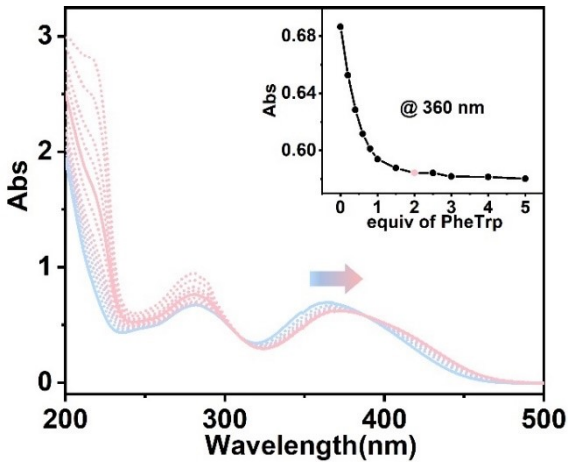

Figure S68. UV/vis titration of **1** (10 μM) with *L*-PheTrp in water. Insert: Plots of Abs vs the equiv of *L*-PheTrp.

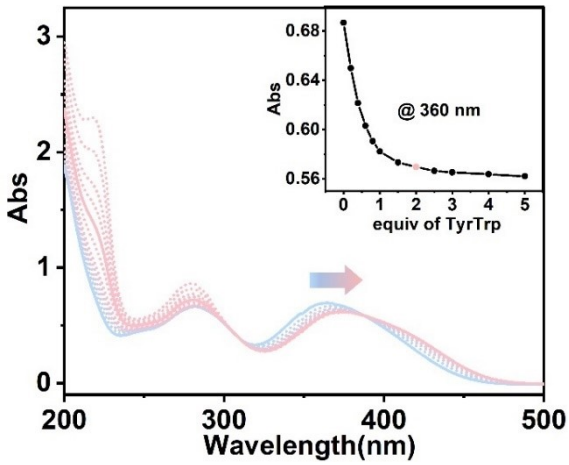

Figure S69. UV/vis titration of **1** (10 μM) with *L*-TyrTrp in water. Insert: Plots of Abs vs the equiv of *L*-TyrTrp.

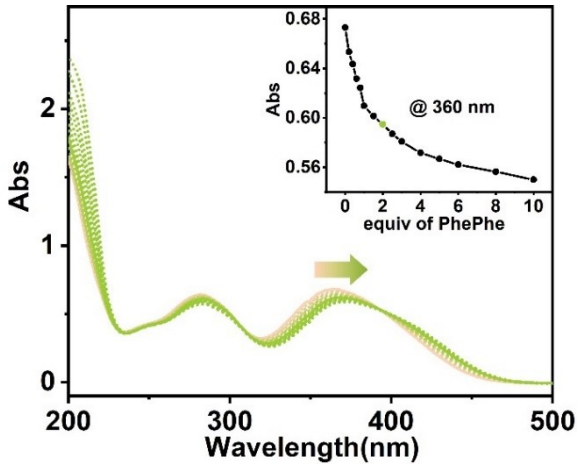

Figure S70. UV/vis titration of **1** (10 μM) with *L*-PhePhe in water. Insert: Plots of Abs vs the equiv of *L*-PhePhe.

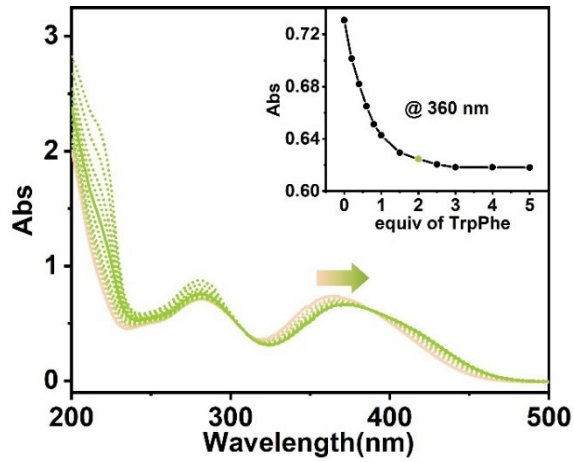

Figure S71. UV/vis titration of **1** (10 μM) with *L*-TrpPhe in water. Insert: Plots of Abs vs the equiv of *L*-TrpPhe.

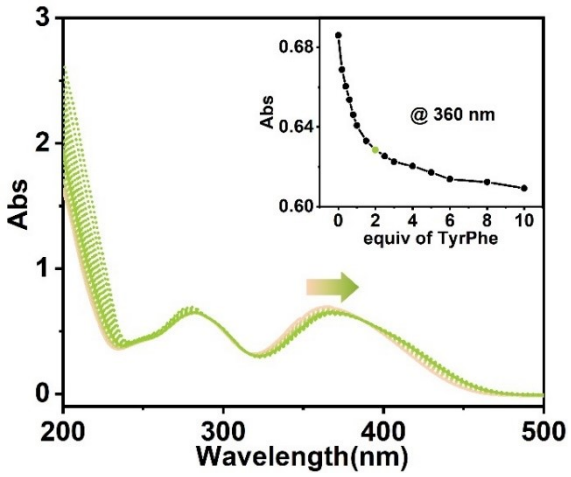

Figure S72. UV/vis titration of **1** (10 μM) with *L*-TyrPhe in water. Insert: Plots of Abs vs the equiv of *L*-TyrPhe.

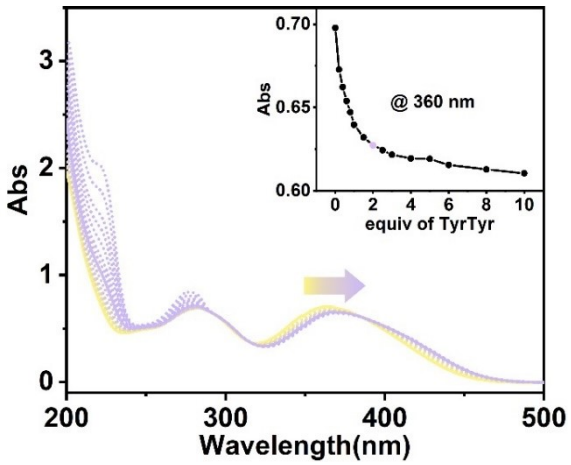

Figure S73. UV/vis titration of **1** (10 μM) with *L*-TyrTyr in water. Insert: Plots of Abs vs the equiv of *L*-TyrTyr.

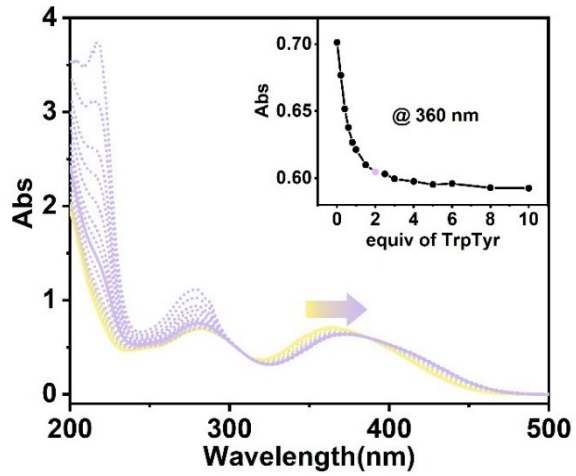

Figure S74. UV/vis titration of **1** (10 μM) with *L*-TrpTyr in water. Insert: Plots of Abs vs the equiv of *L*-TrpTyr.

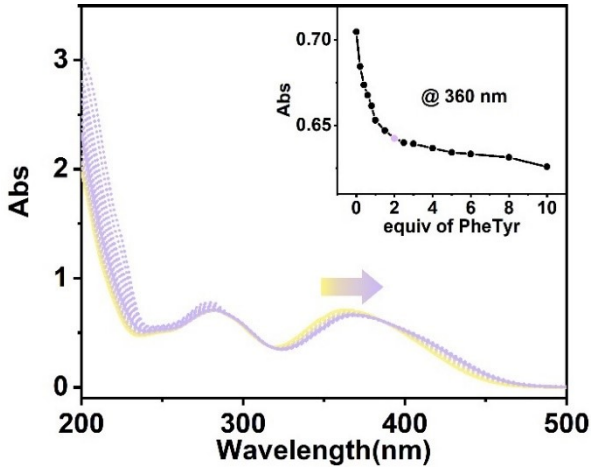

Figure S75. UV/vis titration of **1** (10 μM) with *L*-PheTyr in water. Insert: Plots of Abs vs the equiv of *L*-PheTyr.

3.2 DFT calculated structures of 1⊃(*L*-PhePhe)$_2$

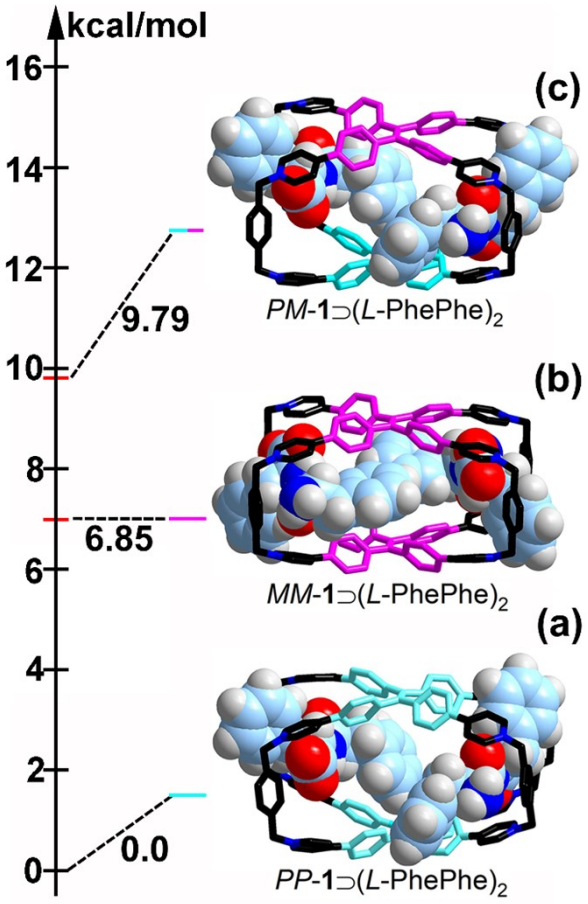

Figure S76. DFT calculated structures of a) *PP*-**1**⊃(*L*-PhePhe)$_2$, b) *MM*-**1**⊃(*L*-PhePhe)$_2$ and c) *PM*-**1**⊃(*L*-PhePhe)$_2$. The geometries of the host-guest complexes were optimized by B3LYP-D3 (the hybrid functionals B3LYP augmented with dispersion correction) with 6-31G(d) basis set, and the energies were corrected using the solvation model density (SMD) method at M06-2x/def2-SVP level.

