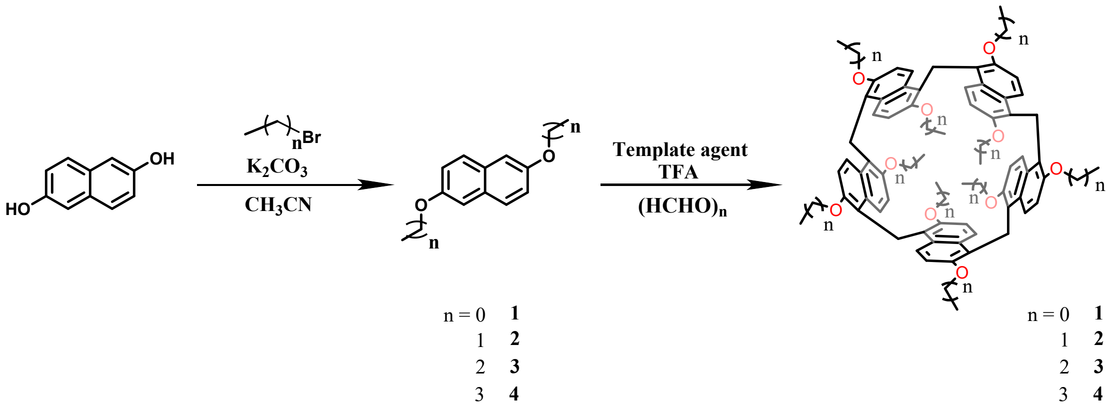
1 General

Chemicals and instruments:

All commercial reagents and solvents (analytical grade) are used as received. The amino acid derivatives were synthesized according to the reported procedure[1]. ^{1}H NMR and ^{13}C NMR spectra were measured at room temperature on a Bruker AMX–400 (operating at 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR) in $CDCl_3$ with TMS as the internal standard. HR MALDI mass spectra were recorded on a Bruker Solarix FT-ICR mass spectrometer equipped with a 7T magnet. CD spectra and binding constants with CD titration were acquired using J-1500 CD spectrometer. UV-vis spectra were obtained on a Jasco V-650 UV-vis spectrometer. Fluorescence spectra were acquired using a Fluoromax-4 spectrofluorometer. All the chemicals were obtained from suppliers and used without further purification in case of analysis investigation.

2, 6-Alkoxy naphthalene (2-4), Prism[5]arenes (N1-N3) and 1,4-C-prism[5]arene CN were synthesized following a literature process[1].

2 Synthesis of host



Scheme S1 Synthesis route of hosts.

Synthesis and characterization of **2**:

2,6-Naphthol (10 mmol, 1.6 g), K_2CO_3 (50 mmol, 6.9 g), and iodoethane (80 mmol, 12.5 g) were mixed and refluxed in acetonitrile (250 mL) under a nitrogen atmosphere for 24h. After cooling, the reaction mixture was filtered and evaporated by rotary evaporation to give a white solid. The crude product was purified on a silica gel column (PE/DCM= 1/1, V/V), and the eluent was removed under vacuum to give compond **2** as a white solid (yield: 65%) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.7 Hz, 1H), 7.24 – 6.97 (m, 2H), 4.15 (q, J = 7.0 Hz, 2H), 1.49 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.37 (s), 129.73 (s), 128.07 (s), 119.18 (s), 106.95 (s), 63.48 (s), 14.89 (s).

Synthesis and characterization of **3**:

2,6-Naphthol (10 mmol, 1.6 g), K_2CO_3 (50 mmol, 6.9 g) and n-Propyl iodide (80 mmol, 13.5 g) were mixed and refluxed in acetonitrile (250 mL) under a nitrogen atmosphere for 12h. After cooling, the reaction mixture was filtered and evaporated by rotary evaporation to give a white solid. The crude product was purified on a silica gel column (PE/DCM= 5/1, V/V), and the eluent was removed under vacuum to give compond **3** as a white solid (yield: 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.8 Hz, 2H), 7.17 – 7.10 (m, 4H), 4.04 (t, J = 6.6 Hz, 4H), 1.89

(dd, *J* = 14.1, 6.8 Hz, 4H), 1.10 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.53 (s), 129.72 (s), 128.02 (s), 119.19 (s), 106.98 (s), 69.59 (s), 22.65 (s), 10.62 (s).

Synthesis and characterization of **4**:

2,6-Naphthol (10 mmol, 1.6 g), K2CO3 (50 mmol, 6.9 g) and n-butyl bromide (80 mmol, 10.96 g) were mixed and refluxed in acetonitrile (250 mL) under a nitrogen atmosphere for 12h. After cooling, the reaction mixture was filtered and evaporated by rotary evaporation to give a white solid. The crude product was purified on a silica gel column (PE/DCM= 9/1, V/V), and the eluent was removed under vacuum to give compond **4** as a white solid (yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.7 Hz, 2H), 7.11 – 7.06 (m, 4H), 4.03 (t, *J* = 6.5 Hz, 4H), 1.84 – 1.77 (m, 4H), 1.51 (dd, *J* = 14.2, 6.7 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.55 (s), 129.71 (s), 128.02 (s), 119.20 (s), 106.95 (s), 67.76 (s), 31.40 (s), 19.36 (s), 13.92 (s).

Synthesis and characterization of **N1** and **CN**[1a] :

2,6-Dimethoxynaphthalene (250 mg, 1.33 mmol), paraformaldehyde (48 mg, 1.60 mmol, 1.2 eq.), and template 1,4-dihexyl-1,4-diazabicyclo[2.2.2]octane hydroiodide (1.33 mmol, 1.0 eq.) were heated to 70°C in 530 mL dried 1,2-dichloroethane, and then trifluoroacetic acid (1.5 mL, 0.02 mol, 15 eq.) was added. The solution was stirred at 70 °C for 22 h, and the solvent was removed under reduced pressure. The solid was dissolved in CH_2Cl_2 (30 mL) and washed with a 30 mL $NaHCO_3$ saturated aqueous solution. Finally, the organic layer was washed with brine (2 x 20 mL), dried on sodium sulfate, and evaporated under the vaccum to give a light brown solid. The crude product was purified on a silica gel column (PE/DCM= 1/9, V/V), and the eluent was removed under vacuum to give compond **N1** (125 mg, yield: 47%) and **CN** (42 mg, yield: 16%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 9.4 Hz, 10H), 6.97 (d, *J* = 9.4 Hz, 10H), 4.73 (s, 10H), 3.76 (s, 30H).

Synthesis and characterization of **N2**[1b] :

2,6-Diethoxynaphthalene (1.00 g, 4.6 mmol), paraformaldehyde (1.2 eq.), and template 1,4-dihexyl-1,4-diazabicyclo[2.2.2]octane hydroiodide (4.6 mmol, 1.0 eq.) were heated to 70°C in 530 mL dried 1,2-dichloroethane, and then trifluoroacetic acid (15 eq.) was added. The solution was stirred at 70°C for 22 h, and the solvent was removed under reduced pressure. The solid was dissolved in CH_2Cl_2 (30 mL) and washed with a 30 mL $NaHCO_3$ saturated aqueous solution. Finally, the organic layer was washed with brine (2 x 20 mL), dried on sodium sulfate, and evaporated under the vaccum to give a light brown solid. The crude product was purified on a silica gel column (PE/toluene/DCM= 1/2/7, V/V/V), and the eluent was removed under vacuum to give compond **N2** as a white solid (110 mg, yield: 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.3 Hz, 10H), 6.83 (d, *J* = 9.4 Hz, 10H), 4.76 (s, 10H), 3.88 (dd, *J* = 9.3, 7.1 Hz, 10H), 3.69 (dd, *J* = 15.2, 8.1 Hz, 10H), 0.96 (t, *J* = 7.0 Hz, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.55 (s), 129.57 (s), 124.68 (s), 124.05 (s), 114.47 (s), 65.26 (s), 14.99 (s), 0.08 (s).

Synthesis and characterization of **N3**[1b] :

2,6-Dipropoxynaphthalene (1.00 g, 4.6 mmol), paraformaldehyde (1.2 eq.), and template 1,4-dihexyl-1,4-diazabicyclo[2.2.2]octane hydroiodide (1.0 eq.) were heated to 70°C in 530 mL dried 1,2-dichloroethane, and then trifluoroacetic acid (15 eq.) was added. The solution was stirred at 70°C for 22 h, and the solvent was removed under reduced pressure. The solid was dissolved in CH_2Cl_2 (30 mL) and washed with a 30 mL $NaHCO_3$ saturated aqueous solution. Finally, the organic layer was washed with brine (2 x 20 mL), dried on sodium sulfate, and evaporated under the vaccum to give a light brown solid. The crude product was purified on a silica gel column (PE/toluene/DCM= 2.5/2.5/5, V//V/V), and the eluent was removed under vacuum to give compond **N3** as a white solid (270 mg, yield: 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 9.4 Hz, 10H), 6.93 (d, *J* = 9.4 Hz, 10H), 4.75 (s, 10H), 3.93 (qd, *J* = 6.8, 2.5 Hz, 20H), 1.78 – 1.69 (m, 20H), 1.00 (t, *J* = 7.4 Hz, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.42 (s), 130.00 (s), 125.21 (s), 123.70 (s), 114.45 (s), 71.33 (s), 23.13 (s), 10.86 (s).

Synthesis and characterization of **N4**:

2,6-dibutoxynaphthalene (408 mg,1.5 mmol), paraformaldehyde (54 mg, 1.80 mmol, 1.2 eq.), and template 1,4-dihexyl-1,4-diazabicyclo[2.2.2]octane hydroiodide (1.5 mmol, 1.0 eq.) were heated to 80°C in 530 mL of dried 1,2-dichloroethane, and then trifluoroacetic acid (1.5 mL, 0.02 mmol, 15 eq.) was added. The solution was stirred at 80°C for 24 h, and the solvent was removed under reduced pressure. The solid was dissolved in CH_2Cl_2 (30 mL) and washed with a 30 mL $NaHCO_3$ saturated aqueous solution. Finally, the organic layer was washed with brine (2 x 20 mL), dried on sodium sulfate, and evaporated under the vaccum to give a light brown solid. The crude product was purified on a silica gel column (PE/DCM= 1/3, V/V), and the eluent was removed under vacuum to give 227 mg white solid (yield: 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 9.4 Hz, 1H), 6.96 (d, J = 9.5 Hz, 1H), 4.70 (s, 1H), 4.11 – 3.97 (m, 2H), 1.85 (dq, J = 13.4, 6.6 Hz, 2H), 1.59 (dt, J = 9.9, 4.8 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.27 (s), 130.25 (s), 125.41 (s), 123.71 (s), 114.61 (s), 69.50 (s), 31.99 (s), 19.59 (s), 14.02 (s).

3 NMR and HRMS spectra

Fig. S1 ^{1}H NMR of **2** in $CDCl_3$ at 298 K (400 MHz).

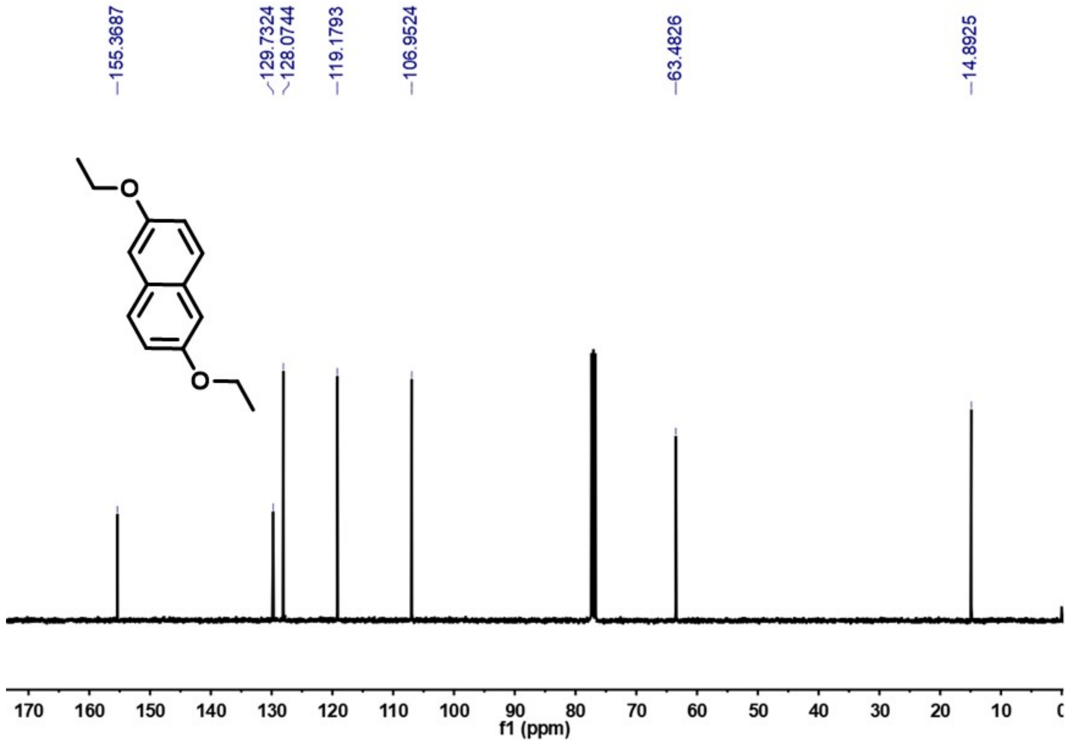


Fig. S2 ^{13}C NMR of **2** in $CDCl_3$ at 298 K (101 MHz).

Fig. S3 ^{1}H NMR of **3** in $CDCl_3$ at 298 K (400 MHz).

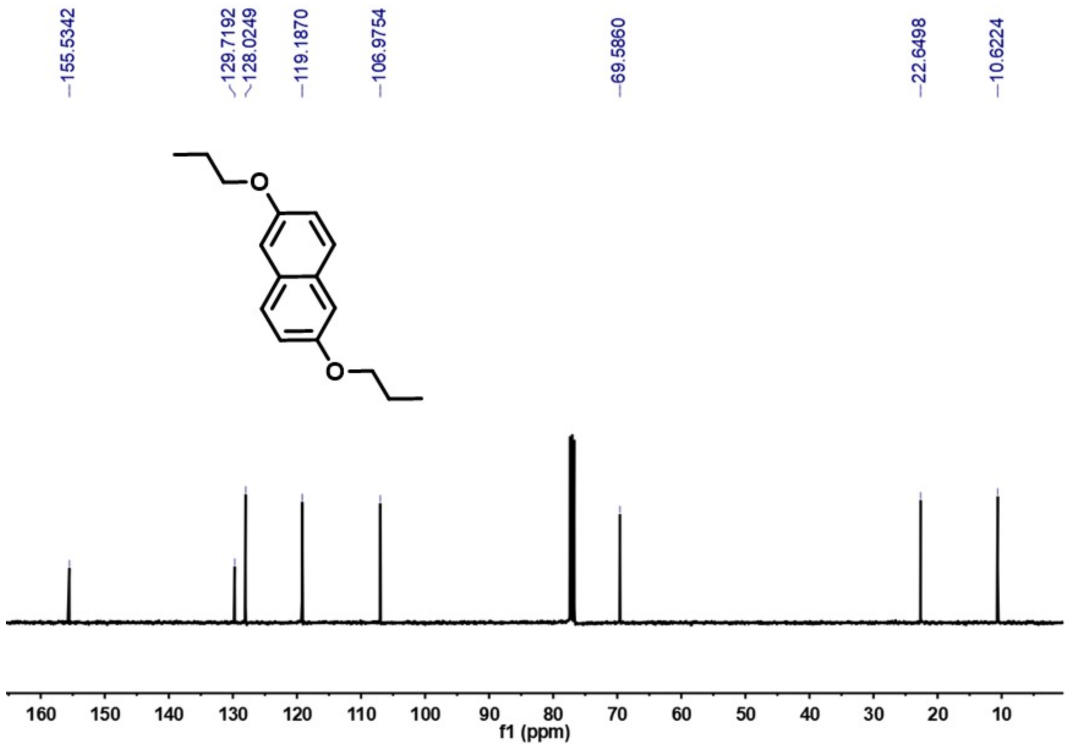


Fig. S4 ^{13}C NMR of **3** in $CDCl_3$ at 298 K (101 MHz).

Fig. S5 ^{1}H NMR of **4** in $CDCl_3$ at 298 K (400 MHz).

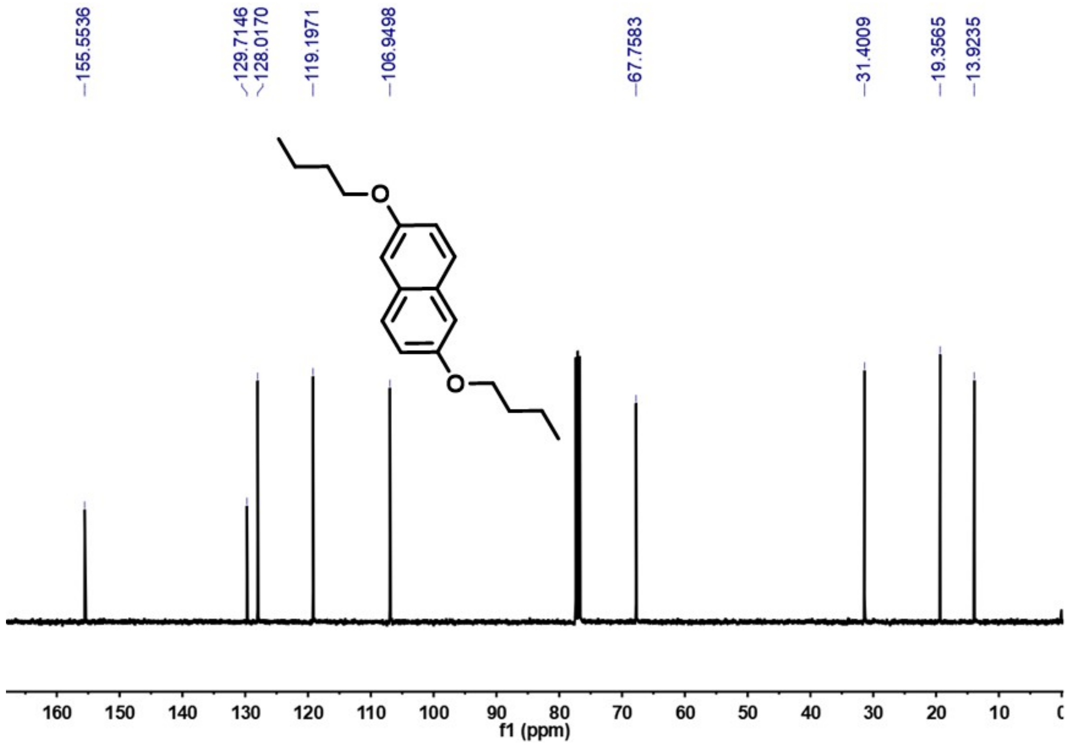


Fig. S6 ^{13}C NMR of **4** in $CDCl_3$ at 298 K (101 MHz).

Fig. S7 ^{1}H NMR of **N1** in $CDCl_3$ at 298 K (400 MHz).

