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Electronic Supplementary Information for

Room-Temperature Phosphorescent γ-Cyclodextrin- Cucurbit [6]uril-Cowheeled [4]Rotaxanes for Specific Sensing of Tryptophan

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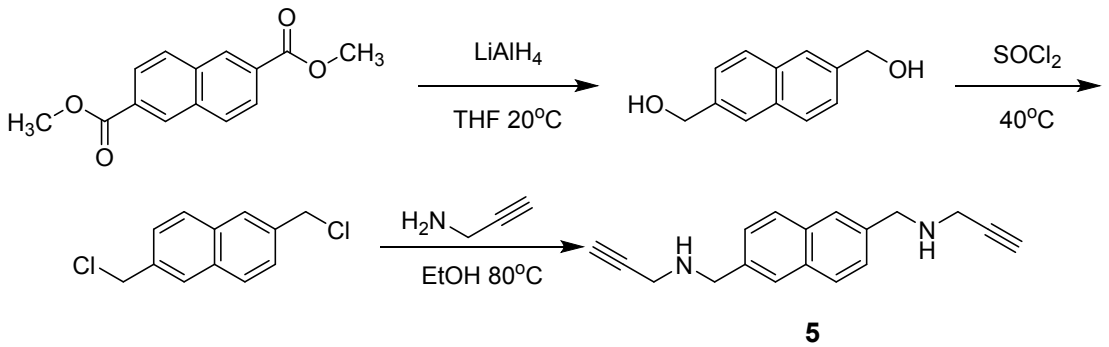
1. Synthesis and Characterization of Rotaxanes

Materials and Instruments

γ-Cyclodextrin, dimethyl naphthalene-2, 6-dicarboxylate, 2-(*Tert*-butylamino) ethanol were purchased from Tokyo Chemical Industry and were vacuum-dried before use. Amino acids and HAS were purchased from Solarbio (Shanghai, China). CB [6] and compound **6** was prepared according to the literature method.[1] ^{1}H and ^{13}C NMR spectra were recorded at room temperature on Bruker AMX-400 (operating at 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR) with TMS as the internal standard. HRMS data were measured in waters-Q-TOF Premiers (ESI) and MALDI-TOF-MS spectrometers. UV-vis. spectra were recorded using a JASCO V650 spectrometer. Circular dichroism spectra were measured on a JASCO J-1500 spectrometer. Fluorescence and phosphorescence spectra were taken on a Fluoromax-4 spectrofluorometer or a JASCO FP-8500 spectrofluorometer. The bandwidth for the measurement was not fixed. Fluorescence and phosphorescence lifetime decay were taken on the Fluoromax-4 spectrofluorometer. The phosphorescence spectra were measured by bubbling Ar gas over 10 min in an ice bath to remove dissolved oxygen. Titration calorimetry measurements were performed with a VP-ITC calorimeter.

Synthesis and characterizations of 1, 2, 3, 4, 5, Rot0, Rot1, Rot2, Rot3, Rot4:

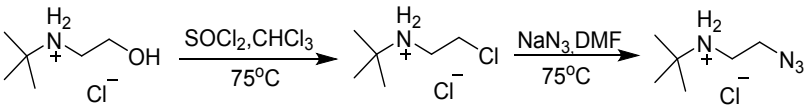


Naphthalene -2, 6-diyldimethanol: Dimethyl naphthalene-2, 6-dicarboxylate (2 g) was dissolved in THF (50 ml), and the resulting solution was cooled with ice-bath. $LiAlH_4$ (2.3 g) was then added in batches under stirring. The reaction mixture was stirred at room temperature for 30h. Methanol (50 ml) was added to quench the reaction and NaOH (1.0 g) was added. The precipitate was filtered and washed by dichloromethane, and the filtrate was collected. The solvent was removed under reduced pressure, and the resulting white solid (965 mg) were collected. ^{1}H NMR (400 MHz, CD_3OD): δ =7.78 (s, 1H), 7.75 (d, J = 6.7 Hz, 3H), 7.44 (d, J = 1.3 Hz, 1H), 7.42 (d, J = 1.3 Hz, 1H), 4.71 (s, 4H).

2, 6-bis (chloromethyl) naphthalene: Naphthalene-2, 6-diyldimethanol (800 mg) was dissolved in $SOCl_2$ (5 ml), and the mixture was reacted at 40 °C for 6 h. $SOCl_2$ was removed under reduced pressure, and the crude product was purified by column chromatography to give the product as white solid (320.5 mg). ^{1}H NMR (400 MHz, CD_3OD) δ =7.87 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 1.3 Hz, 1H), 7.54 (d, J = 1.5 Hz, 1H), 4.80 (s, 4H).

Compound 5: 2, 6-bis (chloromethyl) naphthalene (160 mg) was dissolved in ethanol (1.0 ml) and 2-propynylamine (2 ml) was added under stirring. The mixture was reacted at 80 °C for 10 h under nitrogen, then the solvent was removed under reduced pressure. The crude product was

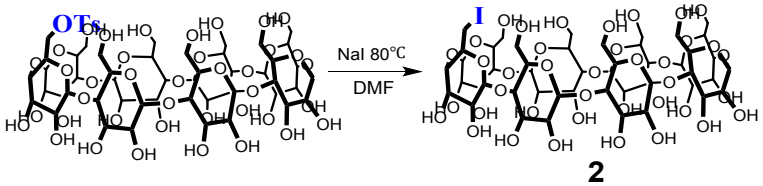
purified by column chromatography (ethyl acetate: methanol=8:1) to afford the product (102 mg) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.80 – 7.76 (m, 3H), 7.48 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.26 (s, 1H), 4.05 (s, 4H), 3.47 (d, *J* = 2.4 Hz, 4H), 2.29 (t, *J* = 2.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.67, 132.74, 128.02, 126.97, 126.71, 82.04, 71.70, 52.34, 37.34, 29.71. HRMS (ESI). calcd for $[M + H]^+$ m/z = 263.1543, found m/z = 263.1544.



4

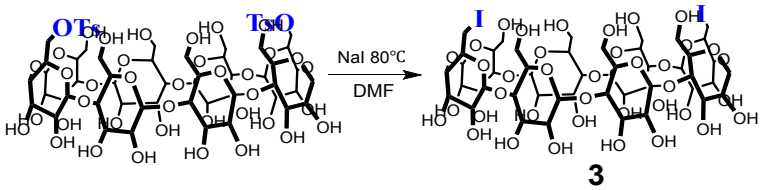
***N*-(2-Chloroethyl)-2-methylpropan-2-aminium chloride**: 2-(*Tert*-butylamino) ethanol (10.0 g, 85.5 mmol) was dissolved in $CHCl_3$ (150 ml). To the resulting ice-bath cooled solution was added dropwise $SOCl_2$ (15 ml, 197.5 mmol). The mixture was heated to reflux for 24 h, after which excess $SOCl_2$ and solvent were removed under reduced pressure. The resulting crude product was recrystallized from acetone to yield the compound as a white powder (8.5 g, 54.4%). ^{1}H NMR (400 MHz, D_2O) *δ* =3.87 (t, *J* = 5.3 Hz, 2H), 3.45 (t, *J* = 5.2 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, D_2O) *δ* 57.9, 43.2, 39.9, 24.8. HRMS (ESI): calcd for $[M - Cl]^+$, m/z =136.0888, found m/z =136.0878.

Compound 4: Sodium azide (2 g, 30.8 mmol) was add to a solution of *N*-(2-chloroethyl)-2-methylpropan-2-aminium chloride (2.0 g, 11.6 mmol) in 80 ml ethanol, and the mixture was stirred at 75 °C for 15 h. After the removal of solvent under reduced pressure, 10 ml water was added to dissolve the crude product, which was then subjected to a reverse-phase flash column chromatography (cosmosil $75C_{18}$-PREP) with pure water to afford **4** as a white powder (1.3 g, 63%). ^{1}H NMR (400 MHz, D_2O) *δ* =3.87 (t, *J* = 5.3 Hz, 2H), 3.45 (t, *J* = 5.2 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, D_2O) *δ* 57.9, 43.2, 39.9, 24.8. HRMS (ESI): calcd for $[M - Cl]^+$, m/z =143.1291, found m/z = 143.1295.



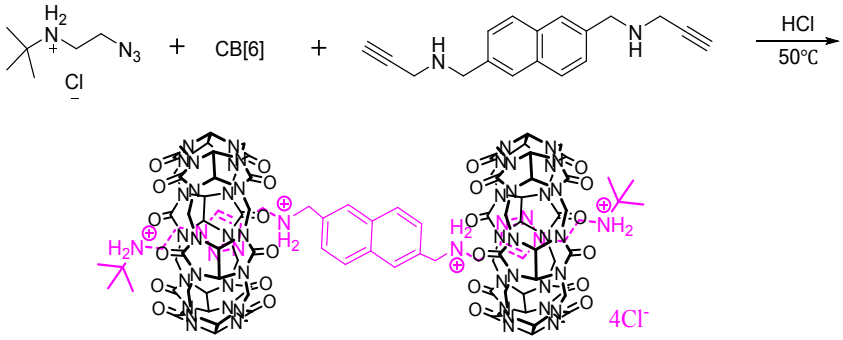
2

Compound 2: 6-mono-sulfonylation-γ-CD(100 mg) was dissolved in DMF(2 ml), After the mixture was stirred, sodium iodide (600 mg) was added. The mixture was reacted to 80 °C and refluxed for 10h. The solvent were removed under reduced pressure. The crude product was subjected to reversed-phase flash column chromatography (cosmosil $75C_{18}$-PREP) with a gradient elution from 0 % aqueous ethanol to 35 % aqueous ethanol to afford **2** (55.5 mg) as a white solid. ^{1}H NMR (400 MHz, D_2O) δ= 5.08 (d, *J* = 3.9 Hz, 1H), 4.98 (d, *J* = 3.3 Hz, 7H), 3.87 – 3.68 (m, 30H), 3.61 – 3.32 (m, 20H). ^{13}C NMR (101 MHz, D_2O) δ 101.51, 84.36, 80.74, 79.99, 72.8, 72.22, 71.92, 71.67, 70.09, 60.52, 60.30, 16.82, 16.62. HRMS (ESI). calcd for $[M + Na]^+$, m/z = 1429.3141, found m/z = 1429.3940. $[M+K]^+$, m/z = 1445.2880, found m/z = 1445.3777.

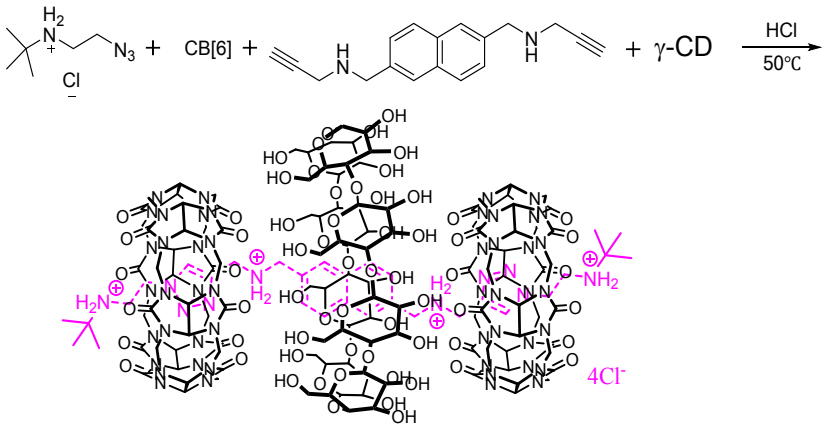


3

Compound 3: 6^A, 6^E-Dideoxy-6^A, 6^E-disulfonylation-γ-CD (100 mg) was dissolved in DMF(1.5 ml). After the mixture was stirred, sodium iodide (600 mg) was added. The mixture was reacted to 80 °C and refluxed for 10 h.The solvent were removed under reduced pressure. The crude product was subjected to reversed-phase flash column chromatography (cosmosil $75C_{18}$-PREP) with a gradient elution from 0% aqueous ethanol to 35% aqueous ethanol to afford **3** (40 mg) as a white solid. ^{1}H NMR (400 MHz, D_2O) δ= 5.12 (d, J = 3.8 Hz, 1H), 5.01 (dd, J = 6.5, 3.8 Hz, 3H), 3.93–3.69 (m, 13H), 3.66 – 3.33 (m, 11H), 3.25 (s, 1H). ^{13}C NMR (101 MHz, D2O) δ 101.49, 84.32, 80.51, 72.83, 72.20, 71.81, 71.67 – 71.33, 70.64, 70.12, 60.88 – 59.84, 7.09. HRMS (ESI). calcd for $[M + Na]^+$, m/z =1539.2158, found m/z =1539.0883.

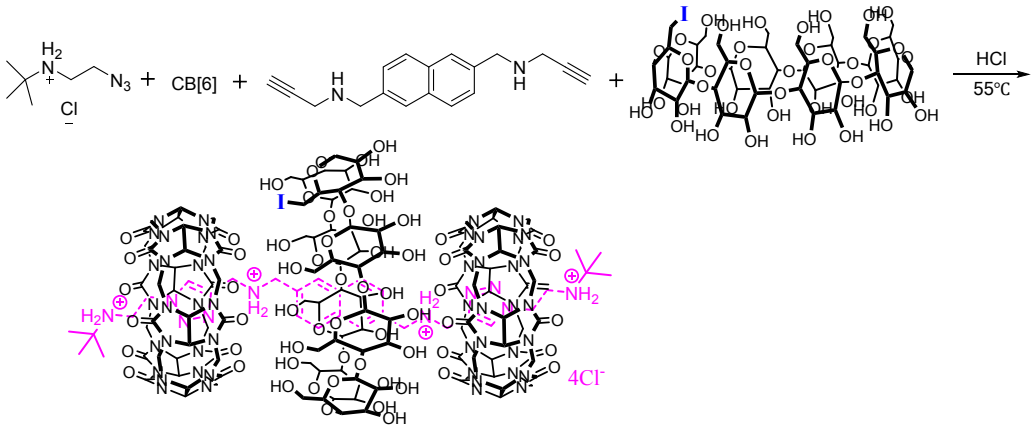


Rot0: Compound **4** (10 mg), compound **5** (10 mg), and CB [6] (100 mg) were mixed in 5 ml water. The reaction mixture was stirred at 50 °C for 4 h to give a homogenous solution. Then the mixture was subjected to reversed-phase flash column chromatography (cosmosil $75C_{18}$-PREP) with pure water to afford the targeted rotaxane. ^{1}H NMR (400 MHz, D_2O) δ 8.36 (s, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.94 (dd, J = 8.5, 1.3 Hz, 2H), 6.47 (s, 2H), 5.60 (dd, J = 21.1, 15.6 Hz, 24H), 5.40 (s, 24H), 4.58 (s, 4H), 4.24 (s, 4H), 4.22 – 3.90 (m, 28H), 3.70 (t, J = 6.4 Hz, 4H), 1.52 (s, 18H). ^{13}C NMR (101 MHz, D_2O) δ 156.56, 156.31, 138.68, 133.01, 130.36, 129.54, 128.72, 128.50, 120.83, 70.20, 58.71, 53.03, 51.32, 51.12, 50.83, 47.46, 42.73, 39.95, 25.25. HRMS (ESI) of compound **Rot0**. calcd for $[M - 4Cl]^{4+}$, m/z = 636.0030, found m/z = 636.0032.