3.3 Circular dichroism, fluorescence, and circularly polarized luminescence experiments

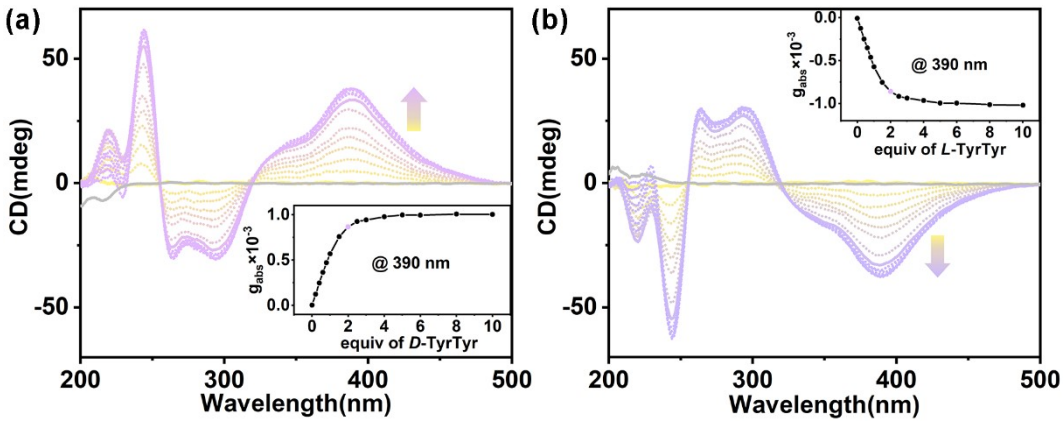

Figure S77. CD titration of **1** (20 μM) with a) *D*-TyrTyr and b) *L*-TyrTyr (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Inset: Plots of g_{abs} vs the equiv of *D*/*L*-TyrTyr.

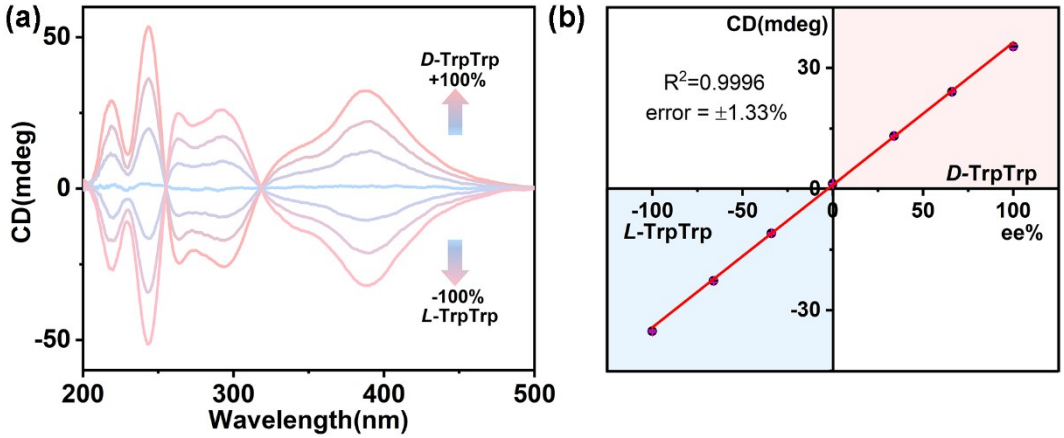

Figure S78. a) CD spectra of **1** (20 μM) in the presence of *D*/*L*-TrpTrp (40 μM) with *ee* ranging from -100% to +100%. b) The calibration curve obtained for the CD signals (390 nm) upon varying *ee* values of *D*/*L*-TrpTrp.

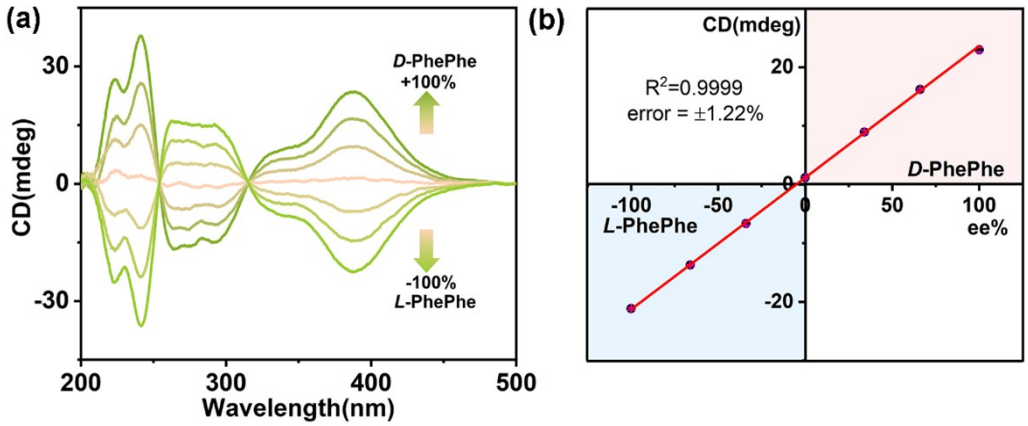

Figure S79. a) CD spectra of **1** (20 μM) in the presence of *D*/*L*-PhePhe (40 μM) with *ee* ranging from -100% to +100%. b) The calibration curve obtained for the CD signals (390 nm) upon varying *ee* values of *D*/*L*-PhePhe.

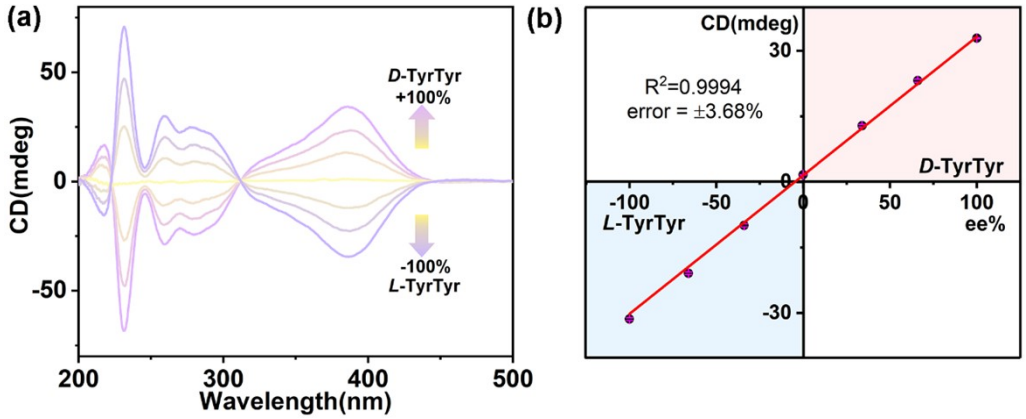

Figure S80. a) CD spectra of **1** (20 μM) in the presence of *D*/*L*-TyrTyr (40 μM) with *ee* ranging from -100% to +100%. b) The calibration curve obtained for the CD signals (390 nm) upon varying *ee* values of *D*/*L*-TyrTyr.

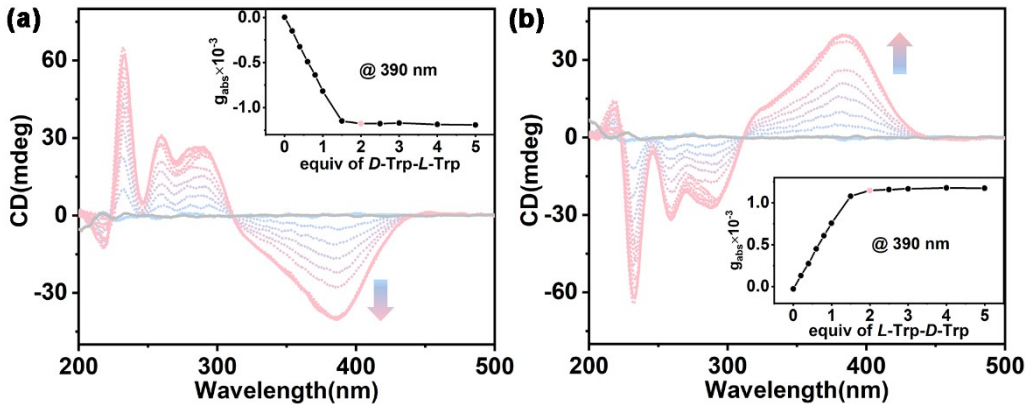

Figure S81. CD titration of **1** (20 μM) with a) *D*-Trp-*L*-Trp and b) *L*-Trp-*D*-Trp (0 – 5.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Inset: Plots of g_{abs} vs the equiv of *D*-Trp-*L*-Trp or *L*-Trp-*D*-Trp.

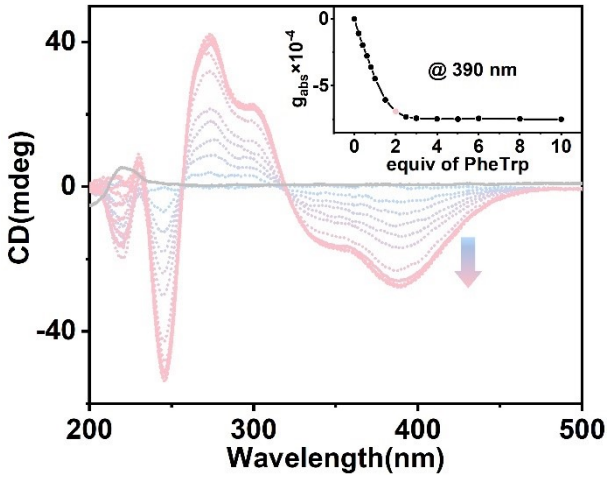

Figure S82. CD titration of **1** (20 μM) with *L*-PheTrp in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of *L*-PheTrp.

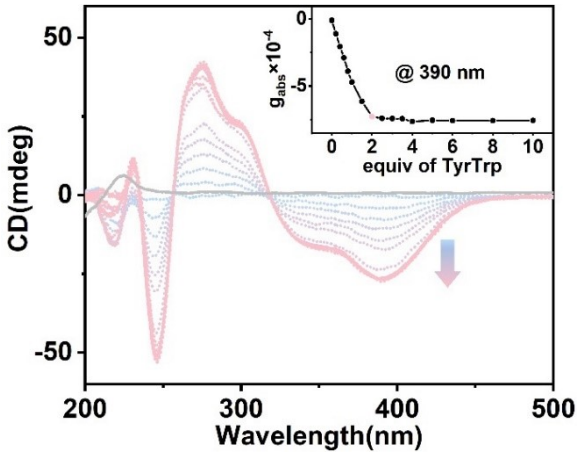

Figure S83. CD titration of **1** (20 μM) with *L*-TyrTrp in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of *L*-TyrTrp.

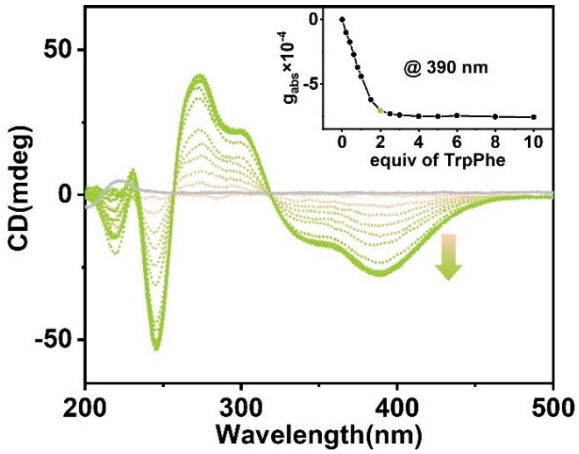

Figure S84. CD titration of **1** (20 μM) with *L*-TrpPhe in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of *L*-TrpPhe.