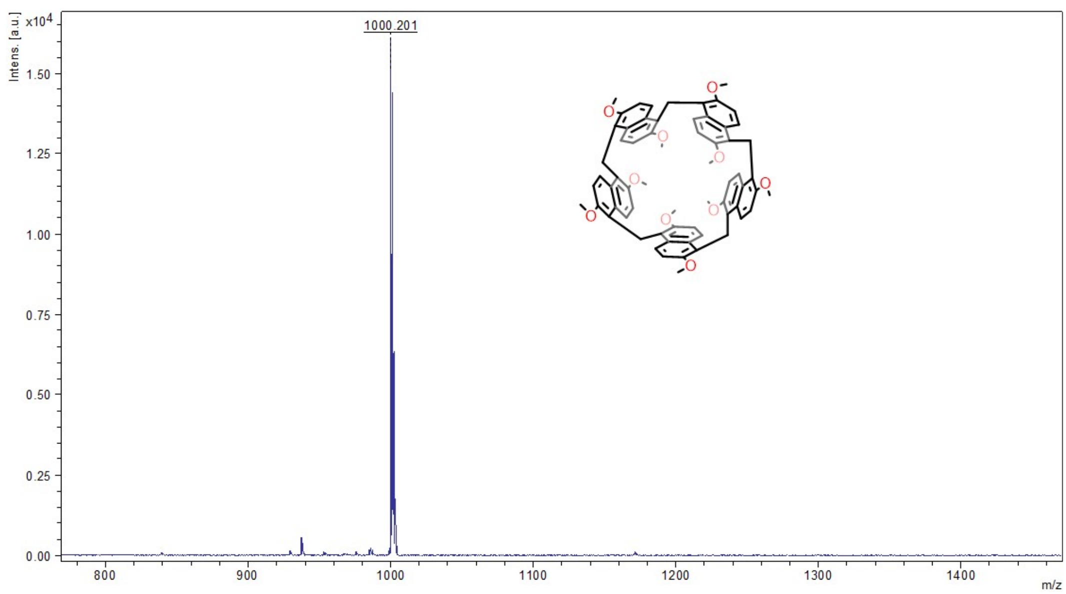


Fig. S9 MALDI-HRMS spectra of **N1**.

Fig. S10 ^{1}H NMR of **N2** in $CDCl_3$ at 298 K (400 MHz).

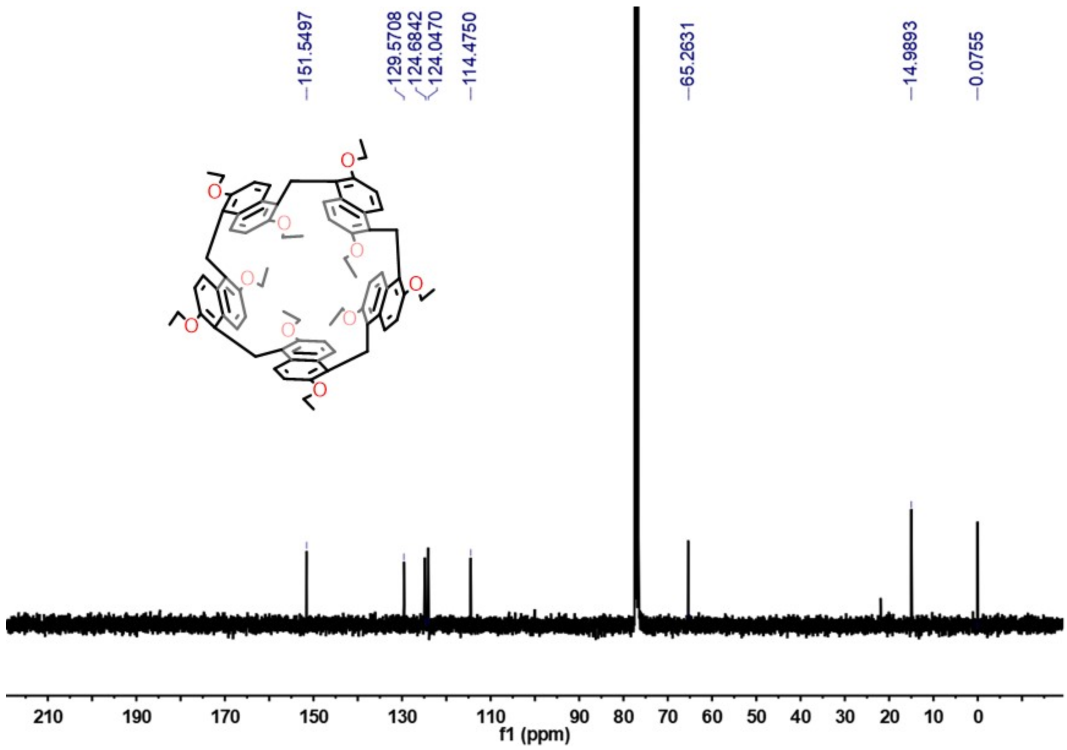


Fig. S11 ^{13}C NMR of **N2** in $CDCl_3$ at 298 K (101 MHz).

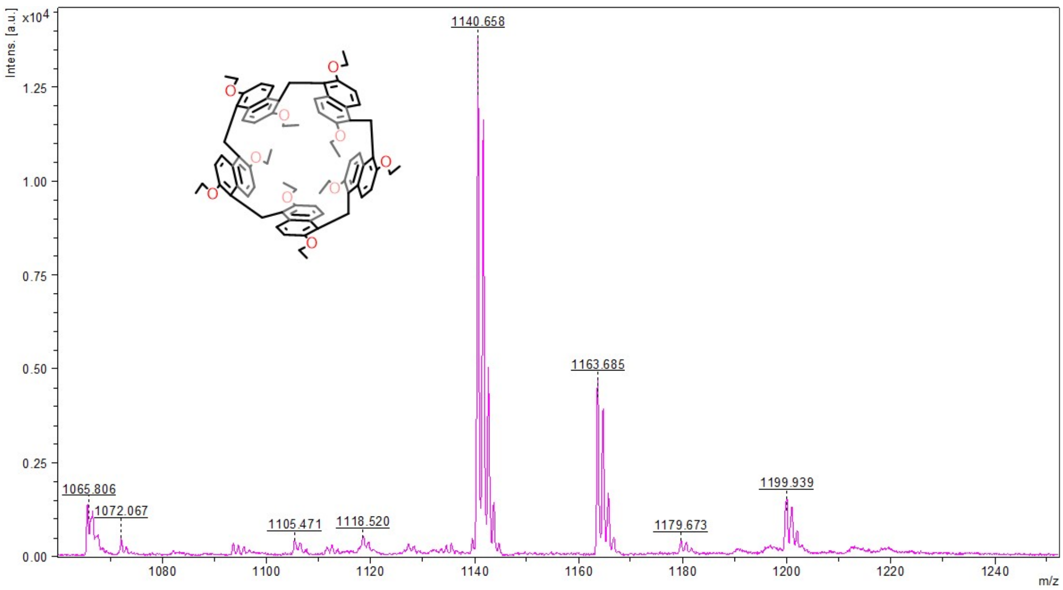


Fig. S12 MALDI-HRMS spectra of **N2**.

Fig. S13 ^{1}H NMR of **N3** in $CDCl_3$ at 298 K (400 MHz).

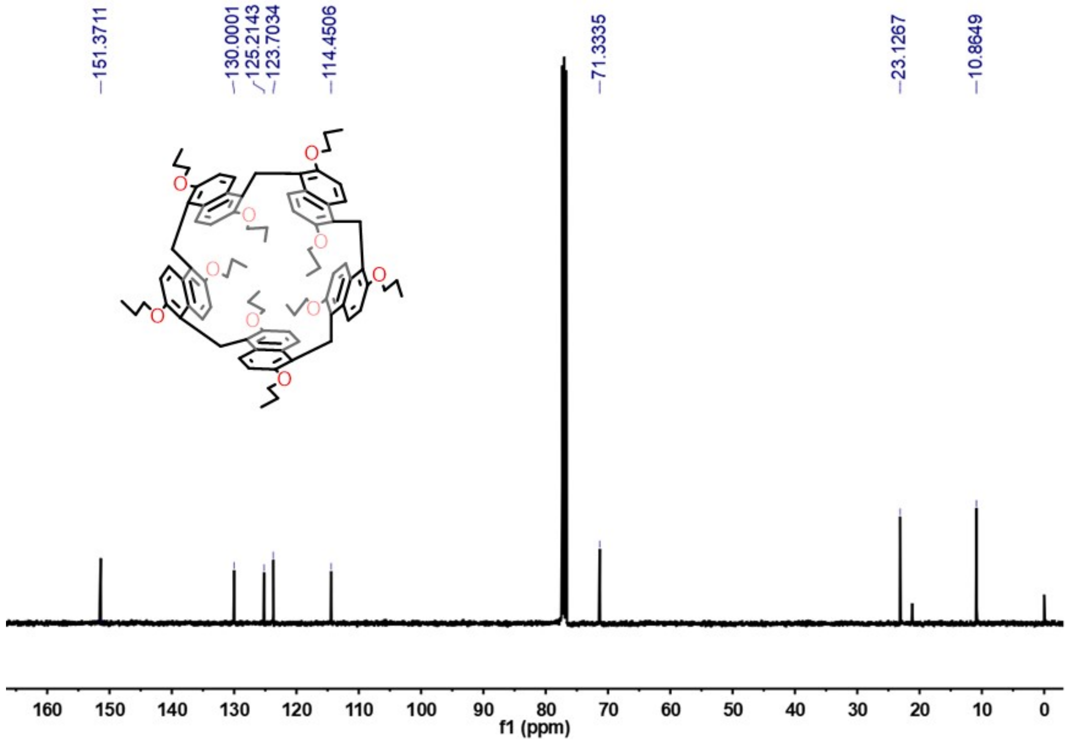


Fig. S14 ^{13}C NMR of **N3** in $CDCl_3$ at 298 K (101 MHz).

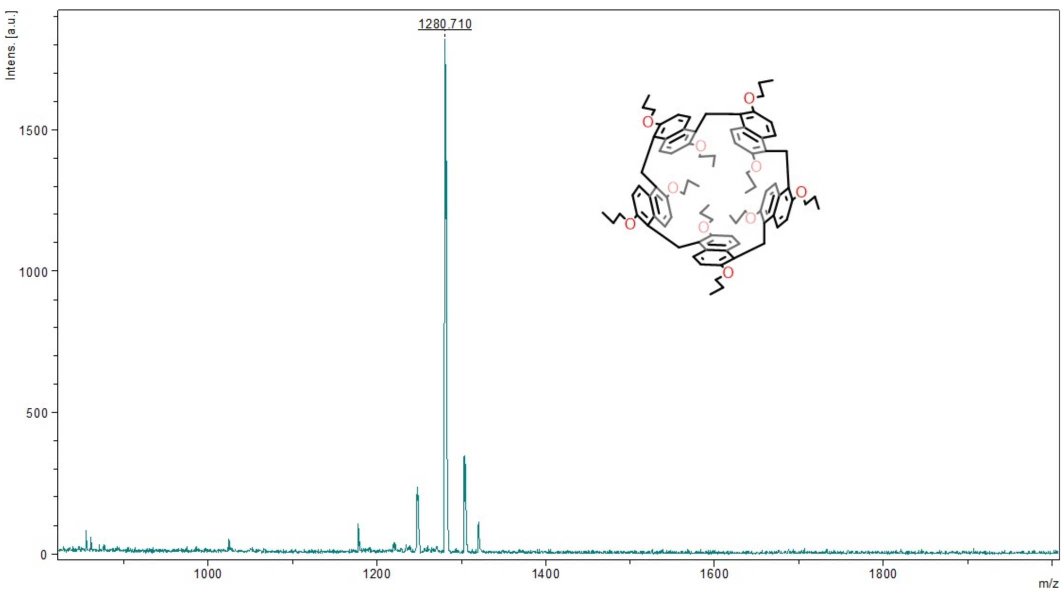


Fig. S15 MALDI-HRMS spectra of **N3**.

Fig. S16 ^{1}H NMR of **N4** in $CDCl_3$ at 298 K (400 MHz).

Fig. S17 ^{13}C NMR of **N4** in $CDCl_3$ at 298 K (101 MHz).

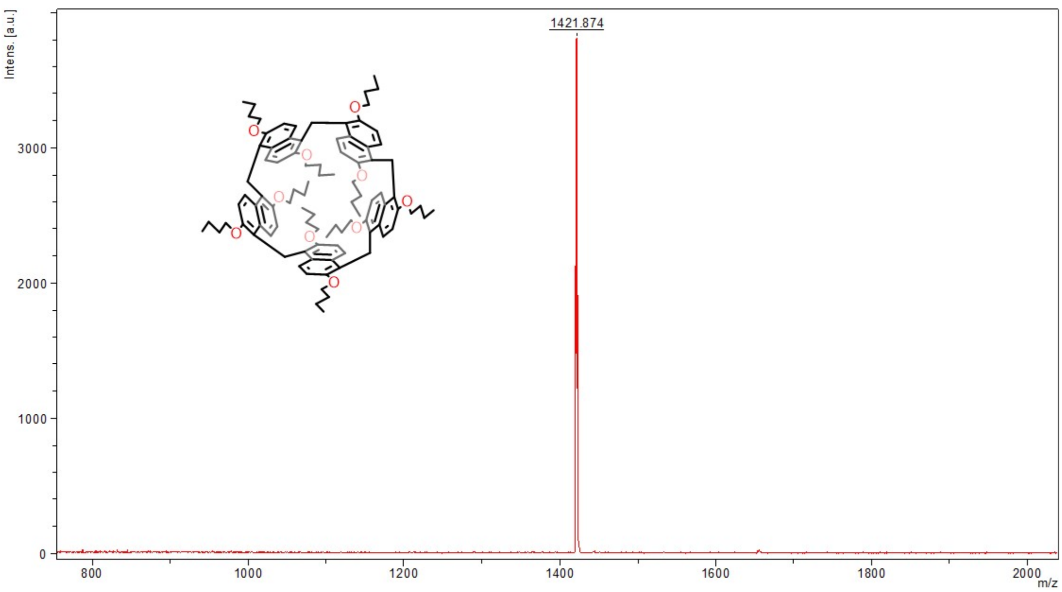


Fig. S18 MALDI-HRMS spectra of **N4.**

4 Spectroscopic properties of prismarene

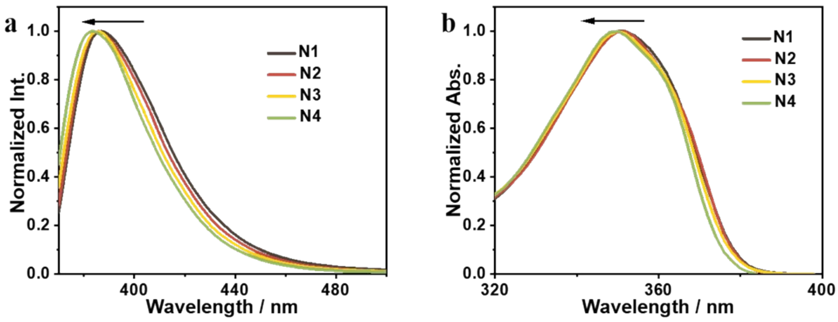


Fig. S19 Normalized Fluorescence (a) and UV-Vis (b) spectra of **N1** (λ_{Abs}=351 nm and λ_{em}=386 nm), **N2** (λ_{Abs}=350 nm and λ_{em}=386 nm), **N3** (λ_{Abs}=349 nm and λ_{em}=385 nm) and **N4** (λ_{Abs}=348 nm and λ_{em}=383 nm) in $CHCl_3$ at room temperature.

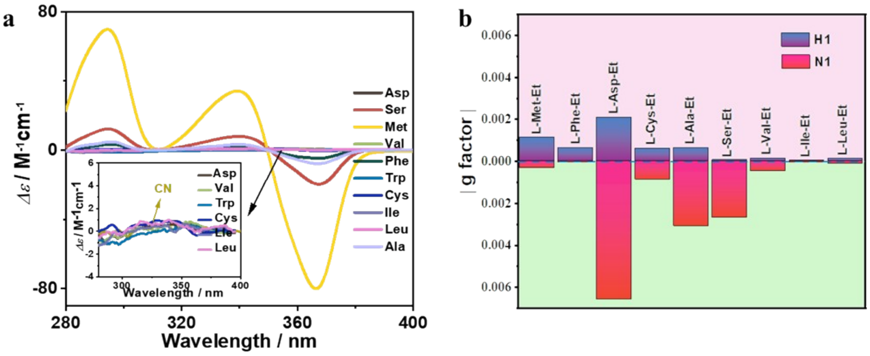


Fig. S20 (a) CD spectra of **CN** with different chiral amino in $CHCl_3$ at room temperature. (b) Comparison of g factor of CD signals of N1 and P1 induced by different amino acids ethyl ester salts. g factor of P1 induced by different amino acids ethyl ester salts reported by Yang et al.[2]

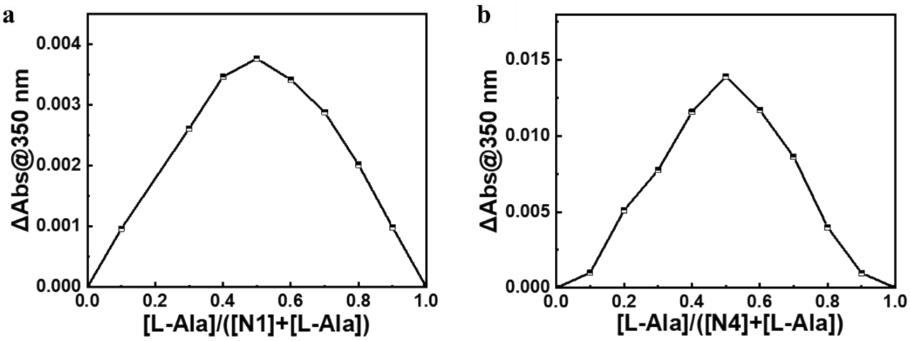


Fig. S21 Job's plot of the change in the UV–vis absorption spectrum at 350 nm showing the stoichiometry of the complexation of *L*-**Ala** with **N1** or **N4** in $CHCl_3$ (rt). $c_{[G] + [H]} = 5.0 \times 10^{-5}$ M.

5 Spectroscopic titrations of the host-guest complexation

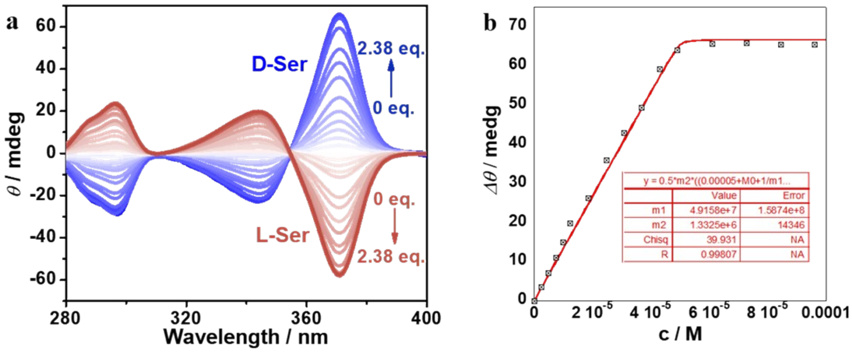


Fig. S22 (a) CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *D-/L*-**Ser** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 370 nm upon the addition of *L*-**Ser**, and the host-guest association constant K_a was estimated to be 3.1×10^7 M^{-1}.