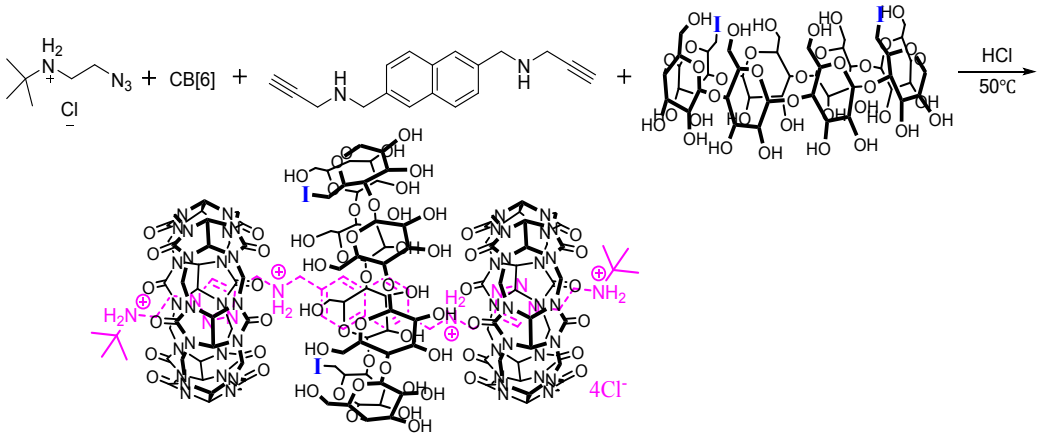


Rot1: Compound **4** (10 mg), compound **5** (10 mg), CB [6] (100 mg), and γ-CD (450 mg) were

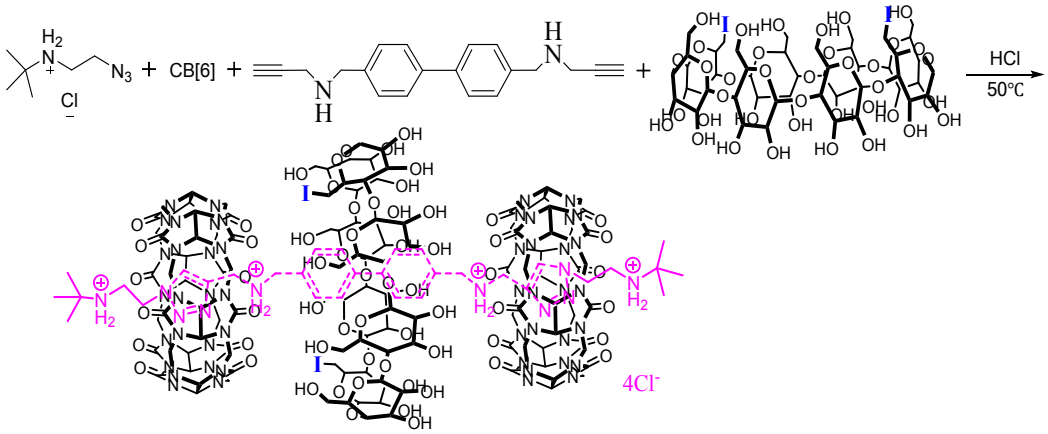
mixed in 5 ml water. The reaction mixture was stirred at 50 °C for 3 h to give a homogenous solution. Then the mixture was subjected to reversed-phase flash column chromatography (cosmosil 75C_{18}-PREP) with pure water to afford the targeted rotaxane. ^{1}H NMR (400 MHz, D_2O) δ 8.26 (s, 1H), 8.20 (s, 1H), 7.91 – 7.84 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 6.47 (d, *J* = 5.0 Hz, 2H), 5.63 (dt, *J* = 15.3, 13.2 Hz, 24H), 5.39 (d, *J* = 7.3 Hz, 24H), 4.94 (d, *J* = 3.7 Hz, 8H), 4.59 – 4.46 (m, 4H), 4.28 – 4.05 (m, 32H), 3.78 (s, 3H), 3.65 (d, *J* = 15.3 Hz, 25H), 3.57 (dd, *J* = 9.8, 3.6 Hz, 8H), 3.47 (d, *J* = 6.5 Hz, 16H), 1.50 (d, *J* = 5.1 Hz, 18H). ^{13}C NMR (151 MHz, D_2O) δ 156.45,156.13, 138.71, 138.37, 133.25, 132.79, 131.13, 130.64, 129.75, 129.14, 128.79, 128.33, 127.83, 127.17, 120.89, 120.63, 102.50, 81.16, 73.09, 72.21, 71.91, 70.15, 59.72, 58.73, 58.43, 53.60, 52.92, 51.33, 51.07 ,50.88, 47.59, 47.43, 42.76, 39.97, 39.78, 25.19, 24.66. HRMS (ESI) of compound **Rot1.** calcd for $[M - 4Cl]^{4+}$, m/z = 960.1087, found m/z = 960.3503.



Rot2： Compound **4** (10 mg), compound **5** (10 mg), CB [6] (100 mg), and compound **2** (120 mg) were mixed in 5 ml water. The reaction mixture was stirred at 55 °C for 5 h to give a homogenous solution. The crude product was subjected to reversed-phase flash column chromatography (cosmosil 75C_{18}-PREP) with a gradient elution from 0% aqueous ethanol to 50% aqueous ethanol to afford **Rot2** (56 mg) as a white solid. ^{1}H NMR (400 MHz, D2O) δ 8.34 (s, 1H), 8.25 (s, 1H), 7.92 (dd, *J* = 15.2, 8.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 6.51 (d, *J* = 6.6 Hz, 2H), 5.67 (dt, *J* = 15.4, 12.0 Hz, 21H), 5.42 (dd, *J* = 7.1, 4.0 Hz, 20H), 5.07 (d, *J* = 4.1 Hz, 1H), 5.04 – 4.92 (m, 6H), 4.62 – 4.48 (m, 6H), 4.32 – 4.07 (m, 28H), 3.91 – 3.45 (m, 40H), 3.37 (dd, *J* = 16.0, 9.6 Hz, 4H), 3.17 – 3.03 (m, 2H), 1.54 (d, *J* = 5.0 Hz, 15H). ^{13}C NMR (101 MHz, D_2O) δ 170.96, 156.58, 156.55, 155.95, 138.71, 120.87, 120.65, 102.69, 102.39, 81.49, 80.95, 73.15, 72.48,72.14, 71.95, 70.55, 69.66, 59.80, 51.52, 51.20, 47.80, 47.61, 47.44, 42.78, 39.96, 25.18. HRMS (ESI) of compound **Rot2.** calcd for $[M - Cl]^+$, m/z = 4055.2446, found m/z = 4055.2655.



Rot3：Compound **4** (10 mg), compound **5** (10 mg), CB [6] (100 mg), and compound **3** (130 mg) were mixed in 5ml water. The reaction mixture was stirred at 55 ℃ for 5 h to give a homogenous solution. The crude product was subjected to reversed-phase flash column chromatography (cosmosil 75C_{18}-PREP) with a gradient elution from 0% aqueous ethanol to 50% aqueous ethanol to afford **Rot3** (50 mg) as a white solid. ^{1}H NMR (400 MHz, D_2O) δ 8.38 – 8.20 (m, 4H), 8.08 – 7.61 (m, 4H), 6.48 (d, J = 8.5 Hz, 2H), 5.79 – 5.53 (m, 24H), 5.42 (d, J = 4.4 Hz, 24H), 5.11 – 4.88 (m, 7H), 4.33 – 4.02 (m, 32H), 3.96 – 2.99 (m, 46H), 1.52 (d, J = 4.7 Hz, 18H). ^{13}C NMR (101 MHz, D_2O) δ 156.5, 156.48, 155.98, 138.69, 138.27, 133.29, 129.86, 129.09, 128.75, 127.20, 120.90, 120.64, 102.39, 81.25, 73.15, 72.19, 70.18, 59.78, 58.72, 58.38, 52.10, 50.59, 47.54, 42.72, 40.46, 39.86, 25.20. HRMS (ESI) of **Rot3**. calcd for $[M-3Cl]^{3+}$, m/z = 1365.0692, found m/z = 1365.0407.



Rot4：Compound **6** (10 mg), compound **4** (10 mg), CB [6] (100 mg), and compound **3** (130 mg) were mixed in 5 ml water. The reaction mixture was stirred at 55 °C for 5 h to give a homogenous solution. The crude product was subjected to reversed-phase flash column chromatography (cosmosil 75C_{18}-PREP) with a gradient elution from 0% aqueous ethanol to 50% aqueous ethanol to afford **Rot4** (50 mg) as a white solid. ^{1}H NMR (400 MHz, D_2O) δ 7.88 (t, J = 7.2 Hz, 4H), 7.64 – 7.56 (m, 4H), 6.48 (d, J = 9.0 Hz, 2H), 5.66 (dt, J = 15.4, 10.5 Hz, 24H), 5.43 (d, J = 8.4 Hz, 24H), 4.99 (dd, J = 34.3, 6.4 Hz, 9H), 4.46 (s, 4H), 4.33 (t, J = 6.0 Hz, 2H), 4.25 – 4.06 (m, 29H), 3.86 – 3.43 (m, 58H), 3.12 – 3.06 (m, 4H), 1.52 (d, J = 6.2 Hz, 17H). ^{13}C NMR (101 MHz, D_2O) δ 156.35, 141.64, 141.02, 138.72, 138.20, 131.89, 131.64, 130.72, 130.06, 126.79, 102.60, 81.27, 73.12, 72.31, 72.00, 70.18, 59.80, 58.73, 58.41, 51.93 – 50.85, 47.60, 42.62, 40.01, 39.77, 25.23. HRMS (ESI) of **Rot4.** calcd for $[M–3Cl]^{3+}$, m/z = 1373.7411, found m/z = 1373.3156.

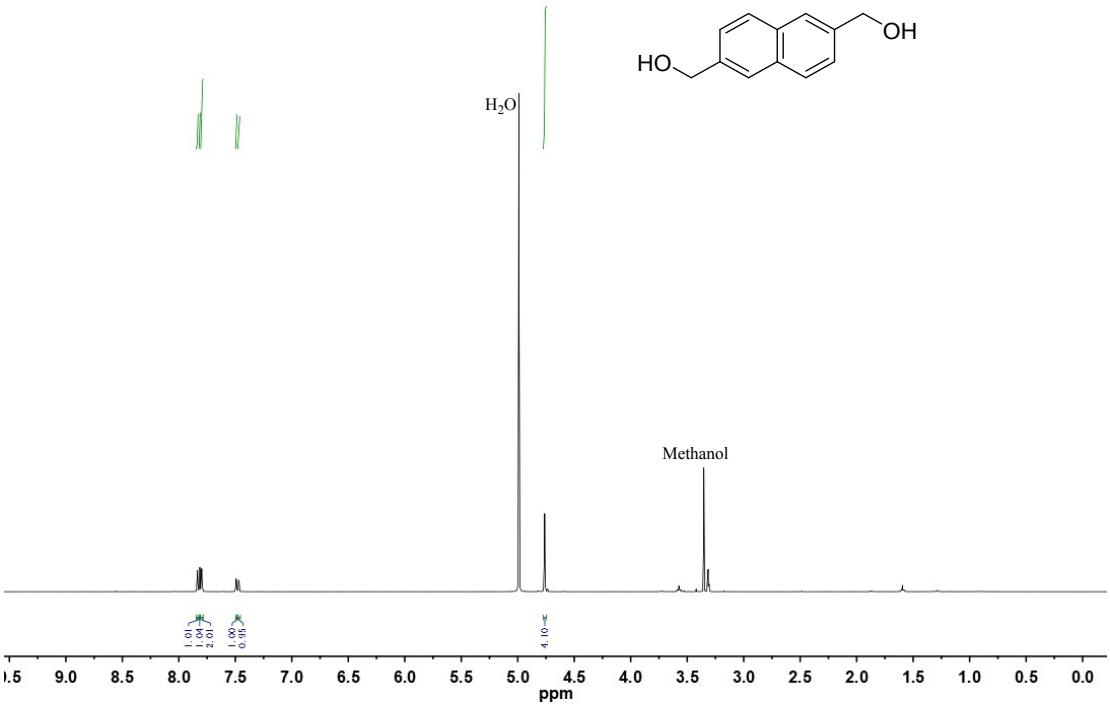


Fig. S1. ^{1}H NMR spectrum of **naphthalene-2,6-diyldimethanol** measured in CD_3OD at 25 °C.

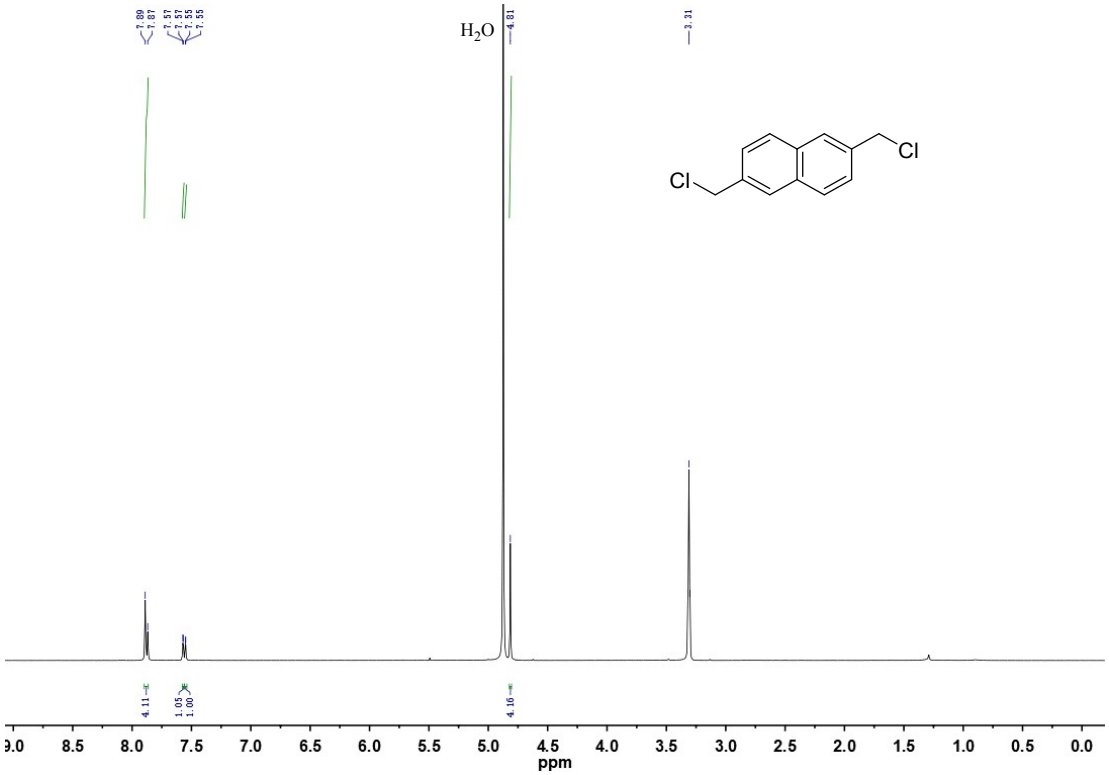


Fig. S2. ^{1}H NMR spectrum of **2,6 –bis(chloromethyl)naphthalene** measured in CD_3OD at 25 °C.

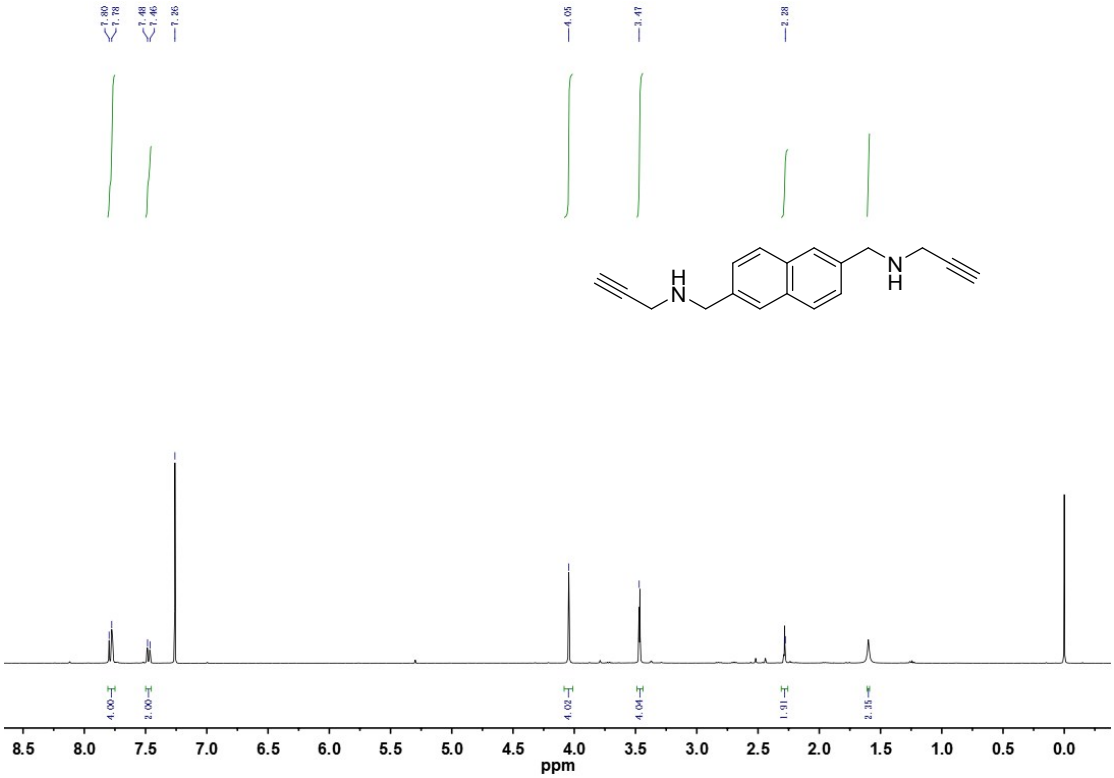


Fig. S3. ^{1}H NMR spectrum of **compound 5** measured in $CDCl_3$ at 25 °C.

