Supporting Information

for

A multifunctional catenated host for efficient binding of Eu^{3+} and Gd^{3+}

Mandira Nandi[a], Somnath Bej[a], Tamal Kanti Ghosh[a] and Pradyut Ghosh*[a]

[a]*School of Chemical Sciences, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Kolkata 700032, India. E-mail: icpg@iacs.res.in*

TABLE OF CONTENTS

Materials and methods

All the reagents and deuterated solvents were purchased from Sigma- Aldrich and used as received. Solvents like THF, acetone, CH_2Cl_2, $CHCl_3$, and CH_3CN were distilled *via* usual procedure prior to use. Reactions were carried out under argon atmosphere and work up procedure was done at ambient conditions. In each case, column chromatography was performed by using 60-120 mesh silica gel which was purchased from Merck private limited. ^{1}H, ^{13}C, COSY and ROESY NMR spectroscopy experiments were carried out on a FT-NMR Bruker DPX 300/400/500 MHz NMR spectrometer and the residual protons of each

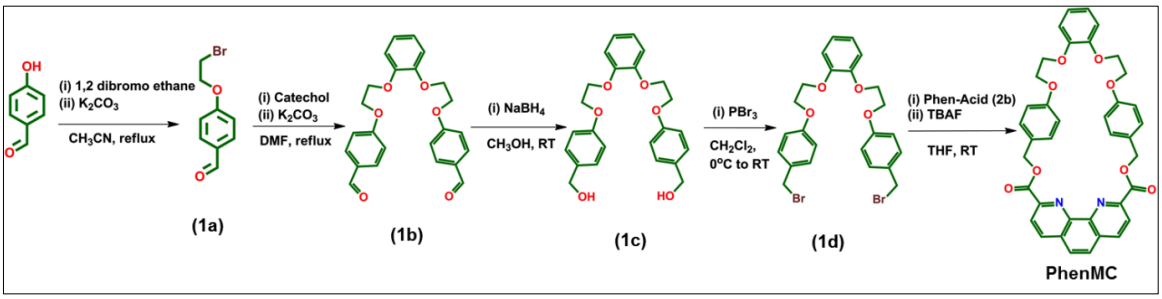
deuterated solvents were granted as the internal standards where the coupling constants were calculated in hertz (Hz) and chemical shifts in ppm. Electrospray ionization mass spectrometry (ESI-MS) analysis was performed with a Waters QtoF Model YA 263 spectrometer in positive ion ESI mode. The absorption studies and emission studies were recorded in a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer (NIR = near-infrared) (with a quartz cuvette of path length 1cm) and PerkinElmer LS-55 spectrofluorimeter respectively.Fourier transform infrared (FT-IR) spectra were recorded on a SHIMADZU FTIR-8400S IR spectrophotometer with KBr pellets. Crystals were solved by using a Bruker SMART APEX diffractometer, equipped with a CCD area detector at 150 K. Compounds **1a**,[1] **1b**,[1] **2a**,[2] **2b**[2] and alkene iodide[3] were prepared by using the known procedure reported in literature. All the characterization data of the known compounds properly matched with the reported characterization details.

X-Ray crystallographic refinement details:

Crystal data of **Axle** and **Na-Catenate** were obtained by using Mo- Kα (λ=0.7107 Å) radiation on a Bruker SMART APEX diffractometer, equipped with a CCD area detector. Data integration and reduction were processed by SAINT[4] software provided with the SMART APEX II software package. The structure was solved using SHELXTL[5] and was refined on F2 by the full- matrix least-squares technique using the SHELXL-2014[6] program package. Empirical absorption correction to the collected reflections has been done by applying SADABS[7]. PLATON-97[8] and MERCURY 3.6[9] were used to generate graphics. Some disordered solvent molecules were removed by the PLATON/SQUEEZE program. In the crystal structures all non-hydrogen atoms were refined with anisotropic displacement coefficients and all hydrogen atoms were geometrically fixed at idealized positions. The CCDC no. of the crystal structures (1871206 and 1871207) contains the supplementary crystallographic data for this paper.

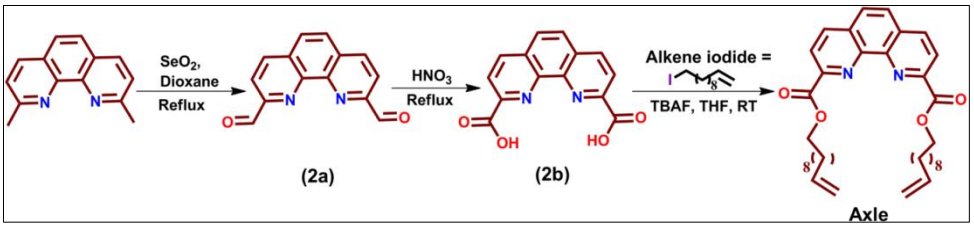
Synthetic Scheme

PhenMC: Compound **1a** and **1b** were prepared by using the known procedure reported in literature. All the characterization data of the known compounds properly matched with the reported characterization details.



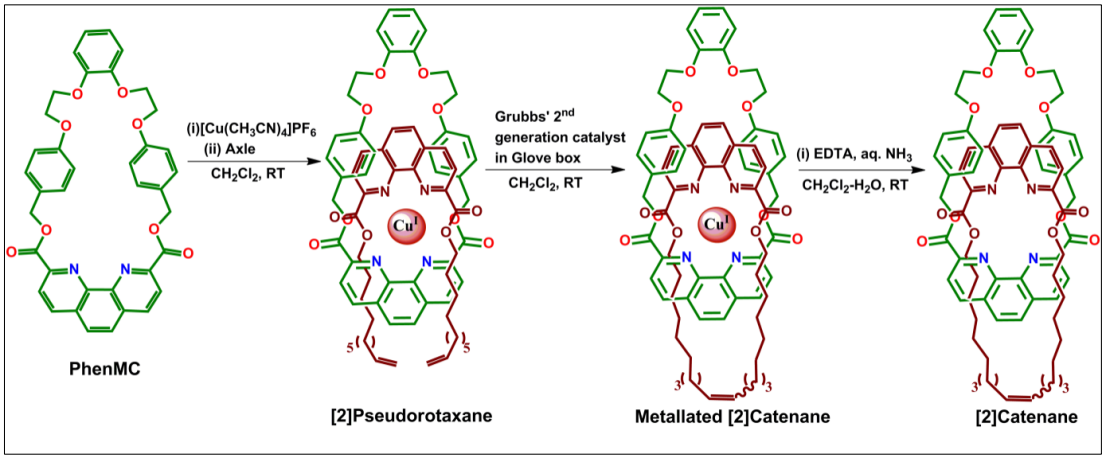
Scheme S1: Synthetic scheme of **PhenMC**

Axle: Compound **2a** and **2b** were prepared by using the known procedure reported in literature. All the characterization data of the known compounds properly matched with the reported characterization details.



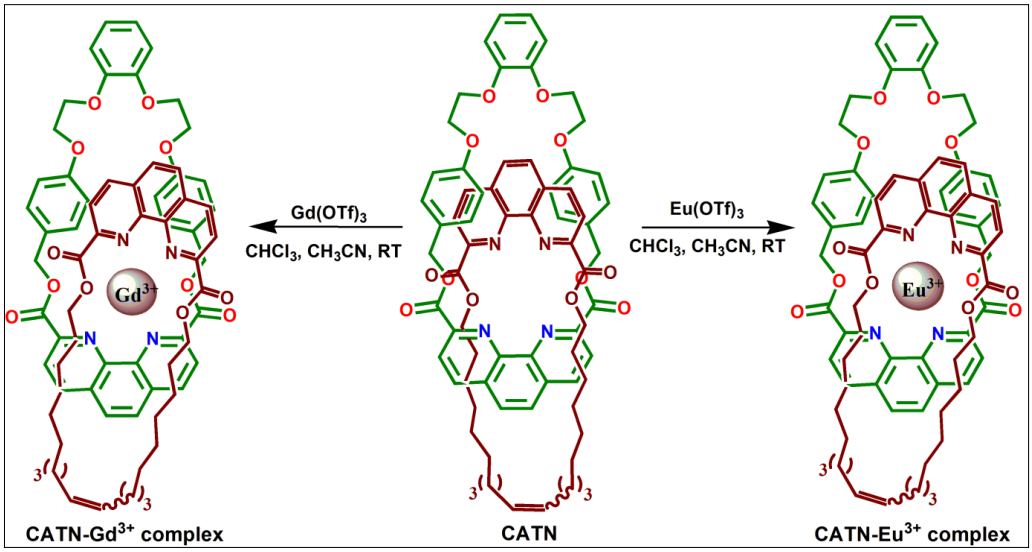
Scheme S2: Synthetic scheme of **Axle**

[2]Catenane:



Scheme S3: Synthetic scheme of **[2]Catenane**

Lanthanide binded [2]Catenane:



Scheme S4: Synthetic scheme of **CATN-Gd^{3+}** and **CATN-Eu^{3+}** complexes

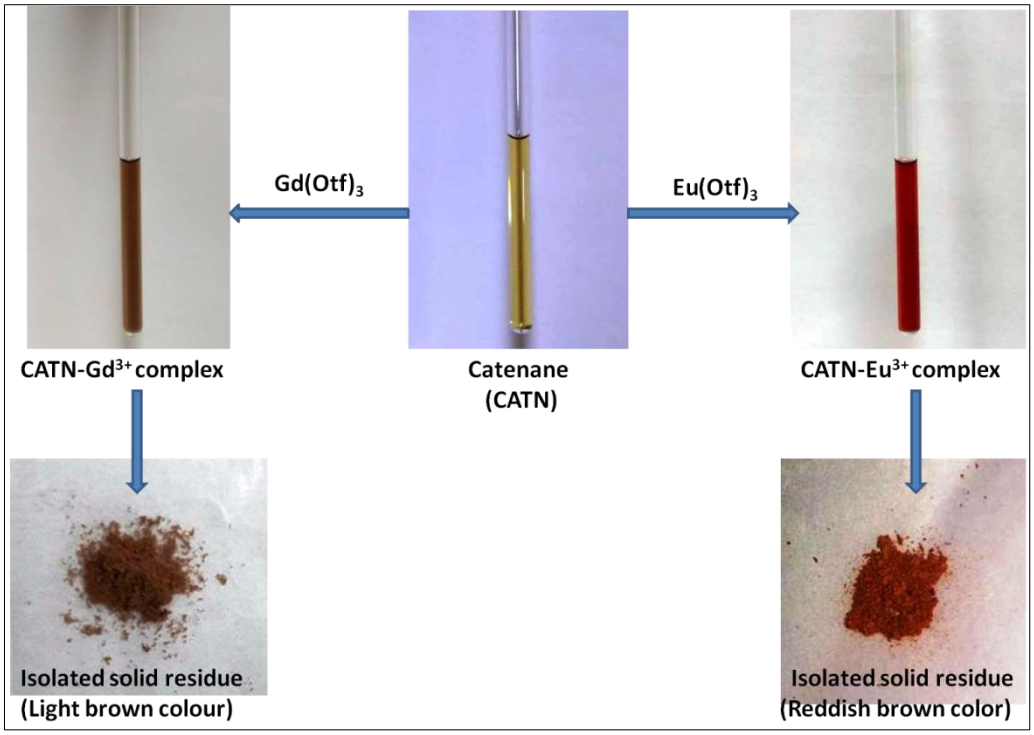


Figure S1: Progress of reaction between catenane with Eu^{3+} and Gd^{3+}

General Procedure:

Synthesis of Compound **1c**: Compound **1b** (406 mg, 1mmol) was dissolved in $CHCl_3$-CH_3OH binary solvent mixture and reacted with $NaBH_4$ (151 mg, 4mmol) for 24h in room temperature. After that, the reaction mixture was evaporated to dryness and extracted with $CHCl_3$ and water by washing the organic layer several times with brine solution. Solid crystalline product was isolated as white solid (Scheme S1). Yield: 82%.

Compound **1c (**$C_{24}H_{26}O_6$, M_w = 410.46**):** HRMS (ESI-MS): $C_{24}H_{27}O_6$ $[M + H]^+$: calcd, *m/z* 411.1808; found, *m/z* 411.1821. Anal. calcd for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38. Found C, 71.05; H, 6.55. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.30 (t, 4H, J = 5 Hz, -CH_2), 4.36 (t, 4H, J = 4.5 Hz, -CH_2), 4.58 (s, 4H, -CH_2), 6.90 (d, 4H, J = 8.5 Hz, Ar-H), 6.95-7.00 (m, 4H, Ar-H), 7.22 (d, 4H, J = 8.5 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 65.15, 67.14, 68.49, 115.05, 115.83, 122.31, 128.78, 130.20, 133.66, 149.30, 158.61.

Synthesis of Compound **1d**: Compound **1c** (410 mg, 1mmol) in dry CH_2Cl_2 was purged with argon gas, then PBr_3 (570 µl, 6mmol) was added drop wise in the atmosphere of argon and the reaction mixture was stirred for 24h. The reaction mixture was quenched with sodium bicarbonate solution and stirred for another 6h. Thereafter, the reaction mixture was evaporated to dryness and extracted with $CHCl_3$ and water by washing the organic layer several times with brine solution. Solid crystalline product was isolated as yellowish white crystalline solid (scheme S1). Yield: 70%

Compound **1d (**$C_{24}H_{24}Br_2O_4$, M_w = 536.25). Anal. calcd for $C_{24}H_{24}Br_2O_4$: C, 53.75; H, 4.51. Found C, 55.11; H, 4.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.30 (t, 4H, J = 5.2 Hz, -CH_2), 4.36 (t, 4H, J = 4 Hz, -CH_2), 4.48 (s, 4H, -CH_2), 6.88 (d, 4H, J = 8.8 Hz, Ar-H), 6.94-7.00 (m, 4H, Ar-H), 7.29 (d, 4H, J = 8.8 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 33.98, 67.03, 68.40, 115.18, 115.91, 122.37, 130.50, 130.61, 149.23, 159.01.

Synthesis of Compound **PhenMC**: Compound **2b** (536 mg, 2mmol) was reacted with TBAF (1.044 g, 4mmol) in dry THF and stirred for 3h in the room temperature. Then the compound **1d** (3.204 g, 3mmol) in dry THF was added drop wise to the reaction mixture *via* pressure equalizer funnel and the reaction was stirred in room temperature for another 48h in the atmosphere of argon. Thereafter, the reaction mixture was evaporated to dryness and extracted with $CHCl_3$ and water by washing the organic layer several times with brine solution. Extracted yellowish semi-solid product was purified in column chromatography by

using 4:1 $CHCl_3$ and ethyl acetate as eluent mixture. Solid crystalline **PhenMC** was isolated as light yellow powder (Scheme S1). Yield: 66%

PhenMC ($C_{38}H_{30}N_2O_8$, M_w=642.65). HRMS (ESI-MS): $C_{38}H_{30}N_2NaO_8$ $[M + Na]^+$: calcd, *m/z* 665.1900; found, *m/z* 665.1904. HRMS (ESI-MS): $C_{38}H_{31}N_2O_8$ $[M + H]^+$: calcd, *m/z* 643.2080; found, *m/z* 643.2081. Anal. calcd for $C_{38}H_{30}N_2O_8$: C, 71.02; H, 4.71; N, 4.36. Found C, 69.91; H, 4.43; N, 4.80. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.32 (s, 8H, -CH_2), 5.56 (s, 4H, -CH_2), 6.97 (t, 8H, J =4 Hz, Ar-H), 7.52 (d, 4H, J = 8.5 Hz, Ar-H), 7.92 (s, 2H, Ar-H), 8.39 (d, 2H, J = 8.5 Hz, Ar-H), 8.49 (d, 2H, J = 8 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 67.26, 67.47, 68.86, 114.21, 115.15, 115.72, 116.29, 122.34, 124.12, 128.43, 130.71, 137.45, 139.44, 149.46, 159.23, 165.86, 170.54.

Synthesis of **Axle**: Compound **2b** (536 mg, 2mmol) was reacted with TBAF (1.044 g, 4mmol) in dry THF and stirred for 3h in the room temperature. Then alkene iodide (1.680 g, 3mmol) in dry THF was added to the reaction mixture *via* pressure equalizer funnel and the reaction was stirred in room temperature for another 48h in the atmosphere of argon. Thereafter, the reaction mixture was evaporated to dryness and extracted with $CHCl_3$ and water by washing the organic layer several times with brine solution. Extracted liquid product was purified in column chromatography by using 9:1 $CHCl_3$ and ethyl acetate as eluent mixture. Pure product was isolated as yellowish oil (Scheme S2). Yield: 74%

Axle ($C_{36}H_{48}N_2O_4$, M_w = 572.77). HRMS (ESI-MS): $C_{36}H_{49}N_2O_4$ $[M + H]^+$: calcd, *m/z* 573.3692; found, *m/z* 573.3698. Anal. calcd for $C_{36}H_{48}N_2O_4$: C, 75.49; H, 8.45; N, 4.89. Found C, 76.33; H, 8.79; N, 5.53. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.28-1.33(m, 12H, -CH_2), 1.36-1.39(m, 8H, -CH_2), 1.45-1.50 (m, 4H, -CH_2), 1.92-1.97 (m, 4H, -CH_2), 2.01-2.05 (m, 4H, -CH_2), 4.53(t, 4H, J = 7 Hz, -CH_2), 4.91-5.00 (m, 4H, -CH_2), 5.76-5.83 (m, 2H, -CH), 7.94 (s, 2H, Ar-H), 8.41-8.46 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.06, 28.76-29.82, 33.92, 66.75, 114.24, 123.99, 128.36, 130.78, 137.53, 139.33, 145.87, 148.75, 165.59.

Synthesis of **[2]Pseudorotaxane**: In the solution of **PhenMC** (128 mg, 0.2mmol) in dry CH_2Cl_2, $[Cu(CH_3CN)_4]PF_6$ (74 mg, 0.2mmol) was added in the atmosphere of argon and the reaction mixture was stirred for 6h in the room temperature. Thereafter **Axle** (114 mg, 0.2mmol) in dry CH_2Cl_2 was added to the **PhenMC-Cu^I** complex in the argon atmosphere and stirred for another 24h. Then the reaction mixture was evaporated to dryness and purple coloured crystalline solid was isolated as [2]pseudorotaxane (Scheme S3). Yield: 82%.

[2]Pseudorotaxane ($C_{74}H_{78}CuF_6N_4O_{12}P$, M_w = 1423.94). HRMS (ESI-MS): $C_{74}H_{78}CuN_4O_{12}$ $[M\text{-}PF_6^-]^+$: calcd, *m/z* 1277.4912; found, *m/z* 1277.4911. Anal. calcd for $C_{74}H_{78}CuF_6N_4O_{12}P$: C, 62.42; H, 5.52; N, 3.93. Found C, 64.01; H, 5.12; N, 3.72.

Synthesis of **[2]Catenane**: In the glove box, [2]Pseudorotaxane (200 mg, 0.15 mmol) was dissolved in dry $CH_2Cl_2$and then catalytic amount of Grubb's 2nd generation catalyst was added to this as a solid. The reaction mixture was stirred for 36h in the glove box to obtain **metallated [2] catenane**. Saturated solution of Na_2EDTA and aq. NH_3 were added to the crude residue and stirred for 48h. Then the reaction mixture was extracted with $CHCl_3$ and water by washing the organic layer with the brine solution. Organic layer was evaporated to obtain red coloured solid residue. The resulting solid was purified by silica column chromatography by using 24:1 $CHCl_3$ and CH_3CN respectively as eluent and by several times washing with diethyl ether, white coloured solid [2]Catenane (**CATN**) was obtained (Scheme S3). Yield: 16%

Metallated [2]catenane ($C_{72}H_{74}CuF_6N_4O_{12}P$, M_w=1395.89). HRMS (ESI-MS): $C_{72}H_{74}CuN_4O_{12}$ $[M\text{-}PF_6^-]^+$: calcd, *m/z* 1249.4599; found, *m/z* 1249.4602. Anal. calcd for $C_{72}H_{74}CuF_6N_4O_{12}P$: C, 61.95; H, 5.34; N, 4.01. Found C, 63.05; H, 5.03; N, 3.67.