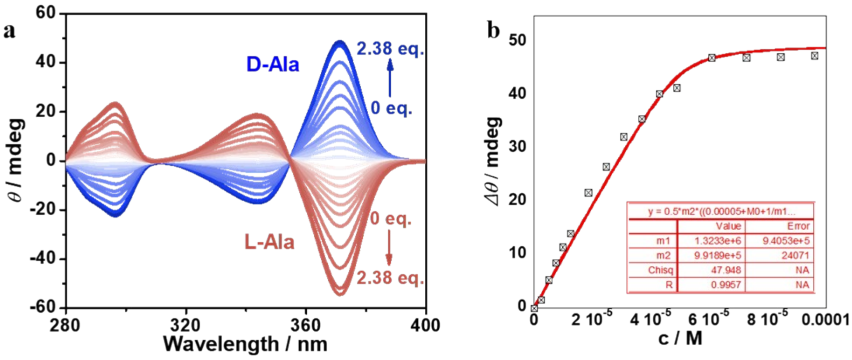


Fig. S23 (a) CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *D-/L*-**Ala** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 370 nm upon the addition of *L*-**Ala**, and the host-guest association constant K_a was estimated to be 1.3×10^6 M^{-1}.

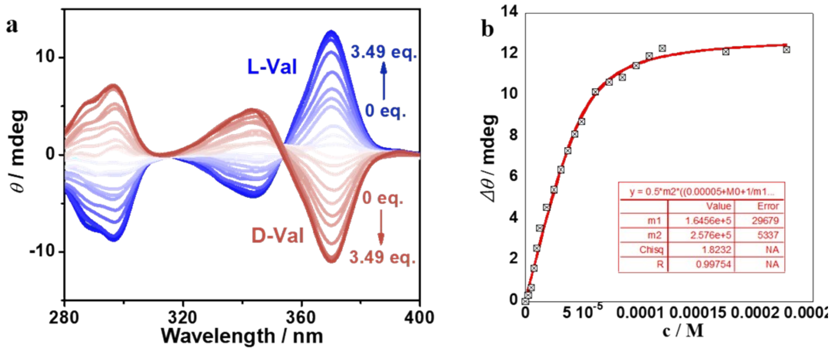


Fig. S24 (a) CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *D*-/*L*-**Val** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 370 nm upon the addition of *L*-**Val**, and the host-guest association constant K_a was estimated to be 1.6×10^5 M^{-1}.

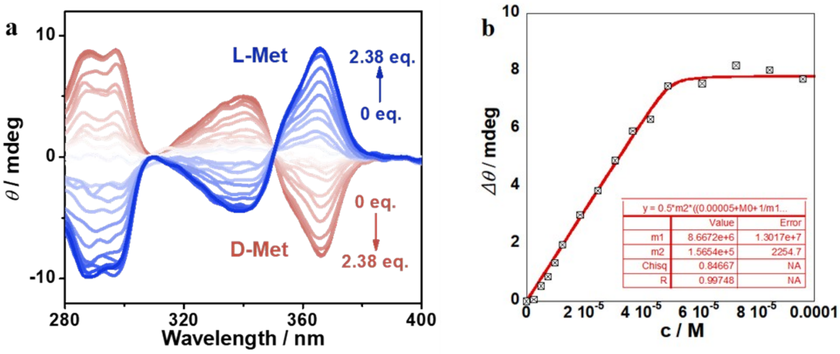


Fig. S25 (a) CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *D*-/*L*-**Met** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 370 nm upon the addition of *L*-**Met**, and the host-guest association constant K_a was estimated to be 8.7×10^6 M^{-1}.

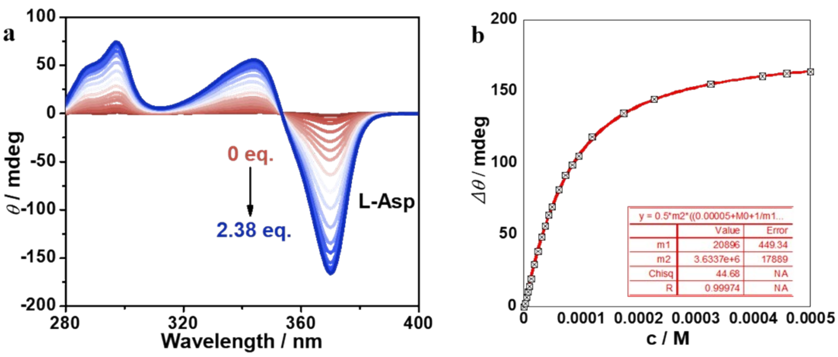


Fig. S26 (a) CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *L*-**Asp** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 369 nm upon the addition of *L*-**Asp**, and the host-guest association constant K_a was estimated to be 2.1×10^4 M^{-1}.

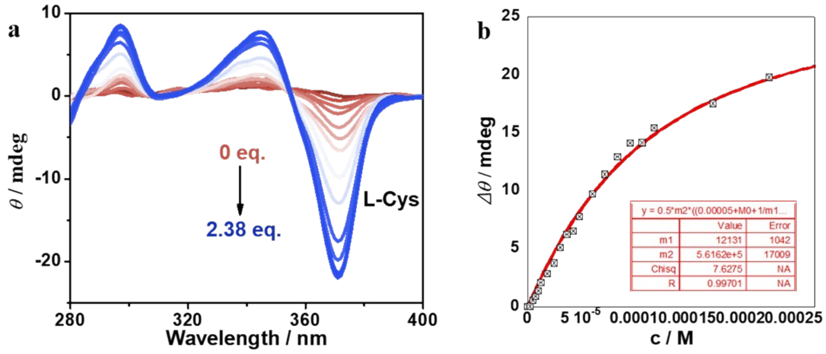


Fig. S27 (a) CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *L*-**Cys** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 371 nm upon the addition of *L*-**Cys**, and the host-guest association constant K_a was estimated to be 1.2×10^4 M^{-1}.

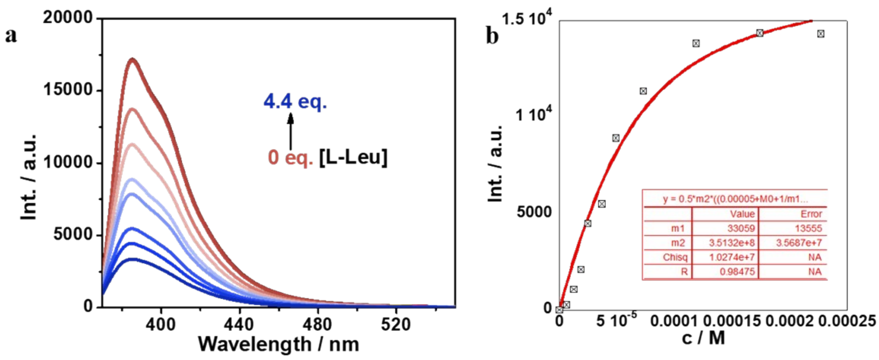


Fig. S28 Fluorescence spectral changes of **N1** (5.0×10^{-5} M) upon titration with *L*-**Leu** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (Fluorescence titrations) for the complexation of *L*-**Leu** and **N1** in $CHCl_3$ at room temperature (b). Curve fitting based on the CD intensity changes. The host-guest association constants (K_a) was estimated to be 3.3×10^4 M^{-1}.

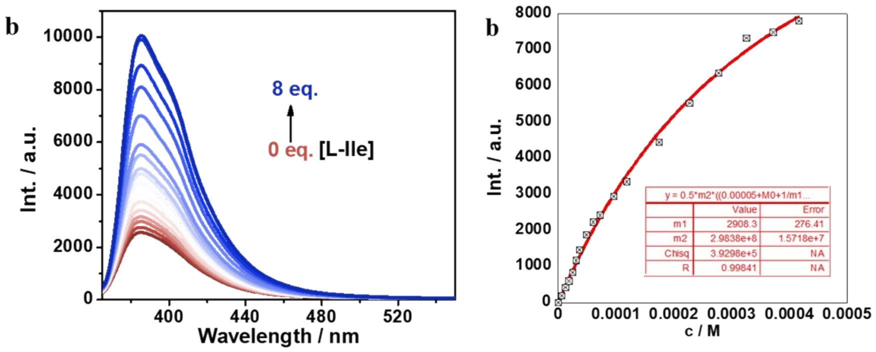


Fig. S29 Fluorescence spectral changes of **N1** (5.0×10^{-5} M) upon titration with *L*-**Ile** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (Fluorescence titrations) for the complexation of *L*-**Ile** and **N1** in $CHCl_3$ at room temperature (b). Curve fitting based on the CD intensity changes. The host-guest association constants (K_a) was estimated to be 2.9×10^3 M^{-1}.

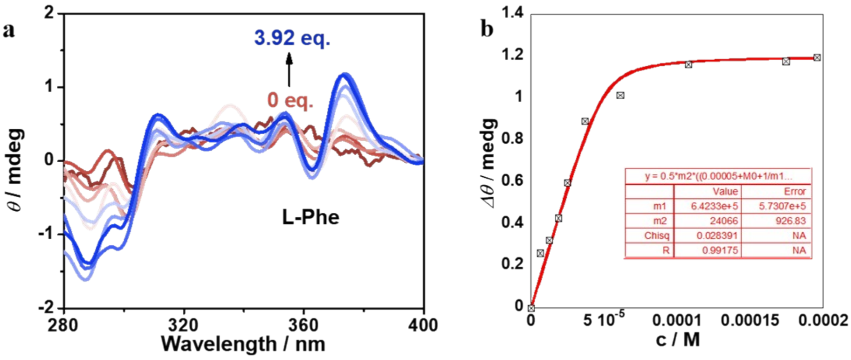


Fig. S30 CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *L*-**Phe** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Phe** and **N1** (371 nm) in $CHCl_3$ at room temperature (b). Curve fitting based on the CD intensity changes. The host-guest association constants (K_a) was estimated to be 6.4×10^5 M^{-1}.

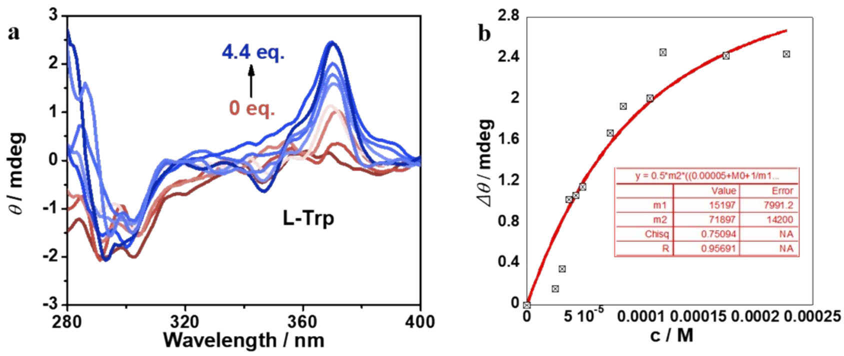


Fig. S31 CD spectral changes of **N1** (5.0×10^{-5} M) upon titration with *L*-**Trp** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Trp** and **N1** (371 nm) in $CHCl_3$ at room temperature (b). Curve fitting based on the CD intensity changes. The host-guest association constants (K_a) was estimated to be 2.1×10^4 M^{-1}.

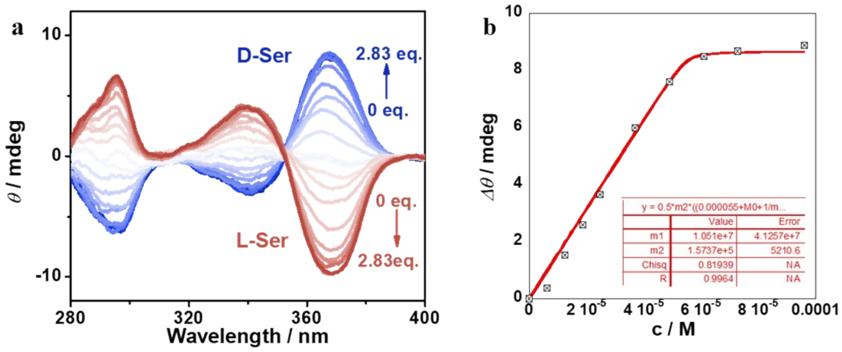


Fig. S32 CD spectral changes of **N2** (5.5×10^{-5} M) upon titration with **Ser** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Ser** and **N2** (368 nm) in $CHCl_3$ at room temperature (b). Curve fitting based on the CD intensity changes. The host-guest association constants (K_a) was estimated to be 1.05×10^7 M^{-1}.

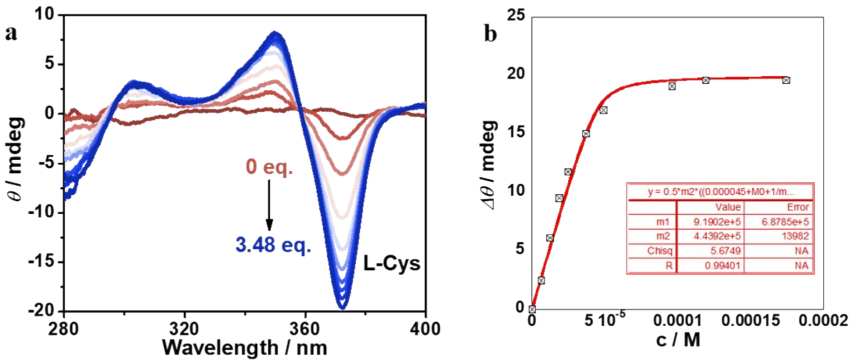


Fig. S33 CD spectral changes of **N2** (4.5×10^{-5} M) upon titration with *L*-**Cys** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Cys** and **N2** (372 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 9.19×10^5 M^{-1}.

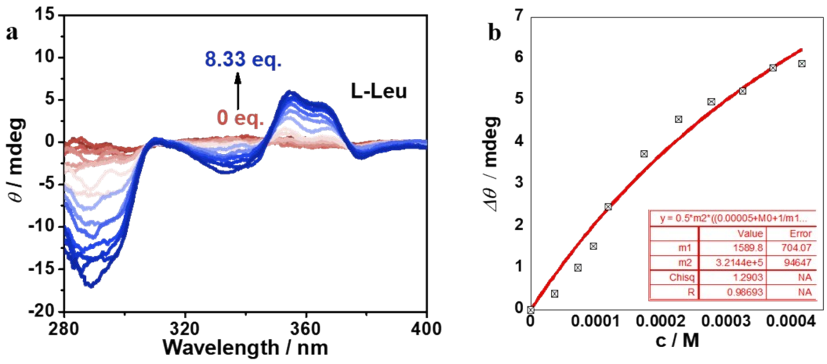


Fig. S34 CD spectral changes of **N2** (5.0×10^{-5} M) upon titration with *L*-**Leu** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Leu** and **N2** (360 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 1.59×10^3 M^{-1}.

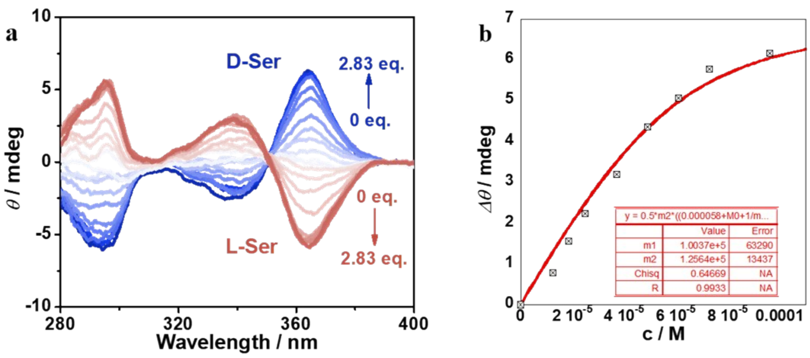


Fig. S35 CD spectral changes of **N3** (5.8×10^{-5} M) upon titration with **Ser** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Ser** and **N3** (364 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 1.00×10^5 M^{-1}.

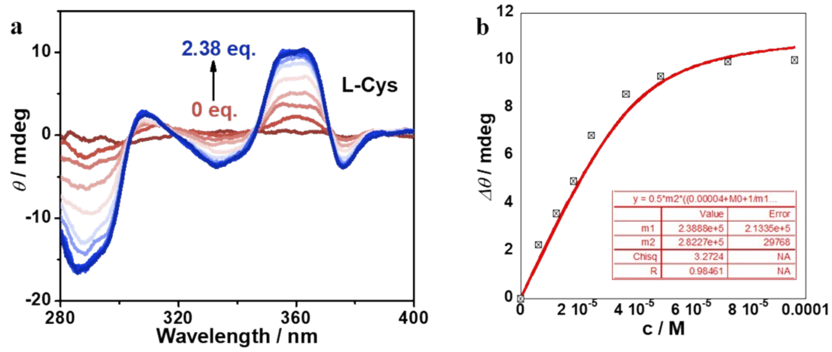


Fig. S36 CD spectral changes of **N3** (5.8×10^{-5} M) upon titration with *L*-**Cys** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Cys** and **N3** (359 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 2.39×10^5 M^{-1}.

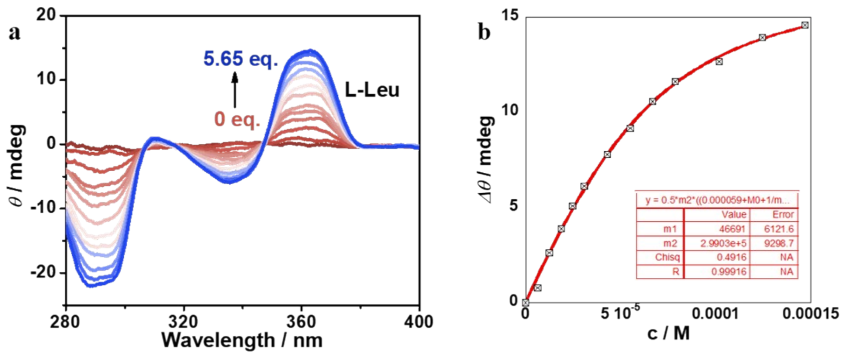


Fig. S37 CD spectral changes of **N3** (5.8×10^{-5} M) upon titration with *L*-**Leu** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Leu** and **N3** (362 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 4.67×10^4 M^{-1}.

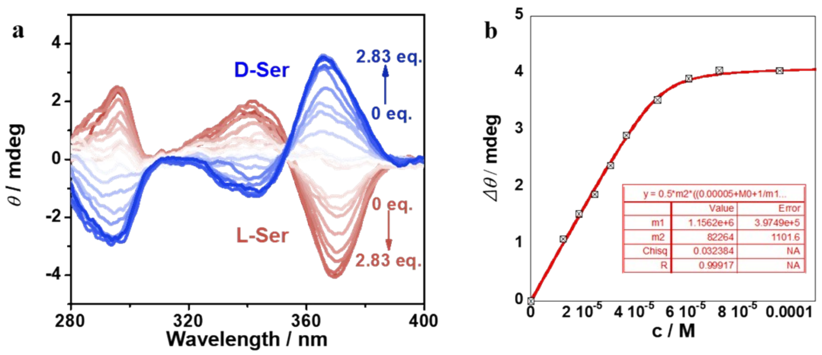


Fig. S38 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with **Ser** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Ser** and **N4** (366 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 1.16×10^6 M^{-1}.

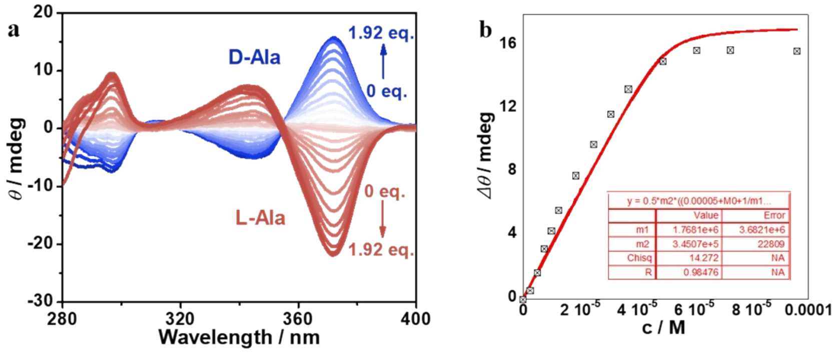


Fig. S39 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with **Ala** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Ala** and **N4** (368 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 1.77×10^6 M^{-1}.