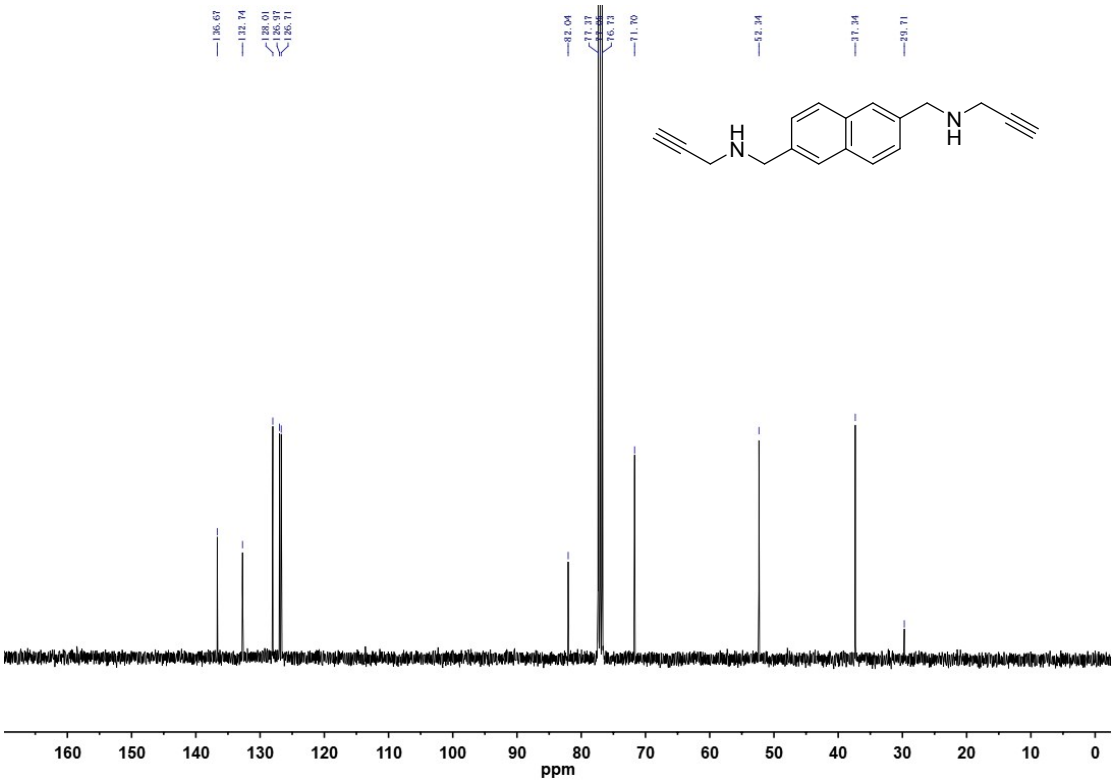


Fig. S4. ^{13}C NMR spectrum of **compound 5** measured in $CDCl_3$ at 25 °C.

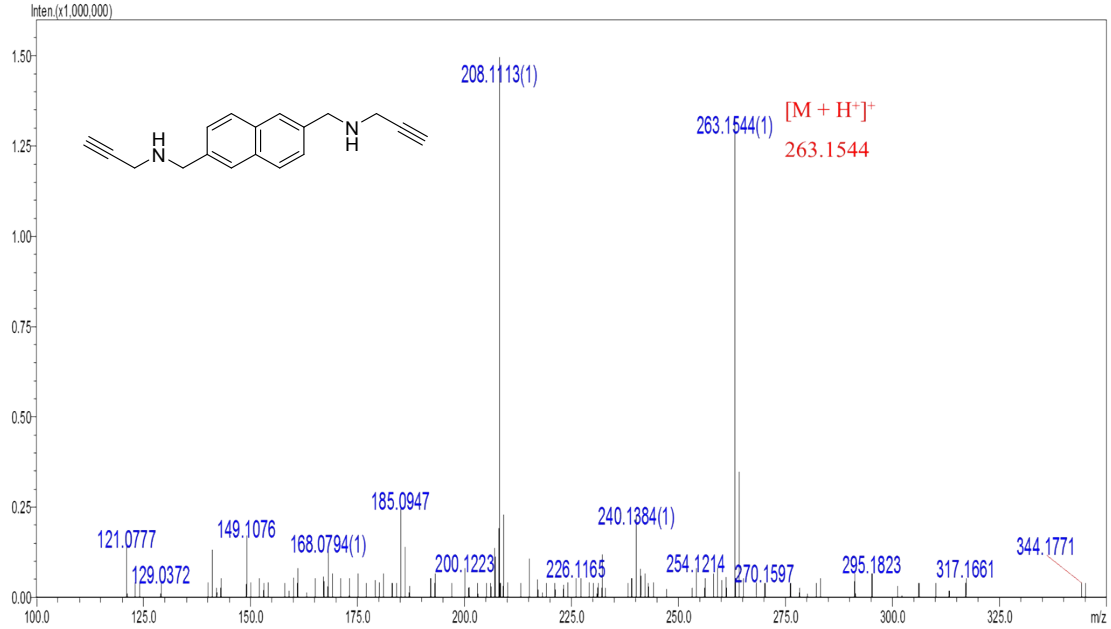


Fig. S5. HRMS spectrum of **compound 5.**

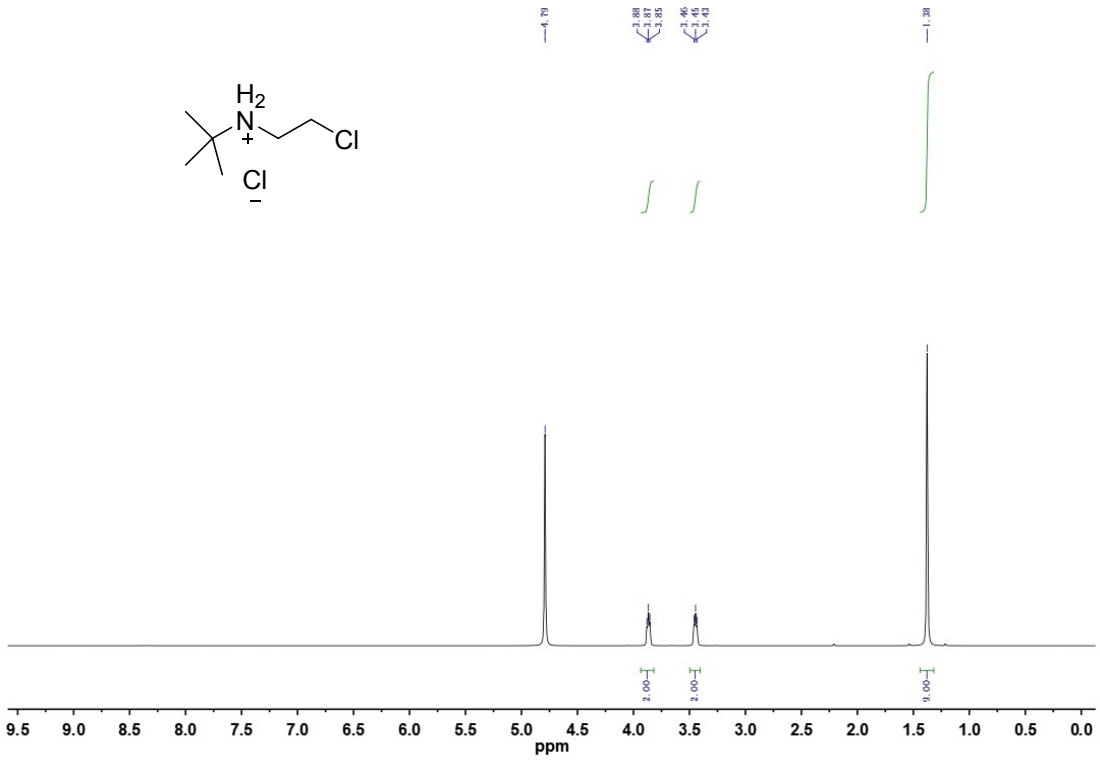


Fig. S6.^{1}H NMR spectrum of ***N*-(2-Chloroethyl)-2-methylpropan-2-aminium chloride** measured in D_2O at 25 °C.

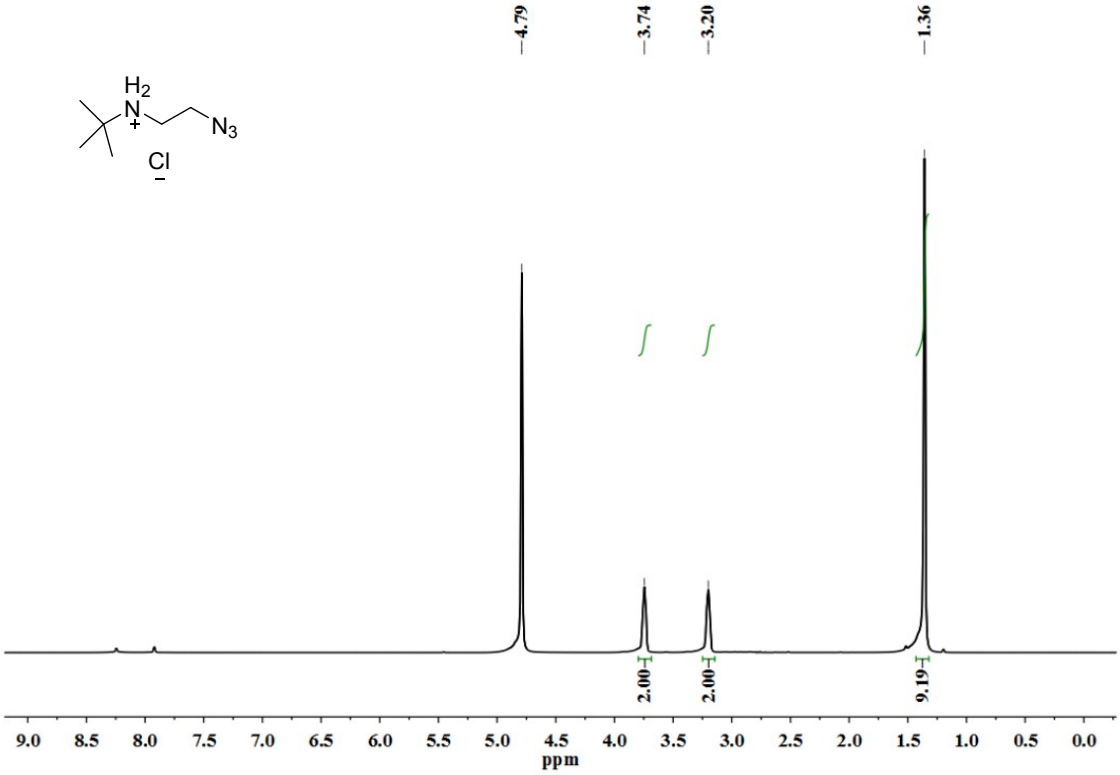


Fig. S7. ^{1}H NMR spectrum of **compound 4** measured in D_2O at 25 °C.

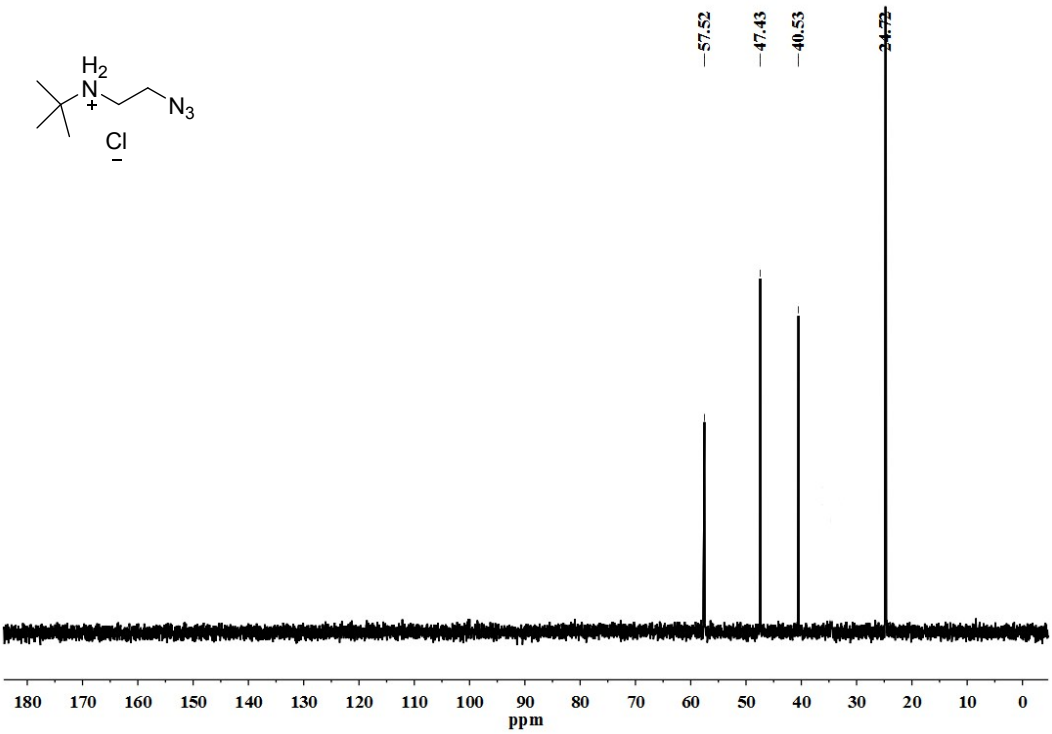


Fig. S8. ^{13}C NMR spectrum of **compound 4** measured in D_2O at 25 °C.

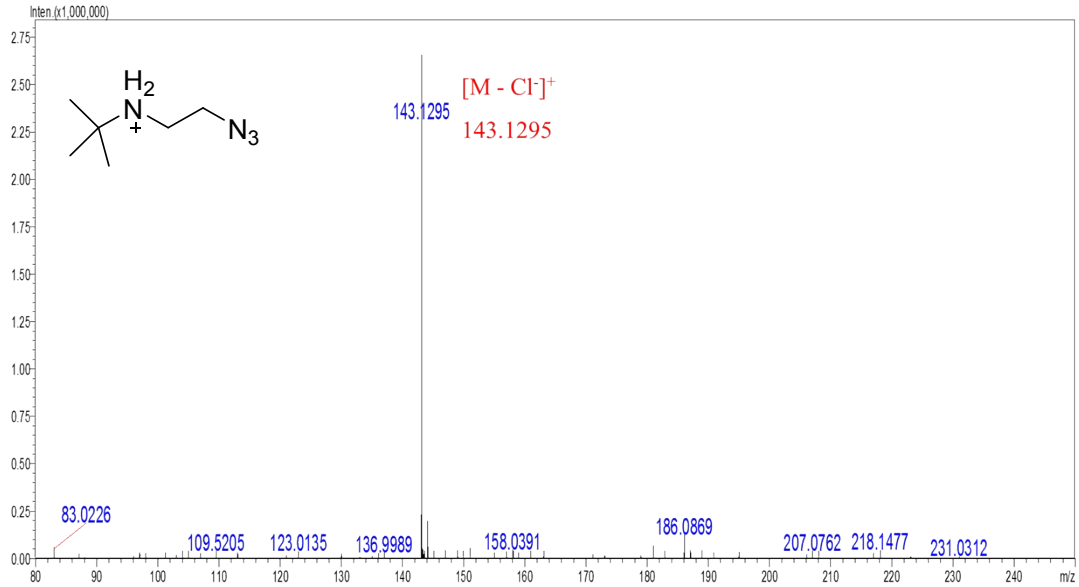


Fig. S9. HRMS spectrum of **compound 4.**

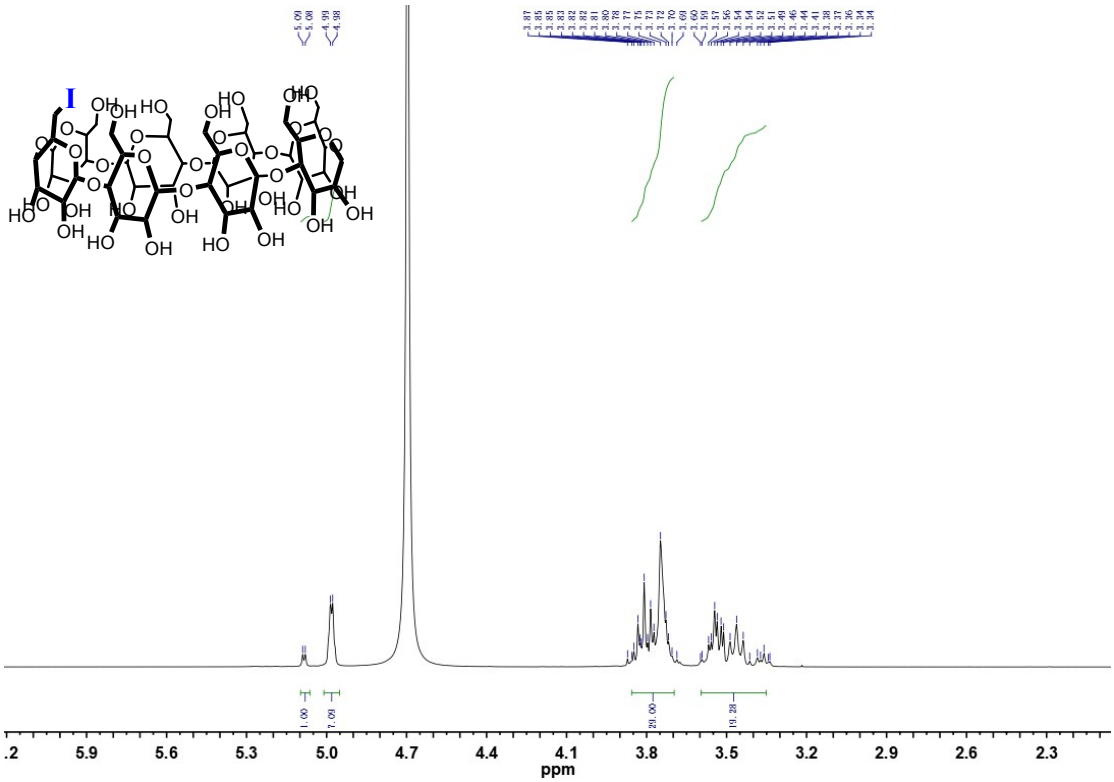


Fig. S10. ^{1}H NMR spectrum of **compound 2** measured in D_2O at 25 °C.