[2]catenane ($C_{72}H_{74}N_4O_{12}$, M_w = 1187.38): HRMS (ESI-MS): $C_{72}H_{74}N_4NaO_{12}$ $[M + Na]^+$: calcd, *m/z* 1209.5201; found, 1209.5208. Anal. calcd for $C_{72}H_{74}N_4O_{12}$: C, 72.83; H, 6.28; N, 4.72. Found C, 71.26; H, 6.05; N, 4.97. Characteristic λ_{max} = 280 nm in (2 x 10^{-5}) M CH_3CN and molar extinction coefficient (ε) value in = 2.2 × 10^4 M^{-1} cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.11-1.43(m, 28H, -CH_2), 2.04 (s, 4H, -CH_2), 3.95 (s, 4H, -CH_2), 4.05 (s, 4H, -CH_2), 4.39 (s, 4H, -CH_2), 4.95 (s, 4H, -CH_2), 5.55 (s, 2H, -CH), 5.69 (d, 4H, J = 8 Hz, Ar-H), 6.07 (d, 4H, J = 8 Hz, Ar-H), 7.04 (s, 4H, Ar-H), 8.26 (d, 4H, J = 7 Hz, Ar-H), 8.32 (d, 2H, J = 8 Hz, Ar-H), 8.57 (d, 2H, J = 8.5 Hz, Ar-H), 8.71 (d, 2H, J = 7 Hz, Ar-H), 8.97 (d, 2H, J = 8 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ (ppm) 25.88, 28.94-33.94, 65.98, 66.35, 67.15, 67.61, 111.74, 112.51, 114.19, 121.30, 123.37, 124.67, 126.24, 127.03,129.24, 130.69, 131.23, 131.48, 138.92, 139.45, 144.57, 145.22, 145.71, 146.85, 148.32, 156.34, 164.62, 165.00. IR (KBr, ν cm^{-1}): 559.32, 721.33, 842.83, 943.13, 1060.78, 1130.21, 1157.21, 1247,86, 1377.08, 1454.23, 1508.23, 1614.31, 1728.10, 2852.52, 2923.88, 3433.06.

Synthesis of **CATN-Eu^{3+}**complex: $Eu(OTf)_3$ (30 mg, 0.05 mmol) was added to the CH_3CN/ $CHCl_3$ binary solvent mixture of **CATN** (50 mg, 0.042 mmol). The reaction mixture was stirred vigorously for 24h. By overnight stirring the solution mixture was turned into reddish

brown color from the light yellow color and the color persisted even after evaporation. The crude solid was washed several times with chloroform and diethylether to obtain reddish brown colored solid Eu-catenate (Scheme S4). Yield: 59%

CATN-Eu^{3+}complex ($C_{75}H_{74}F_9EuN_4O_{21}S_3$, M_w=1786.54). Anal. calcd for $C_{75}H_{74}F_9EuN_4O_{21}S_3$: C, 50.42; H, 4.17; N, 3.14. Found C, 49.43; H, 4.02; N, 3.18. HRMS (ESI-MS): $C_{74}H_{76}EuF_6N_4O_{19}S_2$ $[M - CF_3SO_3^- + H_2O]^+$: calcd, *m/z* 1655.3651; found *m/z* 1655.3649. Characteristic λ_{max} = 294 nm in (2 x 10^{-5}) M CH_3CN and molar extinction coefficient value (ε) = 2.35 × 10^4 M^{-1} cm^{-1}. Characteristic Eu^{3+} centered emission peaks at 589, 614, 651 and 697 nm in (2 x 10^{-5}) M CH_3CN. Characteristic absorption maxima and emission peaks (Fig. S34a, S34b, ESI†) of the isolated **CATN-Eu^{3+}** complex matched well with the corresponding peak values obtained from the UV/Vis and PL titration data respectively, which suggested the formation of 1:1 Eu-catenate complex in the solution state. ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 1.28-1.50 (m), 1.60 (d), 1.76 (d), 1.87-1.89 (m), 2.10-2.19 (m), 2.32 (s), 3.08-3.11 (m), 4.23-4.42 (m), 4.61 (s), 5.56 (bs), 6.90-7.04 (m), 7.08 (s), 7.23 (bs), 7.30-7.33 (m), 7.71-7.87 (m), 8.13 (s), 8.27-8.45 (m), 8.76 (bs), 9.18 (bs), 9.79 (bs). IR (KBr, ν cm^{-1}): 395.38, 516.89, 642.25, 719.40, 815.83, 875.62, 1031.85, 1172.64, 1251.72, 1400.22, 1434.94, 1467.73, 1510.16, 1589.95, 1627.81, 2927.74, 3436.91.

Synthesis of **CATN-Gd^{3+}** complex: $Gd(OTf)_3$ (30 mg, 0.05 mmol) was added to the CH_3CN/ $CHCl_3$ binary solvent mixture of **CATN** (50 mg, 0.042 mmol). The reaction mixture was stirred vigorously for 24h. By overnight stirring the solution mixture was turned into light brown color from the light yellow color and the color persisted even after evaporation. The crude solid was washed several times with chloroform and diethylether to obtain light brown colored solid Gd-catenate (Scheme S4). Yield: 48%

CATN-Gd^{3+}complex ($C_{75}H_{74}F_9GdN_4O_{21}S_3$, M_w=1791.83). Anal. calcd for $C_{75}H_{74}F_9GdN_4O_{21}S_3$: C, 50.27; H, 4.16; N, 3.13. Found C, 49.37; H, 4.33; N, 3.07. HRMS (ESI-MS): $C_{74}H_{76}F_6GdN_4O_{19}S_2$ $[M - CF_3SO_3^- + H_2O]^+$: calcd, *m/z* 1660.3679; found, 1660.3682. Characteristic λ_{max} = 298 nm in (2 x 10^{-5}) M CH_3CN and molar extinction coefficient value (ε) = 2.25 × 10^4 M^{-1} cm^{-1}. Characteristic absorption maxima at λ_{max} = 298 nm (Fig. S35, ESI†) of the isolated **CATN-Gd^{3+}** complex matched well with the λ_{max} value obtained from the UV/Vis titration data, which suggested the formation of 1:1 Gd-catenate complex in the solution state. ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 7.01, 5.89, 4.90, 4.25,3.09, 2.32, 1.97, 1.63, 1.29, -0.68. IR (KBr, ν cm^{-1}): 433.95, 636.47, 715.54, 1031.85, 1170.71, 1253.64, 1384.79, 1465.80, 1569.95, 1625.88, 2554.45, 2923.88, 3431.13.