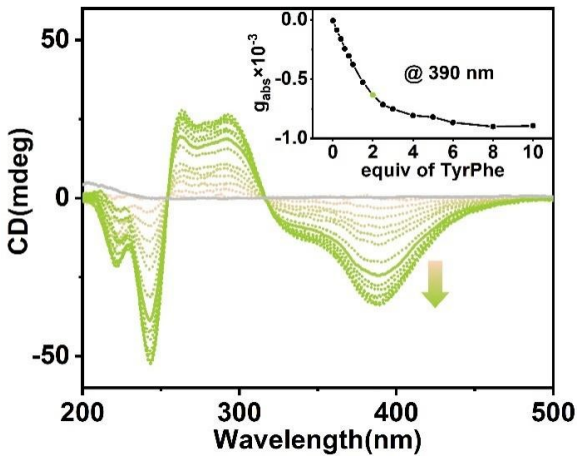

Figure S85. CD titration of **1** (20 μM) with *L*-TyrPhe in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of *L*-TyrPhe.

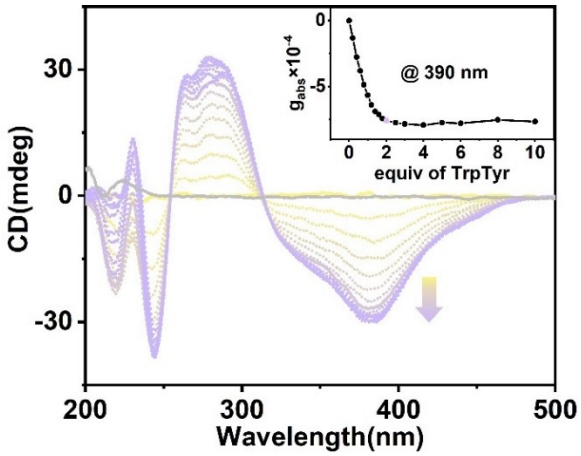

Figure S86. CD titration of **1** (20 μM) with *L*-TrpTyr in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of *L*-TrpTyr.

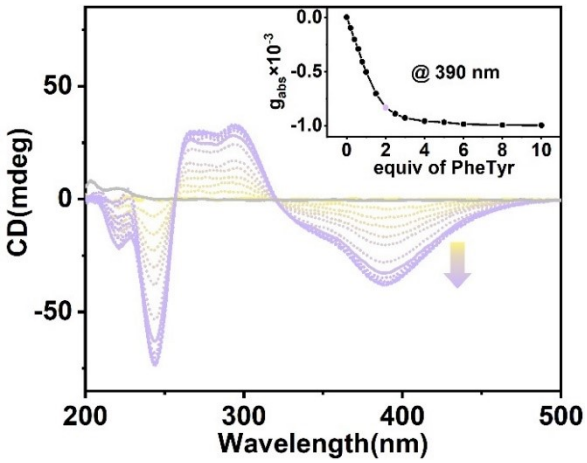

Figure S87. CD titration of **1** (20 μM) with *L*-PheTyr in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of *L*-PheTyr.

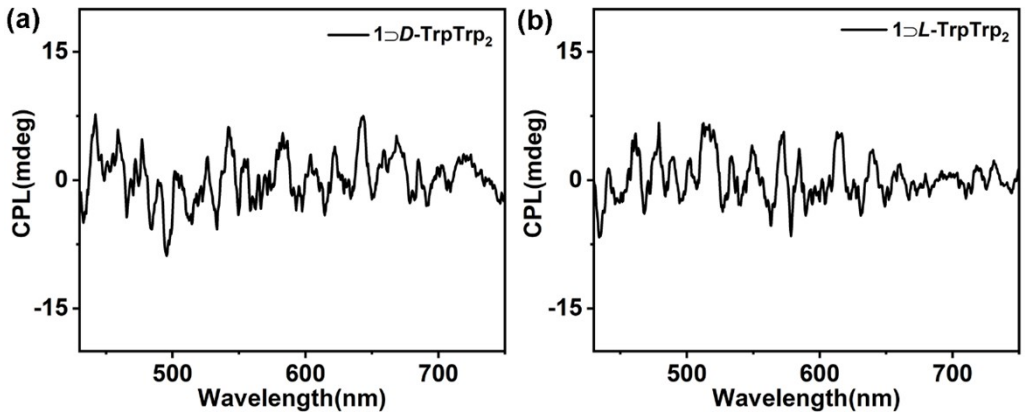

Figure S88. CPL spectra of **1** (20 μM) with *D*/*L*-TrpTrp (40 μM,) in phosphate buffer (10 mM, pH = 7.4). λ_{ex} = 320 nm, E_x/E_m slit = 3000 μm.

4. Recognition of Tetrapeptides

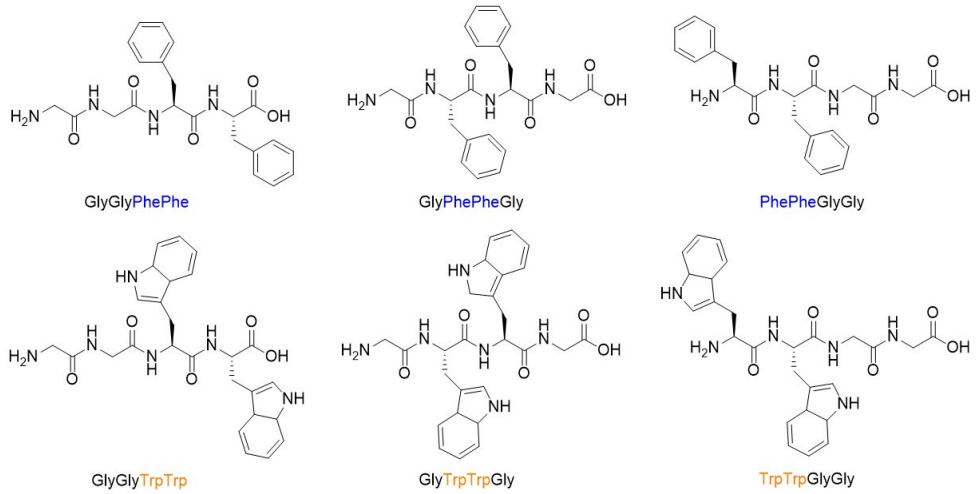

Figure S89. Chemical structures of tetrapeptides.

4.1 NMR and ITC experiments

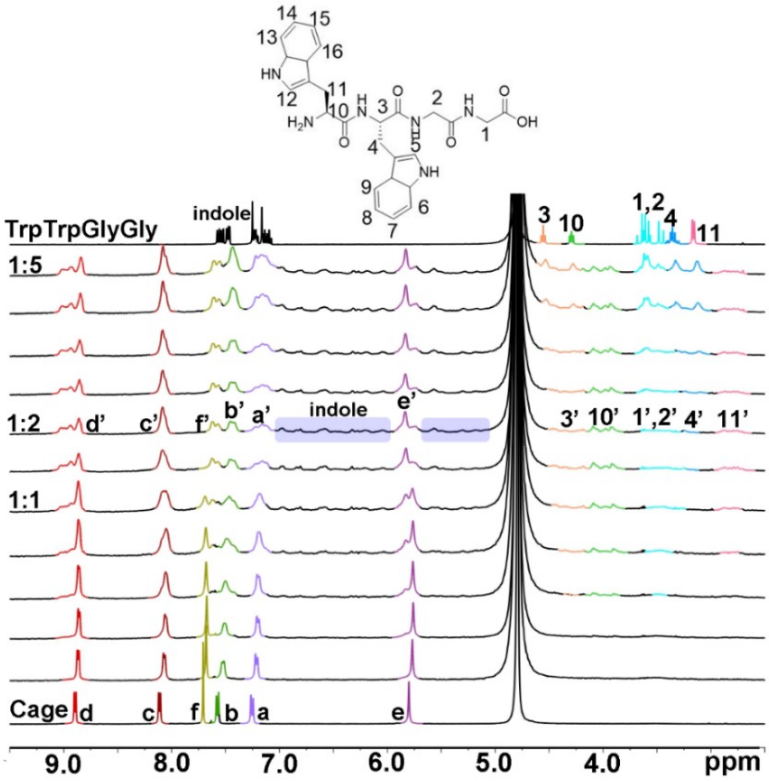

Figure S90. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with TrpTrpGlyGly (0 – 5.0 equiv).

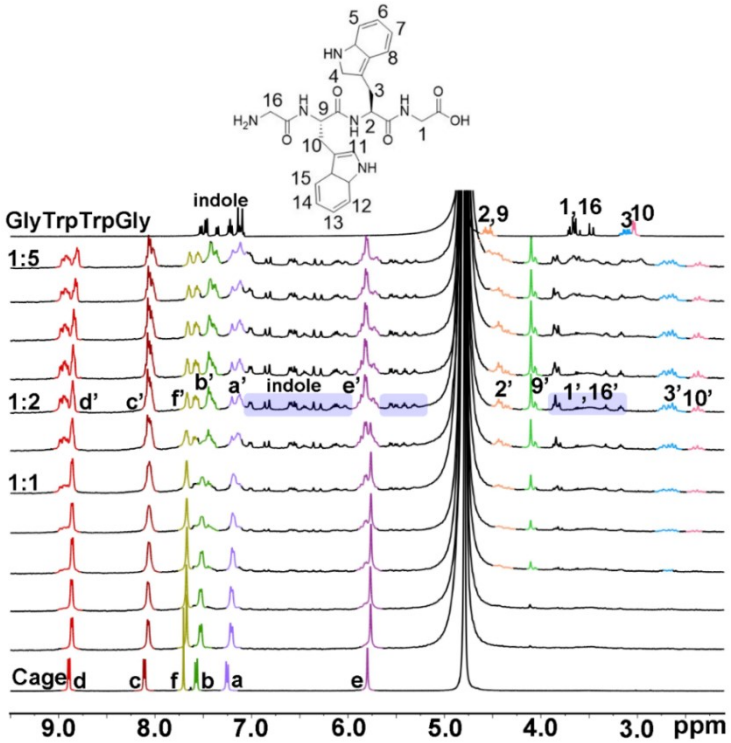

Figure S91. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with

GlyTrpTrpGly (0 – 5.0 equiv).