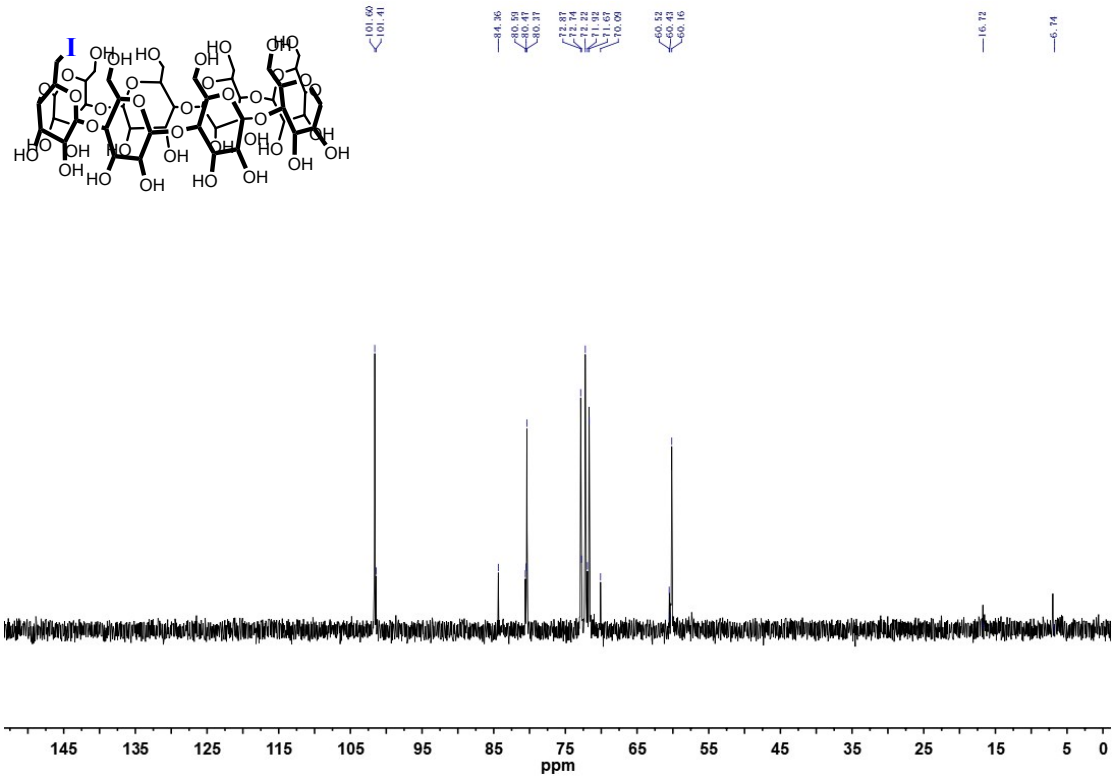


Fig. S11. ^{13}C NMR spectrum of **compound 2** measured in D_2O at 25 °C.

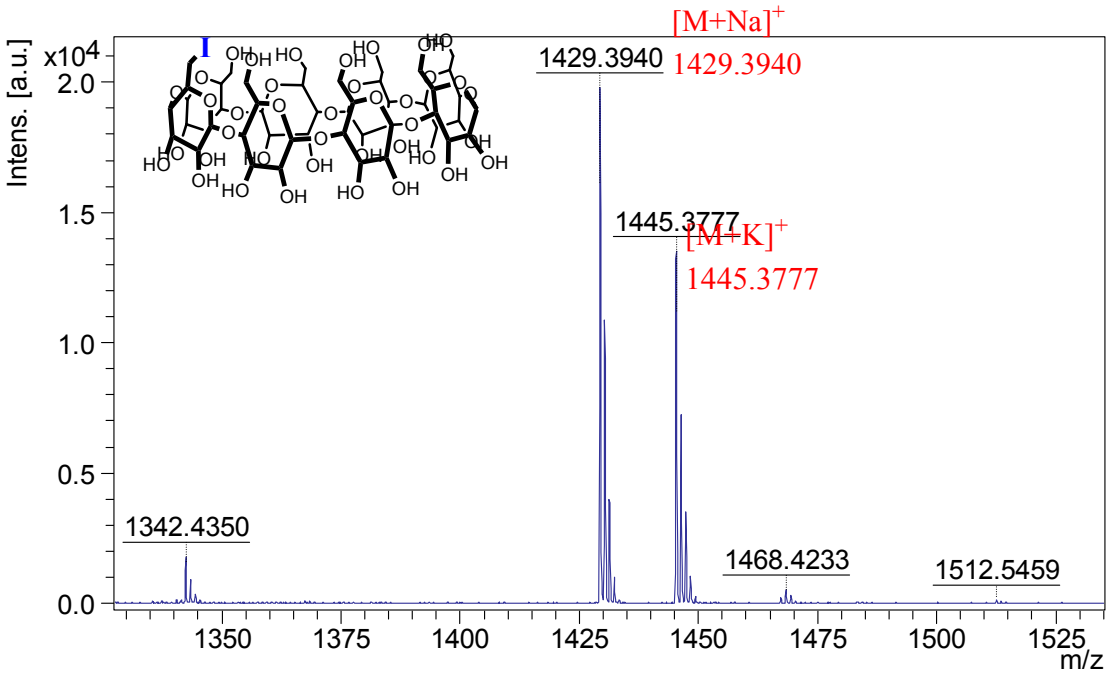


Fig. S12. HRMS spectrum of **compound 2.**

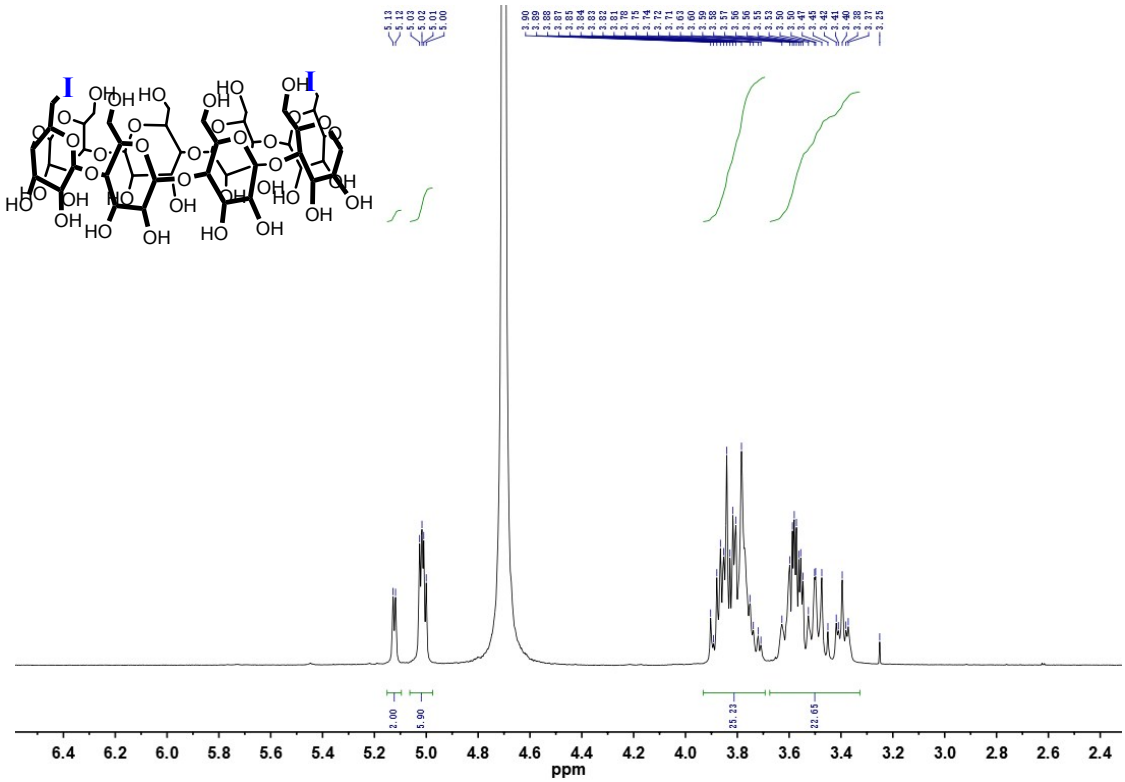


Fig. S13. ^{1}H NMR spectrum of **compound 3** measured in D_2O at 25 °C.

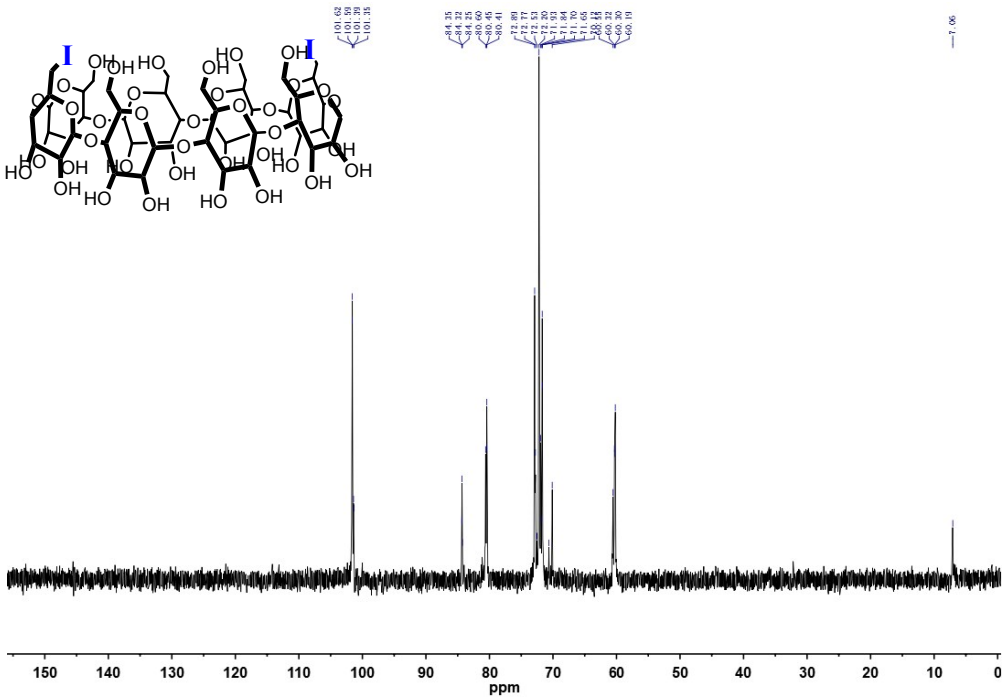


Fig. S14. ^{13}C NMR spectrum of **compound 3** measured in D_2O at 25 °C.

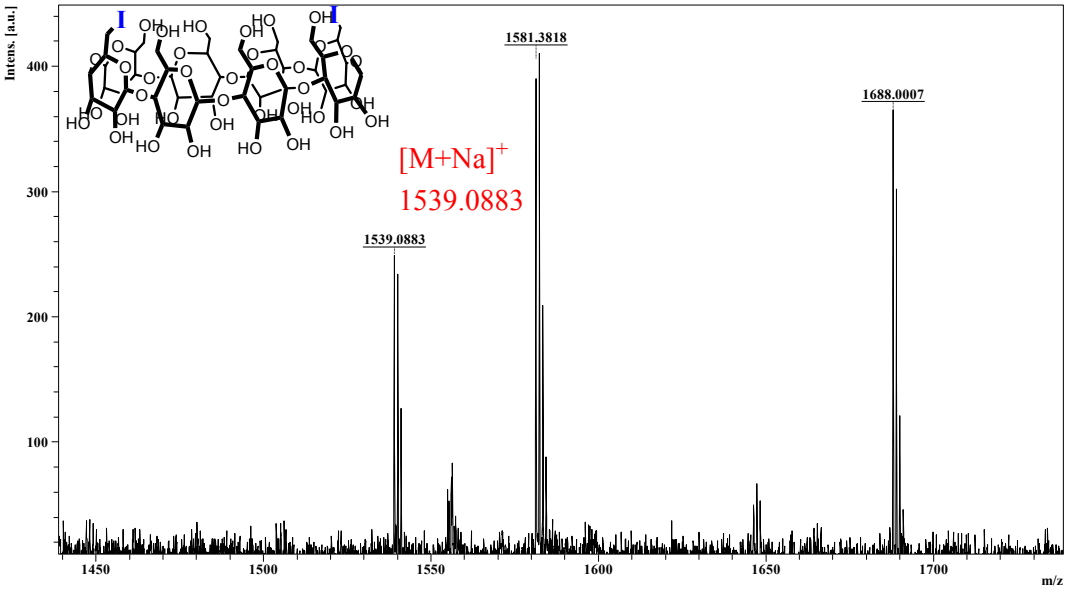


Fig. S15. HRMS spectrum of **compound 3.**

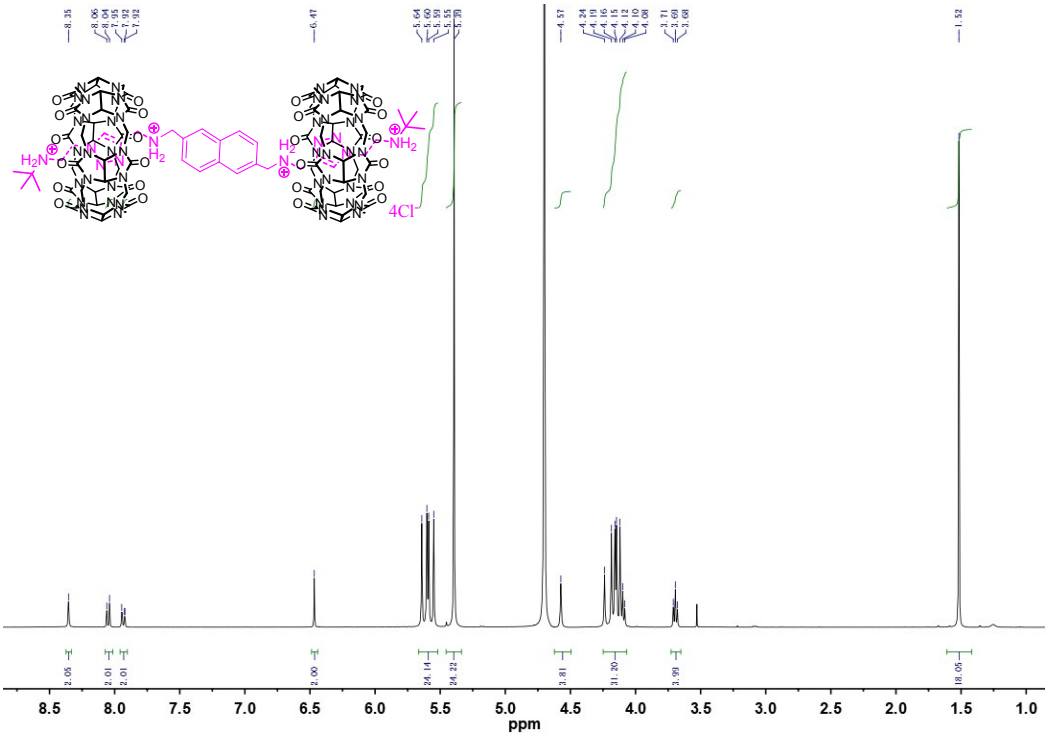


Fig. S16. ^{1}H NMR spectrum of **Rot0** measured in D_2O at 25 °C.