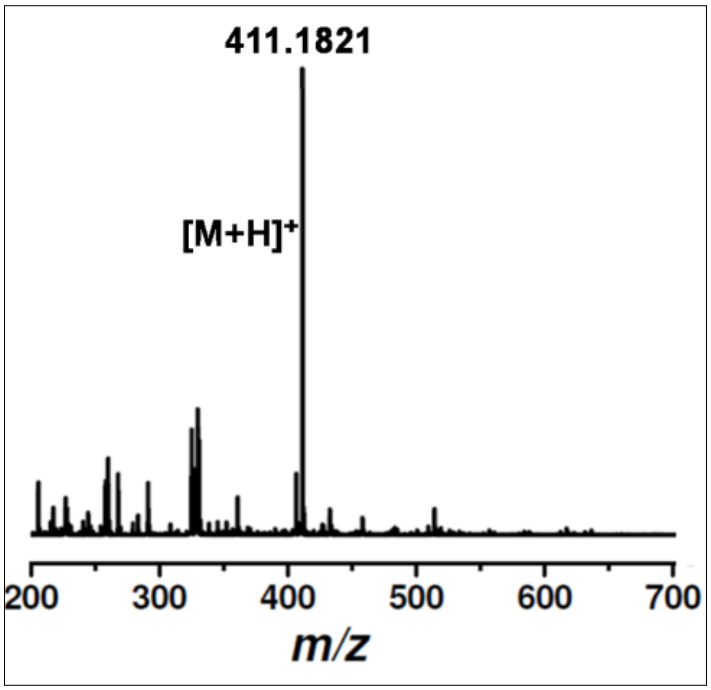


Figure S1a: ESI-MS (+ve) spectrum of Compound **1c**

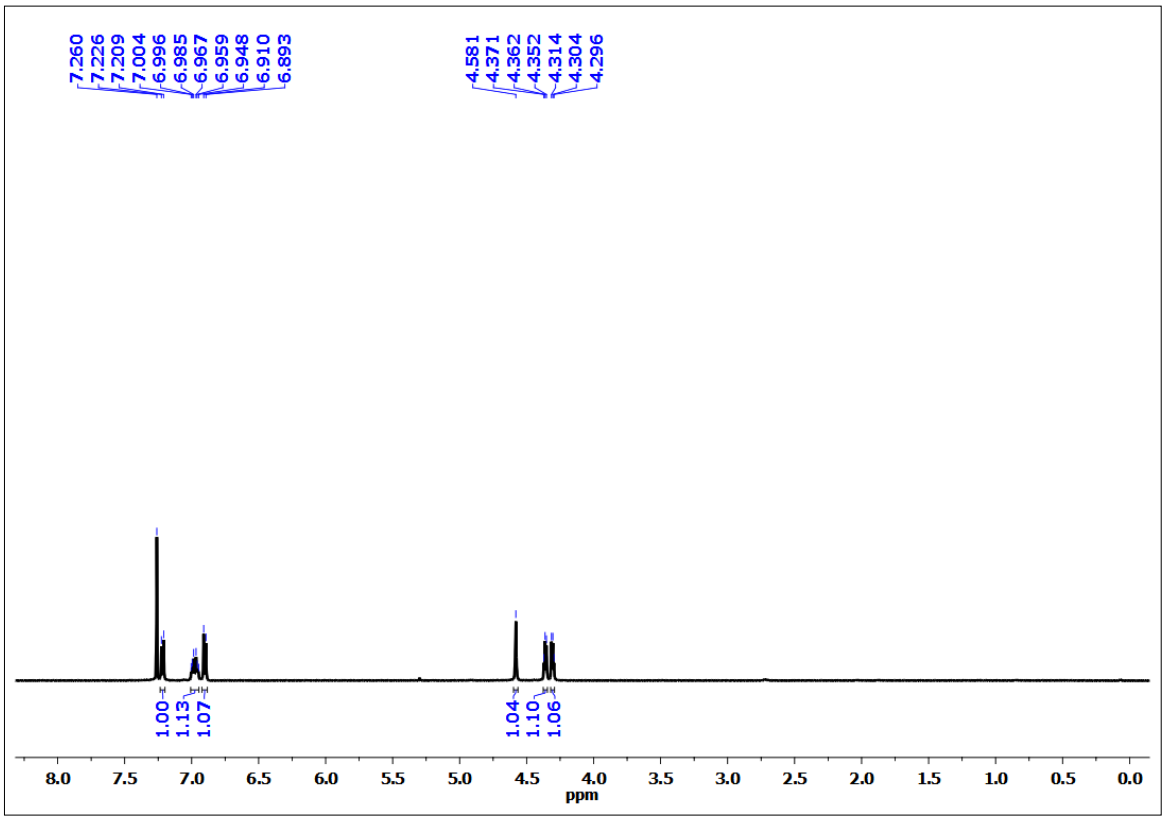


Figure S1b: ^{1}H NMR spectrum of Compound **1c** in $CDCl_3$ (500 MHz) at 298 K

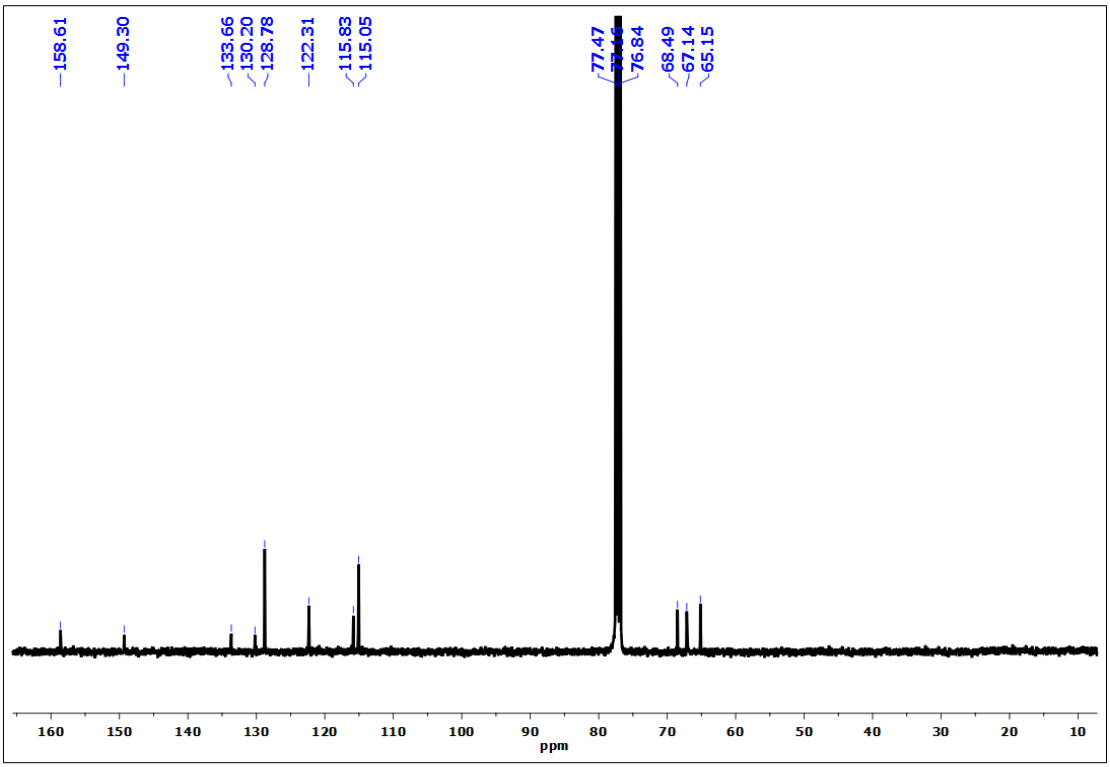


Figure S2: ^{13}C NMR spectrum of Compound **1c** in $CDCl_3$ (100 MHz) at 298 K

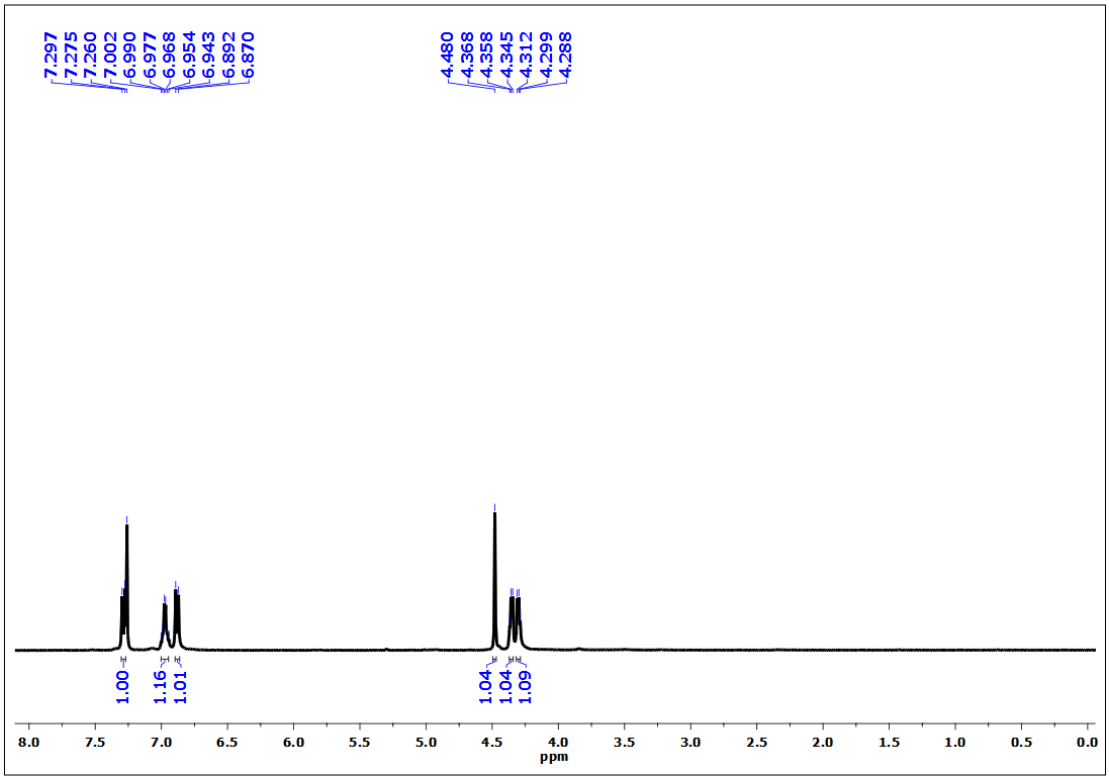


Figure S3: ^{1}H NMR spectrum of Compound **1d** in $CDCl_3$ (400 MHz) at 298 K

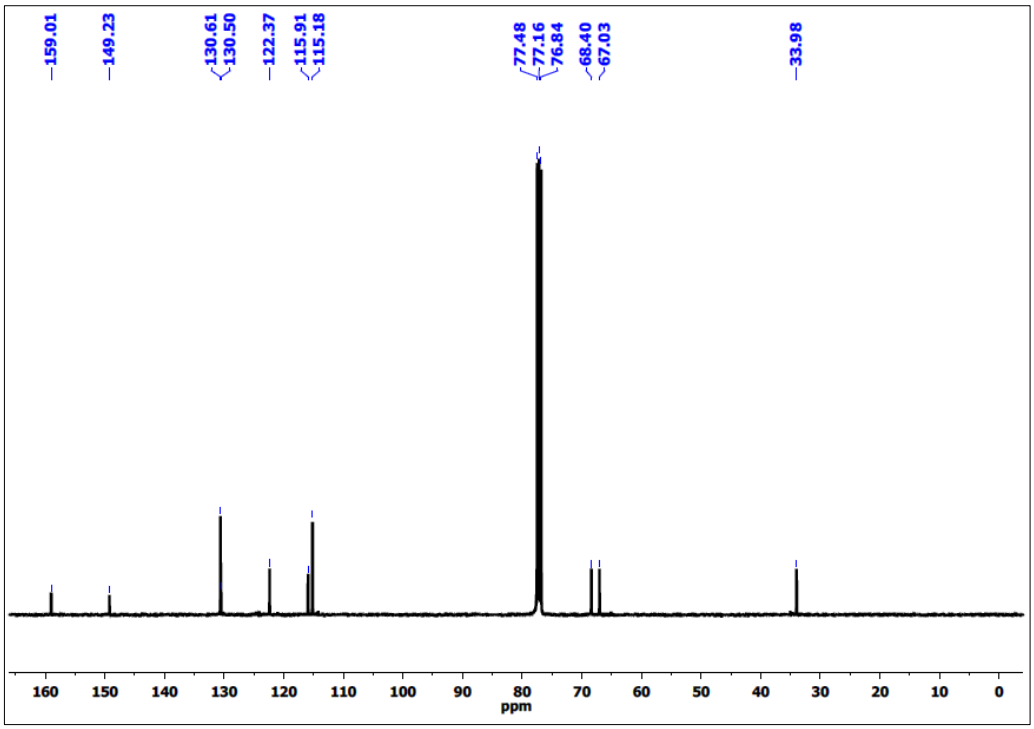


Figure S4: ^{13}C NMR spectrum of Compound **1d** in $CDCl_3$ (100 MHz) at 298 K

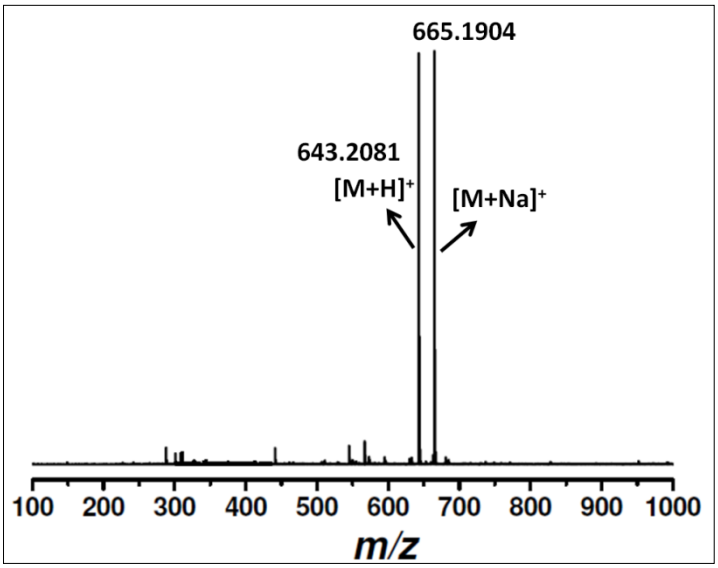


Figure S5: ESI-MS (+ve) spectrum of **PhenMC**

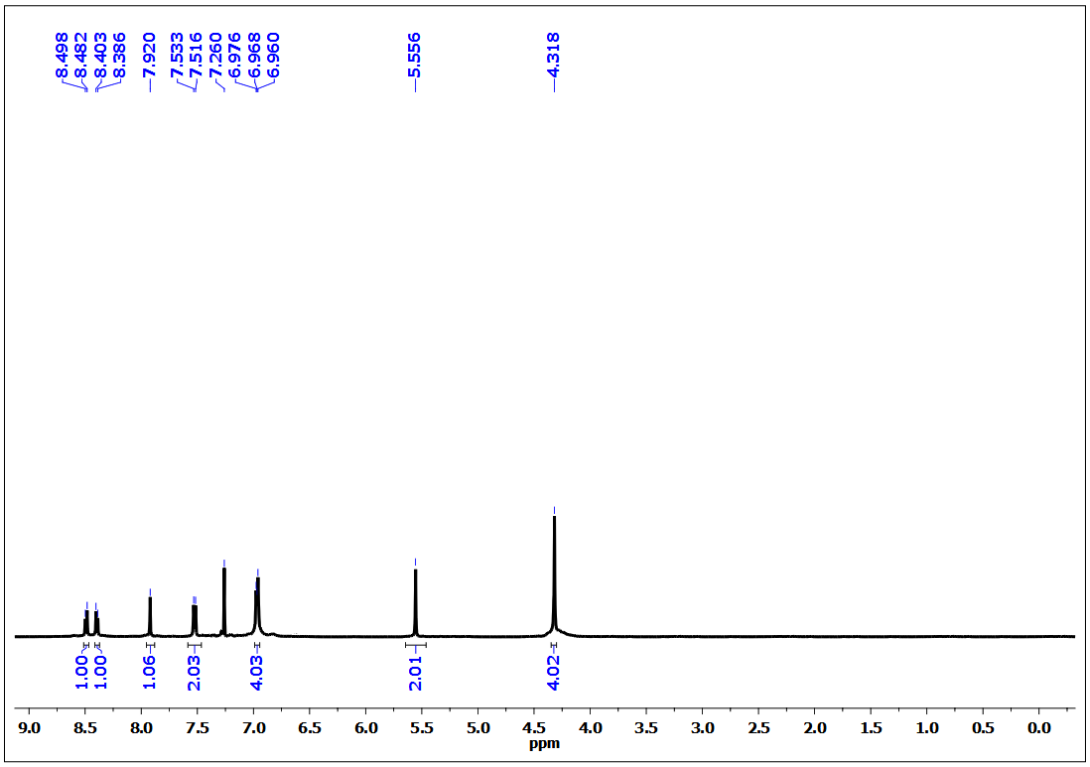