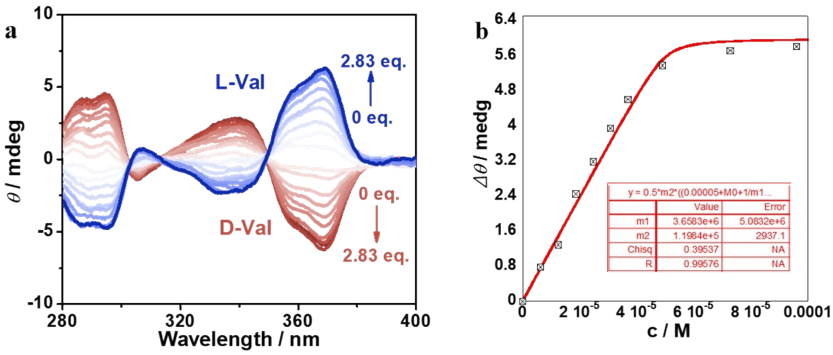


Fig. S40 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with **Val** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Val** and **N4** (369 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 3.66×10^6 M^{-1}.

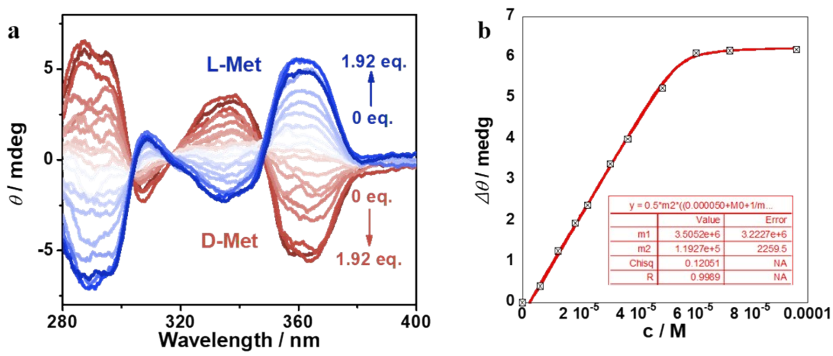


Fig. S41 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with **Met** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Met** and **N4** (369 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 3.51×10^6 M^{-1}.

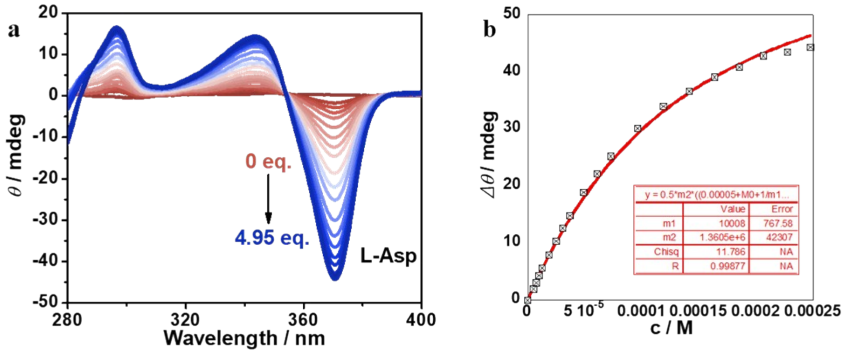


Fig. S42 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with *L*-**Asp** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Asp** and **N4** (370 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 1.00×10^4 M^{-1}.

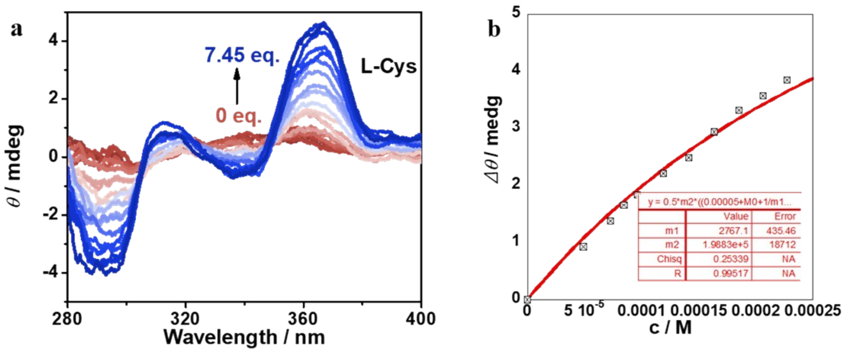


Fig. S43 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with *L*-**Cys** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Cys** and **N4** (370 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 2.77×10^3 M^{-1}.

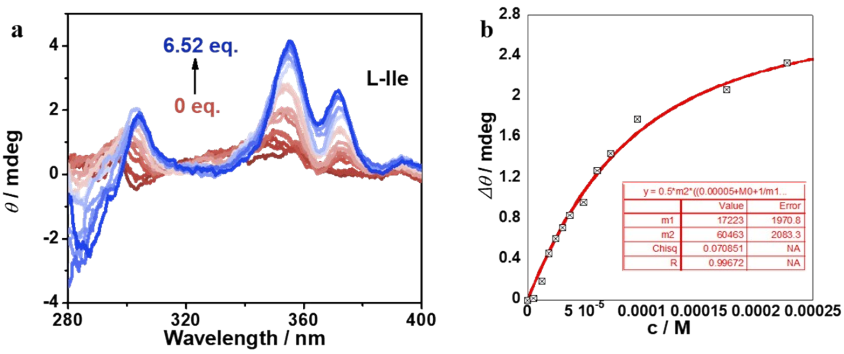


Fig. S44 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with *L*-**Ile** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Ile** and **N4** (360 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 1.72×10^4 M^{-1}.

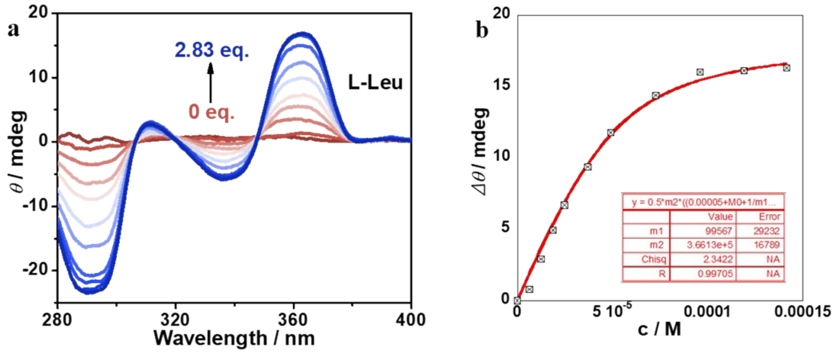


Fig. S45 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with *L*-**Leu** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Leu** and **N4** (365 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 9.96×10^4 M^{-1}.

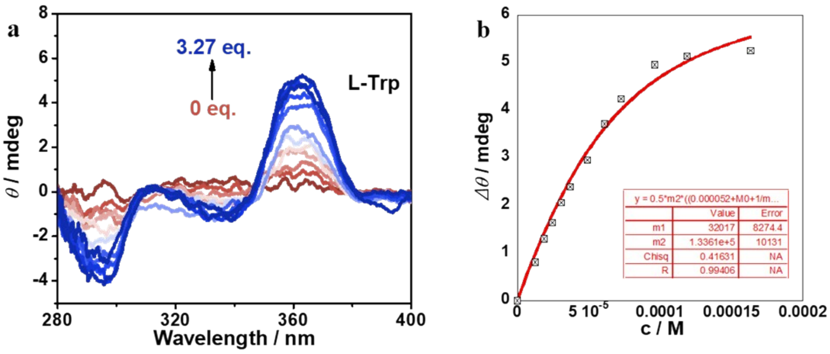


Fig. S46 CD spectral changes of **N4** (5.2×10^{-5} M) upon titration with *L*-**Trp** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Trp** and **N4** (365 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 3.20×10^4 M^{-1}.

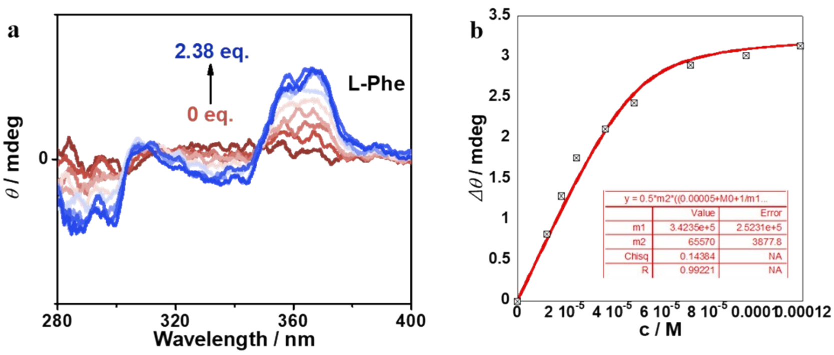


Fig. S47 CD spectral changes of **N4** (5.0×10^{-5} M) upon titration with *L*-**Phe** in $CHCl_3$ at room temperature (a). The non-linear curve-fitting (CD titrations) for the complexation of *L*-**Phe** and **N4** (369 nm) in $CHCl_3$ at room temperature (b). The association constants (Ka) of host and guest is 3.42×10^5 M^{-1}.

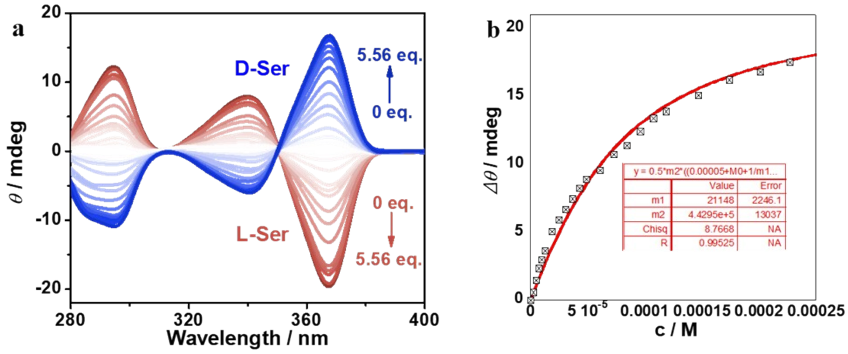


Fig. S48 (a) CD spectral changes of **CN1** (5.0×10^{-5} M) upon titration with *D*-/*L*-**Ser** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 368 nm upon the addition of *L*-**Ser**. The host-guest association constant K_a was estimated to be 2.11×10^4 M^{-1}.

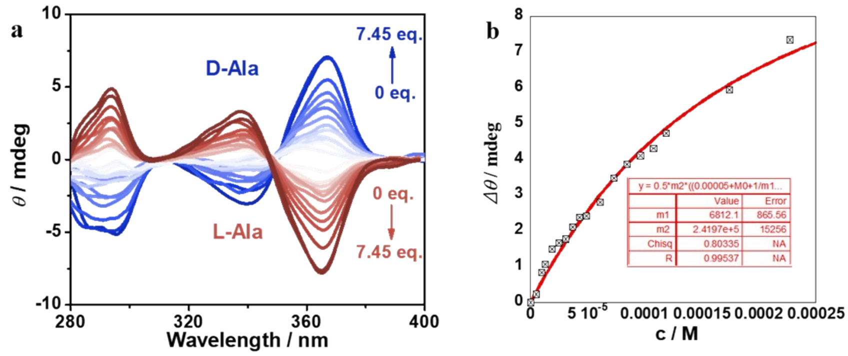


Fig. S49 (a) CD spectral changes of **CN1** (5.0×10^{-5} M) upon titration with *D*-/*L*-**Ala** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 368 nm upon the addition of *L*-**Ala**. The host-guest association constant K_a was estimated to be 6.81×10^3 M^{-1}.

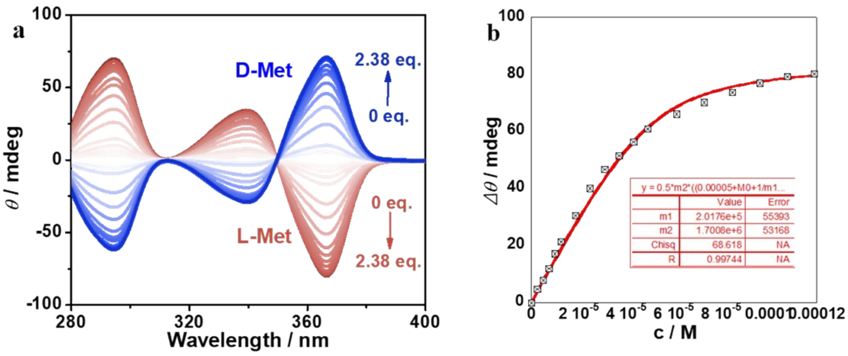


Fig. S50 (a) CD spectral changes of **CN1** (5.0×10^{-5} M) upon titration with *D*-/*L*-**Met** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 368 nm upon the addition of *L*-**Met**. The host-guest association constant K_a was estimated to be 2.02×10^5 M^{-1}.

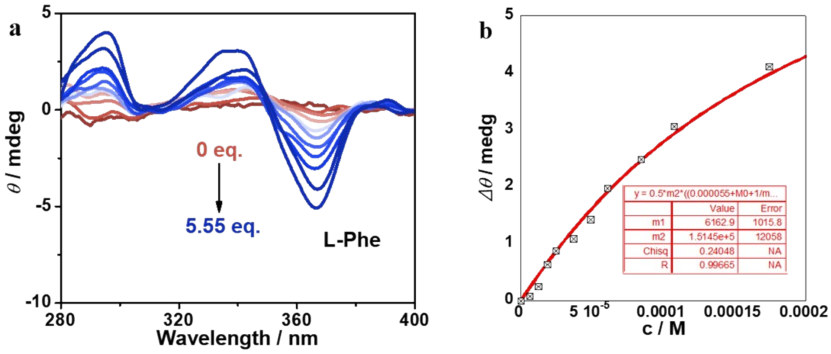


Fig. S51 (a) CD spectral changes of **CN1** (5.5×10^{-5} M) upon titration with *L*-**Phe** in $CHCl_3$ at room temperature. (b) The non-linear curve-fitting based on the CD intensity changes at 368 nm upon the addition of *L*-**Phe**. The host-guest association constant K_a was estimated to be 6.16×10^3 M^{-1}.

Table S1 Association constants and $\Delta\Delta\varepsilon$ values of CD_{max} at the $^{1}L_a$ band upon complexation of amino acid derivatives with **N1**, **CN** and **N4**[a]

Guest	N1		CN		N4	
	K_a / M^{-1}	$\Delta\Delta\varepsilon$ / $M^{-1}cm^{-1}$	K_a / M^{-1}	$\Delta\Delta\varepsilon$ / $M^{-1}cm^{-1}$	K_a / M^{-1}	$\Delta\Delta\varepsilon$ / $M^{-1}cm^{-1}$
L-Ser	4.92×10^{7}	-66.2	2.11×10^{4}	-19.8	1.81×10^{6}	-4.1
L-Ala	1.32×10^{6}	-76.7	1.77×10^{4}	-7.8	1.44×10^{6}	-21.9
L-Val	1.65×10^{5}	+12.2	\	+0.9	3.66×10^{6}	+6.4
L-Met	8.67×10^{6}	+9.3	2.02×10^{5}	-80	1.17×10^{6}	+5.6
L-Asp	2.09×10^{4}	-163.4	\	-0.3	1.00×10^{4}	-43.1
L-Cys	1.21×10^{4}	-21.7	\	-0.3	2.77×10^{3}	+4.7
L-Leu	3.23×10^{4} [b]	-3.2	\	-0.2	1.72×10^{4}	+16.6
L-Lle	2.91×10^{3} [b]	-0.9	\	-0.1	9.96×10^{4}	+4.1
L-Phe	6.42×10^{5}	+1.2	6.16×10^{3}	-5.1	3.42×10^{5}	+3.1
L-Trp	1.52×10^{4}	+2.4	\	+0.8	3.20×10^{4}	+5.2

[a]The CD_{max} were recorded upon complexation of 0.5 mM guest with 0.05 mM host. The association constants K_a were obtained based on the CD spectral titration. [b]K_a were estimated based on the fluorescence titrations data.

6 UV spectra of N1 complexes

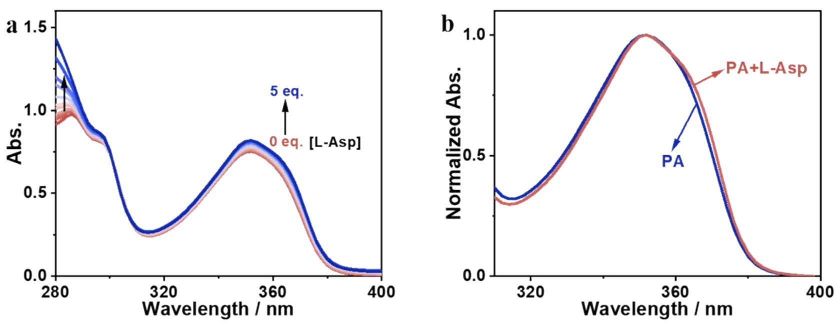


Fig. S52 UV-vis spectral changes of 0.05 mM **N1** upon increasing the concentration of *L*-**Asp** (a). Normalized UV-vis spectra of **N1** (blue line) and **N1**+*L*-**Asp** (red line). All above in $CHCl_3$ at room temperature. (The maximum absorption wavelength is redshifted from 350nm to 351nm)

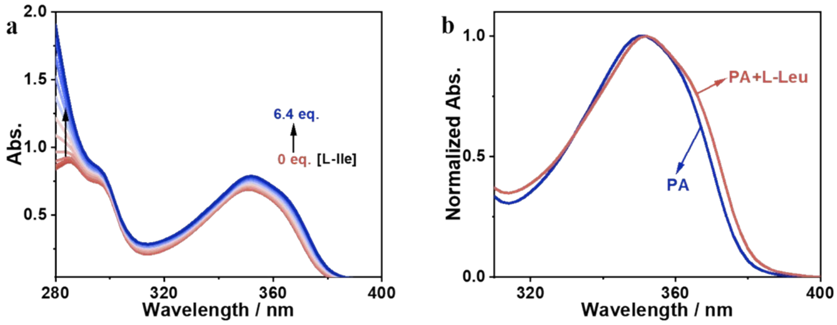


Fig. S53 UV-vis spectral changes of 0.05 mM **N1** upon increasing the concentration of *L*-**Ile** (a). Normalized UV-vis spectra of **N1** (blue line) and **N1**+*L*-**Ile** (red line). All above in $CHCl_3$ at room temperature. (The maximum absorption wavelength is redshifted from 350nm to 352nm)

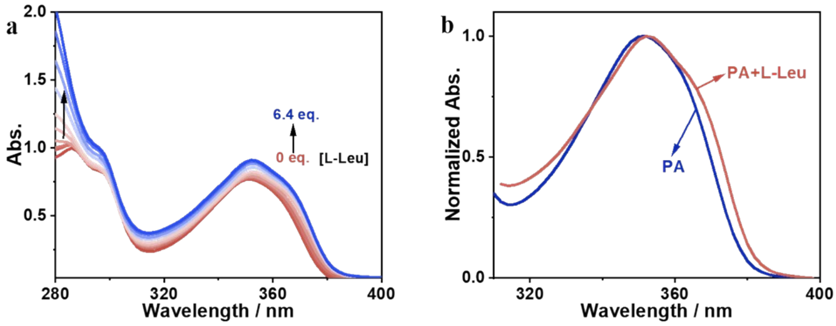


Fig. S54 UV-vis spectral changes of 0.05 mM **N1** upon increasing the concentration of *L*-**Leu** (a). Normalized UV-vis spectra of **N1** (blue line) and **N1**+*L*-**Leu** (red line). All above in $CHCl_3$ at room temperature. (The maximum absorption wavelength is redshifted from 350nm to 353nm)

7 Fluorescence spectra of N1 complexes

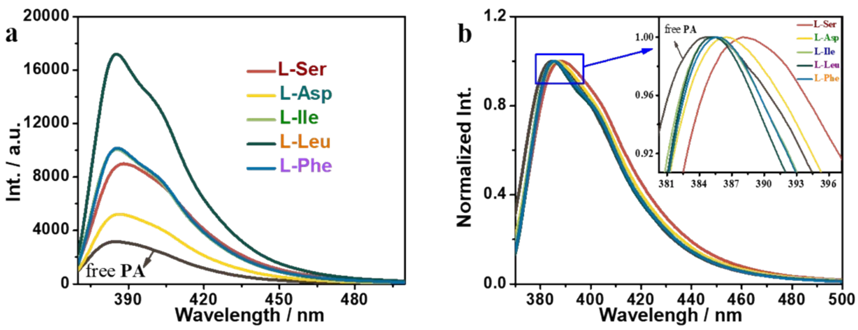


Fig. S55 a) Fluorescence excitation (λem = 350 nm) spectra of the complexes **N1** (0.05 mM) and different amino acid derivatives (0.5 mM) in CHCl3 in CHCl3 at room temperature. b) Normalized Fluorescence excitation (λem = 350 nm) spectra of the complexes N1 and different amino acid derivatives.