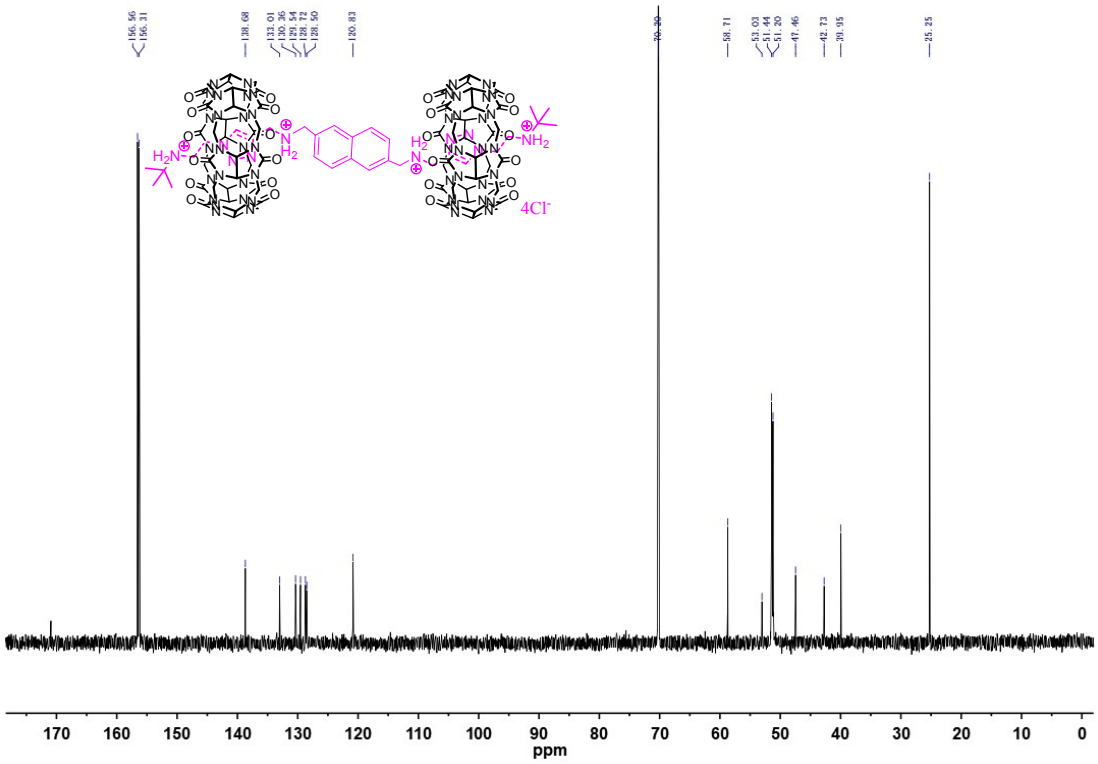


Fig. S17. ^{13}C NMR spectrum of **Rot0** measured in D_2O at 25 °C.

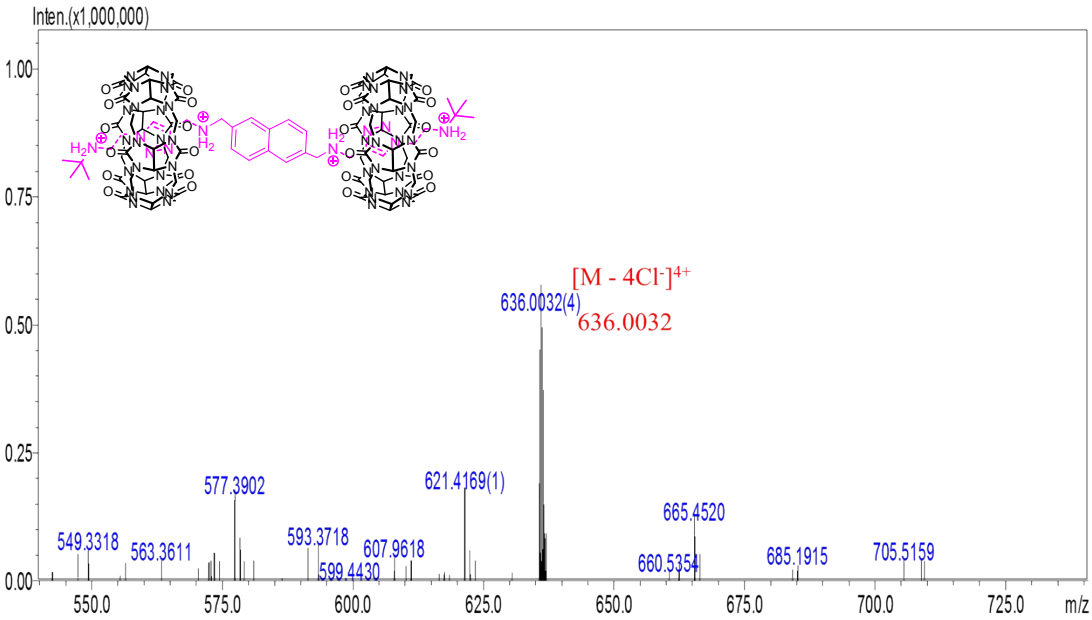


Fig. S18. HRMS spectrum of **Rot0.**

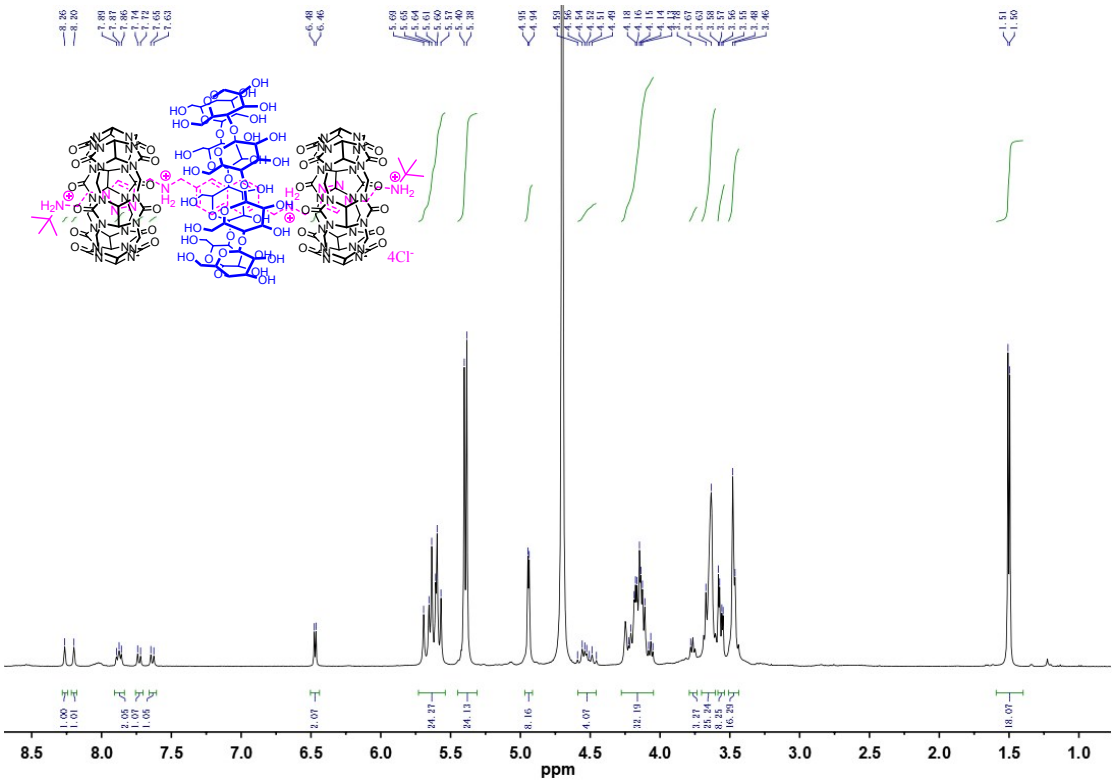


Fig. S19. ^{1}H NMR spectrum of **Rot1** measured in D_2O at 25 °C.

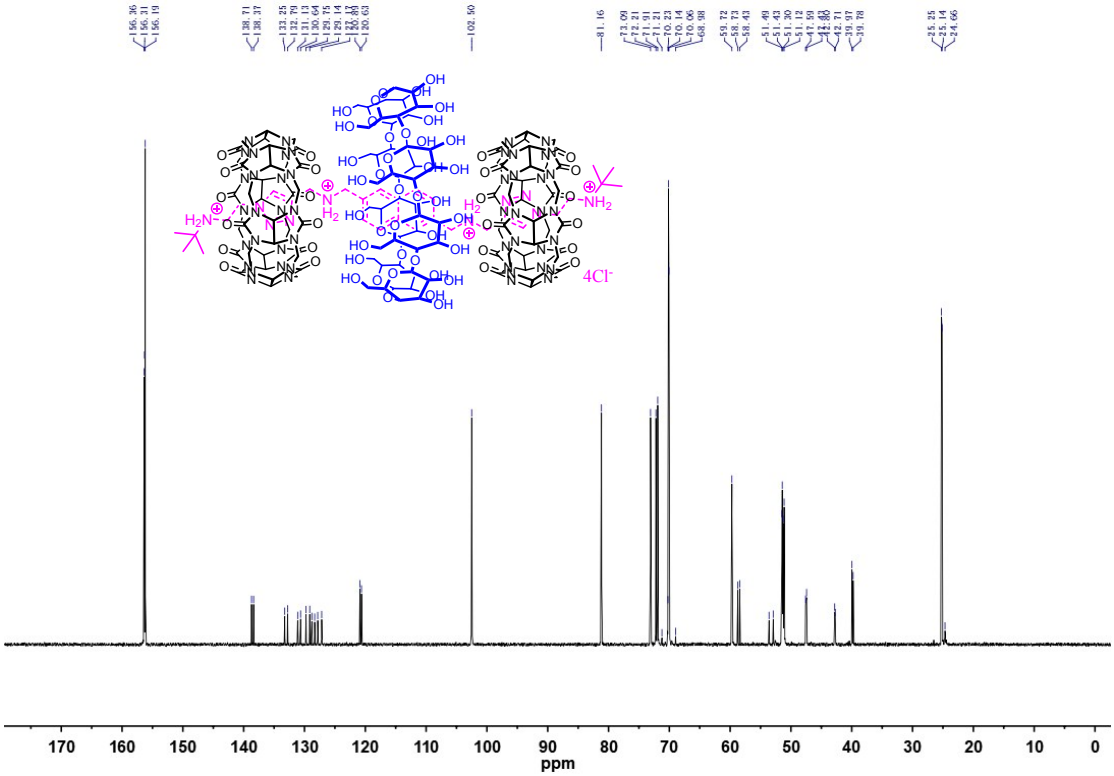


Fig. S20. ^{13}C NMR spectrum of **Rot1** measured in D_2O at 25 °C.

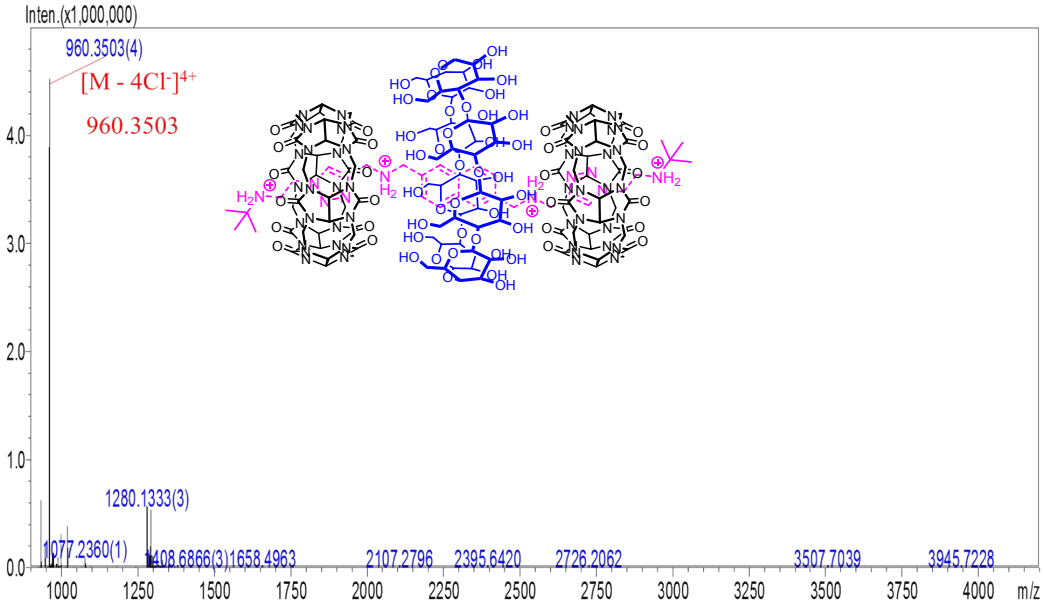


Fig. S21. HRMS spectrum of **Rot1.**

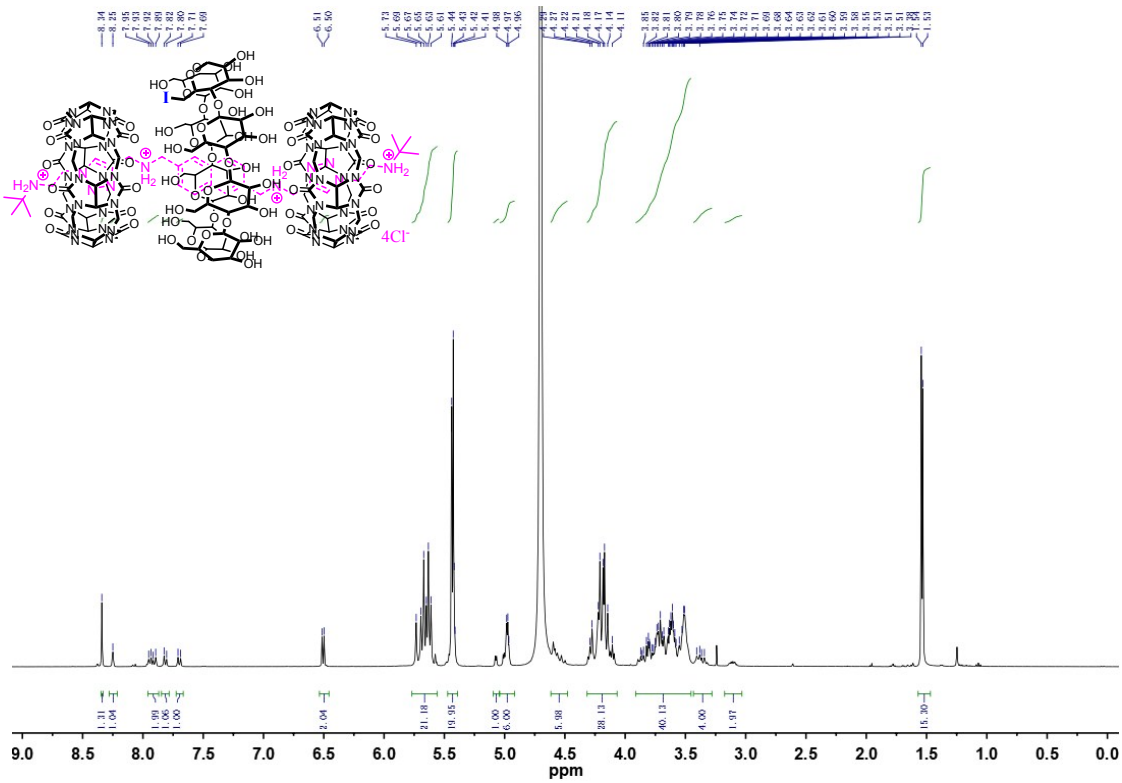


Fig. S22. ^{1}H NMR spectrum of **Rot2** measured in D_2O at 25 °C.