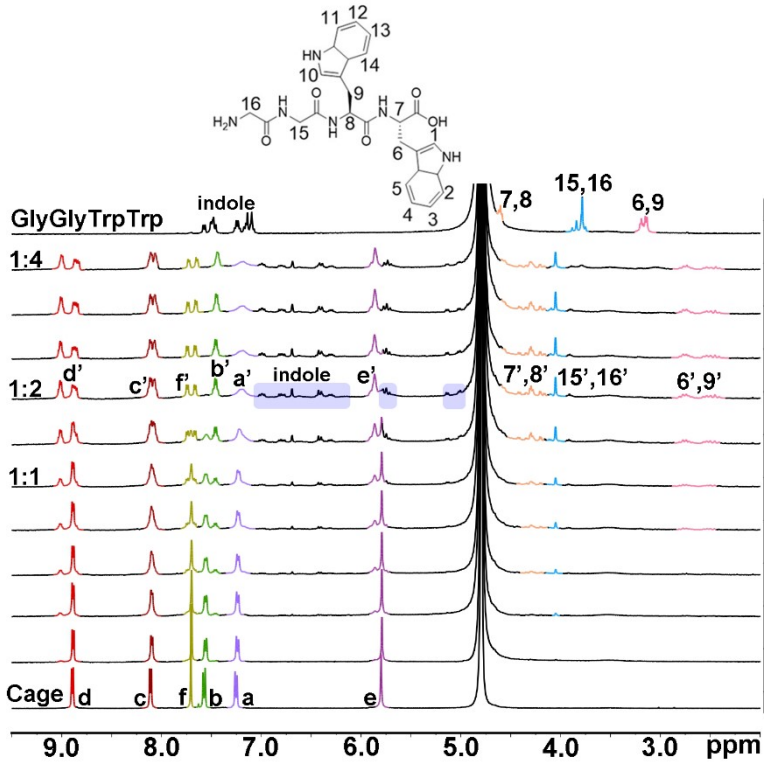

Figure S92. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with GlyGlyTrpTrp (0 – 4.0 equiv).

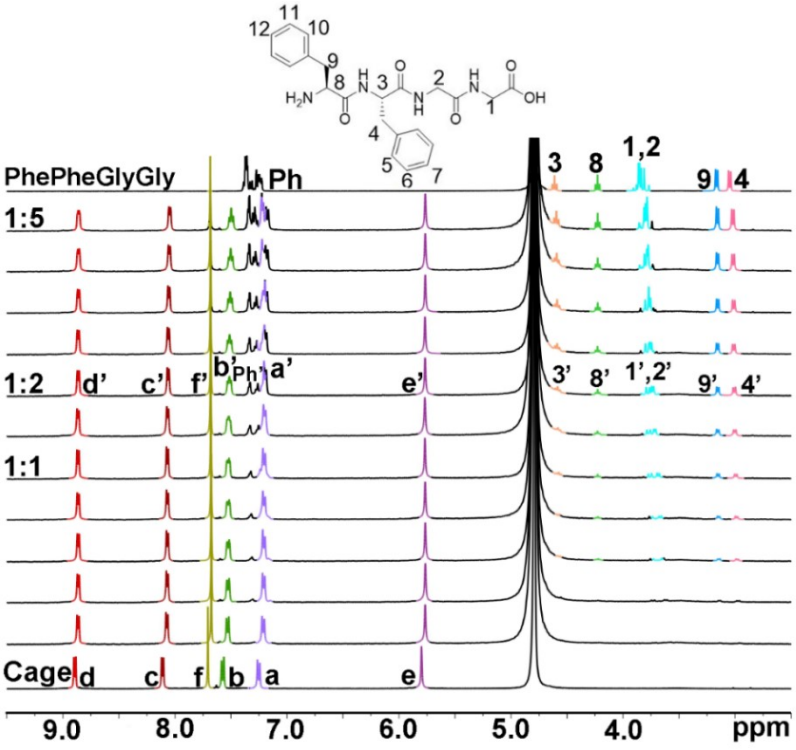

Figure S93. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with

PhePheGlyGly (0 – 5.0 equiv).

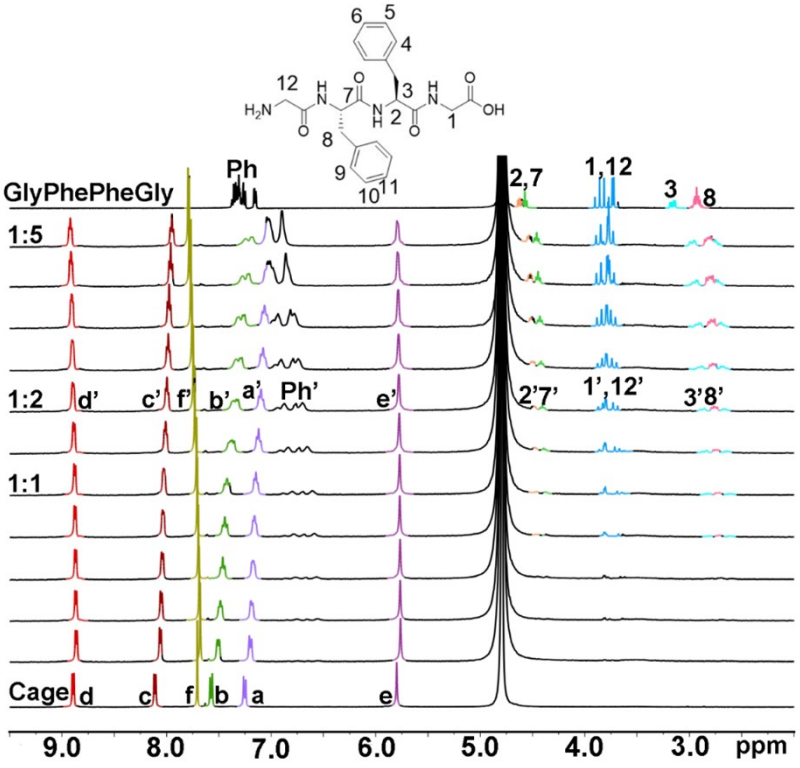

Figure S94. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with GlyPhePheGly (0 – 5.0 equiv).

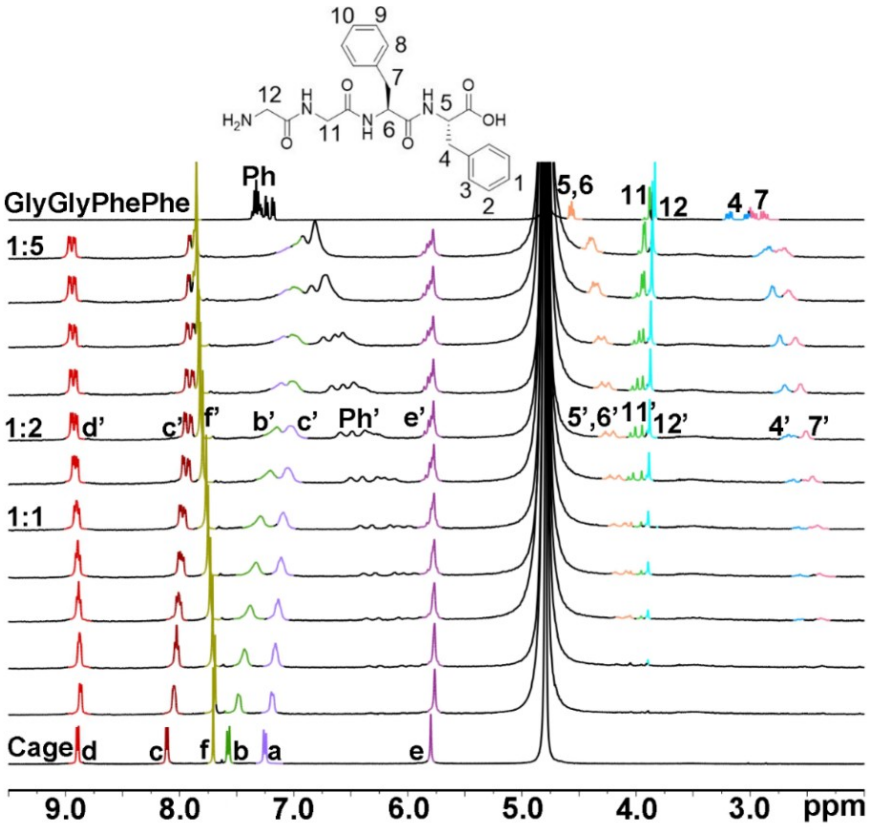

Figure S95. ^{1}H NMR titration (400 MHz, 298 K, D_2O) of **1** (0.40 mM) with

GlyGlyPhePhe (0 – 5.0 equiv).

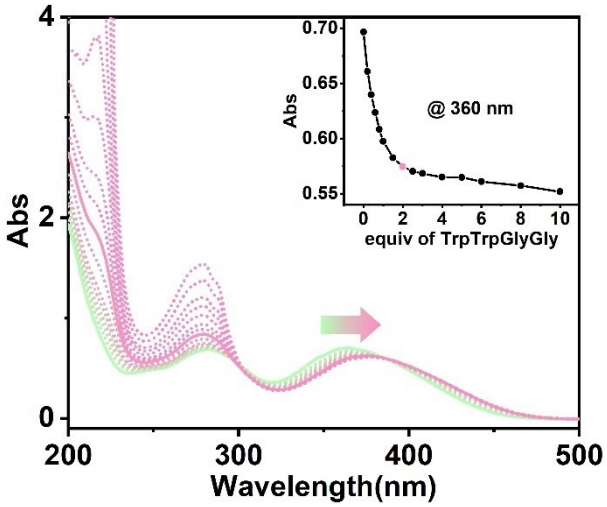

Figure S96. UV/vis titration of **1** (10 μM) with TrpTrpGlyGly (0 – 10.0 equiv) in water. Insert: Plots of Abs vs the equiv of TrpTrpGlyGly.

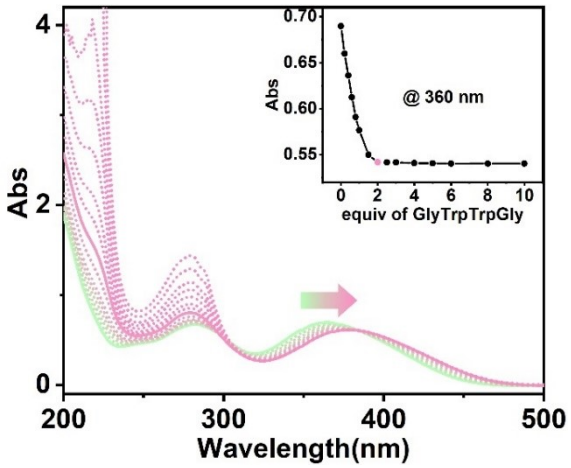

Figure S97. UV/vis titration of **1** (10 μM) with GlyTrpTrpGly (0 – 10.0 equiv) in water. Insert: Plots of Abs vs the equiv of GlyTrpTrpGly.

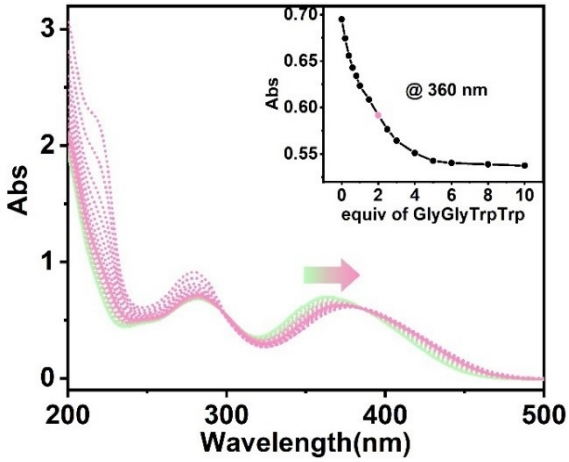

Figure S98. UV/vis titration of **1** (10 μM) with GlyGlyTrpTr**p** (0 – 10.0 equiv)in water. Insert: Plots of Abs vs the equiv of GlyGlyTrpTrp.