8 CD and CPL spectra of complex

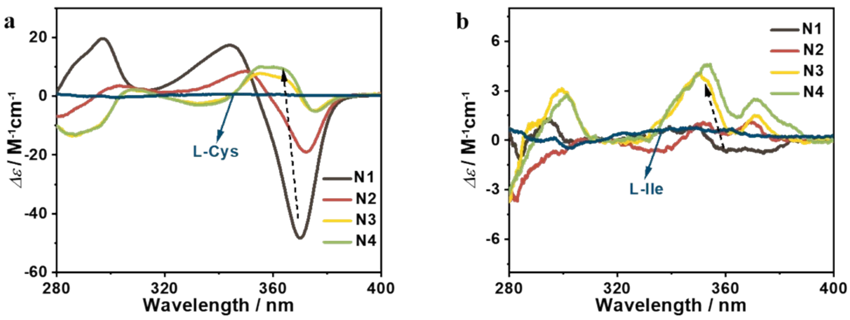


Fig. S56 CD spectra of **N1**~**N4** (5.0×10^{-5} M) in the presence of compound *L*-**Cys** (2.0×10^{-4} M) (a) and *L*-**Ile** (2.0×10^{-4} M) (b) in $CHCl_3$ at 25 °C.

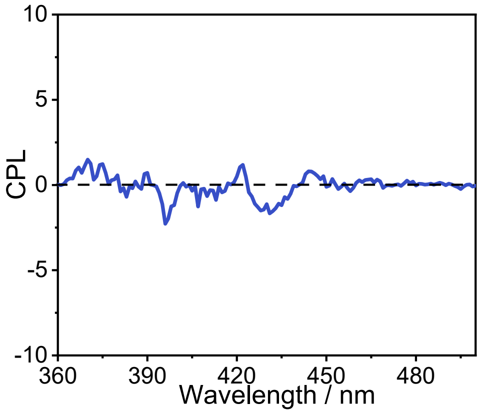


Fig. S57 CPL spectra and corresponding g_{lum} factor of the complexation of **N1** (0.05 mM) with L-**Asp** (0.25 mM) in CH_2Cl_2 at 25 °C.

9 Study on the model of complexes

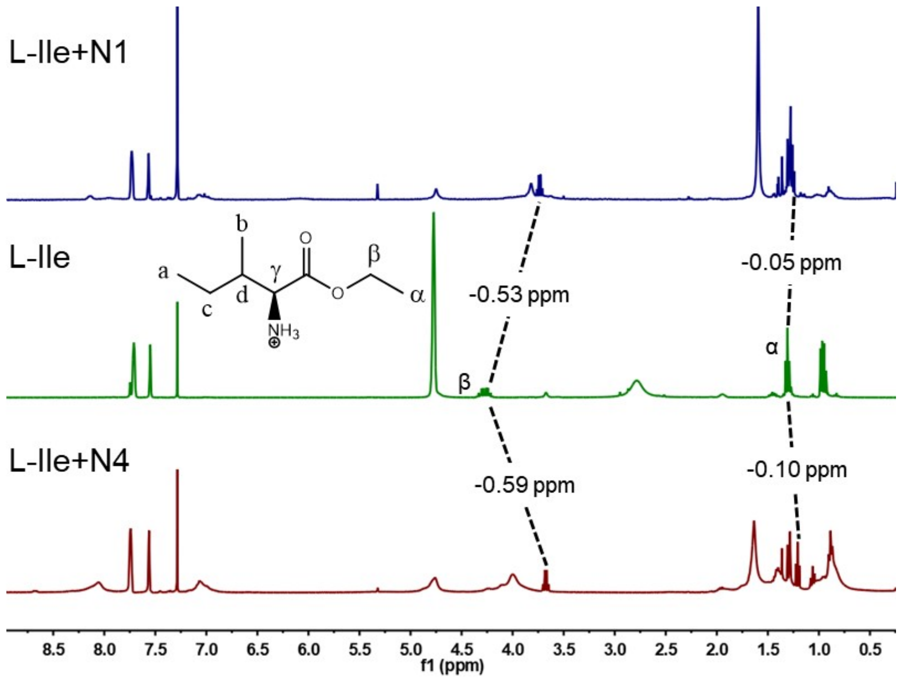


Fig. S58 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298K) of *L*-**Ile** @**N1**, *L*-**Ile** and *L*-**Ile** @**N4**.

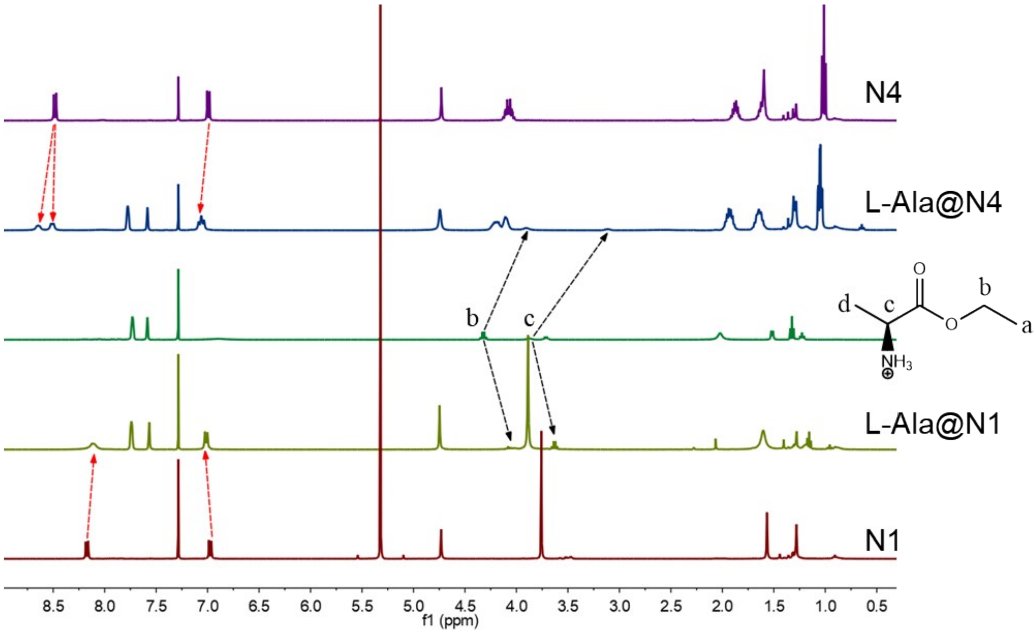


Fig. S59 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of **N1**, *L*-**Al**a@**N1**, *L*-**Ala** and *L*-**Ala**@**N4** and **N4**.

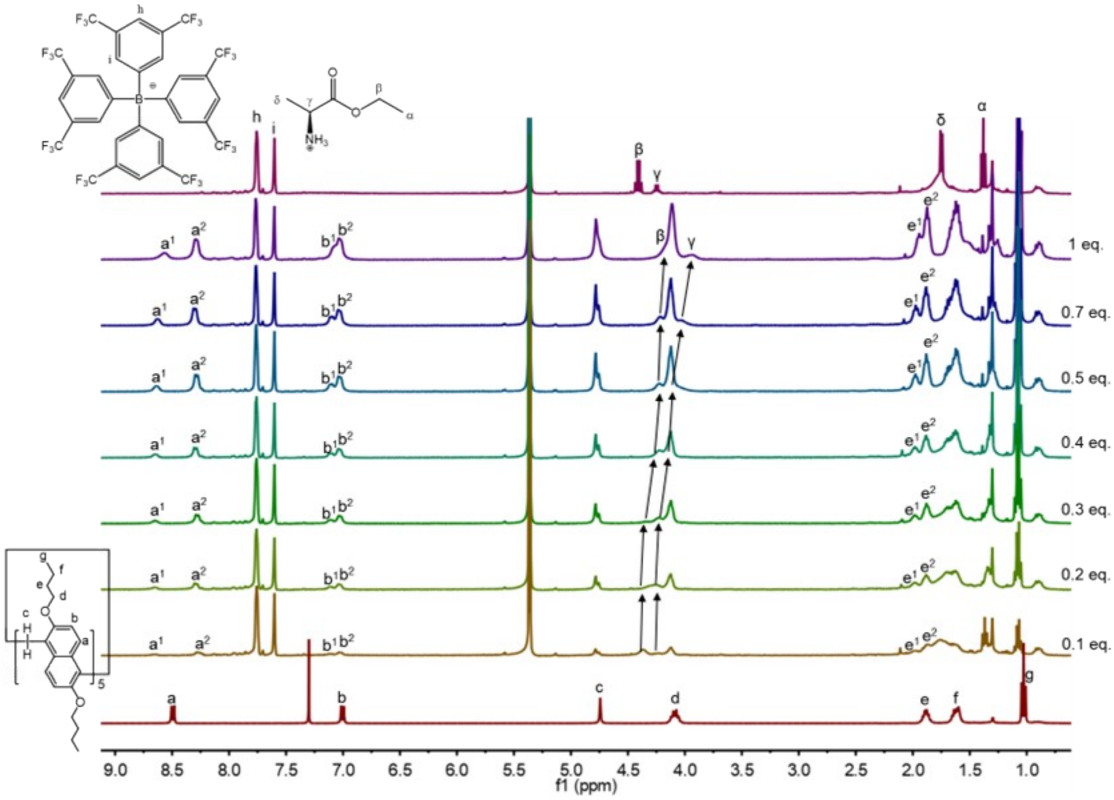


Fig. S60 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of *L*-**Ala** (2 mM) titrated by **N4**.

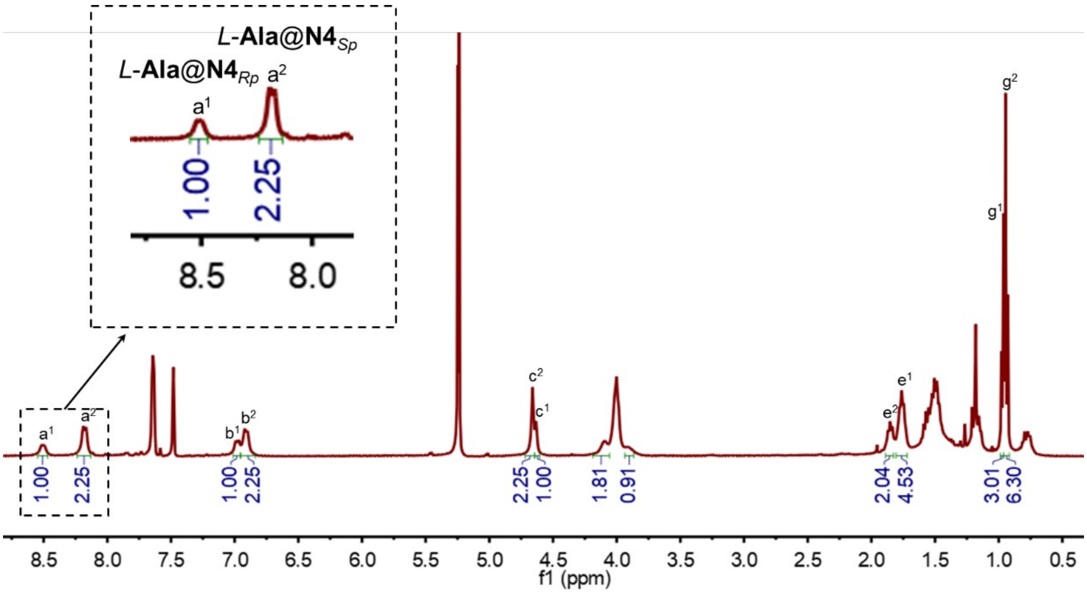


Fig. S61 ^{1}H NMR (400 MHz, 25°C) spectra of *L*-**Ala@N4** (1.25 mM) in CD_2Cl_2 showing the integrals of the methylene bridge (c), the alkyl (e and g) and aromatic protons (a and b) of **N4** detailing the 2.25:1 ratio of major (*L*-**Ala@N4**$_{Rp}$) to minor (*L*-**Ala@N4**$_{Sp}$) isomers..

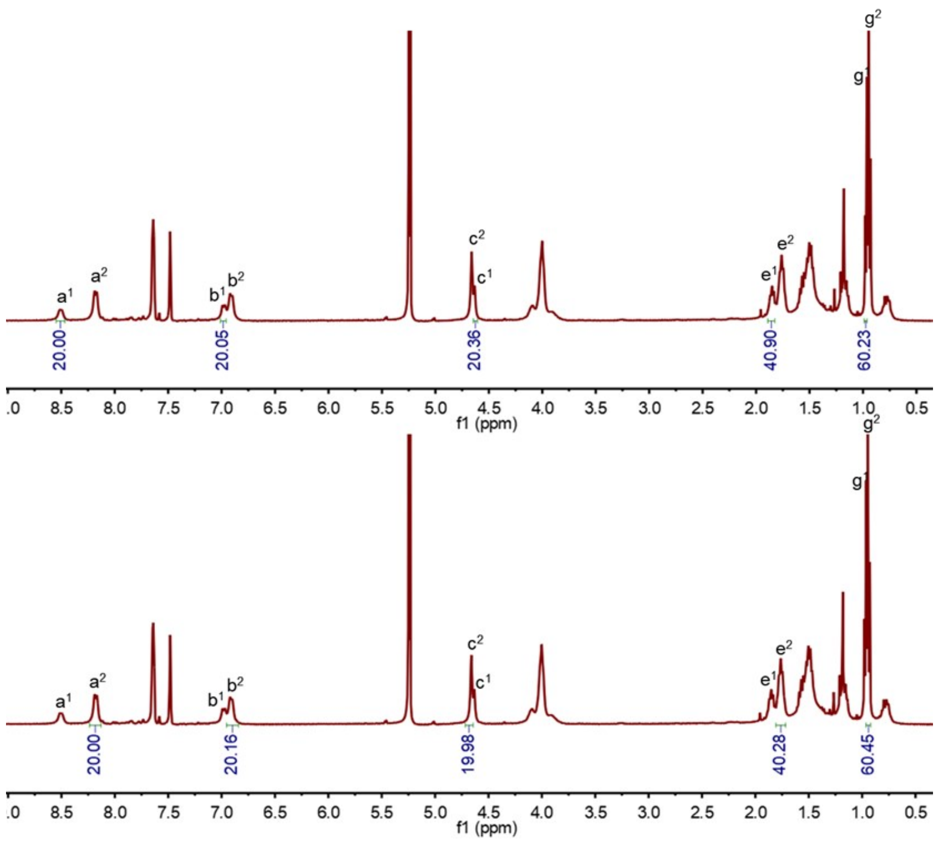


Fig. S62 ^{1}H NMR (400 MHz, 25°C) spectra of *L*-**Ala@N4** (1.25 mM) in CD_2Cl_2 showing the integrals of the methylene bridge (c), the alkyl (e and g) and aromatic protons (a and b) of **N4**. The two sets of signals belonging to the major (*L*-**Ala@N4**$_{Rp}$) and minor (*L*-**Ala@N4**$_{Sp}$) species are integrated separately, (bottom) major species and (up) minor species.

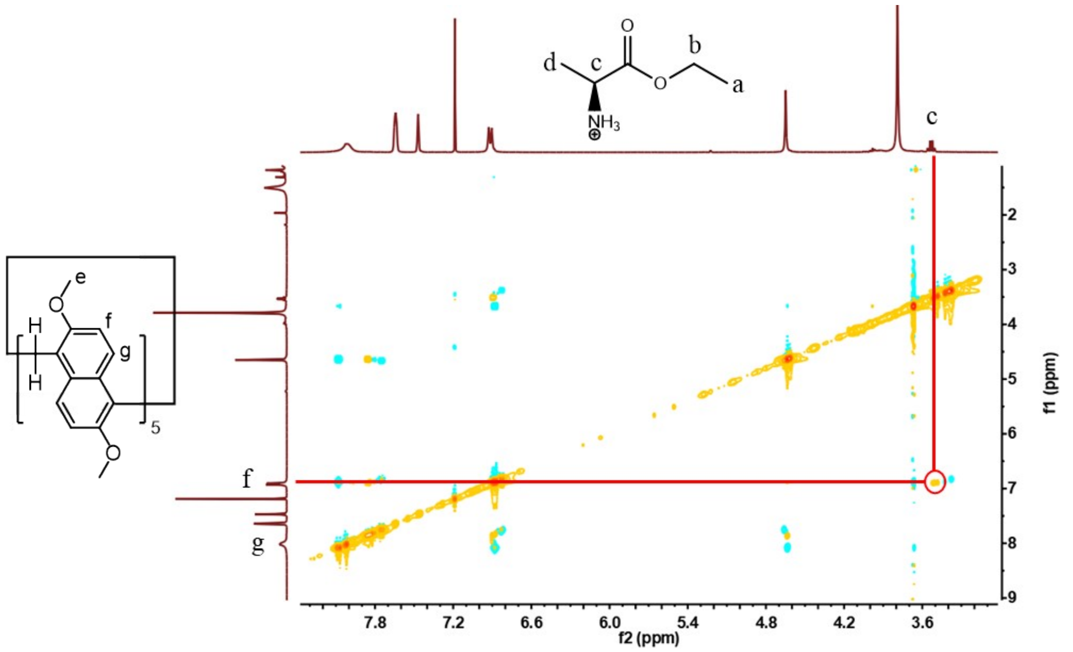


Fig. S63 ^{1}H-^{1}H ROESY NMR spectra of complexes ([**N1**] = [*L*-**Ala**] = 2 mM, 400 MHz, $CDCl_3$).