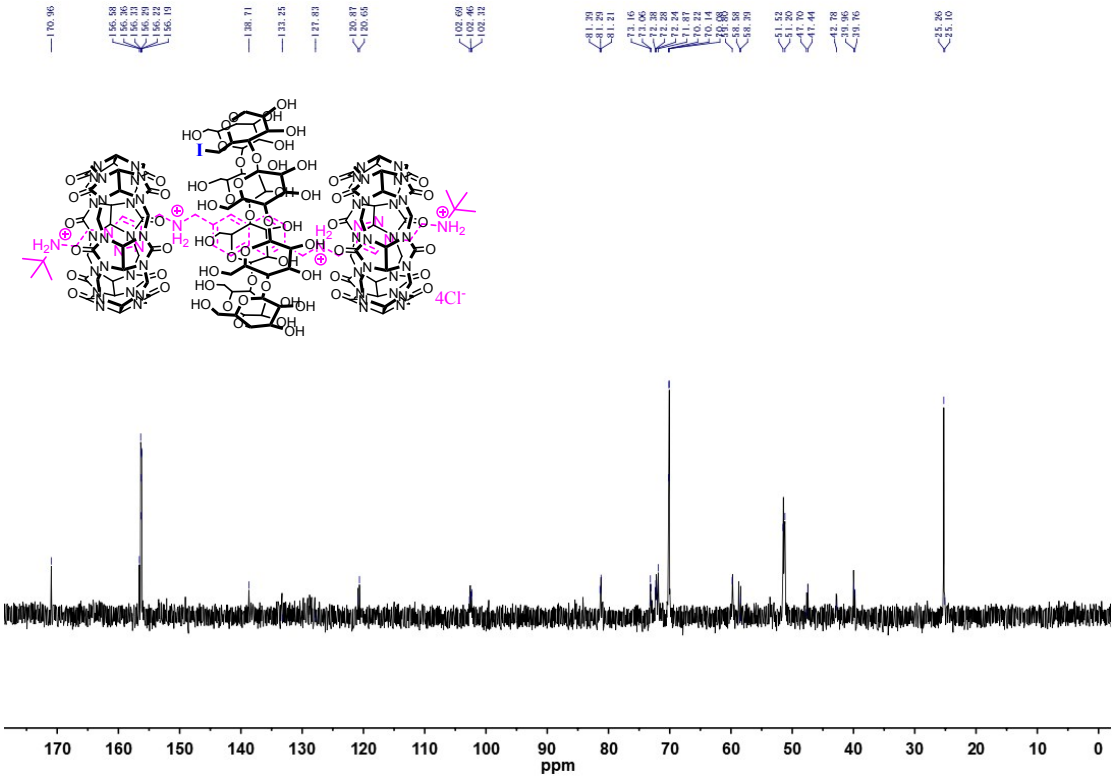


Fig. S23. ^{13}C NMR spectrum of **Rot2** measured in D_2O at 25 °C.

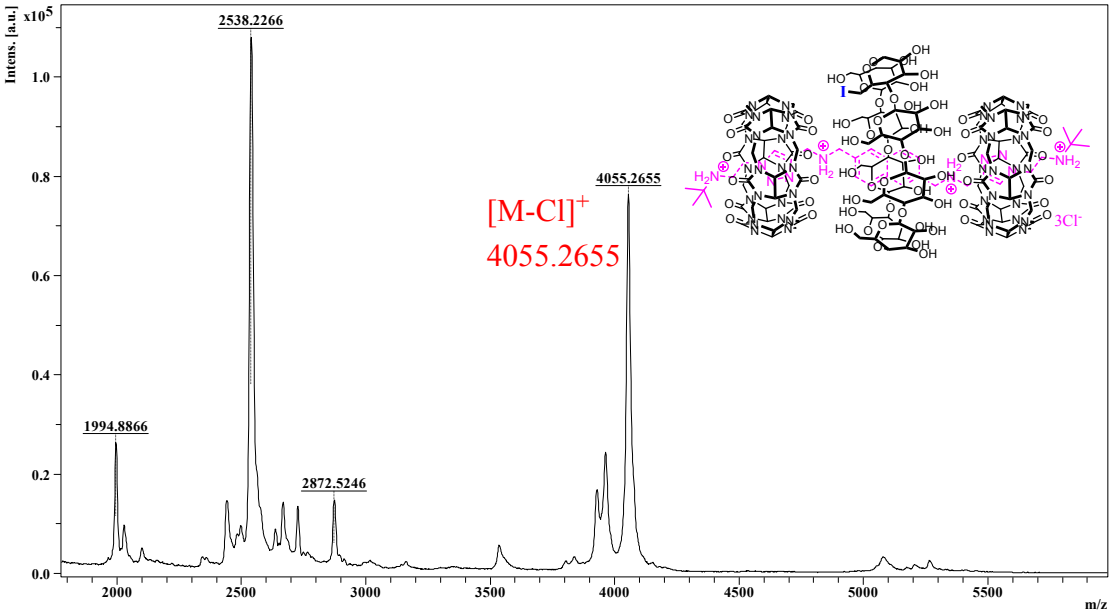


Fig. S24. HRMS spectrum of **Rot2**.

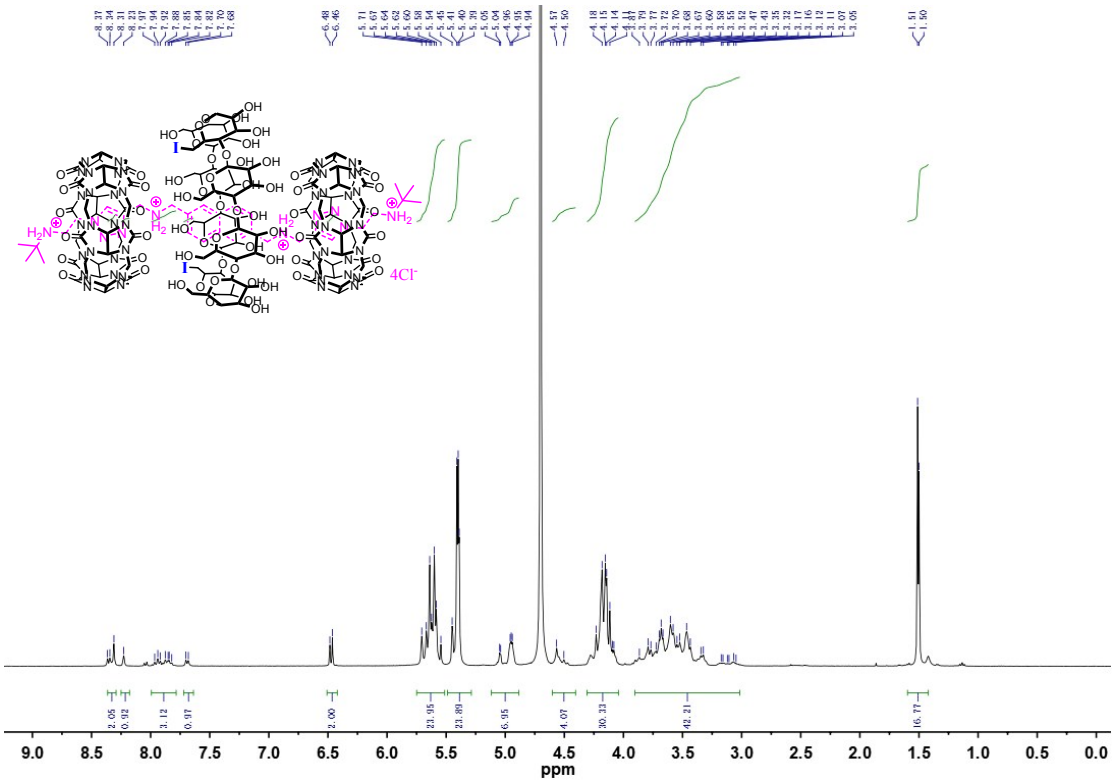


Fig. S25. ^{1}H NMR spectrum of **Rot3** measured in D_2O at 25 °C.

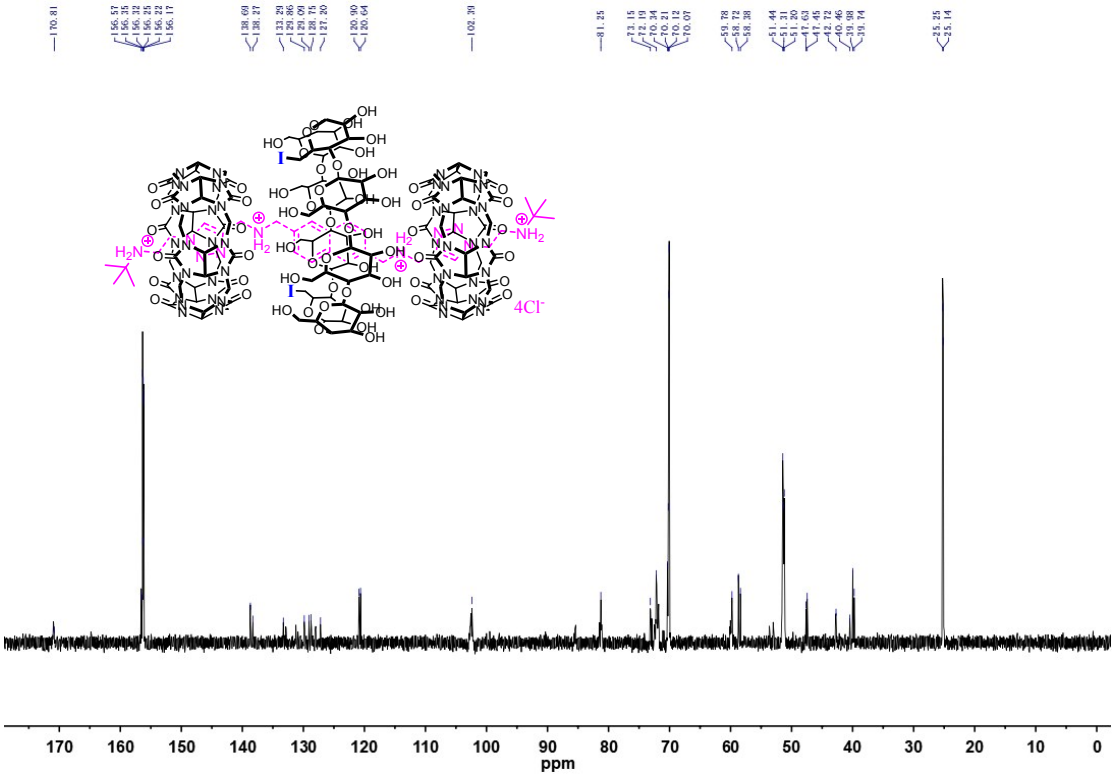


Fig. S26. ^{13}C NMR spectrum of **Rot3** measured in D_2O at 25 °C.

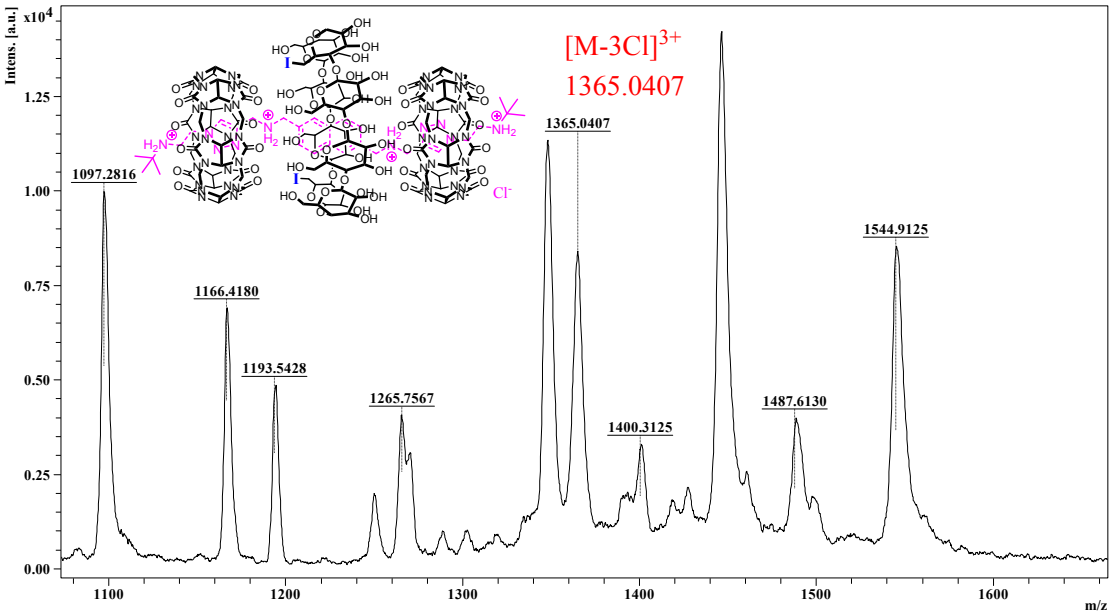


Fig. S27. HRMS spectrum of **Rot3**.

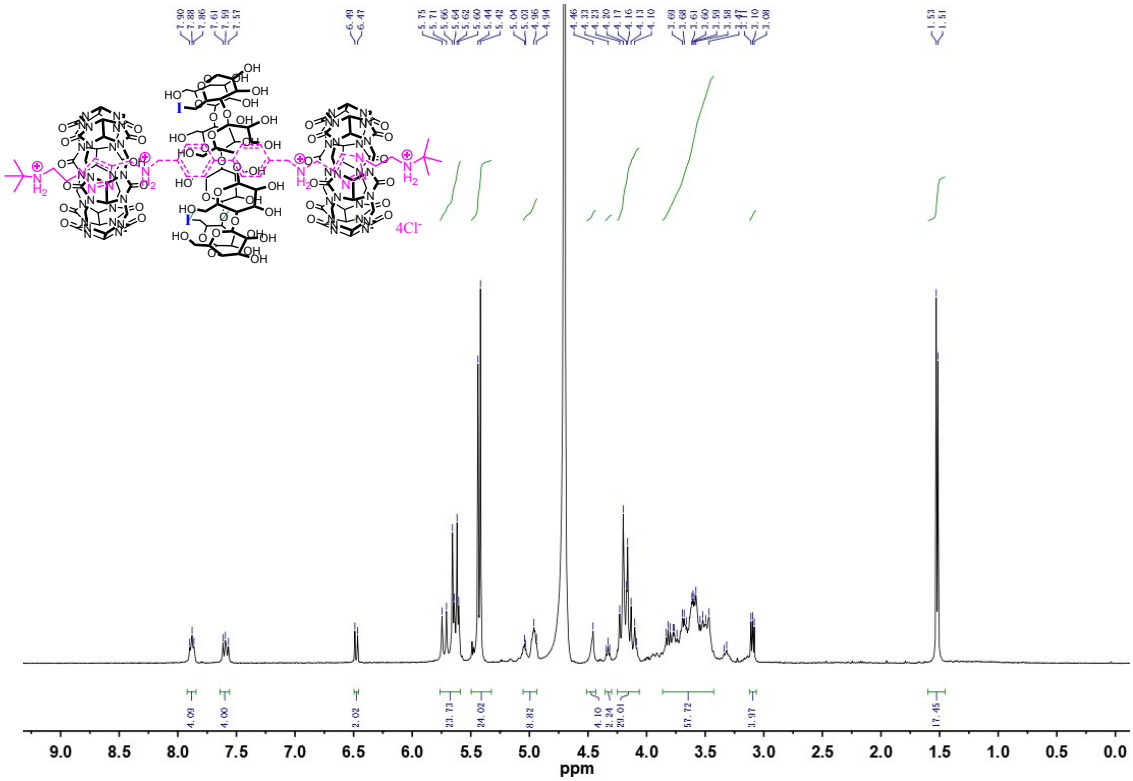


Fig. S28. ^{1}H NMR spectrum of **Rot4** measured in D_2O at 25 °C.

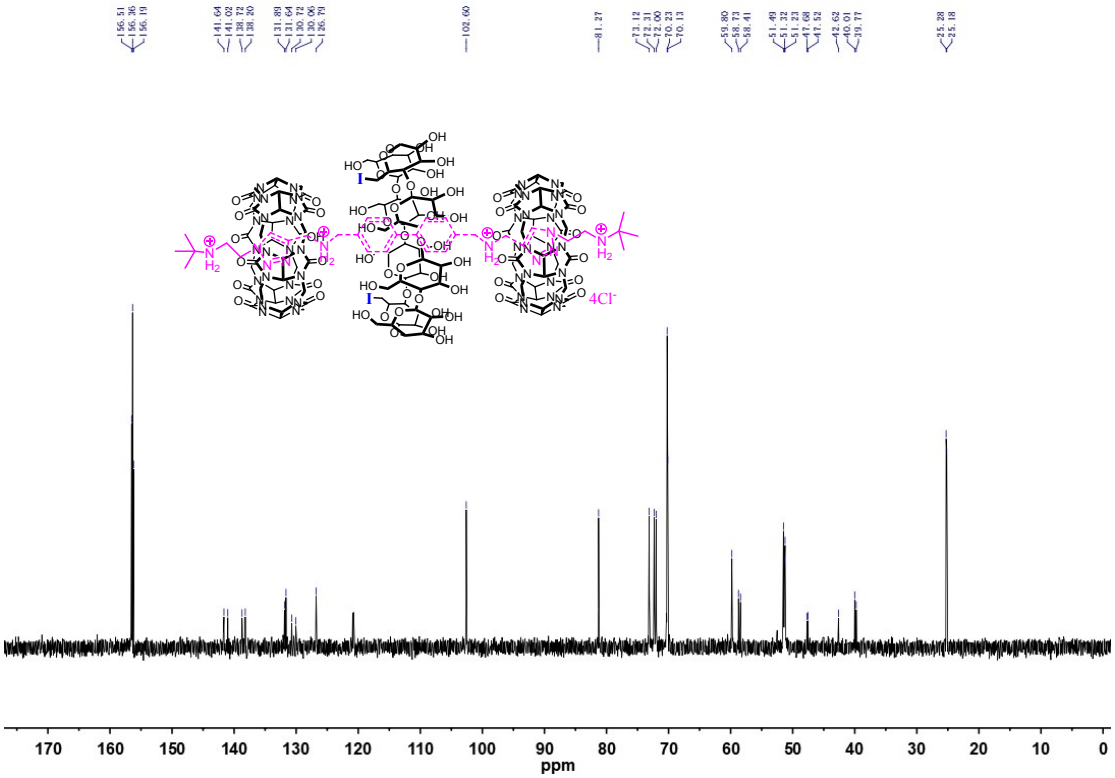


Fig. S29. ^{13}C NMR spectrum of **Rot4** measured in D_2O at 25 °C.