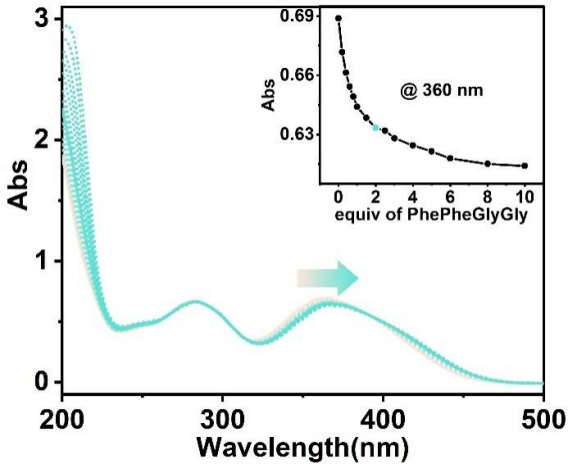

Figure S99. UV/vis titration of **1** (10 μM) with PhePheGlyGly (0 – 10.0 equiv) in water. Insert: Plots of Abs vs the equiv of PhePheGlyGly.

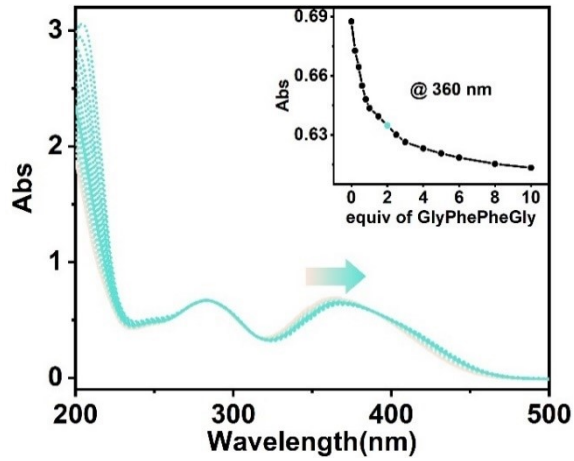

Figure S100. UV/vis titration of **1** (10 μM) with GlyPhePheGly (0 – 10.0 equiv) in water. Insert: Plots of Abs vs the equiv of GlyPhePheGly.

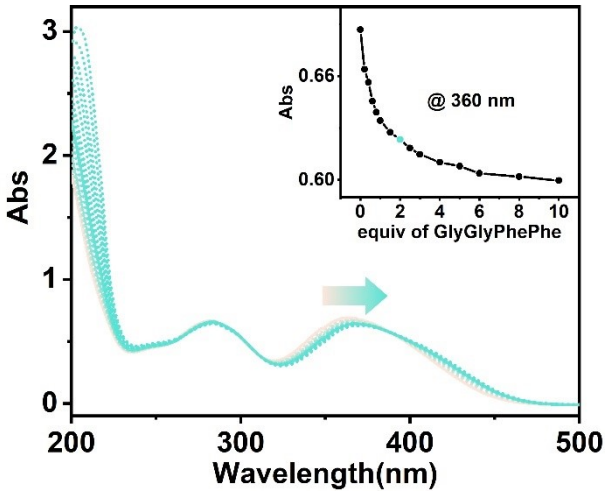

Figure S101. UV/vis titration of **1** (10 μM) with GlyGlyPhePhe (0 – 10.0 equiv) in water. Insert: Plots of Abs vs the equiv of GlyGlyPhePhe.

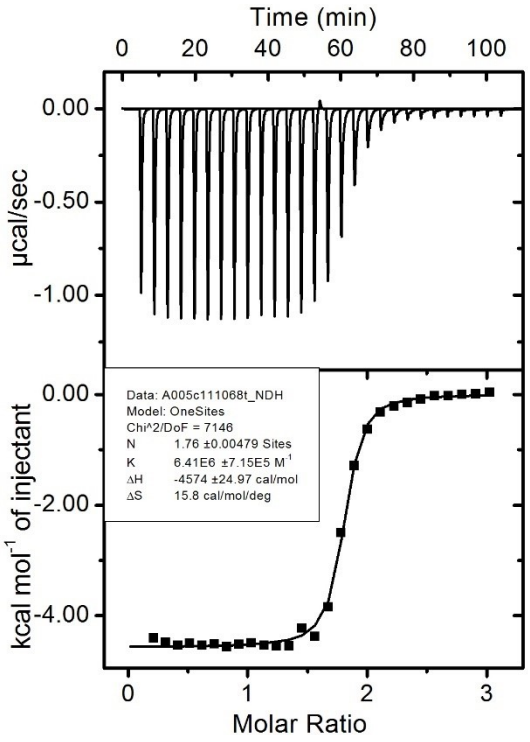

Figure S102. ITC of **1** (50 μM) with TrpTrpGlyGly (750 μM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

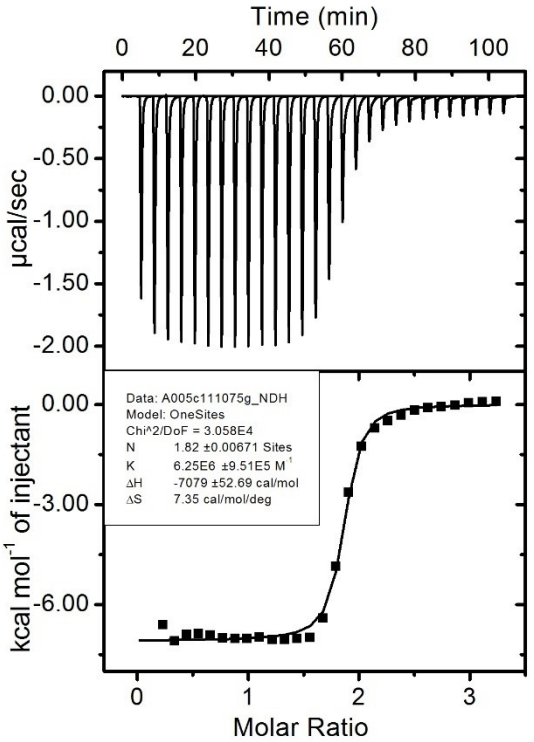

Figure S103. ITC of **1** (30 μM) with GlyTrpTrpGly (450 μM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

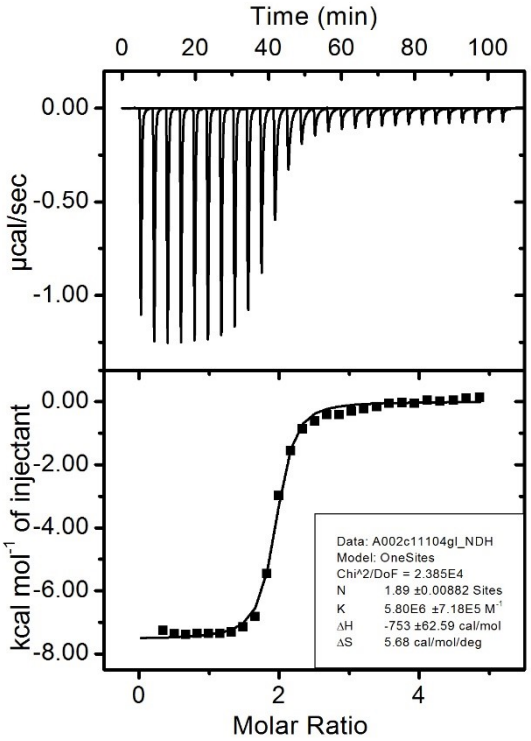

Figure S104. ITC of **1** (30 µM) with GlyGlyTrpTrp (450 µM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

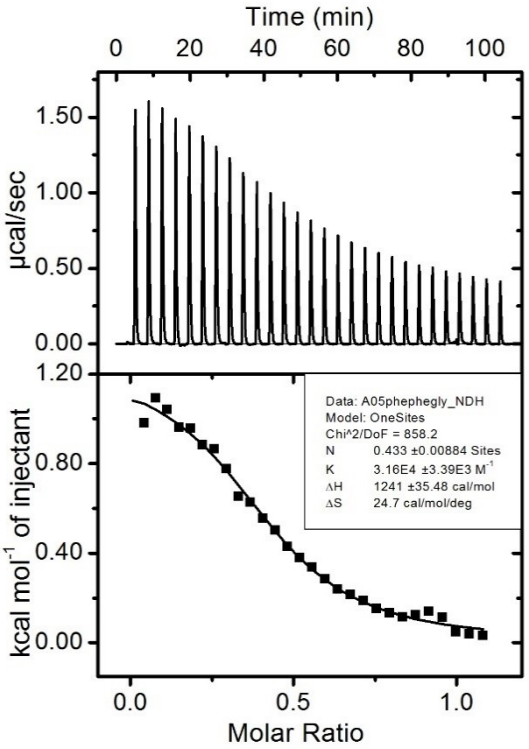

Figure S105. ITC of PhePheGlyGly (0.50 mM) with **1** (2.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

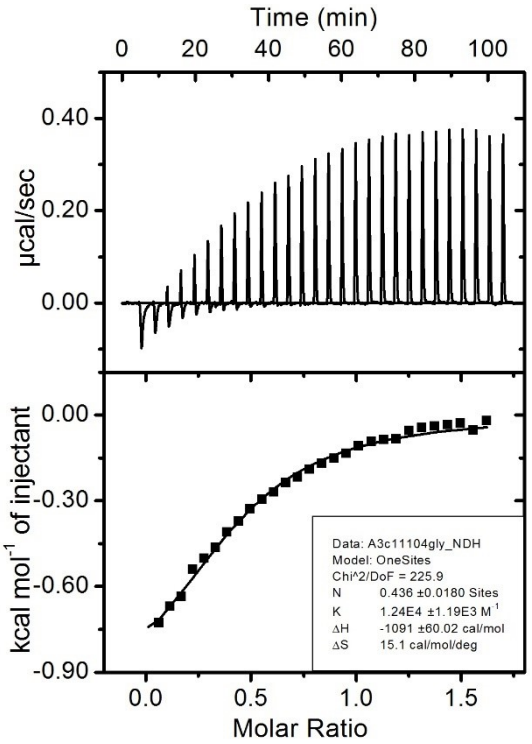

Figure S106. ITC of GlyPhePheGly (0.40 mM) with **1** (3.0 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