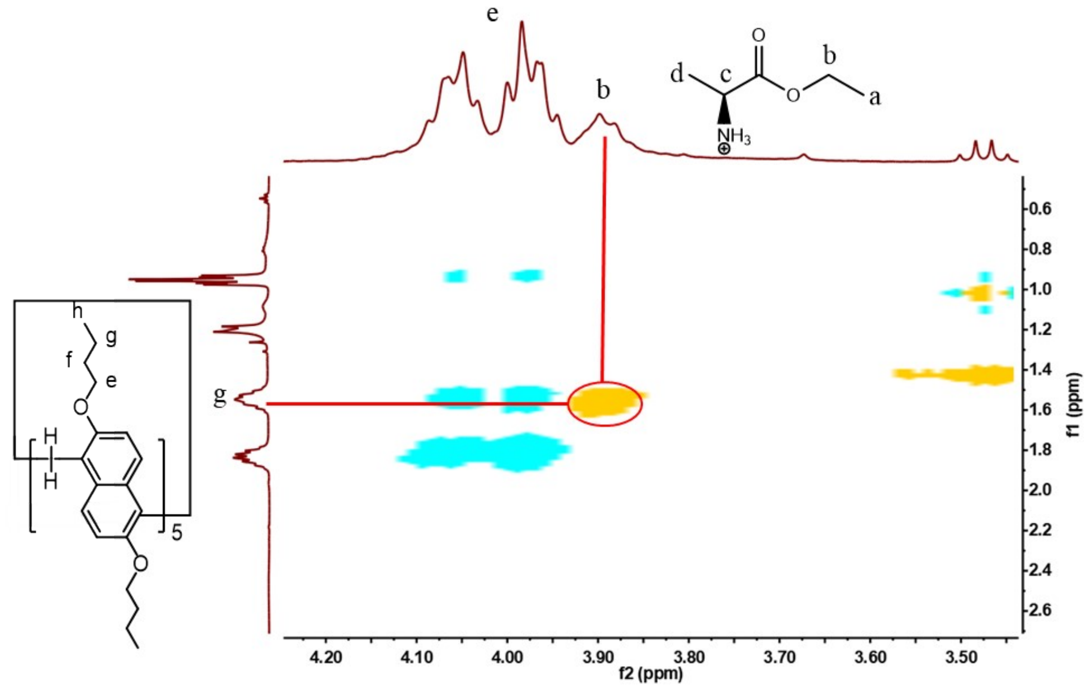


Fig. S64 ^{1}H-^{1}H ROESY NMR spectra of complexes ([**N4**] = [*L*-**Ala**] = 2 mM, 400 MHz, $CDCl_3$).

10 Determination of quantum yield of N1 complex

At room temperature, quinine sulfate in 0.5 mol/L H2SO4 solution as the reference standard (Φ = 0.55) and the prism [5] arene in $CHCl_3$ solution as the solution under test. The UV and fluorescence spectra of 5 × 10^{-6} mol/L standard and sample were determined under the same condition. Absorbance (A_s, A_x) and relative fluorescence intensity (D_s, D_x, Area integral intensity) of standard and sample solutions were obtained respectively. Then through solution refractive correction, the quantum yield (Φ) of prism[5]arene was calculated.

The calculation formula is as follows:

$$\emptyset_x = \frac{{n_x}^2}{{n_s}^2} \cdot \frac{A_s \cdot D_x}{A_x \cdot D_s} \cdot \emptyset_s \quad (A \leq 0.05)$$

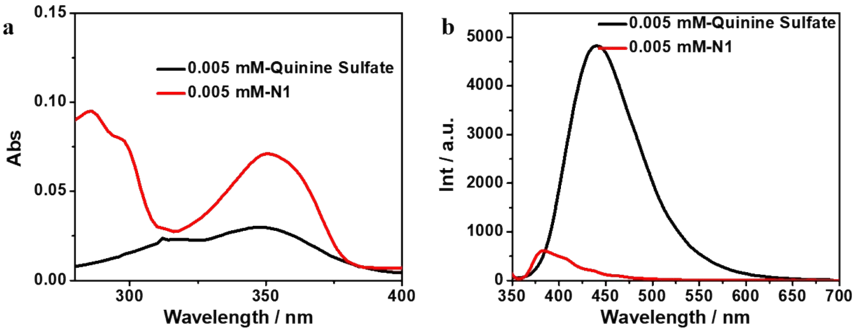


Fig. S65 The UV-vis a) and fluorescenece spectra b) of 0.005 mM **N1** and **qninine sulfate**.

Table S2 The Spectral data of different compounds.

	Solvent	λ_{ab}	λ_{ex}	Φ
Quinine Sulfate	0.5 mol/L H_2SO_4	350	440	0.55
Prism[5]arene	$CHCl_3$	350	384	0.10
Prism[5]arene+Ser	$CHCl_3$	350	388	0.29
Prism[5]arene+Cys	$CHCl_3$	350	385	0.32
Prism[5]arene+Ala	$CHCl_3$	350	391	0.37
Prism[5]arene+Asp	$CHCl_3$	350	386	0.20
Prism[5]arene+Lle	$CHCl_3$	350	385	0.37
Prism[5]arene+Phe	$CHCl_3$	350	385	0.27
Prism[5]arene+Leu	$CHCl_3$	350	385	0.49

12 Calculations for Complexation Between the Hosts and *L*-Ile

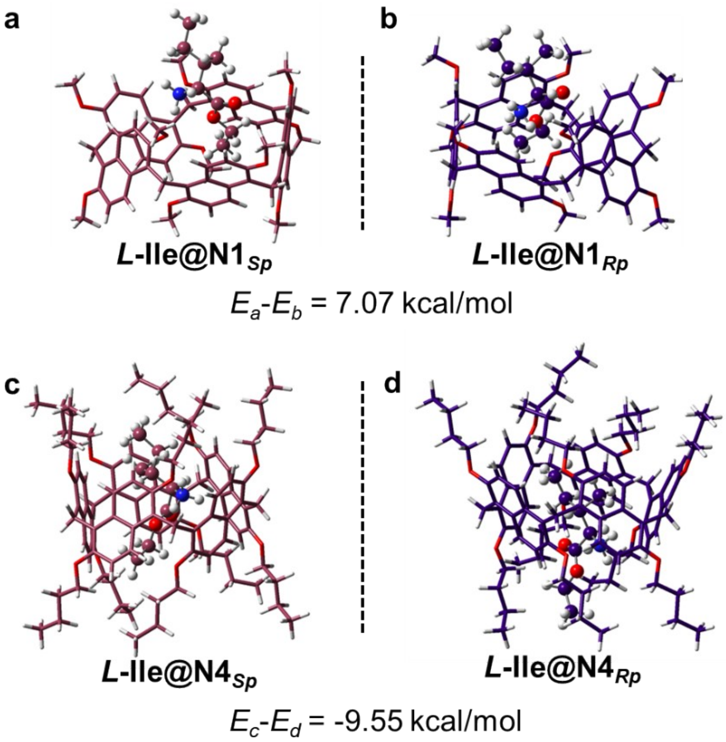


Fig. S66 The calculated optimal structure of enantiomeric complexes of (a) *L*-**Ile**@**N1**$_{Sp}$, (a) *L*-**Ile**@**N1**$_{Rp}$, (c) *L*-**Ile**@**N4**$_{Sp}$, (d) *L*-**Ile**@**N4**$_{Rp}$. Color code: pink for carbon, red for oxygen, blue for nitrogen, and white for hydrogen atoms in (a) and (c); purple for carbon, red for oxygen, blue for nitrogen, and white for hydrogen atoms in (b) and (d). Stability order: *L*-**Ile**@**N1**$_{Sp}$ < *L*-**Ile**@**N1**$_{Rp}$, *L*-**Ile**@**N4**$_{Rp}$ < *L*-**Ile**@**N4**$_{Sp}$. Solvents and the counter anions were omitted.

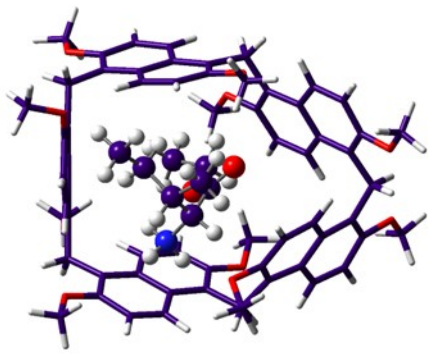


Fig. S67 Calculated structure of complex *L*-**Ile**@*R*-**N1** at B3LYP/6-31G(d) level.

The atomic coordinates of *L*-**Ile**@*R*-**N1**

C	5.69590000	2.48230000	1.76530000
C	5.53380000	1.13410000	1.77570000
C	5.51270000	0.44690000	0.60540000
C	5.53300000	1.05460000	-0.60360000
C	5.57210000	2.39560000	-0.57670000
C	5.67460000	3.08470000	0.56430000
C	5.49810000	-0.89550000	0.59700000
C	5.60070000	-1.57840000	-0.54650000
C	5.69350000	-0.97380000	-1.74180000

1	C	5.54450000	0.37300000	-1.77910000
2	O	5.82720000	3.17690000	2.94890000
3	O	5.75980000	-1.76320000	-2.86430000
4	C	5.88770000	4.58380000	2.93270000
5	C	7.07160000	-2.11830000	-3.23560000
6	C	4.37750000	3.20570000	-3.76950000
7	C	4.23780000	1.88720000	-3.48410000
8	C	3.00910000	1.31270000	-3.55000000
9	C	1.86810000	2.01240000	-3.75980000
10	C	2.03610000	3.32950000	-3.96990000
11	C	3.24670000	3.89950000	-3.98600000
12	C	2.87650000	-0.01590000	-3.41580000
13	C	1.69160000	-0.62090000	-3.50460000
14	C	0.56380000	0.06800000	-3.72220000
15	C	0.64360000	1.41880000	-3.76870000
16	O	5.62660000	3.78620000	-3.77860000
17	O	-0.62070000	-0.61970000	-3.74440000
18	C	5.74330000	5.18920000	-3.81900000
19	C	-0.89130000	-1.26030000	-4.97130000
20	C	-4.82620000	1.90050000	2.59540000
21	C	-4.48230000	0.91580000	1.72930000
22	C	-3.51340000	0.02210000	2.04460000
23	C	-2.76020000	0.14100000	3.16180000
24	C	-3.14310000	1.10300000	4.02000000
25	C	-4.14240000	1.95020000	3.75030000
26	C	-3.26310000	-1.02810000	1.24570000
27	C	-2.30570000	-1.90890000	1.54980000
28	C	-1.50930000	-1.76010000	2.61930000
29	C	-1.69340000	-0.66740000	3.39600000
30	O	-5.82070000	2.79360000	2.26670000
31	O	-0.48390000	-2.64870000	2.82330000
32	C	-6.11740000	3.85820000	3.13990000
33	C	-0.87290000	-3.86820000	3.41260000
34	C	0.52140000	1.53360000	3.64300000
35	C	0.62740000	0.23800000	4.03570000
36	C	1.84050000	-0.37910000	4.00960000
37	C	2.96920000	0.25310000	3.60690000
38	C	2.82690000	1.54590000	3.28260000
39	C	1.64870000	2.17000000	3.29390000
40	C	2.01500000	-1.65080000	4.40780000
41	C	3.21000000	-2.25100000	4.37040000
42	C	4.31920000	-1.63410000	3.92850000
43	C	4.19170000	-0.33760000	3.55010000
44	O	-0.68870000	2.17760000	3.67390000

1	O	5.55060000	-2.24900000	3.92100000
2	C	-0.74820000	3.58120000	3.57000000
3	C	5.77000000	-3.37180000	4.74330000
4	C	-0.98720000	2.98990000	-1.57990000
5	C	-1.49710000	2.20800000	-2.56360000
6	C	-2.65360000	1.52270000	-2.35330000
7	C	-3.32500000	1.56920000	-1.17660000
8	C	-2.83410000	2.41470000	-0.25650000
9	C	-1.70330000	3.09950000	-0.44950000
10	C	-3.22180000	0.76750000	-3.30940000
11	C	-4.33280000	0.05480000	-3.09590000
12	C	-4.96410000	0.04990000	-1.91050000
13	C	-4.44510000	0.83820000	-0.93630000
14	O	0.17780000	3.68770000	-1.78760000
15	O	-6.11500000	-0.66910000	-1.67570000
16	C	0.50770000	4.76640000	-0.94360000
17	C	-6.74290000	-1.34830000	-2.73810000
18	C	5.50240000	1.07460000	-3.14980000
19	C	-0.69050000	2.17110000	-3.87600000
20	C	-0.67420000	-0.43510000	4.51820000
21	C	5.46930000	0.42440000	3.13750000
22	C	-5.22270000	0.86090000	0.39180000
23	H	5.58890000	2.99480000	-1.49130000
24	H	5.75770000	4.17920000	0.47200000
25	H	5.46180000	-1.49560000	1.51460000
26	H	5.63280000	-2.68020000	-0.50060000
27	H	5.96870000	4.93010000	3.98760000
28	H	6.79500000	4.92760000	2.38800000
29	H	4.95230000	5.00640000	2.50260000
30	H	7.01450000	-2.73140000	-4.16250000
31	H	7.67100000	-1.20260000	-3.43760000
32	H	7.54630000	-2.72040000	-2.42900000
33	H	1.20160000	4.01300000	-4.17950000
34	H	3.27760000	4.98070000	-4.19540000
35	H	3.72390000	-0.68660000	-3.25870000
36	H	1.64280000	-1.71640000	-3.39950000
37	H	6.82410000	5.44060000	-3.73090000
38	H	5.37990000	5.58280000	-4.79410000
39	H	5.20980000	5.64650000	-2.95570000
40	H	-1.88560000	-1.75400000	-4.89170000
41	H	-0.91660000	-0.51310000	-5.79540000
42	H	-0.12220000	-2.03680000	-5.17990000
43	H	-2.66520000	1.25460000	4.99840000
44	H	-4.36710000	2.71150000	4.51410000

1	H	-3.84510000	-1.23660000	0.33580000
2	H	-2.16360000	-2.77540000	0.88490000
3	H	-6.92110000	4.46750000	2.66880000
4	H	-6.50390000	3.47020000	4.10850000
5	H	-5.22490000	4.50950000	3.27450000
6	H	0.03910000	-4.48490000	3.57500000
7	H	-1.36300000	-3.67480000	4.39240000
8	H	-1.56430000	-4.41560000	2.73490000
9	H	3.66590000	2.17130000	2.97870000
10	H	1.64690000	3.23050000	2.99610000
11	H	1.20100000	-2.27620000	4.79710000
12	H	3.24810000	-3.29530000	4.72000000
13	H	-1.81030000	3.88650000	3.70210000
14	H	-0.14630000	4.05460000	4.37730000
15	H	-0.42770000	3.91310000	2.55830000
16	H	6.85770000	-3.60640000	4.71150000
17	H	5.49080000	-3.14020000	5.79540000
18	H	5.22290000	-4.25800000	4.35210000
19	H	-3.33160000	2.60470000	0.70090000
20	H	-1.37680000	3.75800000	0.36990000
21	H	-2.82060000	0.68710000	-4.32810000
22	H	-4.71190000	-0.53550000	-3.94540000
23	H	1.42720000	5.24350000	-1.35160000
24	H	-0.31000000	5.52100000	-0.94520000
25	H	0.74150000	4.40910000	0.08330000
26	H	-7.67100000	-1.81560000	-2.33860000
27	H	-7.03340000	-0.63220000	-3.53890000
28	H	-6.08810000	-2.16310000	-3.11990000
29	H	5.64610000	0.38160000	-4.00800000
30	H	6.43960000	1.67170000	-3.20540000
31	H	-1.23250000	1.75740000	-4.74910000
32	H	-0.60350000	3.21990000	-4.22420000
33	H	-0.53590000	-1.38810000	5.06470000
34	H	-1.05270000	0.17720000	5.36150000
35	H	6.39060000	-0.19830000	3.17370000
36	H	5.65310000	1.11740000	3.98960000
37	H	-5.89440000	-0.01900000	0.51870000
38	H	-5.92750000	1.71150000	0.25130000
39	C	2.88080000	-3.69730000	-1.24090000
40	C	1.47170000	-4.20530000	-0.88310000
41	C	3.62310000	-4.57670000	-2.25670000
42	C	0.71020000	-3.27260000	0.07600000
43	C	0.26090000	-1.93360000	-0.48440000
44	O	1.17590000	-1.00170000	-0.12170000

C	0.78820000	0.34240000	-0.09130000
C	2.04170000	1.20080000	0.00250000
O	-0.78630000	-1.72690000	-1.05500000
N	1.54940000	-3.03500000	1.30840000
C	0.60710000	-4.48370000	-2.12660000
H	2.82810000	-2.65520000	-1.62890000
H	3.49470000	-3.66660000	-0.31020000
H	1.60440000	-5.18490000	-0.35390000
H	3.17610000	-4.49700000	-3.27310000
H	4.68990000	-4.27240000	-2.35090000
H	3.61120000	-5.64650000	-1.94720000
H	-0.21210000	-3.80400000	0.40810000
H	0.22320000	0.60530000	-1.01060000
H	0.13690000	0.49780000	0.80000000
H	2.70550000	0.83850000	0.81580000
H	2.63190000	1.15950000	-0.93730000
H	1.79570000	2.26730000	0.20180000
H	1.52230000	-3.88250000	1.91890000
H	2.53680000	-2.84180000	1.02970000
H	1.19290000	-2.20740000	1.83510000
H	-0.42230000	-4.79880000	-1.84060000
H	0.51420000	-3.58270000	-2.77160000
H	1.02380000	-5.30620000	-2.74940000

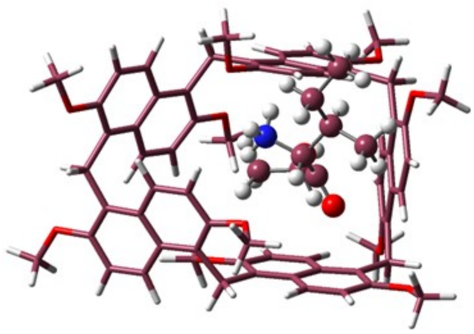


Fig. S68 Calculated structure of complex *L*-**Ile**@*S*-**N1** at B3LYP/6-31G(d) level.