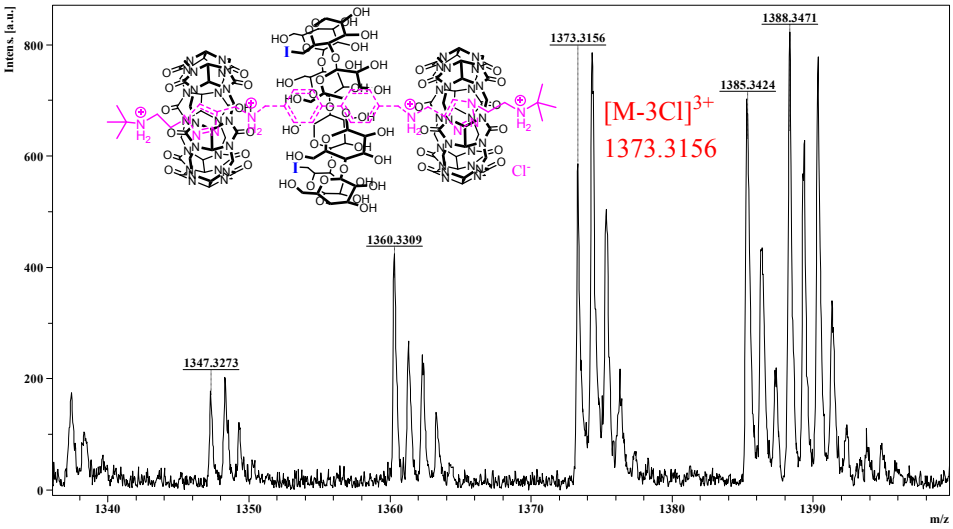


Fig. S30. HRMS spectrum of **Rot4**.

2. UV-vis, fluorescence, and RTP spectra of rotaxanes

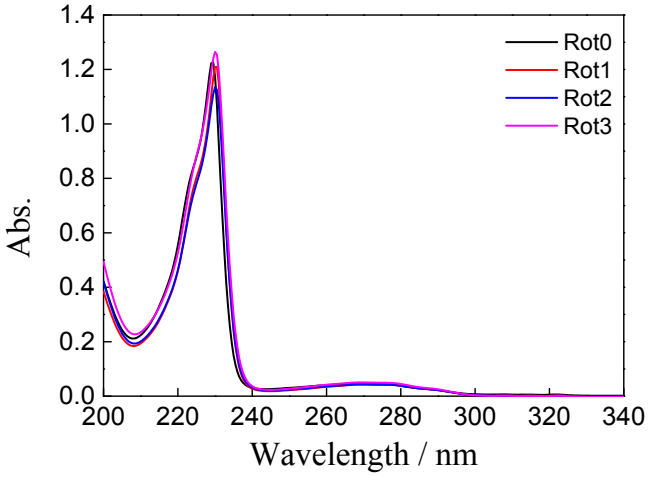


Fig. S31. UV-vis spectra of **Rot0** (10 μM), **Rot1** (10 μM), **Rot2** (10 μM) and **Rot3** (10 μM) in water at 25℃.

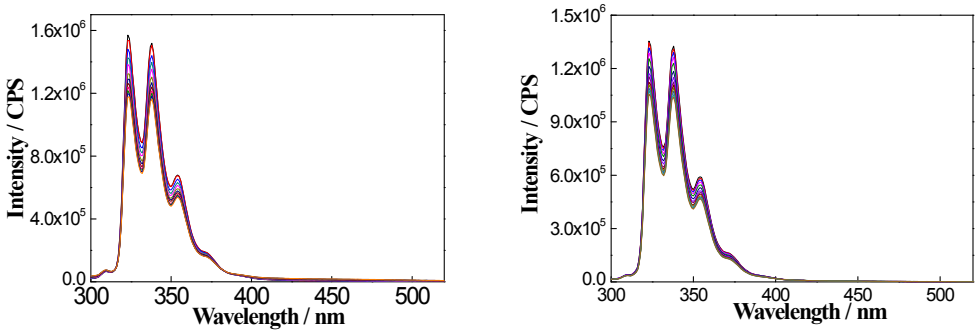


Fig. S32. Left: Fluorescence spectra of **Rot3** (10 μM) upon addition of L-His from 0-0.0222 M at λ_{ex} = 280 nm in water at 25℃. Excitation and emission bandwidths are 2.5 nm. Right: Fluorescence spectra of **Rot3** (10 μM) upon addition of L-Met from 0-0.0237 M at λ_{ex} = 280 nm in water at 25 ℃. Excitation and emission bandwidths are 2.5 nm and 2.0 nm, respectively. All spectra were measured with the Fluoromax-4 spectrofluorometer.

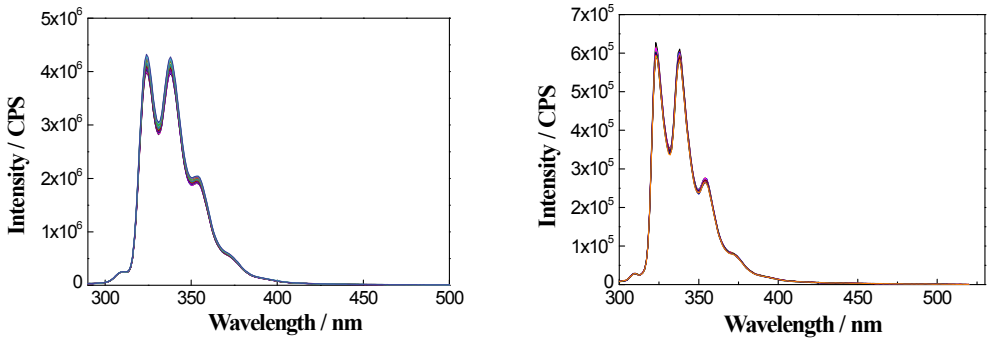


Fig. S33. Left: Fluorescence spectra of **Rot3** (10 μM) upon addition of L-Lys from 0-0.0237 M at λ_{ex} = 280 nm in water at 25℃. Excitation and emission bandwidths are 3.0 nm and 3.0 nm, respectively. Right: Fluorescence spectra of **Rot3** (10 μM) upon addition of L-Leu from 0-0.0222M at λ_{ex} = 280 nm in water at 25 ℃, Excitation and emission bandwidths are 2.5 nm and 1.0 nm,

respectively. All spectra were measured with the Fluoromax-4 spectrofluorometer.

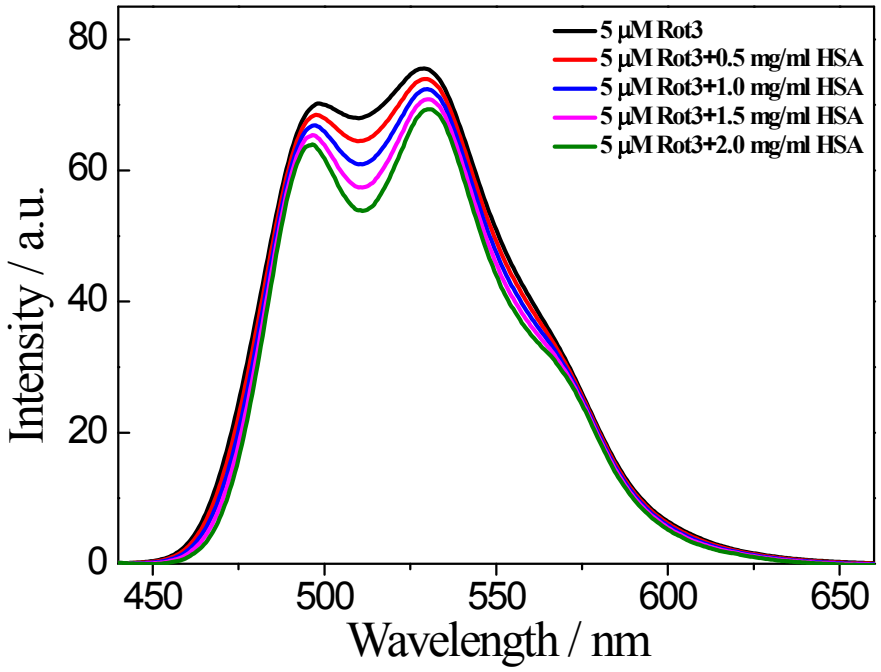


Fig. S34. Phosphorescence spectra of **Rot3** 5 μM and **Rot3** 5 μM mixed **HSA** (0.5, 1.0, 1.5, 2.0 mg / ml) in deaerated water at λ_{ex} = 280 nm at 25 °C.

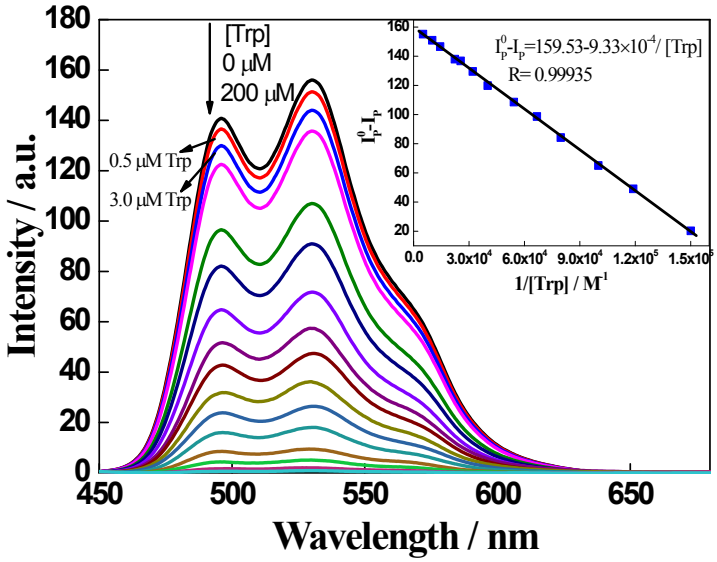


Fig. S35. Phosphorescence spectra of **Rot3** (20 μM) in the simulated human blood serum solution upon addition of Trp (0-200 μM) at 25 °C. λ_{ex} = 280 nm. Inset: Phosphorescence intensity change at 530 nm as a function of the reciprocal of Trp concentration.

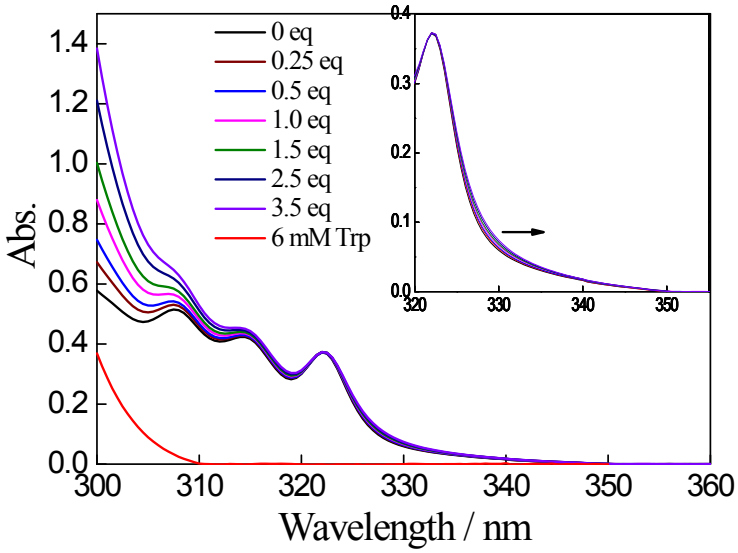


Fig. S36 UV-vis spectra of 6 mM **Rot3**(black) upon addition of L-Trp (0 eq, 0.25 eq, 0.5 eq, 1.0 eq, 1.5 eq, 2.5 eq and 3.5 eq) and 6 mM Trp(red) in water at 25℃. Inset: partial UV-vis spectra in the wavelength range from 320 nm to 355 nm.

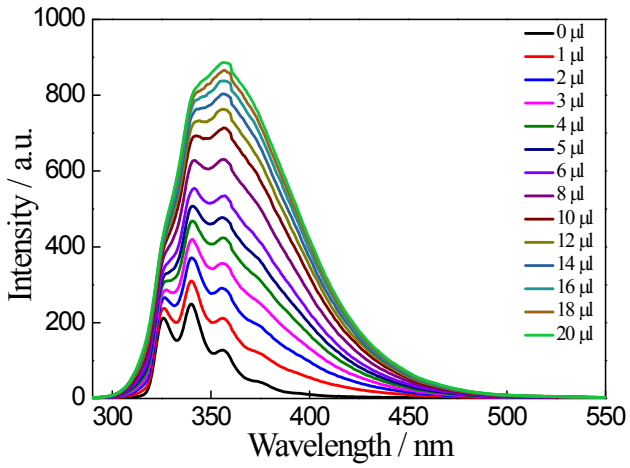


Fig. S37. Fluorescence spectra of **Rot3** (5 μM) upon increasing the concentration of of L-Trp in water (5 μM~10 μM) at λ_{ex} = 280 nm at 25 °C, measured with the JASCO FP-8500 spectrofluorometer.

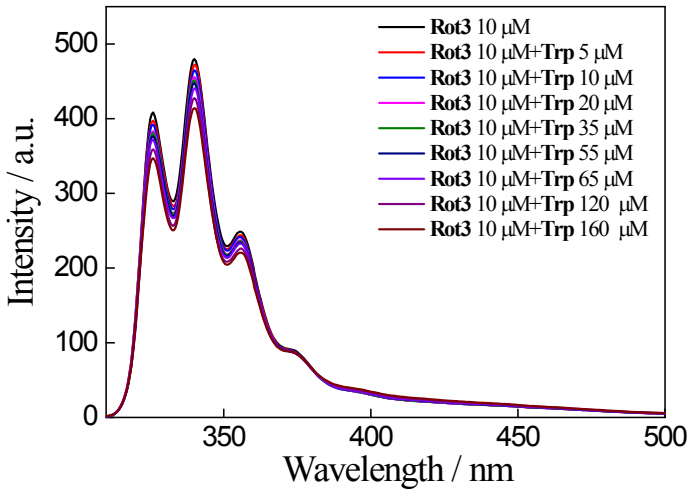


Fig.38 Fluorescence spectra of 10 μM **Rot3** (black) upon addition of L-Trp (5 μM~160 μM) at λ_{ex} = 322 nm in water at 25℃, measured with the JASCO FP-8500 spectrofluorometer.

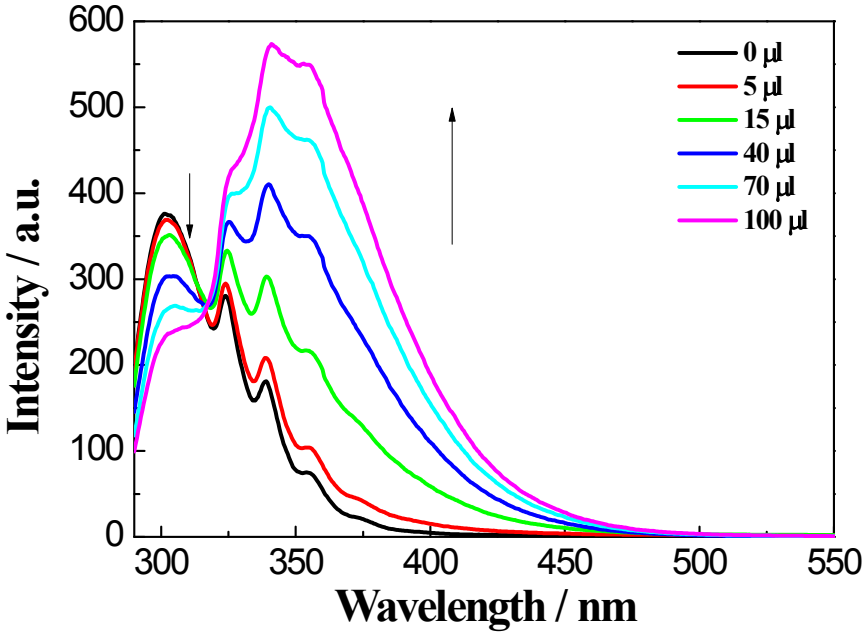


Fig. S39. Fluorescence spectra of **Rot3** (5 μM) mixed amino acid that mimic of the human bloodstream without L-Tryptophan in water with the addition of Tryptophan (0~0.5 mM) at λ_{ex} = 280 nm at 25 °C, measured with the JASCO FP-8500 spectrofluorometer.