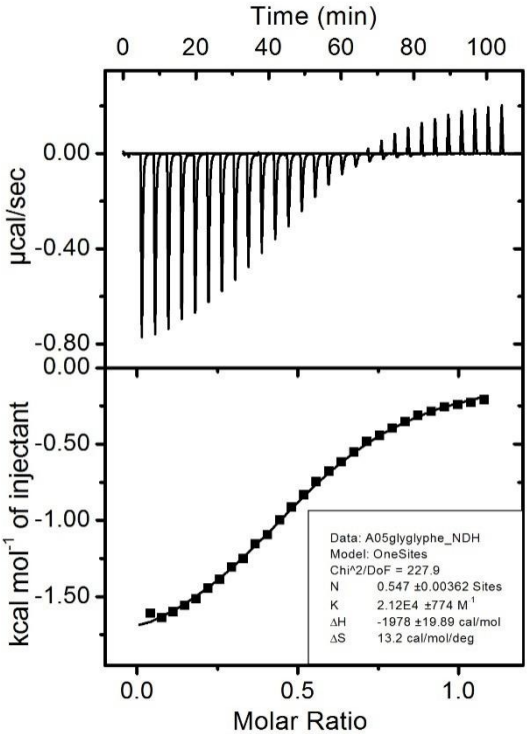

Figure S107. ITC of GlyGlyPhePhe (0.50 mM) with **1** (2.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

4.2 Fluorescence and circular dichroism experiments

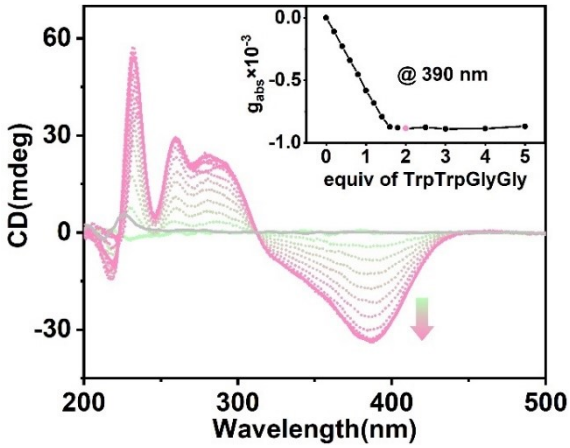

Figure S108. CD titration of **1** (20 μM) with TrpTrpGlyGly (0 – 5.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of TrpTrpGlyGly.

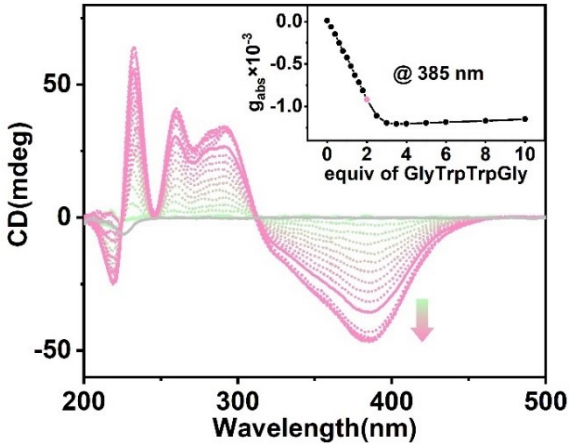

Figure S109. CD titration of **1** (20 μM) with GlyTrpTrpGly (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of GlyTrpTrpGly.

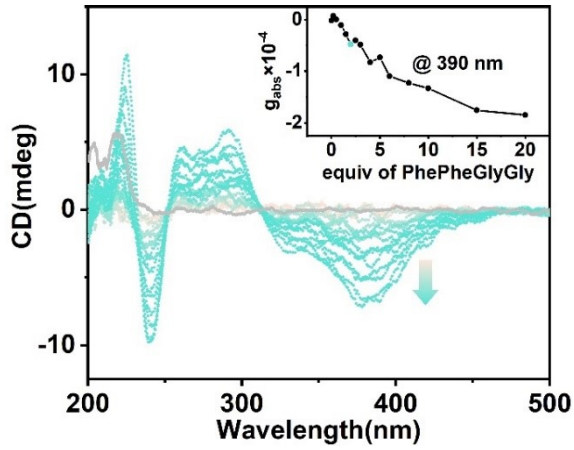

Figure S110. CD titration of **1** (20 μM) with PhePheGlyGly (0 – 20.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of PhePheGlyGly.

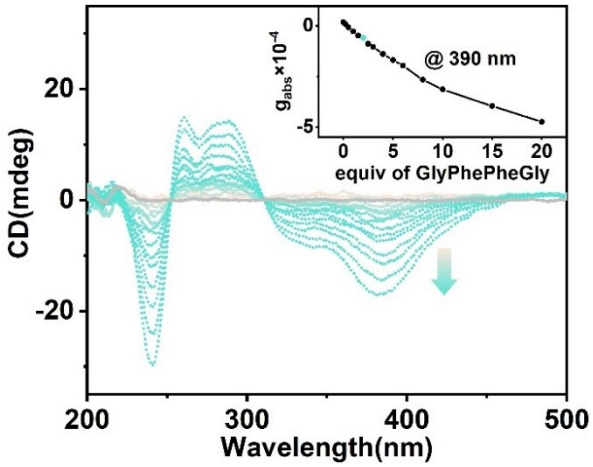

Figure S111. CD titration of **1** (20 μM) with GlyPhePheGly (0 – 20.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of GlyPhePheGly.

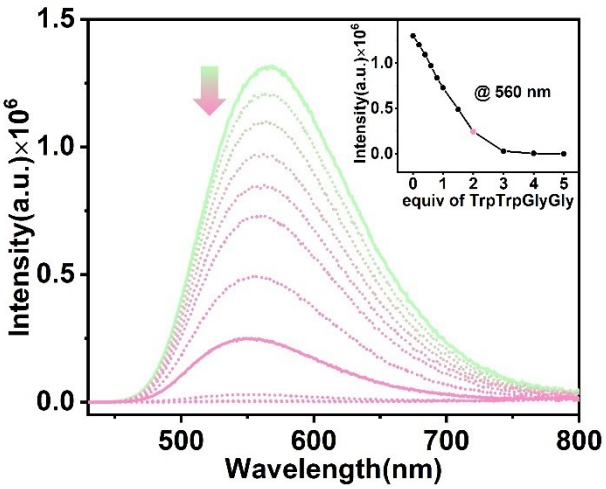

Figure S112. Fluorescence titration of **1** (10 μM) with TrpTrpGlyGly (0 – 5.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of fluorescence intensity versus the equiv of TrpTrpGlyGly. λ_{ex} = 410 nm, E_x/E_m slit = 1.2 nm.

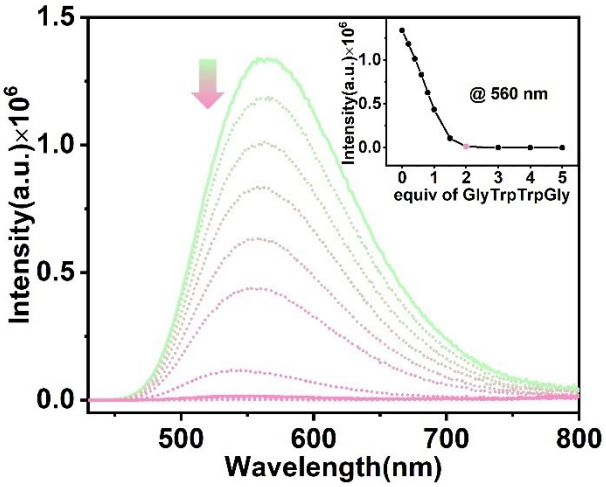

Figure S113. Fluorescence titration of **1** (10 μM) with GlyTrpTrpGly (0 – 5.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of fluorescence intensity versus the equiv of GlyTrpTrpGly. λ_{ex} = 410 nm, E_x/E_m slit = 1.2 nm.

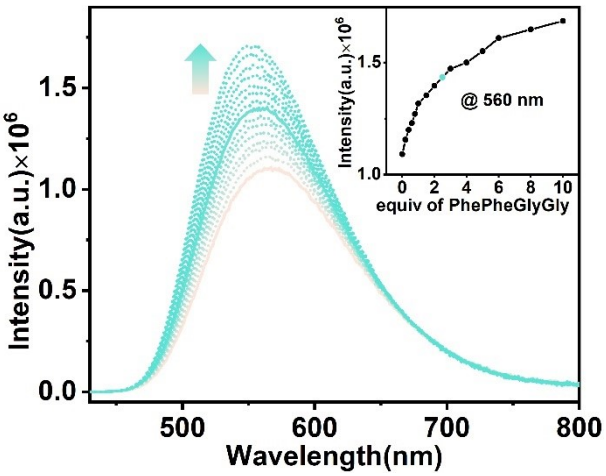

Figure S114. Fluorescence titration of **1** (10 μM) with PhePheGlyGly (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of fluorescence intensity versus the equiv of PhePheGlyGly. λ_{ex} = 410 nm, E_x/E_m slit = 1.2 nm.

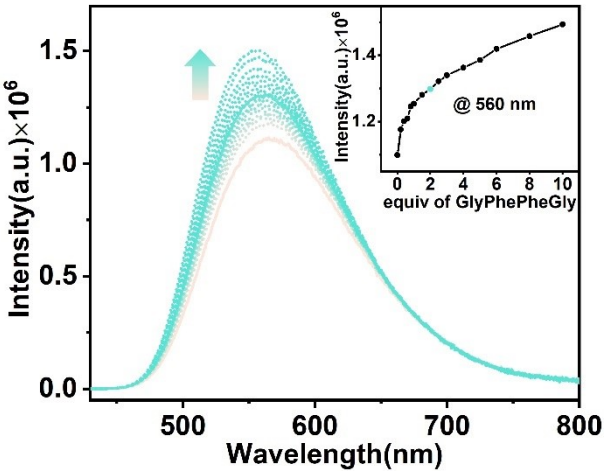

Figure S115. Fluorescence titration of **1** (10 μM) with GlyPhePheGly (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of fluorescence intensity versus the equiv of GlyPhePheGly. λ_{ex} = 410 nm, E_x/E_m slit = 1.2 nm.