Figure S6: ^{1}H NMR spectrum of **PhenMC** in $CDCl_3$ (500 MHz) at 298 K

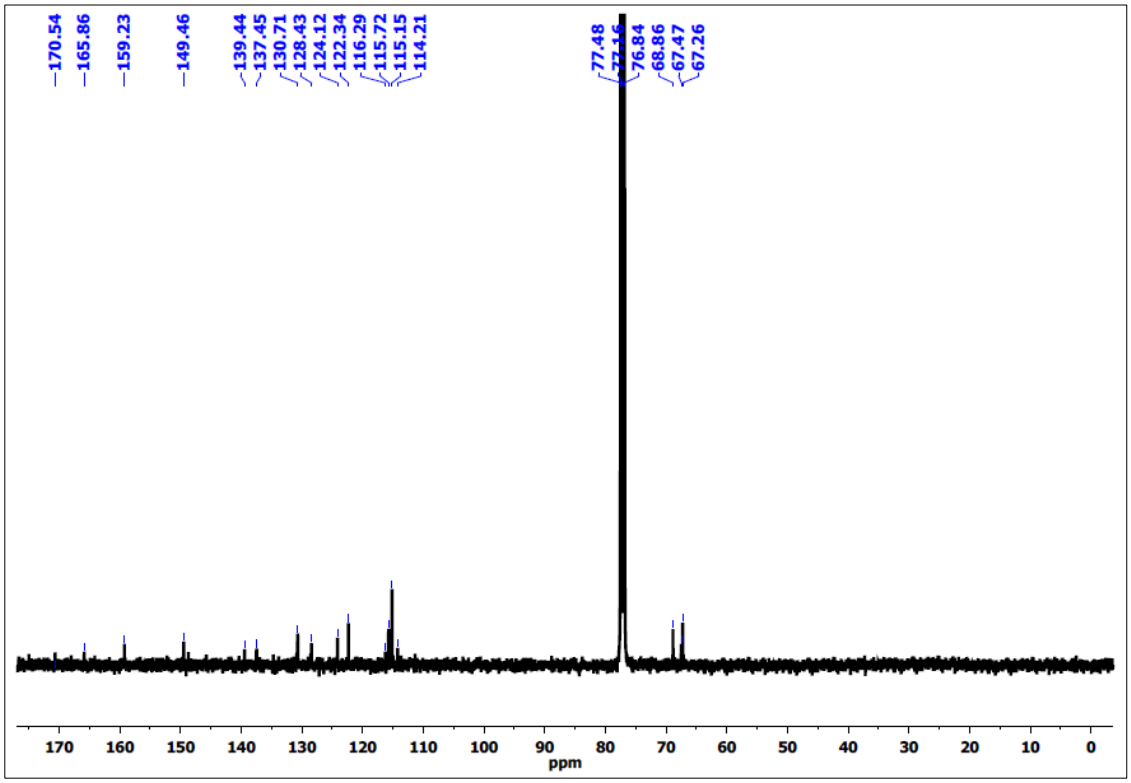


Figure S7: ^{13}C NMR spectrum of **PhenMC** in $CDCl_3$ (100 MHz) at 298 K

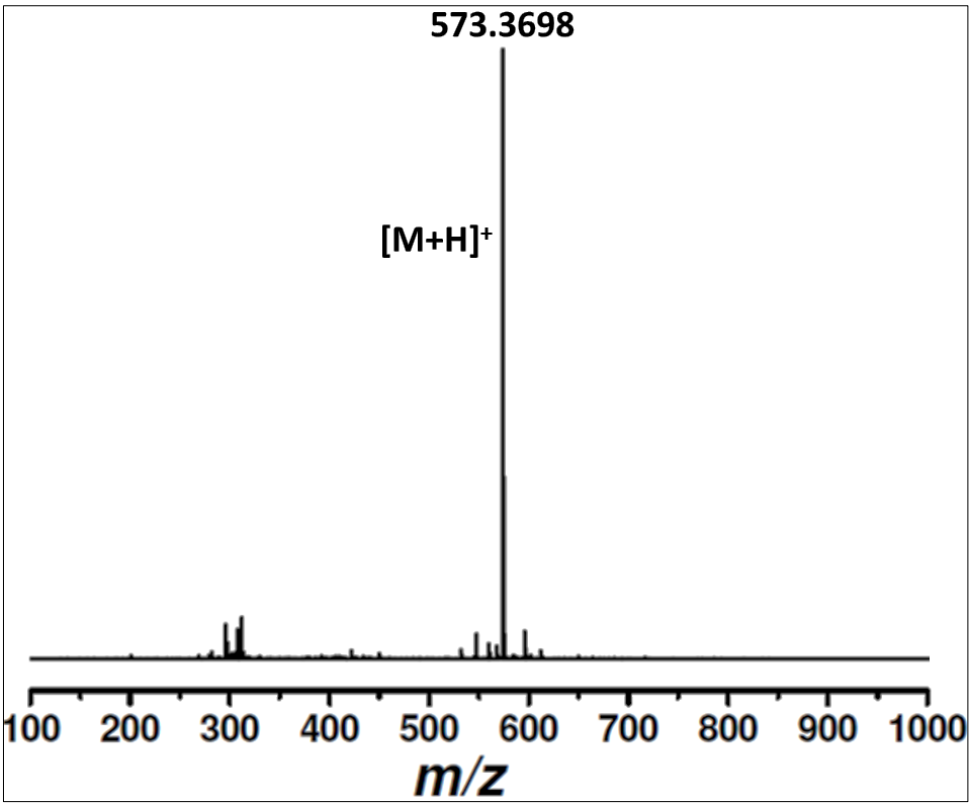


Figure S8: ESI-MS (+ve) spectrum of **Axle**

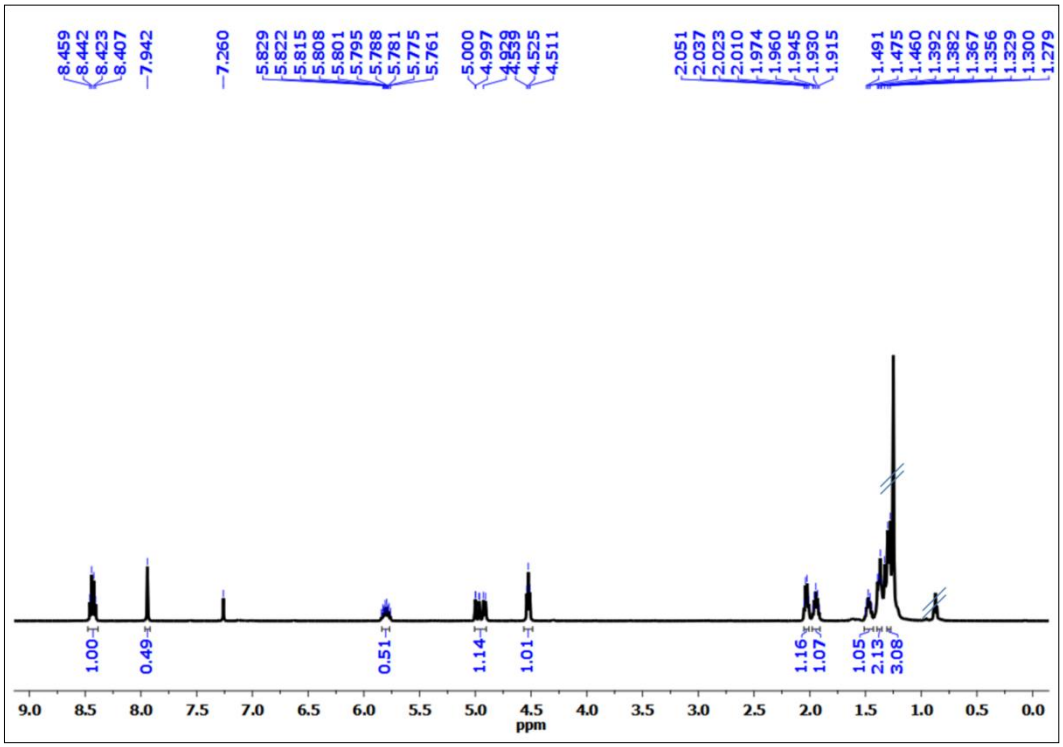


Figure S9: ^{1}H NMR spectrum of **Axle** in $CDCl_3$ (500 MHz) at 298 K

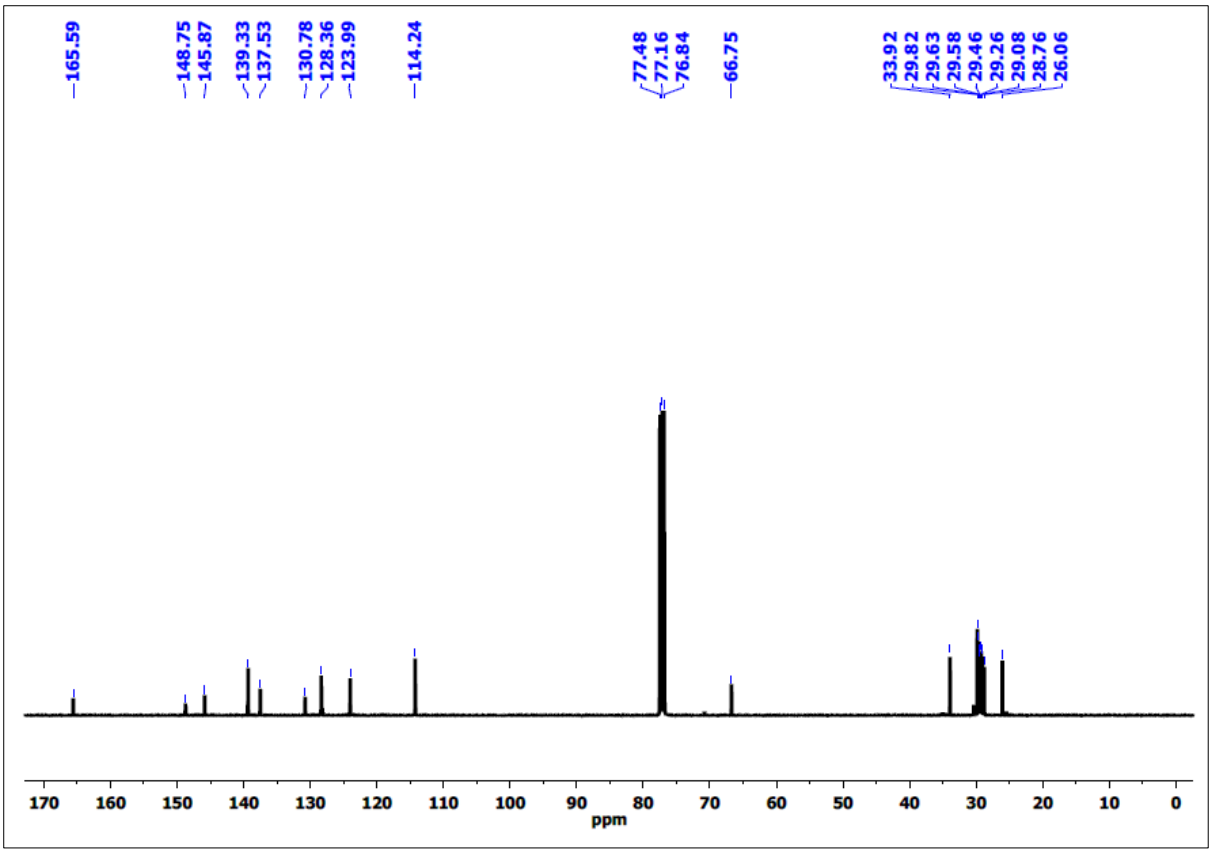


Figure S10: ^{13}C NMR spectrum of **Axle** in $CDCl_3$ (100 MHz) at 298 K

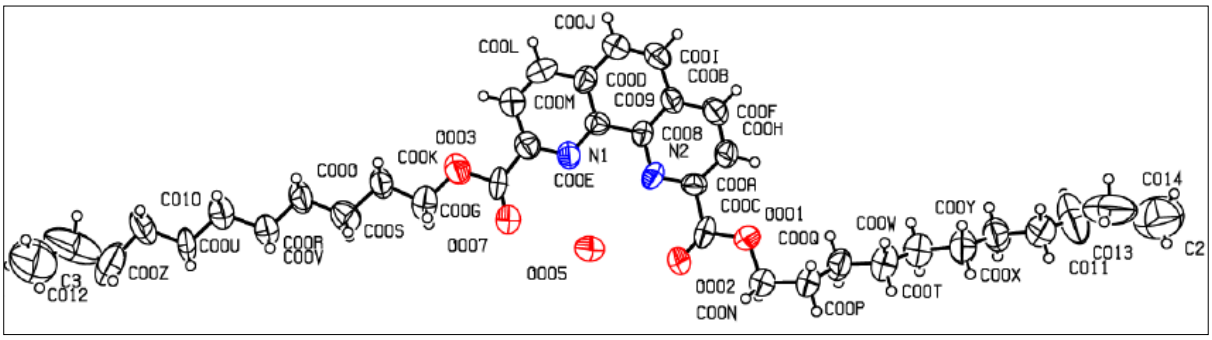


Figure S11: Single Crystal X-ray structure of **Axle** (ellipsoid model using platon version)

Table 1S: Crystallographic details of **Axle**

Compound reference	AXLE