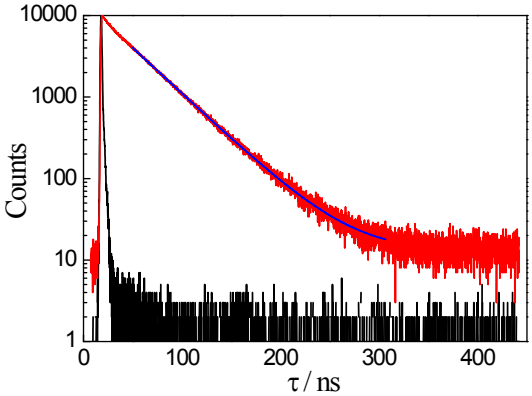


Fig. S40. Lifetime decay curves of **Compound 5** in water, excited at 280 nm and monitoring at 340 nm. CHISQ=1.06, τ =38.7 ns.

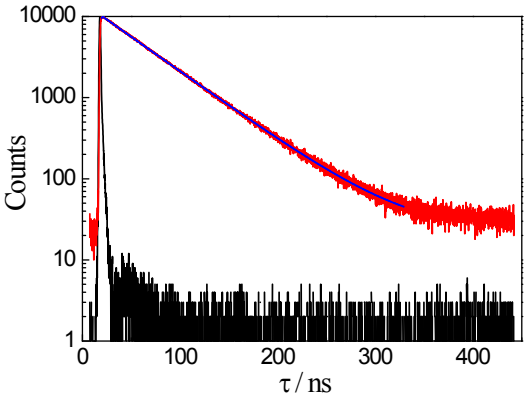


Fig. S41. Lifetime decay curves of **Rot0** in water, excited at 280 nm and monitoring at 340 nm. CHISQ=1.13, τ =39.0 ns

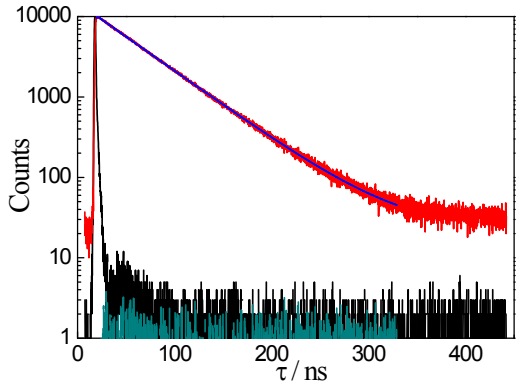


Fig. S42. Lifetime decay curves of **Rot1** in water, excited at 280 nm and monitoring at 340 nm. CHISQ=1.10, τ=50.9 ns.

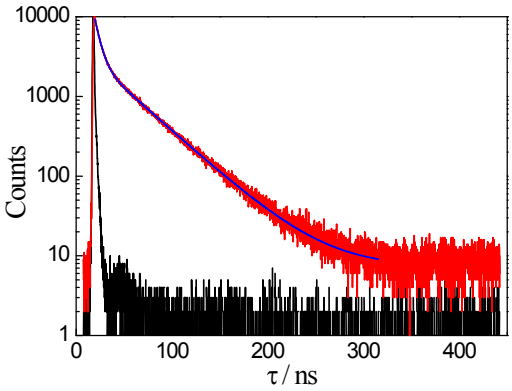


Fig. S43. Lifetime decay curves of **Rot2** in water, excited at 280 nm and monitoring at 340 nm. CHISQ=1.05. τ_1=5.7 ns, τ_2=40.6 ns, A_1=35.31%, A_2=64.69%

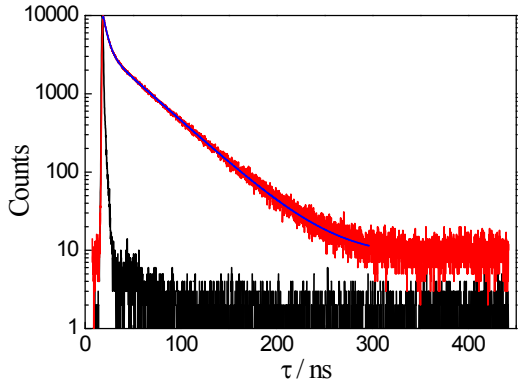


Fig. S44. Lifetime decay curves of **Rot3** in water, excited at 280 nm and monitoring at 340 nm. CHISQ=1.11. τ_1=4.7 ns, τ_2=39.7 ns, A_1=21.02%, A_2=78.98%.

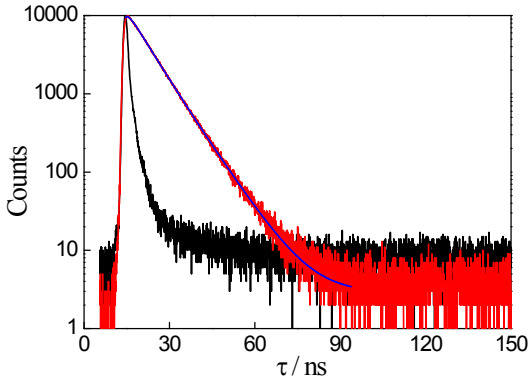


Fig. S45. Lifetime decay curves of **Rot4** in water, excited at 280 nm and monitoring at 315 nm. CHISQ=1.01. τ_1=5.0 ns, τ_2=8.2 ns, A_1=27.23%, A_2=72.77%.

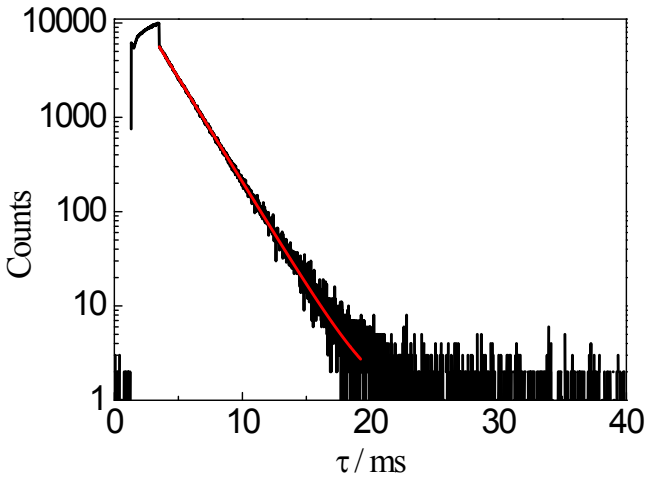


Fig. S46. Phosphorescence lifetime decay curves of **Rot2** (10 μM) in deaerated water, excited at 280 nm and monitoring at 530 nm. CHISQ=1.09. Average lifetime=2.0 ms.

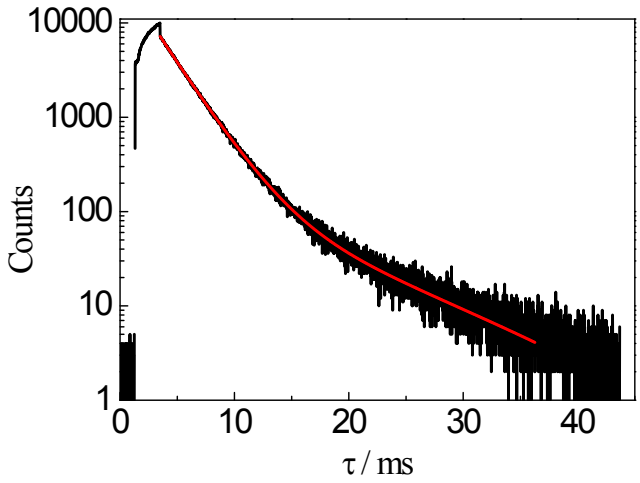


Fig. S47. Phosphorescence lifetime decay curves of **Rot3** (10 μM) in deaerated water, excited at 280 nm and monitoring at 530 nm. CHISQ=1.10. Average lifetime=2.5 ms.

3. Complexation Studies of Rotaxanes with Amino Acids

Calculation of the Gibbs free energy change of photoinduced electron transfer.

Compounds	$E_{1/2}(X^+/X)$	$E_{1/2}(X/X^-)$
L-Tryptophan	+0.97V	-
Naphthalene,2,7-dimethyl-	-	-2.49V

$$\Delta G = 23.05[(E_{1/2}(D^+/D) - E_{1/2}(A/A^-) - \frac{e^2}{\varepsilon\alpha} - \Delta E_{0,0}]$$

Where $e^2/\varepsilon\alpha$ is Coulomb energy released by ion entering collision distance, the value is probably 0.06V. $\Delta E_{0\text{-}0}$ is the excited state energy of the electron donor or acceptor. It is estimated from its fluorescence emission and UV spectra, the value is probably 4.19V (404.2 kJ·mol^{-1}). Hence, the value of ΔG is -76.2 kJ·mol^{-1}.

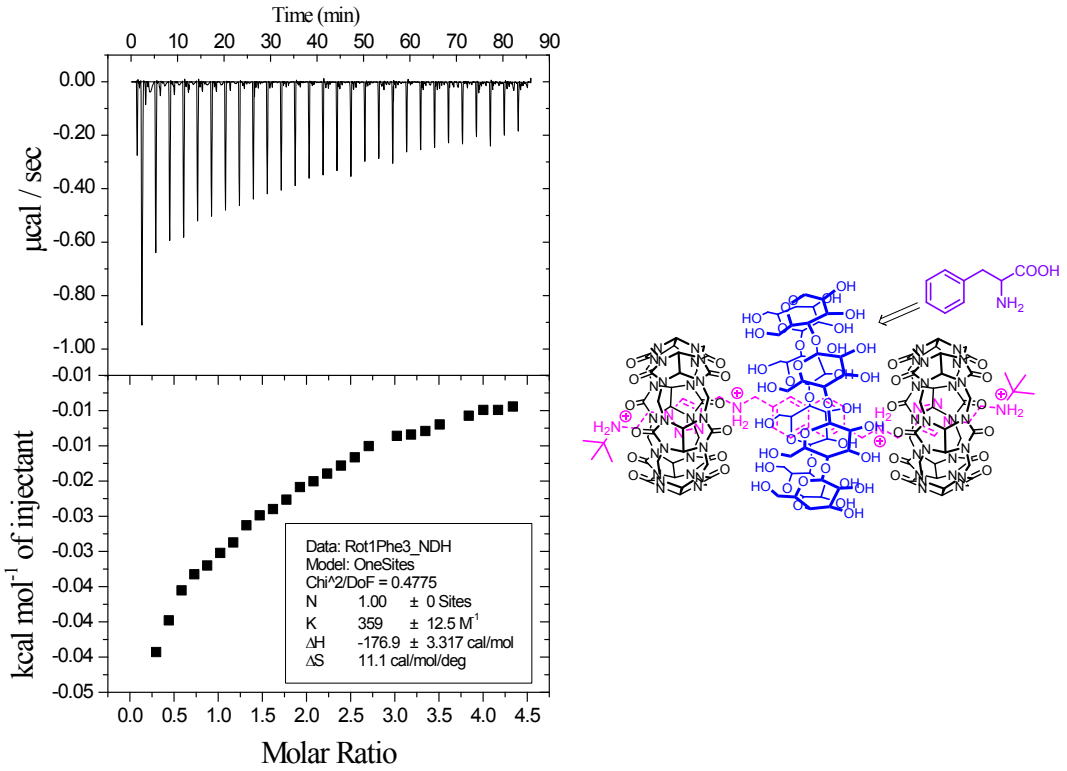


Fig. S48. ITC titration date for the complexation of host **Rot3** (1 mM) with for L-Phe (20 mM) in aqueous solution at 25 °C.

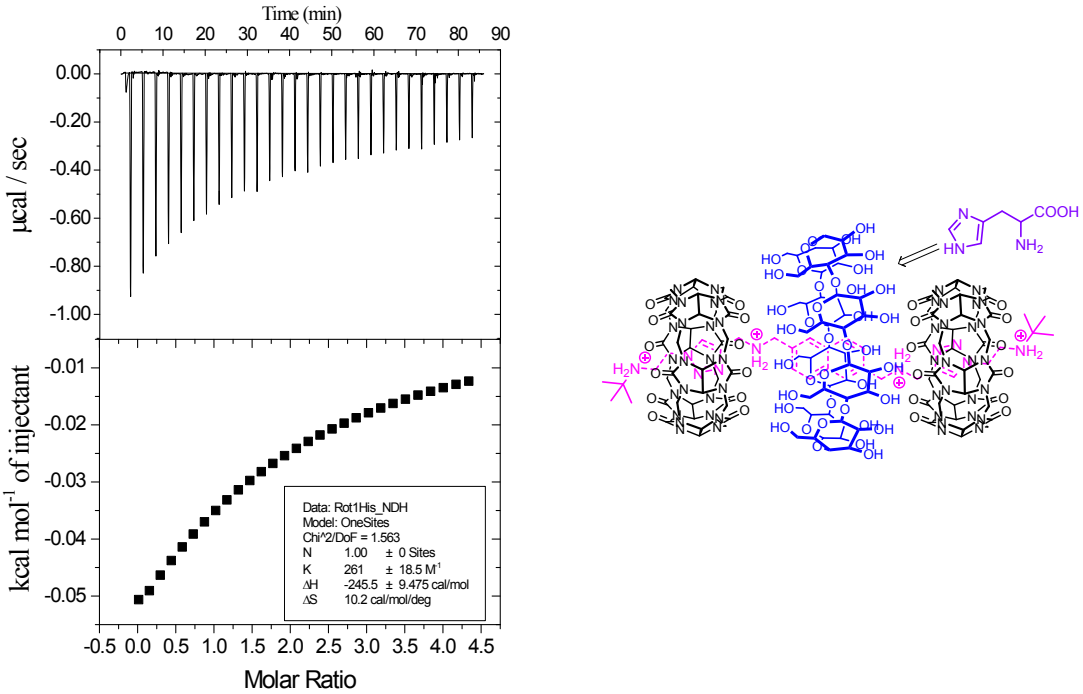


Fig. S49. ITC titration date for the complexation of host **Rot3** (1 mM) with for L-His (20 mM) in aqueous solution at 25 °C.

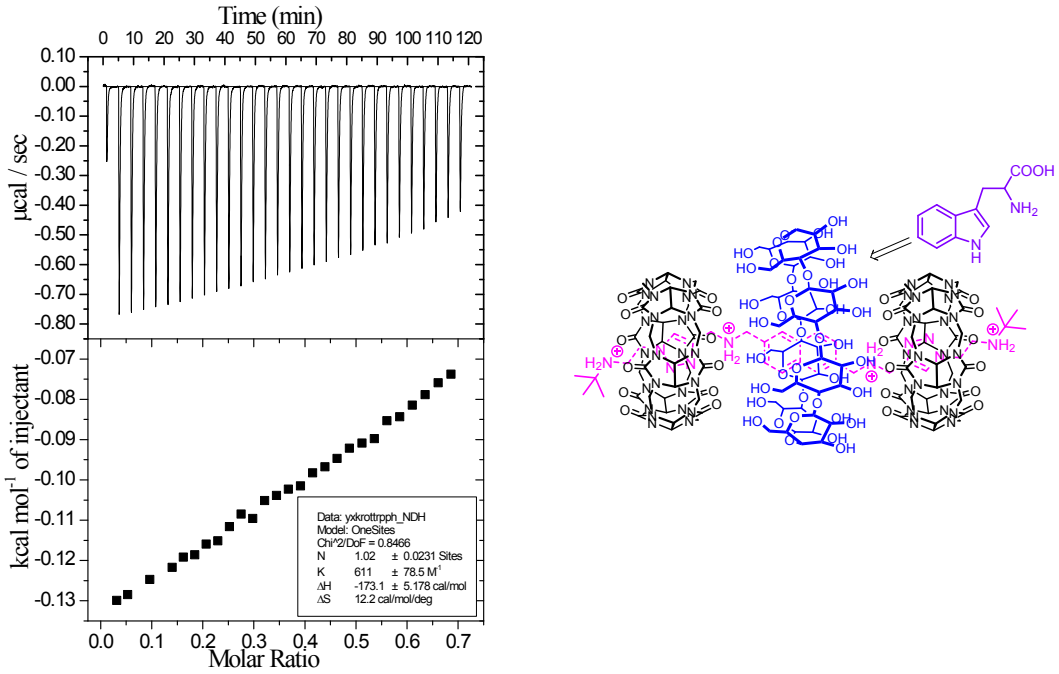


Fig. S50. ITC titration date for the complexation of host **Rot3** (5 mM) with for L-Trp (15 mM) in aqueous solution at 25 °C.

Reference

1. (a)Jon, S. Y.; Selvapalam, N.; Oh, D. H.; Kang, J.-K.; Kim, S.-Y.; Jeon, Y. J.; Lee, J. W.; Kim, K. *J. Am. Chem. Soc.,* **2003**, *125*, 10186. (b) Ke, C.; Smaldone, R. A.; Kikuchi, T.; Li, H.; Davis, A. P.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2013**, *52*, 381.