5. Recognition of Polypeptides and Proteins

5.1 NMR and ITC experiments

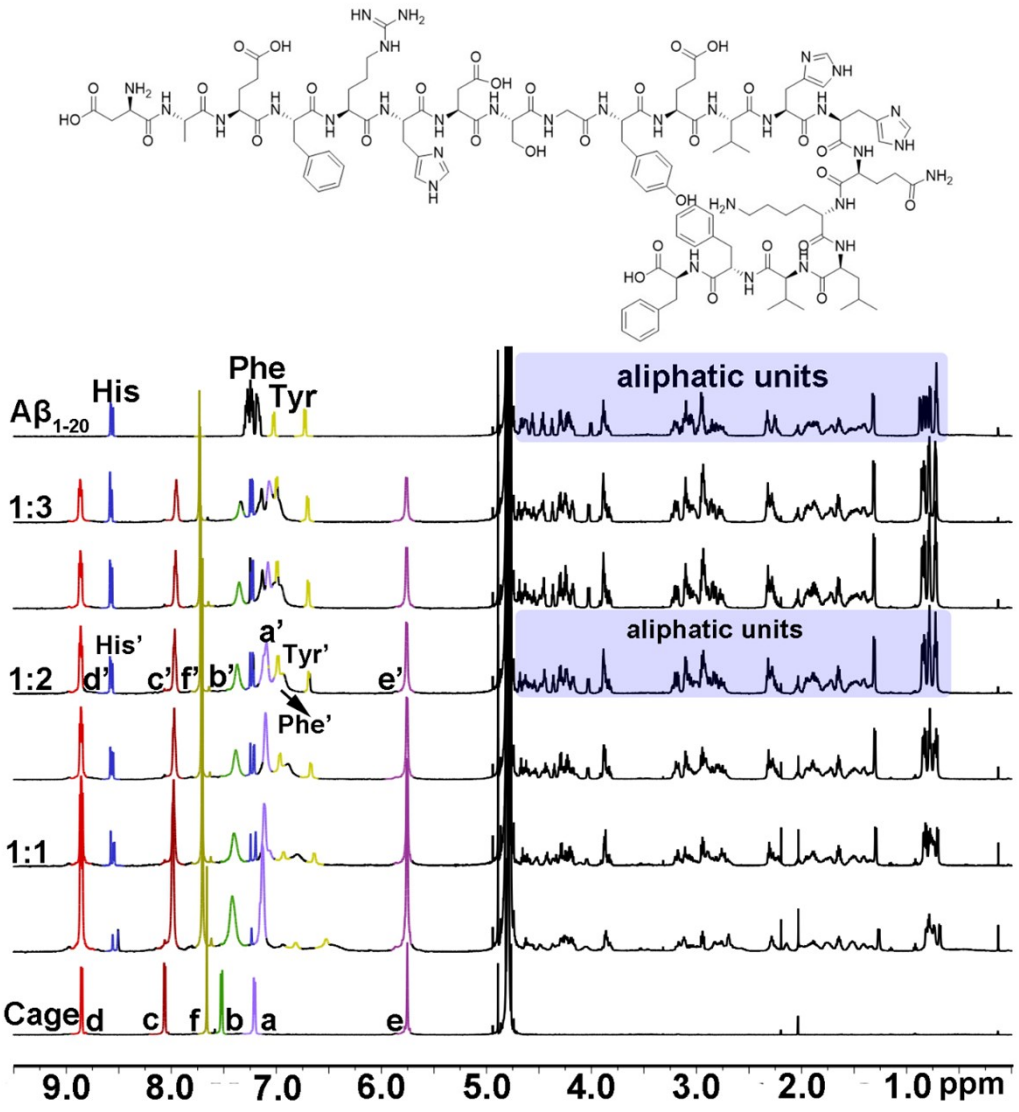

Figure S116. ^{1}H NMR titration (600 MHz, 298 K, D_2O) of **1** (0.40 mM) with $A\beta_{1\text{-}20}$ (0 – 3.0 equiv).

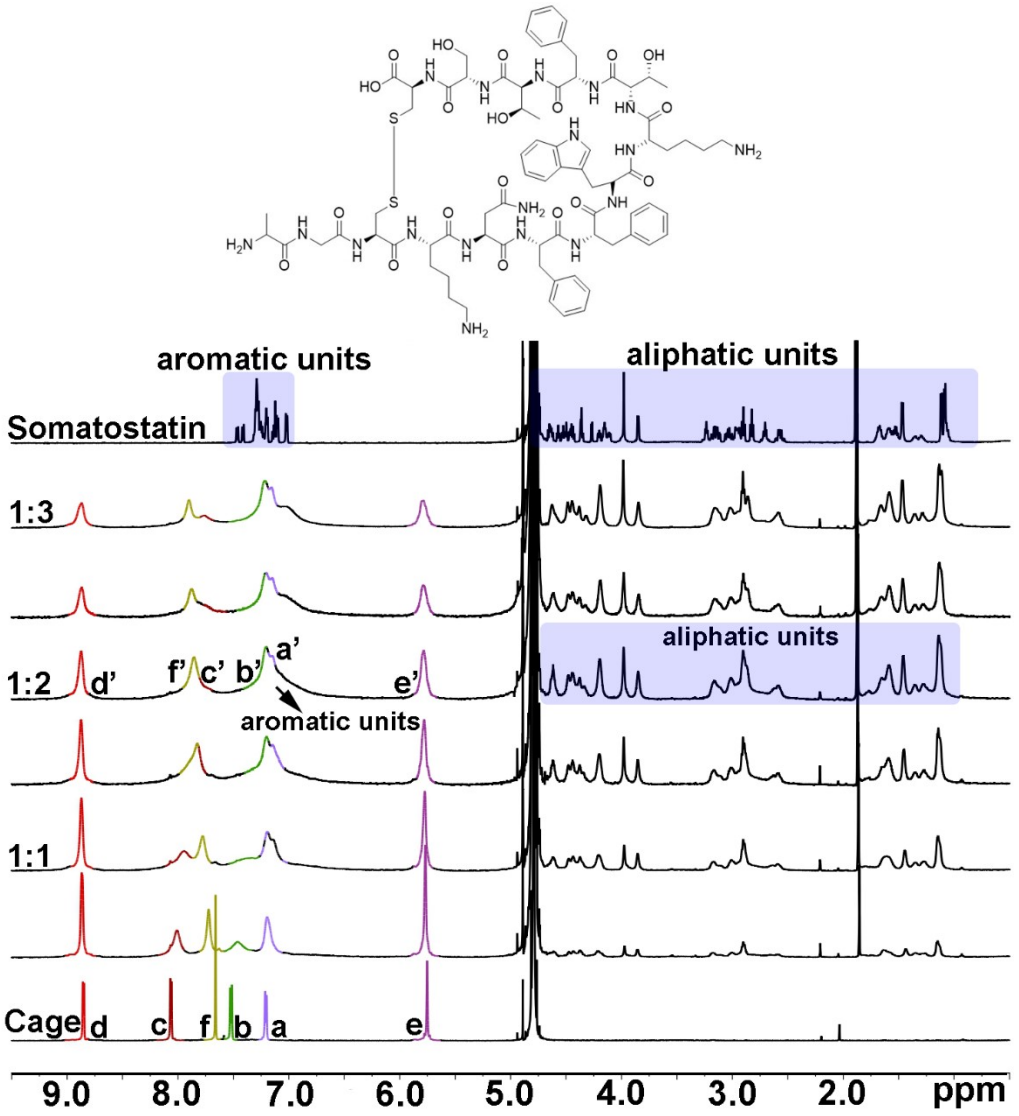

Figure S117. ^{1}H NMR titration (600 MHz, 298 K, D_2O) of **1** (0.40 mM) with somatostatin (0 – 3.0 equiv).

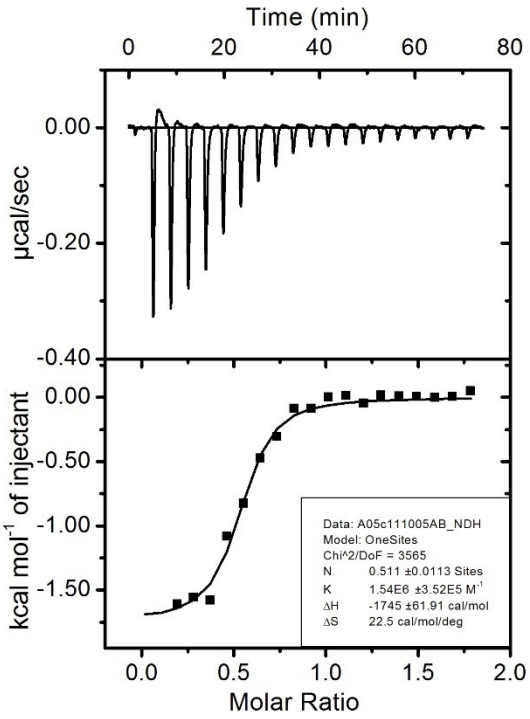

Figure S118. ITC of $A\beta_{1\text{-}20}$ (50 µM) with **1** (0.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

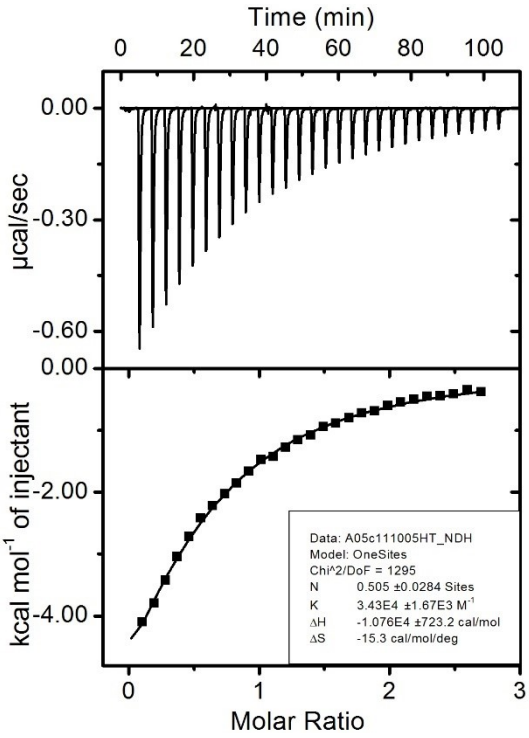

Figure S119. ITC of somatostatin (50 µM) with **1** (0.50 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

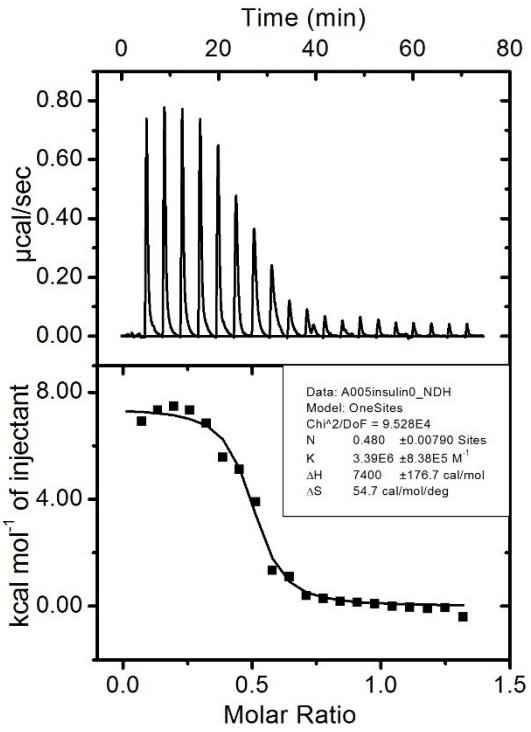

Figure S120. ITC of human insulin (50 µM) with**1** (0.35 mM) at 298 K in phosphate buffer (10 mM, pH = 7.4).

5.2 UV-vis, fluorescence, and circular dichroism experiments

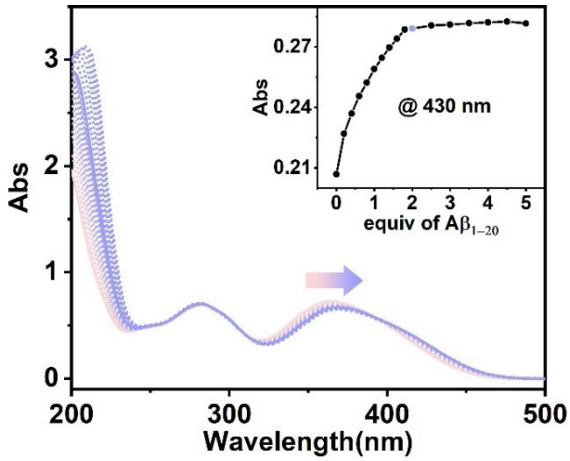

Figure S121. UV/vis titration of **1** (10 µM) with $A\beta_{1\text{-}20}$ (0 – 5.0 equiv) in water. Insert: Plots of Abs vs the equiv of $A\beta_{1\text{-}20}$.