Chemical formula	$C_{36}H_{48}N_2O_5$
Formula Mass	588.76
Crystal system	Monoclinic
a/Å	15.881(7)
b/Å	17.389(7)
c/Å	13.796(6)
α/°	90
β/°	114.134(13)
γ/°	90
Unit cell volume/Å^3	3477(3)
Temperature/K	150(2)
Space group	*P*21/*c*
No. of formula units per unit cell, *Z*	4
No. of reflections measured	21382
No. of independent reflections	2721
R_{int}	0.1034
Final R_1 values ($I > 2\sigma(I)$)	0.0642
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1317
Final R_1 values (all data)	0.1173
Final $wR(F^2)$ values (all data)	0.1463
Goodness of fit on F^2	1.579
CCDC number	1871206

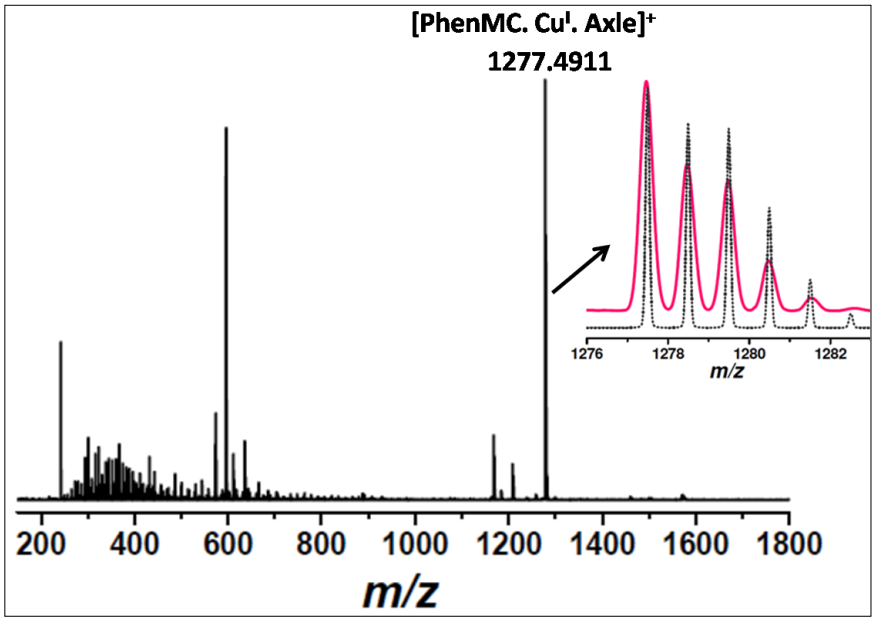


Figure S12: ESI-MS (+ve) spectrum of **[2]Pseudorotaxane** with the isotopic distribution pattern given in inset