The atomic coordinates of *L*-**Ile**@*S*-**N1**

C	-5.28020000	3.45950000	-0.98410000
C	-5.34340000	2.11350000	-0.82080000
C	-4.86750000	1.29270000	-1.79240000
C	-4.21860000	1.74490000	-2.89020000
C	-4.09780000	3.07870000	-2.97650000
C	-4.62840000	3.90700000	-2.07080000
C	-5.05790000	-0.03390000	-1.72970000
C	-4.66220000	-0.84790000	-2.71300000
C	-3.99720000	-0.40630000	-3.79390000

1	C	-3.74290000	0.92580000	-3.86570000
2	O	-5.84900000	4.30040000	-0.05170000
3	O	-3.63050000	-1.26260000	-4.80840000
4	C	-5.77610000	5.69540000	-0.23120000
5	C	-4.44600000	-2.38020000	-5.07660000
6	C	-1.46500000	3.44750000	-5.21150000
7	C	-1.62400000	2.15770000	-4.82420000
8	C	-0.58340000	1.50050000	-4.25200000
9	C	0.58840000	2.09050000	-3.91610000
10	C	0.69400000	3.38220000	-4.27430000
11	C	-0.28540000	4.02430000	-4.92290000
12	C	-0.66930000	0.18190000	-4.02580000
13	C	0.32000000	-0.50460000	-3.45500000
14	C	1.45570000	0.08420000	-3.05930000
15	C	1.58360000	1.41550000	-3.27750000
16	O	-2.46830000	4.09250000	-5.90090000
17	O	2.38640000	-0.67370000	-2.39350000
18	C	-2.19690000	5.31810000	-6.53950000
19	C	3.09500000	-1.58060000	-3.20930000
20	C	3.57650000	1.81110000	4.85550000
21	C	3.63990000	0.92540000	3.83200000
22	C	2.57020000	0.15320000	3.51950000
23	C	1.36230000	0.31270000	4.10880000
24	C	1.33640000	1.17630000	5.14040000
25	C	2.40750000	1.88660000	5.51240000
26	C	2.67350000	-0.80980000	2.59020000
27	C	1.61350000	-1.53180000	2.22300000
28	C	0.39880000	-1.34190000	2.76110000
29	C	0.25710000	-0.35370000	3.67750000
30	O	4.68560000	2.55330000	5.19230000
31	O	-0.64360000	-2.06250000	2.23820000
32	C	4.67200000	3.32910000	6.36780000
33	C	-0.95960000	-3.25130000	2.92700000
34	C	-1.62120000	2.02390000	2.96780000
35	C	-2.05530000	0.76960000	3.24990000
36	C	-3.24170000	0.33350000	2.74540000
37	C	-4.01440000	1.10510000	1.94370000
38	C	-3.56930000	2.35040000	1.72030000
39	C	-2.41710000	2.80170000	2.21850000
40	C	-3.74010000	-0.88630000	3.01130000
41	C	-4.91740000	-1.29720000	2.52480000
42	C	-5.67880000	-0.53230000	1.72300000
43	C	-5.18590000	0.68820000	1.39720000
44	O	-0.44090000	2.48540000	3.49240000

1	O	-6.88830000	-0.94940000	1.21280000
2	C	-0.17170000	3.86800000	3.50740000
3	C	-7.30540000	-2.28010000	1.41050000
4	C	2.26160000	3.06830000	-0.69150000
5	C	3.07690000	2.17550000	-1.30400000
6	C	3.98110000	1.46470000	-0.58000000
7	C	4.07470000	1.58220000	0.76550000
8	C	3.30450000	2.52320000	1.33630000
9	C	2.42930000	3.24490000	0.62910000
10	C	4.84590000	0.60710000	-1.14970000
11	C	5.70460000	-0.12650000	-0.43330000
12	C	5.74820000	-0.06820000	0.90780000
13	C	4.90880000	0.81090000	1.50870000
14	O	1.35740000	3.78800000	-1.43560000
15	O	6.60750000	-0.82940000	1.66750000
16	C	0.71320000	4.90560000	-0.87150000
17	C	7.60390000	-1.59700000	1.03330000
18	C	-2.97700000	1.46890000	-5.09180000
19	C	2.90370000	2.05170000	-2.82420000
20	C	-1.16110000	-0.06070000	4.18810000
21	C	-6.02080000	1.57400000	0.45180000
22	C	4.95340000	0.86340000	3.04390000
23	H	-3.60410000	3.56340000	-3.82390000
24	H	-4.51090000	4.98540000	-2.26250000
25	H	-5.59060000	-0.51180000	-0.89960000
26	H	-4.89940000	-1.91690000	-2.59650000
27	H	-6.30310000	6.17370000	0.62480000
28	H	-4.71610000	6.03390000	-0.21320000
29	H	-6.29800000	5.99440000	-1.16730000
30	H	-4.12240000	-2.80990000	-6.05110000
31	H	-4.30810000	-3.16630000	-4.30330000
32	H	-5.51080000	-2.06810000	-5.16120000
33	H	1.59740000	3.98120000	-4.09460000
34	H	-0.08470000	5.06980000	-5.20650000
35	H	-1.54000000	-0.41230000	-4.30920000
36	H	0.18440000	-1.58560000	-3.30190000
37	H	-3.10510000	5.60730000	-7.11470000
38	H	-2.00340000	6.11460000	-5.78710000
39	H	-1.35260000	5.20350000	-7.25540000
40	H	3.86530000	-2.08050000	-2.58030000
41	H	2.41220000	-2.35820000	-3.61650000
42	H	3.59730000	-1.03430000	-4.03850000
43	H	0.43880000	1.35680000	5.74850000
44	H	2.27980000	2.56820000	6.36850000

1	H	3.61850000	-1.06790000	2.09440000
2	H	1.74970000	-2.30140000	1.44450000
3	H	5.67870000	3.79090000	6.47940000
4	H	3.92660000	4.15090000	6.28240000
5	H	4.48530000	2.68440000	7.25540000
6	H	-1.90750000	-3.65670000	2.50870000
7	H	-0.14530000	-3.99490000	2.77540000
8	H	-1.09080000	-3.06470000	4.01320000
9	H	-4.12770000	3.07720000	1.12730000
10	H	-2.14620000	3.84110000	1.97520000
11	H	-3.22690000	-1.61780000	3.64890000
12	H	-5.24030000	-2.31000000	2.81440000
13	H	0.79110000	4.02060000	4.04470000
14	H	-0.04470000	4.25680000	2.47460000
15	H	-0.97230000	4.40960000	4.05880000
16	H	-8.26880000	-2.41610000	0.86960000
17	H	-6.56280000	-2.98640000	0.97600000
18	H	-7.48980000	-2.47480000	2.49040000
19	H	3.35820000	2.76220000	2.40680000
20	H	1.83790000	3.99000000	1.18160000
21	H	4.90870000	0.44770000	-2.23440000
22	H	6.36680000	-0.80440000	-0.99530000
23	H	0.09900000	5.37800000	-1.67090000
24	H	0.02430000	4.59040000	-0.05710000
25	H	1.46410000	5.64810000	-0.52110000
26	H	8.21910000	-2.07500000	1.82840000
27	H	7.14370000	-2.40760000	0.42540000
28	H	8.26880000	-0.94320000	0.42600000
29	H	-2.77560000	0.70080000	-5.87070000
30	H	-3.70430000	2.12260000	-5.62300000
31	H	3.70420000	1.49240000	-3.34750000
32	H	3.10680000	3.05820000	-3.24190000
33	H	-1.59260000	-1.02340000	4.51490000
34	H	-1.19680000	0.46490000	5.16370000
35	H	-6.95860000	1.08970000	0.09950000
36	H	-6.42300000	2.37820000	1.10800000
37	H	5.47950000	-0.00700000	3.49840000
38	H	5.61780000	1.73560000	3.24220000
39	C	-0.34180000	-4.77550000	-2.44230000
40	C	-1.44980000	-3.76960000	-2.06650000
41	C	-0.56590000	-5.47970000	-3.78800000
42	C	-1.15930000	-3.04750000	-0.73560000
43	C	-2.03700000	-1.82520000	-0.51610000
44	O	-1.38390000	-0.78170000	-1.08100000

C	-1.64850000	0.54120000	-0.71660000
C	-0.42600000	1.10160000	-0.00170000
O	-3.07390000	-1.79460000	0.10450000
N	0.27920000	-2.59070000	-0.73430000
C	-2.82560000	-4.45670000	-1.98120000
H	0.63710000	-4.24350000	-2.51500000
H	-0.24180000	-5.53780000	-1.63390000
H	-1.50990000	-3.00280000	-2.87790000
H	-1.43500000	-6.17370000	-3.75620000
H	-0.73750000	-4.74050000	-4.60370000
H	0.32270000	-6.09150000	-4.06820000
H	-1.28950000	-3.74670000	0.12050000
H	-1.83050000	1.12600000	-1.64560000
H	-2.55480000	0.61480000	-0.08680000
H	-0.24460000	0.57410000	0.95950000
H	0.49020000	0.97670000	-0.61900000
H	-0.54770000	2.18630000	0.21450000
H	0.42510000	-1.90750000	0.04200000
H	0.50990000	-2.13470000	-1.64280000
H	0.90530000	-3.41520000	-0.59330000
H	-3.14410000	-4.87810000	-2.95990000
H	-2.81310000	-5.28670000	-1.23900000
H	-3.62420000	-3.74570000	-1.67480000

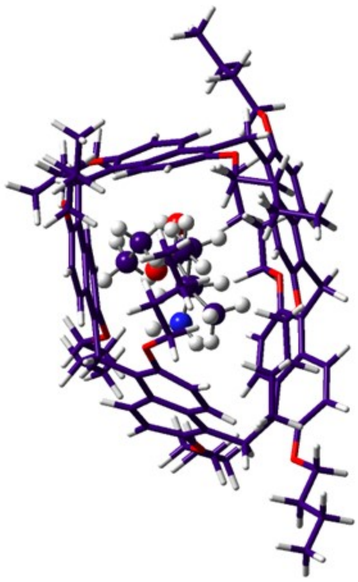


Fig. S69 Calculated structure of complex *L*-**Ile**@*R*-**N4** at B3LYP/6-31G(d) level.

The atomic coordinates of *L*-**Ile**@*R*-**N4**

C	-2.80430000	-0.52820000	-4.44110000
C	-3.10050000	0.43600000	-3.53590000
C	-2.10030000	1.15800000	-2.96700000

1	C	-0.78420000	0.91160000	-3.17730000
2	C	-0.53620000	0.00450000	-4.13650000
3	C	-1.50650000	-0.68340000	-4.74850000
4	C	-2.37820000	2.19830000	-2.16820000
5	C	-1.41360000	2.86930000	-1.53350000
6	C	-0.11180000	2.54390000	-1.63210000
7	C	0.21060000	1.54830000	-2.49790000
8	O	-3.81260000	-1.25370000	-5.03420000
9	O	0.86430000	3.19060000	-0.90480000
10	C	-3.51440000	-2.14530000	-6.07660000
11	C	0.47700000	4.15770000	0.04150000
12	C	2.23570000	-0.94680000	-1.63490000
13	C	2.44030000	0.39610000	-1.61200000
14	C	3.30100000	0.91520000	-0.68880000
15	C	3.87670000	0.16700000	0.28450000
16	C	3.67860000	-1.15300000	0.19640000
17	C	2.91100000	-1.69130000	-0.74740000
18	C	3.66480000	2.20880000	-0.67090000
19	C	4.52270000	2.69370000	0.23510000
20	C	5.05790000	1.94610000	1.21660000
21	C	4.66260000	0.65090000	1.28140000
22	O	1.39120000	-1.57430000	-2.51990000
23	O	5.91450000	2.47840000	2.15390000
24	C	1.86690000	-2.73560000	-3.16410000
25	C	5.79680000	3.84230000	2.47040000
26	C	-1.22290000	-2.14560000	6.27740000
27	C	-0.84300000	-0.87740000	5.98570000
28	C	-1.62930000	-0.13730000	5.16040000
29	C	-2.75760000	-0.58730000	4.55730000
30	C	-3.11330000	-1.83460000	4.90730000
31	C	-2.36650000	-2.58440000	5.72520000
32	C	-1.30590000	1.13570000	4.90340000
33	C	-2.00500000	1.89120000	4.05720000
34	C	-3.08230000	1.43130000	3.39860000
35	C	-3.48070000	0.16140000	3.67640000
36	O	-0.45520000	-2.96190000	7.07680000
37	O	-3.75640000	2.21640000	2.48850000
38	C	-0.38850000	-4.32200000	6.72220000
39	C	-3.27420000	3.51660000	2.24290000
40	C	-4.07010000	-1.84570000	1.14100000
41	C	-4.64010000	-0.65940000	1.47280000
42	C	-5.06400000	0.17740000	0.48860000
43	C	-4.77990000	-0.04480000	-0.81560000
44	C	-4.20950000	-1.22090000	-1.11960000

1	C	-3.91270000	-2.11180000	-0.16840000
2	C	-5.80700000	1.27010000	0.73620000
3	C	-6.19030000	2.10940000	-0.23250000
4	C	-5.80880000	1.95030000	-1.51040000
5	C	-5.06520000	0.85270000	-1.79080000
6	O	-3.71050000	-2.73640000	2.12580000
7	O	-6.12330000	2.84070000	-2.51110000
8	C	-3.50030000	-4.09100000	1.81000000
9	C	-6.81990000	4.01910000	-2.20480000
10	C	3.88610000	-2.18290000	3.40730000
11	C	4.07960000	-0.83830000	3.38190000
12	C	3.34700000	-0.06480000	4.22800000
13	C	2.34480000	-0.53860000	5.00590000
14	C	2.13120000	-1.86030000	4.93780000
15	C	2.90560000	-2.65600000	4.19560000
16	C	3.59780000	1.24600000	4.36040000
17	C	2.93060000	2.02130000	5.21980000
18	C	1.93830000	1.54820000	5.99310000
19	C	1.59980000	0.24240000	5.83150000
20	O	4.66820000	-3.04330000	2.67230000
21	O	1.23870000	2.36920000	6.85100000
22	C	5.04880000	-4.26550000	3.25040000
23	C	1.16220000	3.74020000	6.54890000
24	C	1.71360000	1.23870000	-2.68030000
25	C	5.16240000	-0.24110000	2.44590000
26	C	-4.76610000	-0.33850000	2.97470000
27	C	-4.59370000	0.66820000	-3.23910000
28	C	0.42990000	-0.31980000	6.66400000
29	C	0.86830000	-4.94000000	7.33620000
30	C	1.05820000	-6.39670000	6.88400000
31	C	2.33120000	-7.01550000	7.47590000
32	C	-4.06160000	4.20250000	1.12940000
33	C	-3.50050000	5.60510000	0.83750000
34	C	-4.19950000	6.27230000	-0.35340000
35	C	-3.12730000	-4.84340000	3.08760000
36	C	-2.73840000	-6.30510000	2.82080000
37	C	-2.27430000	-7.00560000	4.10550000
38	C	-6.88660000	4.88780000	-3.46130000
39	C	-7.58810000	6.22790000	-3.18990000
40	C	-7.65010000	7.10400000	-4.44790000
41	C	-4.81470000	-2.79910000	-6.54640000
42	C	-4.56560000	-3.81760000	-7.67020000
43	C	-5.86750000	-4.48160000	-8.13750000
44	C	1.65840000	4.58060000	0.91560000

1	C	1.19250000	5.47350000	2.07950000
2	C	2.32790000	5.78860000	3.06140000
3	C	0.89900000	-3.14370000	-4.27350000
4	C	1.21870000	-4.52580000	-4.86330000
5	C	0.22940000	-4.90020000	-5.97590000
6	C	6.50110000	4.10810000	3.80160000
7	C	6.32300000	5.56550000	4.25580000
8	C	7.01830000	5.83360000	5.59690000
9	C	6.16730000	-4.87490000	2.40420000
10	C	6.60140000	-6.24950000	2.93640000
11	C	7.72180000	-6.86170000	2.08560000
12	C	0.02890000	4.36430000	7.36350000
13	C	-0.13580000	5.85920000	7.04640000
14	C	-1.27430000	6.49140000	7.85740000
15	H	0.47780000	-0.22020000	-4.48790000
16	H	-1.19300000	-1.40450000	-5.51900000
17	H	-3.40240000	2.55110000	-1.99610000
18	H	-1.75600000	3.69680000	-0.89460000
19	H	-3.05160000	-1.58570000	-6.92240000
20	H	-2.82780000	-2.93990000	-5.70080000
21	H	-0.28560000	3.71400000	0.71980000
22	H	0.06380000	5.04880000	-0.48540000
23	H	4.16130000	-1.86740000	0.86260000
24	H	2.82470000	-2.78650000	-0.74130000
25	H	3.31590000	2.93910000	-1.41310000
26	H	4.78470000	3.76040000	0.14240000
27	H	1.91950000	-3.58170000	-2.44250000
28	H	2.87800000	-2.53500000	-3.58710000
29	H	6.26480000	4.45790000	1.66830000
30	H	4.71810000	4.09860000	2.57820000
31	H	-4.02850000	-2.32050000	4.54670000
32	H	-2.73300000	-3.59990000	5.94790000
33	H	-0.44050000	1.62210000	5.35490000
34	H	-1.62010000	2.91420000	3.92300000
35	H	-0.32060000	-4.40940000	5.61190000
36	H	-1.29200000	-4.85580000	7.09620000
37	H	-3.36500000	4.12510000	3.17300000
38	H	-2.21490000	3.45290000	1.90120000
39	H	-3.99160000	-1.51930000	-2.15580000
40	H	-3.47710000	-3.06220000	-0.51410000
41	H	-6.16600000	1.53690000	1.73960000
42	H	-6.81090000	2.96650000	0.07350000
43	H	-2.64740000	-4.19380000	1.10200000
44	H	-4.42860000	-4.51610000	1.36400000

1	H	-7.84980000	3.76330000	-1.86410000
2	H	-6.27180000	4.57790000	-1.41360000
3	H	1.34970000	-2.35720000	5.52130000
4	H	2.69040000	-3.73510000	4.24190000
5	H	4.38700000	1.74540000	3.79600000
6	H	3.23930000	3.07770000	5.27200000
7	H	4.18530000	-4.96810000	3.26260000
8	H	5.41180000	-4.08450000	4.28850000
9	H	2.12540000	4.23650000	6.80930000
10	H	0.93450000	3.86910000	5.46420000
11	H	2.20800000	2.21210000	-2.87510000
12	H	1.95170000	0.77140000	-3.65750000
13	H	5.89810000	0.27390000	3.10190000
14	H	5.82620000	-1.01180000	1.99660000
15	H	-5.54490000	0.41430000	3.21040000
16	H	-5.24940000	-1.20510000	3.46810000
17	H	-4.84830000	1.53120000	-3.89500000
18	H	-5.25230000	-0.14330000	-3.62380000
19	H	0.03820000	0.42470000	7.39360000
20	H	0.89920000	-1.04380000	7.36690000
21	H	1.76390000	-4.34700000	7.03220000
22	H	0.80050000	-4.89340000	8.44910000
23	H	1.11830000	-6.43790000	5.76970000
24	H	0.17260000	-7.00240000	7.19200000
25	H	2.29830000	-7.01350000	8.58930000
26	H	3.23730000	-6.45110000	7.15680000
27	H	2.45490000	-8.07130000	7.14150000
28	H	-5.13550000	4.28350000	1.41950000
29	H	-3.99560000	3.58650000	0.20300000
30	H	-3.61560000	6.24810000	1.74260000
31	H	-2.40760000	5.53870000	0.62030000
32	H	-5.29000000	6.39200000	-0.16140000
33	H	-3.77870000	7.28550000	-0.54790000
34	H	-4.06930000	5.67120000	-1.28250000
35	H	-2.25750000	-4.33510000	3.56550000
36	H	-3.97840000	-4.80640000	3.80810000
37	H	-1.91260000	-6.34400000	2.07020000
38	H	-3.61090000	-6.85020000	2.38830000
39	H	-3.07270000	-6.99210000	4.88210000
40	H	-1.37350000	-6.50770000	4.53200000
41	H	-2.00880000	-8.06950000	3.90760000
42	H	-7.42910000	4.33640000	-4.26600000
43	H	-5.85110000	5.08360000	-3.83050000
44	H	-8.62430000	6.03880000	-2.82050000