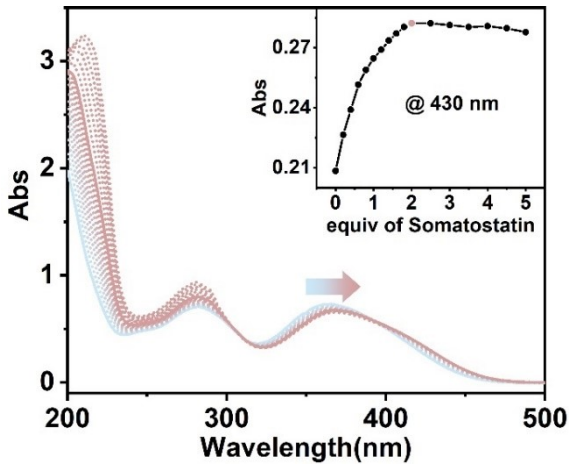

Figure S122. UV/vis titration of **1** (10 μM) with somatostatin (0 – 5.0 equiv) in water. Insert: Plots of Abs vs the equiv of somatostatin.

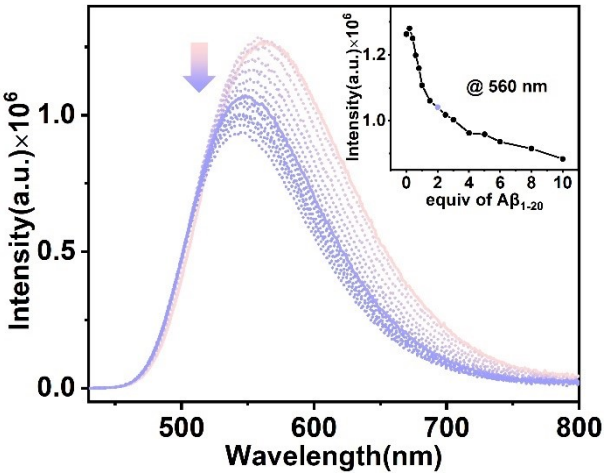

Figure S123. Fluorescence titration of **1** (10 μM) with $A\beta_{1\text{-}20}$ (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of fluorescence intensity versus the equiv of $A\beta_{1\text{-}20}$. λ_{ex} = 410 nm, E_x/E_m slit = 1.2 nm.

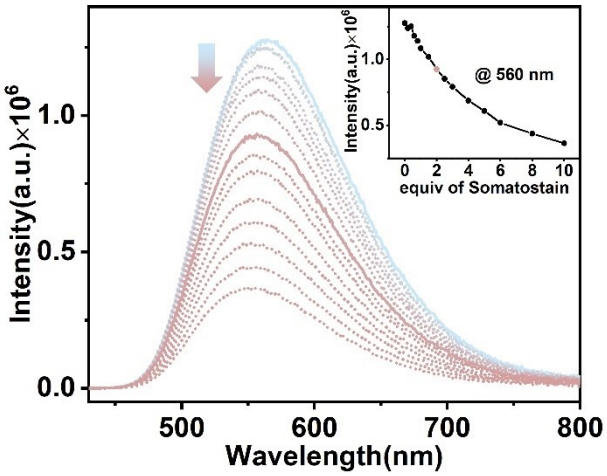

Figure S124. Fluorescence titration of **1** (10 μM) with somatostatin (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of fluorescence intensity versus the equiv of somatostatin. λ_{ex} = 410 nm, E_x/E_m slit = 1.2 nm.

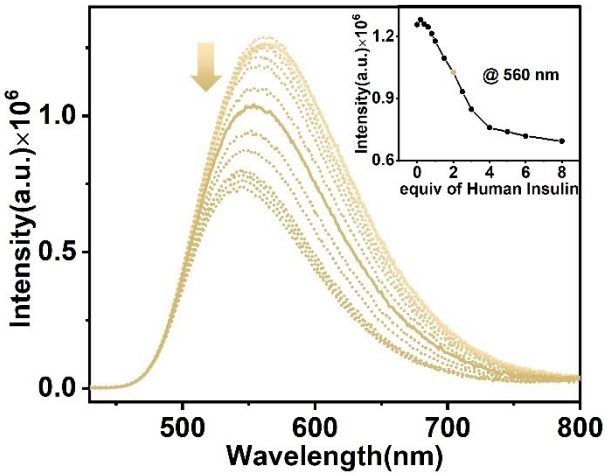

Figure S125. Fluorescence titration of **1** (10 μM) with human insulin (0 – 8.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of fluorescence intensity versus the equiv of human insulin. λ_{ex} = 410 nm, E_x/E_m slit = 1.2 nm.

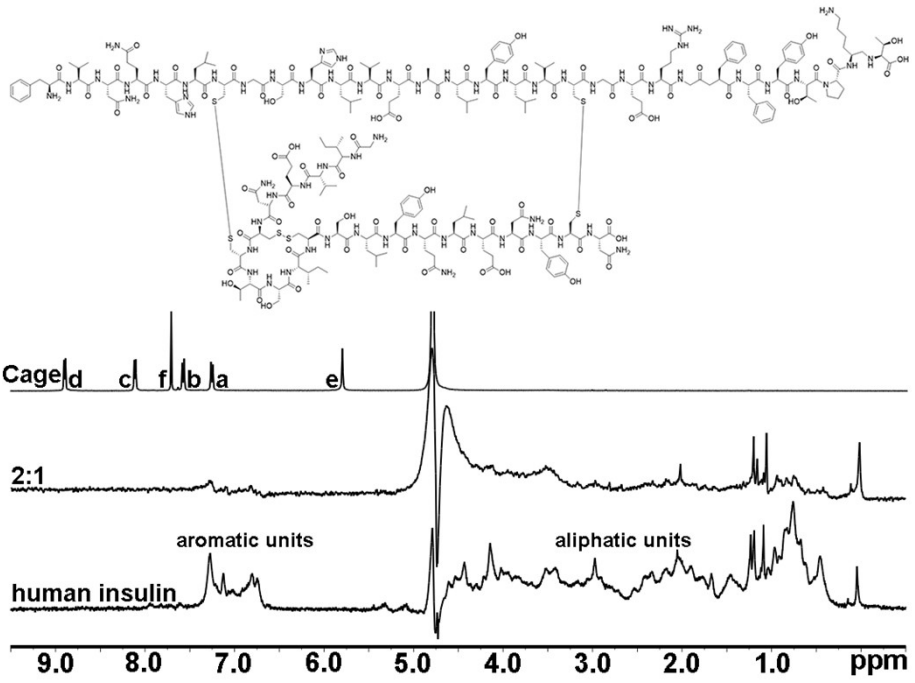

Figure S126. ^{1}H NMR titration (600 MHz, 298 K, D_2O) of human insulin (50 μM) with **1** (0.5 equiv).

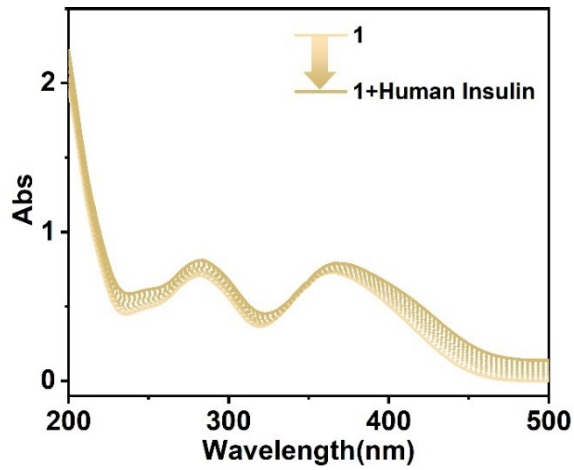

Figure S127. UV/vis titration of **1** (10 μM) with human insulin (0 – 2.0 equiv) in water. Insert: Plots of Abs vs the equiv of human insulin.

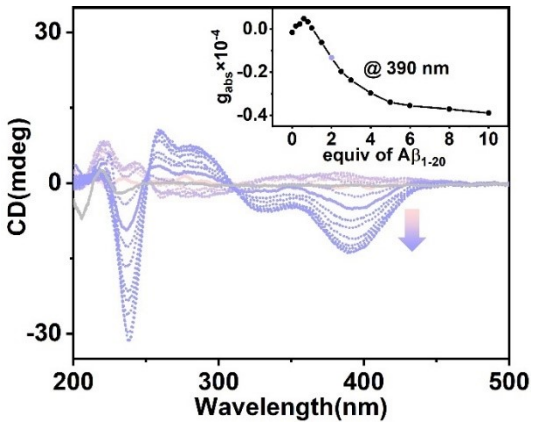

Figure S128. CD titration of **1** (20 μM) with $A\beta_{1-20}$ (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of $A\beta_{1-20}$.

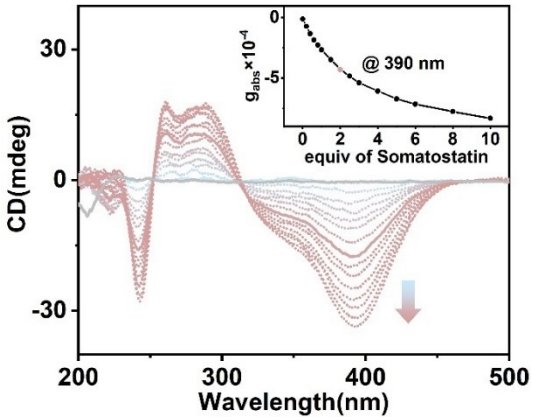

Figure S129. CD titration of **1** (20 μM) with somatostatin (0 – 10.0 equiv) in phosphate buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of somatostatin.

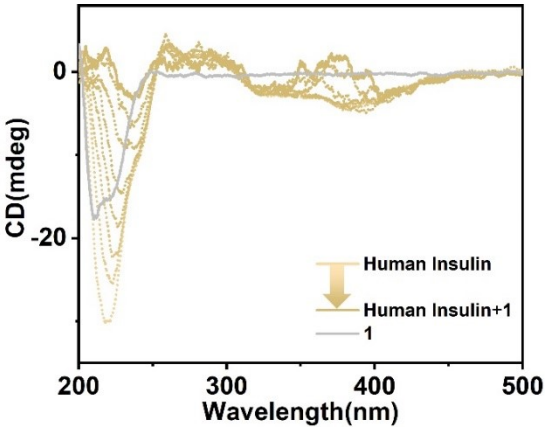

Figure S130. CD titration of human insulin (20 μM) with **1** (0 – 2.5 equiv) in phosphate

buffer (10 mM, pH = 7.4). Insert: Plots of g_{abs} vs the equiv of human insulin.