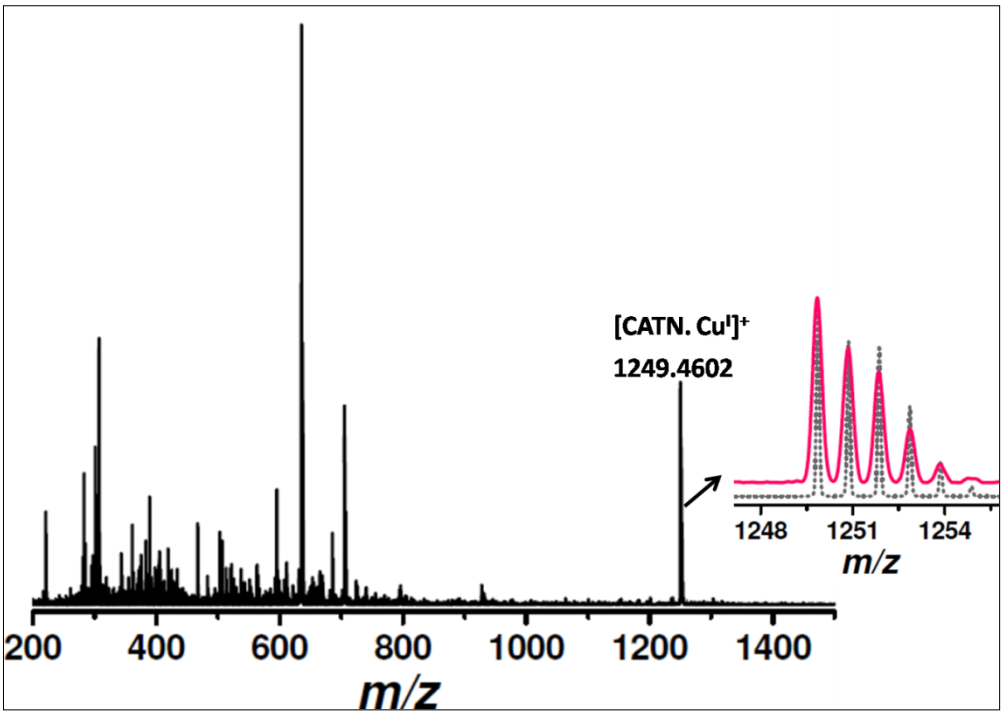


Figure S13: ESI-MS (+ve) spectrum of metallated **[2]Catenane** with the isotopic distribution pattern given in inset

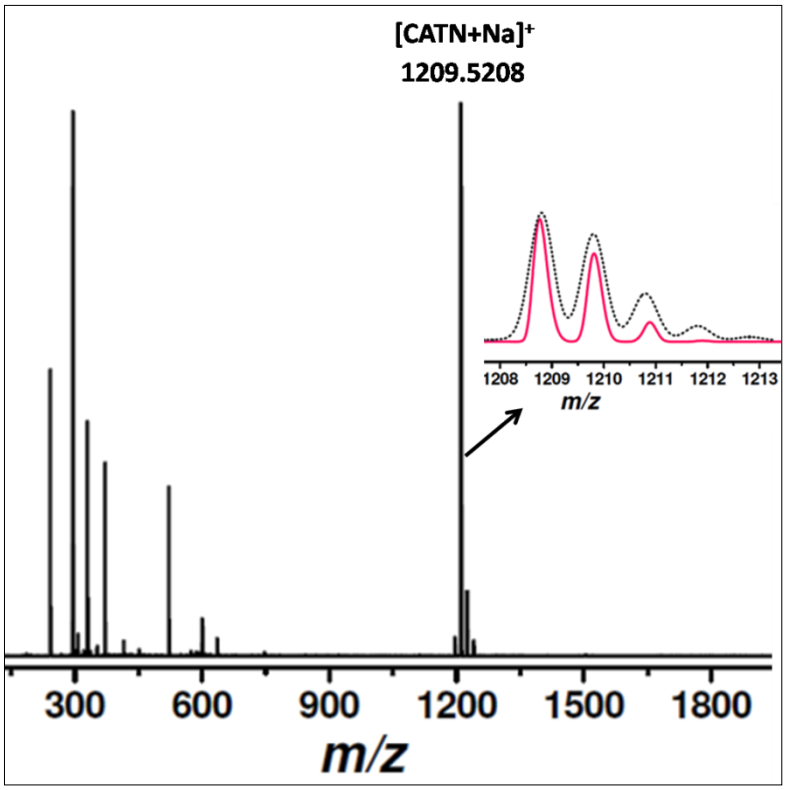


Figure S14: ESI-MS (+ve) spectrum of **[2]Catenane** with the isotopic distribution pattern given in inset