1	H	-7.04320000	6.77920000	-2.38630000
2	H	-8.21170000	6.59520000	-5.26440000
3	H	-8.16130000	8.07130000	-4.23650000
4	H	-6.62830000	7.33640000	-4.82620000
5	H	-5.51810000	-2.01080000	-6.90670000
6	H	-5.30350000	-3.31260000	-5.68390000
7	H	-4.08110000	-3.30700000	-8.53660000
8	H	-3.86030000	-4.60540000	-7.31180000
9	H	-6.58590000	-3.72570000	-8.52930000
10	H	-5.67140000	-5.21680000	-8.95170000
11	H	-6.36310000	-5.02630000	-7.30160000
12	H	2.15390000	3.68000000	1.34430000
13	H	2.41750000	5.11620000	0.29840000
14	H	0.37380000	4.96400000	2.64360000
15	H	0.77300000	6.42400000	1.67200000
16	H	3.18060000	6.28560000	2.54510000
17	H	2.70590000	4.85880000	3.54380000
18	H	1.97840000	6.46480000	3.87540000
19	H	-0.14130000	-3.15650000	-3.86810000
20	H	0.94790000	-2.39240000	-5.09580000
21	H	1.17470000	-5.29860000	-4.05880000
22	H	2.25750000	-4.52690000	-5.27180000
23	H	0.26310000	-4.16220000	-6.80980000
24	H	-0.81580000	-4.93220000	-5.59110000
25	H	0.46560000	-5.90300000	-6.40030000
26	H	7.58740000	3.87360000	3.70020000
27	H	6.08650000	3.43110000	4.58650000
28	H	6.73750000	6.25230000	3.47970000
29	H	5.23520000	5.79550000	4.35760000
30	H	8.11290000	5.63910000	5.52770000
31	H	6.88110000	6.89340000	5.91320000
32	H	6.60320000	5.18380000	6.40100000
33	H	5.81920000	-4.98150000	1.34920000
34	H	7.04400000	-4.18410000	2.39550000
35	H	5.72550000	-6.94180000	2.94170000
36	H	6.95250000	-6.14770000	3.99120000
37	H	8.62430000	-6.20860000	2.07970000
38	H	7.39290000	-7.00340000	1.03060000
39	H	8.02640000	-7.85750000	2.48240000
40	H	0.23650000	4.23110000	8.45200000
41	H	-0.92680000	3.83260000	7.13760000
42	H	0.81740000	6.39580000	7.26930000
43	H	-0.34380000	5.99010000	5.95720000
44	H	-1.08530000	6.40250000	8.95170000

1	H	-1.38130000	7.57470000	7.61880000
2	H	-2.24780000	5.99750000	7.63510000
3	C	0.45500000	-0.22450000	2.17100000
4	C	-0.12430000	-0.57910000	0.79720000
5	C	0.84170000	1.25400000	2.28230000
6	C	-0.43610000	-2.07420000	0.62270000
7	C	0.24510000	-3.07890000	1.53870000
8	O	1.13230000	-3.79600000	0.81180000
9	C	1.57020000	-5.02730000	1.31300000
10	C	2.66420000	-5.56640000	0.39820000
11	O	-0.02540000	-3.26630000	2.70420000
12	N	-0.19980000	-2.39910000	-0.83560000
13	C	-1.38940000	0.23460000	0.49550000
14	H	-0.27730000	-0.49630000	2.96180000
15	H	1.37350000	-0.83350000	2.33730000
16	H	0.64110000	-0.27160000	0.05250000
17	H	-0.02070000	1.93770000	2.15060000
18	H	1.24720000	1.49930000	3.28310000
19	H	1.61630000	1.51320000	1.52850000
20	H	-1.51570000	-2.23010000	0.81980000
21	H	1.97380000	-4.89630000	2.34120000
22	H	0.70320000	-5.72710000	1.34180000
23	H	2.28830000	-5.69750000	-0.64250000
24	H	3.53450000	-4.87210000	0.36340000
25	H	3.03480000	-6.55350000	0.75840000
26	H	-0.43970000	-1.56750000	-1.42160000
27	H	0.79880000	-2.67450000	-0.95330000
28	H	-0.80670000	-3.20440000	-1.10960000
29	H	-1.81270000	-0.03940000	-0.49480000
30	H	-2.15910000	0.05140000	1.27140000
31	H	-1.21370000	1.32780000	0.48680000

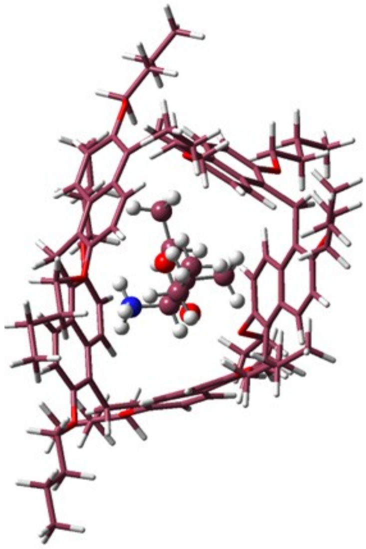


Fig. S70 Calculated structure of complex *L*-**Ile**@*S*-**N4** at B3LYP/6-31G(d) level.

The atomic coordinates of *L*-**Ile**@*S*-**N4**

C	2.58260000	-6.01480000	1.17650000
C	2.77880000	-5.26090000	0.06740000
C	1.75410000	-5.03320000	-0.79090000
C	0.47930000	-5.41050000	-0.53720000
C	0.33420000	-6.20880000	0.53300000
C	1.34390000	-6.49860000	1.36100000
C	1.97800000	-4.43310000	-1.96870000
C	0.97550000	-4.17990000	-2.81450000
C	-0.31280000	-4.40160000	-2.49530000
C	-0.56840000	-5.02860000	-1.31770000
O	3.62580000	-6.25790000	2.04080000
O	-1.34380000	-4.04000000	-3.32930000
C	3.39110000	-6.92770000	3.25150000
C	-1.07600000	-3.64650000	-4.65210000
C	-2.54530000	-3.97100000	1.16930000
C	-2.71890000	-4.05560000	-0.17430000
C	-3.52140000	-3.12560000	-0.76750000
C	-4.02810000	-2.04620000	-0.11770000
C	-3.71220000	-1.94530000	1.18030000
C	-3.00100000	-2.88260000	1.80600000
C	-3.91090000	-3.23760000	-2.04770000
C	-4.71170000	-2.33930000	-2.63000000
C	-5.19470000	-1.26460000	-1.98460000
C	-4.82340000	-1.10210000	-0.68980000
O	-1.80670000	-4.85270000	1.91320000
O	-6.00910000	-0.35690000	-2.62390000
C	-2.59590000	-5.75420000	2.65430000

1	C	-5.76550000	-0.10990000	-3.98760000
2	C	0.11390000	4.66790000	2.46580000
3	C	-0.10950000	4.42070000	1.15170000
4	C	0.83880000	3.73770000	0.45680000
5	C	1.93420000	3.14820000	1.00040000
6	C	2.10730000	3.41150000	2.30600000
7	C	1.23500000	4.15180000	3.00100000
8	C	0.72080000	3.63670000	-0.87180000
9	C	1.60130000	2.97100000	-1.61190000
10	C	2.64930000	2.34510000	-1.06270000
11	C	2.79390000	2.36590000	0.28520000
12	O	-0.78800000	5.37850000	3.22520000
13	O	3.37970000	1.57910000	-1.92360000
14	C	-0.93470000	5.01620000	4.57620000
15	C	4.43360000	2.19900000	-2.61090000
16	C	3.07710000	-0.35130000	2.22220000
17	C	3.75780000	0.02780000	1.11040000
18	C	4.25510000	-0.93890000	0.28830000
19	C	4.01240000	-2.26230000	0.45910000
20	C	3.32660000	-2.59360000	1.56290000
21	C	2.89960000	-1.66820000	2.42600000
22	C	5.06960000	-0.65290000	-0.74070000
23	C	5.53960000	-1.58470000	-1.57690000
24	C	5.23110000	-2.88520000	-1.45160000
25	C	4.45450000	-3.22470000	-0.39290000
26	O	2.63990000	0.59320000	3.11950000
27	O	5.70140000	-3.85670000	-2.30700000
28	C	2.22330000	0.20410000	4.40570000
29	C	6.54220000	-3.50750000	-3.37520000
30	C	-4.59790000	1.31410000	2.10440000
31	C	-4.55480000	1.17710000	0.75290000
32	C	-3.83940000	2.07310000	0.02350000
33	C	-3.07050000	3.04500000	0.56680000
34	C	-3.09100000	3.10680000	1.90700000
35	C	-3.84290000	2.28540000	2.64680000
36	C	-3.90340000	2.07330000	-1.31480000
37	C	-3.31750000	3.02070000	-2.05230000
38	C	-2.54700000	3.98090000	-1.51290000
39	C	-2.35910000	3.94220000	-0.16700000
40	O	-5.40770000	0.49520000	2.86120000
41	O	-1.98200000	4.97770000	-2.27860000
42	C	-5.53840000	0.70890000	4.24180000
43	C	-2.45630000	5.21620000	-3.57850000
44	C	-2.04980000	-5.24180000	-0.91850000

1	C	-5.42830000	0.08220000	0.10140000
2	C	3.96000000	1.55070000	0.89500000
3	C	4.19470000	-4.72790000	-0.18370000
4	C	-1.39970000	4.96870000	0.48490000
5	C	-2.24940000	5.58730000	5.10850000
6	C	-2.50230000	5.15810000	6.56270000
7	C	-3.82860000	5.71280000	7.09820000
8	C	4.78570000	1.34440000	-3.82770000
9	C	6.07600000	1.81230000	-4.51550000
10	C	6.43850000	0.91450000	-5.70610000
11	C	1.85610000	1.44670000	5.21750000
12	C	1.38110000	1.10470000	6.63780000
13	C	0.93940000	2.36250000	7.39930000
14	C	6.85690000	-4.76960000	-4.17990000
15	C	7.74600000	-4.46310000	-5.39550000
16	C	8.05140000	-5.72570000	-6.21210000
17	C	4.69000000	-6.93980000	4.05910000
18	C	4.51270000	-7.64010000	5.41550000
19	C	5.81330000	-7.64440000	6.22960000
20	C	-2.38900000	-3.25360000	-5.32980000
21	C	-2.18140000	-2.75070000	-6.76620000
22	C	-3.50090000	-2.27270000	-7.38820000
23	C	-1.71610000	-6.54820000	3.61850000
24	C	-2.54550000	-7.44260000	4.55320000
25	C	-1.65160000	-8.25700000	5.49820000
26	C	-6.39030000	1.23180000	-4.37320000
27	C	-6.05240000	1.61670000	-5.82230000
28	C	-6.64020000	2.98260000	-6.20020000
29	C	-6.52040000	-0.32360000	4.79850000
30	C	-6.71770000	-0.16560000	6.31430000
31	C	-7.70250000	-1.20160000	6.87200000
32	C	-1.76140000	6.46360000	-4.12660000
33	C	-2.20200000	6.77620000	-5.56530000
34	C	-1.50070000	8.02410000	-6.11790000
35	H	-0.61910000	-6.69500000	0.77390000
36	H	1.11850000	-7.15770000	2.21310000
37	H	2.98530000	-4.14570000	-2.30220000
38	H	1.26410000	-3.70890000	-3.76720000
39	H	3.07490000	-7.97570000	3.04140000
40	H	2.60810000	-6.38320000	3.82960000
41	H	-0.41960000	-2.74710000	-4.65440000
42	H	-0.59460000	-4.48990000	-5.19850000
43	H	-4.03400000	-1.11060000	1.80420000
44	H	-2.78800000	-2.75330000	2.88200000

1	H	-3.63750000	-4.08990000	-2.68140000
2	H	-4.99960000	-2.53130000	-3.67620000
3	H	-3.35230000	-5.18500000	3.24260000
4	H	-3.12940000	-6.43620000	1.95320000
5	H	-6.21310000	-0.92160000	-4.60580000
6	H	-4.66470000	-0.05560000	-4.16070000
7	H	2.98060000	3.05820000	2.87010000
8	H	1.47430000	4.32940000	4.06200000
9	H	-0.08260000	4.10460000	-1.43340000
10	H	1.44280000	2.91630000	-2.70280000
11	H	-0.96570000	3.90380000	4.65560000
12	H	-0.08620000	5.42460000	5.17160000
13	H	5.29540000	2.32680000	-1.92200000
14	H	4.11120000	3.20920000	-2.95310000
15	H	3.11450000	-3.63440000	1.83540000
16	H	2.37530000	-2.04660000	3.31750000
17	H	5.42480000	0.36220000	-0.94470000
18	H	6.20990000	-1.23720000	-2.37860000
19	H	1.31700000	-0.43900000	4.33390000
20	H	3.05440000	-0.34030000	4.91100000
21	H	7.48820000	-3.07240000	-2.97740000
22	H	6.01640000	-2.78030000	-4.03750000
23	H	-2.52930000	3.86560000	2.46010000
24	H	-3.81870000	2.45430000	3.73520000
25	H	-4.49670000	1.33760000	-1.86310000
26	H	-3.49370000	2.96900000	-3.13850000
27	H	-4.54800000	0.56930000	4.73480000
28	H	-5.93480000	1.73500000	4.42290000
29	H	-3.55830000	5.38110000	-3.54670000
30	H	-2.20380000	4.35240000	-4.23600000
31	H	-2.61920000	-5.56830000	-1.81160000
32	H	-2.20090000	-6.15960000	-0.31560000
33	H	-6.19880000	0.63420000	-0.48210000
34	H	-6.08960000	-0.41570000	0.84670000
35	H	4.86360000	1.78310000	0.29770000
36	H	4.32040000	1.97790000	1.85290000
37	H	4.56400000	-5.36370000	-1.01970000
38	H	4.90610000	-4.98820000	0.63270000
39	H	-1.05620000	5.74640000	-0.23350000
40	H	-2.01410000	5.59460000	1.16850000
41	H	-3.09620000	5.23470000	4.47240000
42	H	-2.22490000	6.70100000	5.04230000
43	H	-2.52050000	4.04350000	6.62590000
44	H	-1.66440000	5.51380000	7.20880000

1	H	-3.99780000	5.39510000	8.15290000
2	H	-3.83710000	6.82650000	7.07380000
3	H	-4.68980000	5.34840000	6.49260000
4	H	4.90170000	0.28050000	-3.52140000
5	H	3.93900000	1.37200000	-4.55470000
6	H	6.91610000	1.79820000	-3.78030000
7	H	5.95270000	2.86550000	-4.86390000
8	H	6.59930000	-0.13910000	-5.38050000
9	H	7.37510000	1.26310000	-6.19910000
10	H	5.63000000	0.91780000	-6.47230000
11	H	1.03160000	1.99040000	4.70120000
12	H	2.73440000	2.13270000	5.27390000
13	H	0.52410000	0.39110000	6.58520000
14	H	2.20430000	0.59860000	7.19610000
15	H	1.77440000	3.09500000	7.48370000
16	H	0.09110000	2.86910000	6.88430000
17	H	0.60430000	2.10830000	8.43120000
18	H	7.36780000	-5.51230000	-3.52160000
19	H	5.90310000	-5.23400000	-4.52800000
20	H	8.70440000	-4.00560000	-5.05160000
21	H	7.23800000	-3.71650000	-6.05200000
22	H	8.58520000	-6.48410000	-5.59490000
23	H	8.69590000	-5.48800000	-7.08970000
24	H	7.11530000	-6.19190000	-6.59610000
25	H	5.48650000	-7.45840000	3.47360000
26	H	5.03100000	-5.88990000	4.22710000
27	H	4.17700000	-8.69210000	5.25200000
28	H	3.71510000	-7.12360000	6.00160000
29	H	6.62600000	-8.17770000	5.68550000
30	H	5.66970000	-8.15480000	7.20980000
31	H	6.16130000	-6.60650000	6.43610000
32	H	-2.86710000	-2.43360000	-4.74490000
33	H	-3.08910000	-4.12250000	-5.33020000
34	H	-1.45300000	-1.90430000	-6.76610000
35	H	-1.74580000	-3.56760000	-7.38940000
36	H	-4.25010000	-3.09630000	-7.42170000
37	H	-3.94130000	-1.43240000	-6.80320000
38	H	-3.34400000	-1.91310000	-8.43120000
39	H	-1.10010000	-5.84460000	4.22780000
40	H	-1.01640000	-7.19380000	3.04100000
41	H	-3.24050000	-6.81190000	5.15750000
42	H	-3.17060000	-8.13970000	3.94520000
43	H	-0.96310000	-8.92140000	4.92740000
44	H	-1.03110000	-7.58930000	6.13880000

1	H	-2.26330000	-8.90080000	6.17130000
2	H	-7.49720000	1.17870000	-4.24280000
3	H	-6.01470000	2.03110000	-3.69090000
4	H	-6.44540000	0.83680000	-6.51750000
5	H	-4.94370000	1.65020000	-5.95200000
6	H	-7.74990000	2.98290000	-6.10260000
7	H	-6.39170000	3.24700000	-7.25380000
8	H	-6.23630000	3.78830000	-5.54500000
9	H	-6.14150000	-1.35060000	4.57870000
10	H	-7.50450000	-0.21490000	4.28290000
11	H	-5.73530000	-0.27630000	6.83290000
12	H	-7.09780000	0.86020000	6.53670000
13	H	-8.70440000	-1.10090000	6.39540000
14	H	-7.33890000	-2.23910000	6.69210000
15	H	-7.83600000	-1.07500000	7.97110000
16	H	-1.99080000	7.33600000	-3.46910000
17	H	-0.65560000	6.31060000	-4.10330000
18	H	-3.30710000	6.93210000	-5.59220000
19	H	-1.97280000	5.90480000	-6.22450000
20	H	-1.82900000	8.23810000	-7.16110000
21	H	-0.39480000	7.89050000	-6.13150000
22	H	-1.73110000	8.92140000	-5.49920000
23	C	0.23040000	0.42150000	-3.90380000
24	C	-0.25430000	0.14240000	-2.46540000
25	C	-0.54260000	1.54050000	-4.61800000
26	C	0.60540000	-0.92570000	-1.75830000
27	C	0.13230000	-1.29880000	-0.36650000
28	O	0.07270000	-0.18380000	0.39950000
29	C	-0.41990000	-0.35120000	1.70020000
30	C	-0.60670000	1.01030000	2.34100000
31	O	-0.12440000	-2.41740000	0.01040000
32	N	2.02350000	-0.44300000	-1.66170000
33	C	-1.72340000	-0.31410000	-2.45680000
34	H	1.30580000	0.71570000	-3.88550000
35	H	0.16690000	-0.51100000	-4.51110000
36	H	-0.19930000	1.09560000	-1.88740000
37	H	-1.58370000	1.23850000	-4.86920000
38	H	-0.59110000	2.46080000	-3.99320000
39	H	-0.04900000	1.81190000	-5.57950000
40	H	0.60900000	-1.83430000	-2.39230000
41	H	-1.41810000	-0.83620000	1.64220000
42	H	0.26720000	-0.99300000	2.29130000
43	H	0.36160000	1.51330000	2.51730000
44	H	-1.17330000	1.66700000	1.65170000

H	-1.14410000	0.94580000	3.31450000
H	2.63020000	-1.23830000	-1.36110000
H	2.06830000	0.31440000	-0.94580000
H	2.34660000	-0.09990000	-2.59280000
H	-2.11020000	-0.42220000	-1.41970000
H	-1.83880000	-1.29390000	-2.96730000
H	-2.39570000	0.40710000	-2.96620000

Table S3 Computed energies.

Energy (Hartree/Particle)	G
free *R*-N1+free *L*-Ile	-3786.389112
free *S*-N1+free *L*-Ile	-3786.389112
free *R*-N4+free *L*-Ile	-4966.021962
free *S*-N4+free *L*-Ile	-4966.021962
L-Ile@*R*-N1	-3786.451264
L-Ile@*S*-N1	-3786.440000
L-Ile@*R*-N4	-4966.079923
L-Ile@*S*-N4	-4966.095142

Table S4 Computed free energies for host-guest complexes.

Complexes	ΔG (kcal mol^{-1})
L-Ile@*R*-N1	-39.00
L-Ile@*S*-N1	-31.93
L-Ile@*R*-N4	-36.37
L-Ile@*S*-N4	-45.92

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