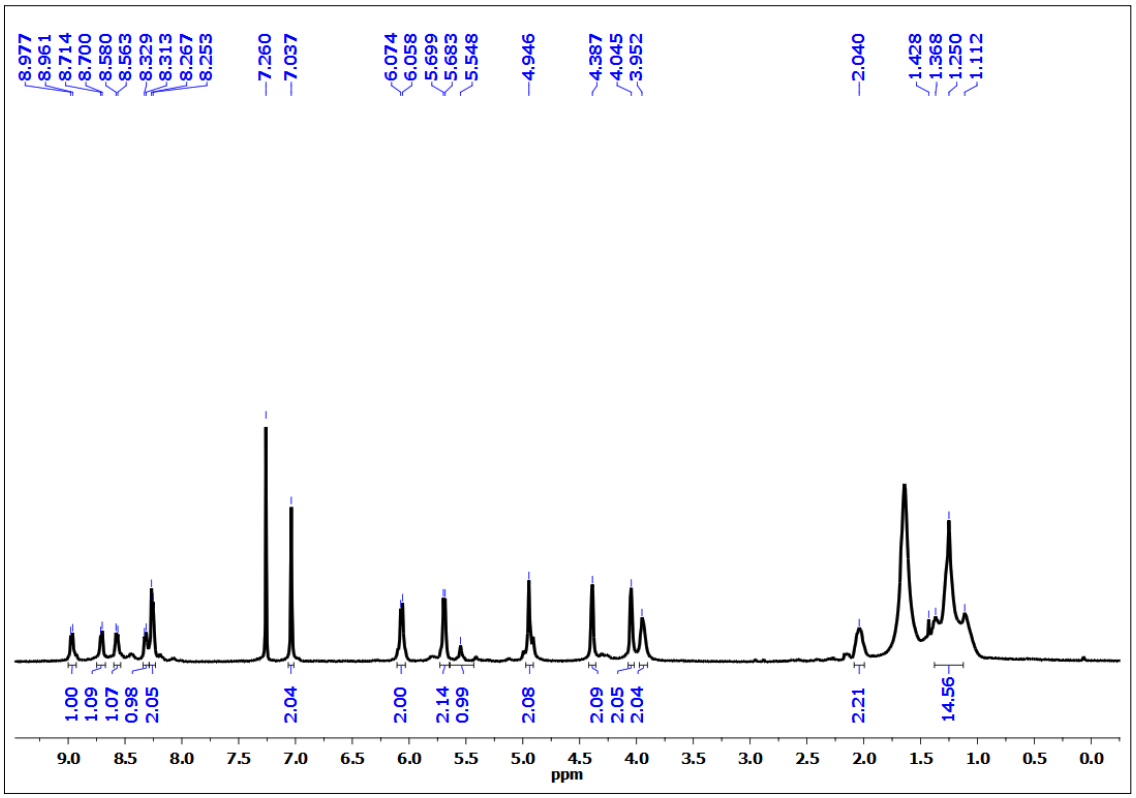


Figure S15: ^{1}H NMR spectrum of **[2]Catenane** in $CDCl_3$ (500MHz) at 298 K

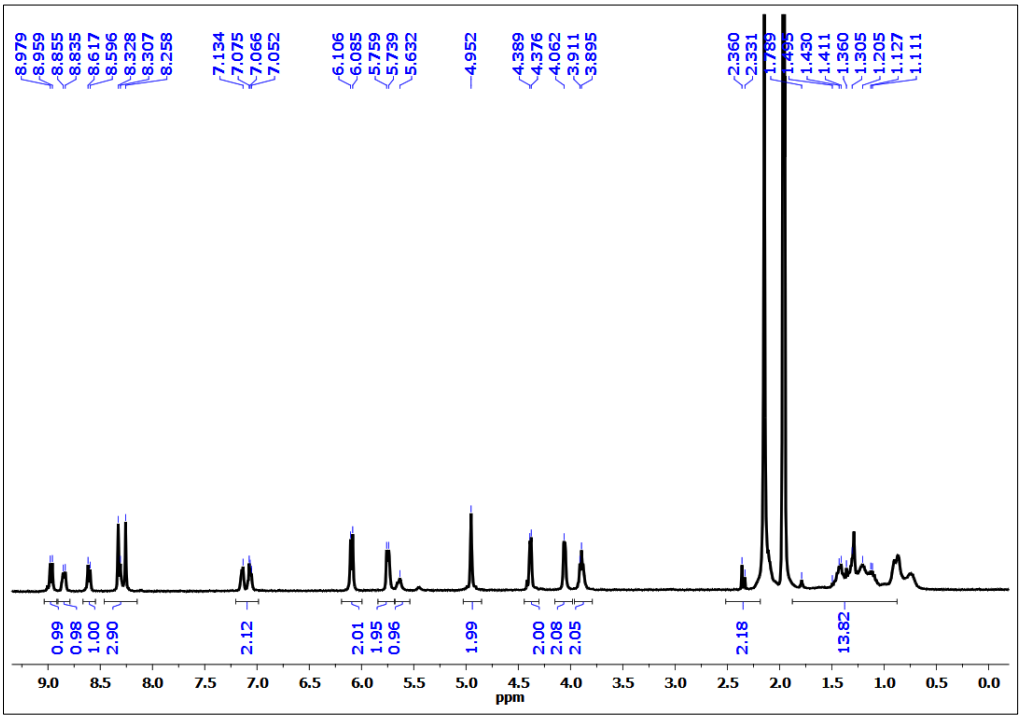


Figure S16: ^{1}H NMR spectrum of **[2]Catenane** in CD_3CN (400MHz) at 298 K

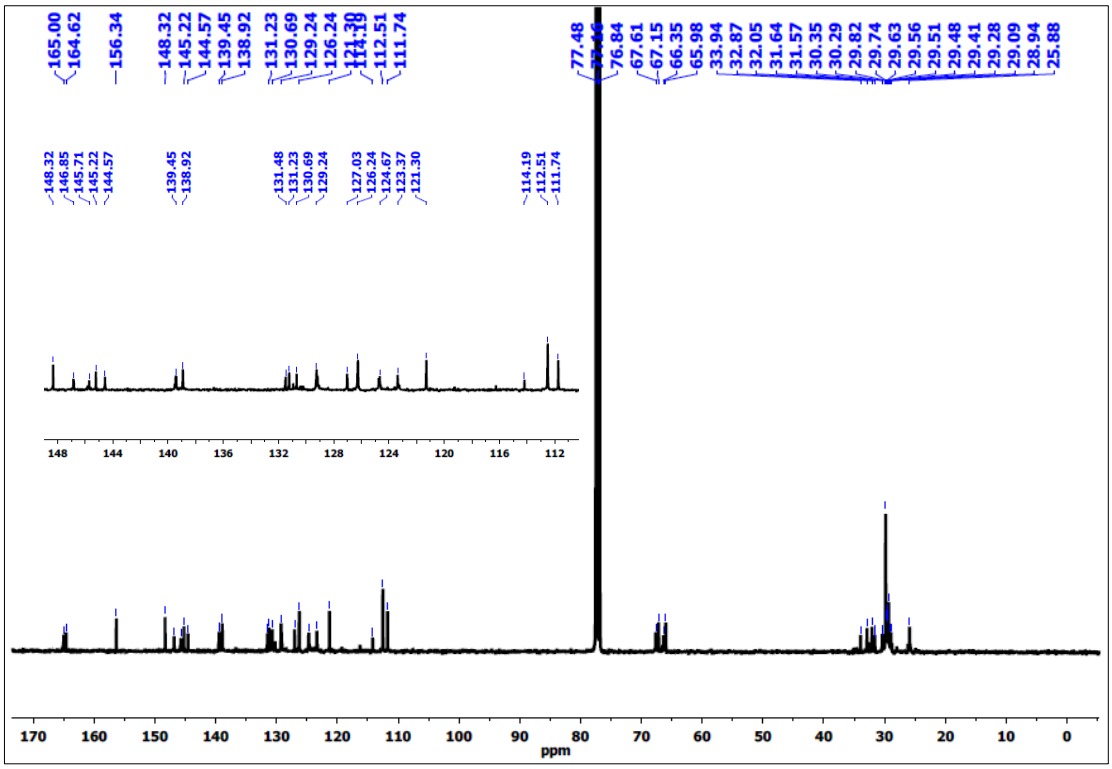


Figure S17: ^{13}C NMR spectrum of **[2]Catenane** in $CDCl_3$ (100MHz) at 298 K

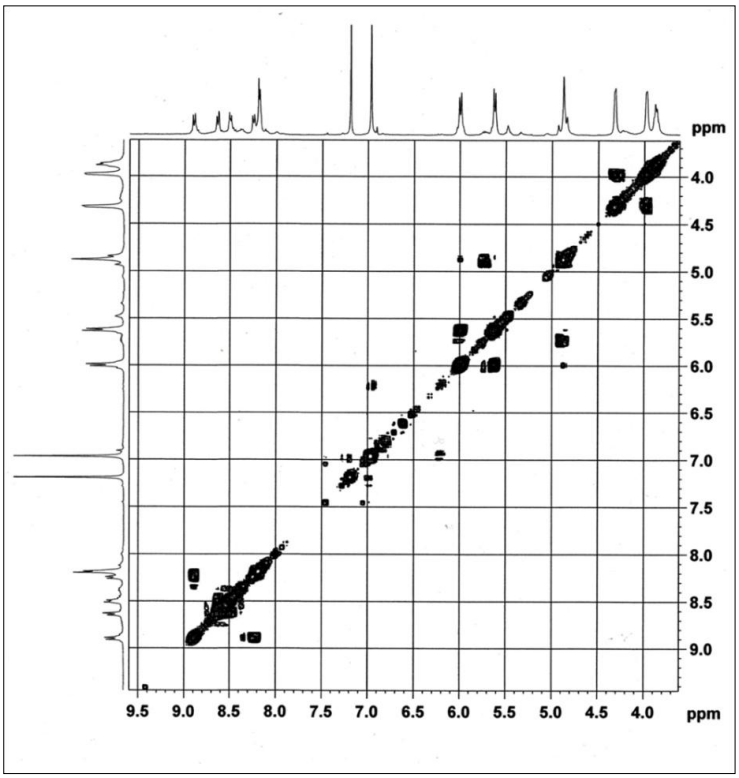


Figure S18: ^{1}H-^{1}H COSY spectrum of **[2]catenane** in $CDCl_3$ (400 MHz) at 298 K

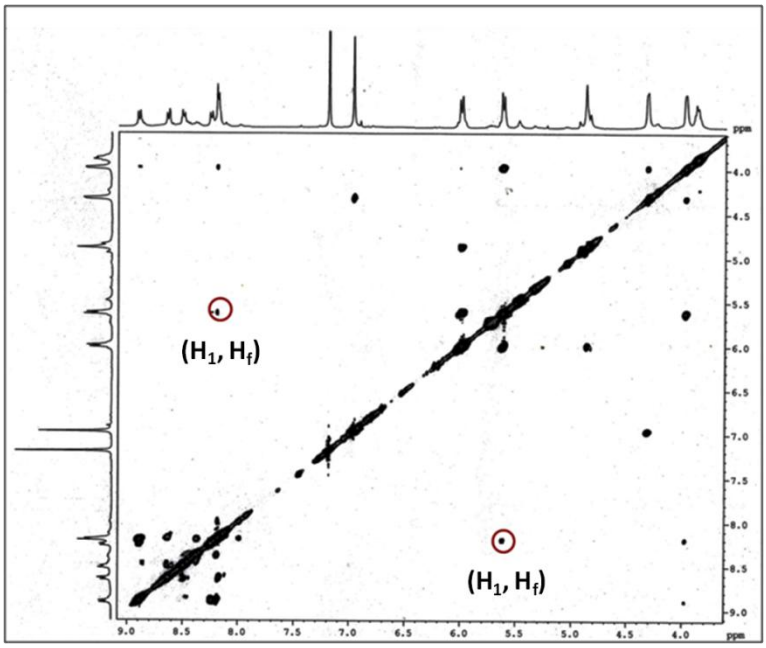


Figure S19: ^{1}H-^{1}H ROESY spectrum of **[2]catenane** in $CDCl_3$ (400 MHz) at 298 K. Assignable through space coupling interactions are highlighted.

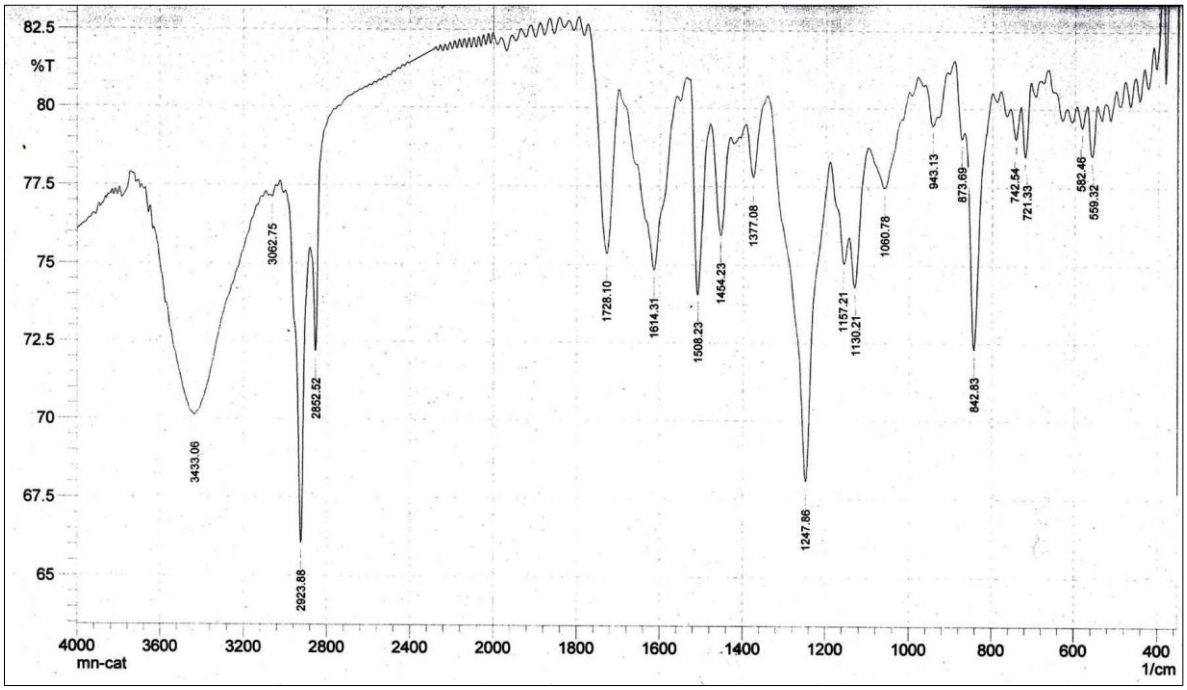


Figure S20: FTIR (KBr, ν cm^{-1}) spectrum of **[2]catenane**

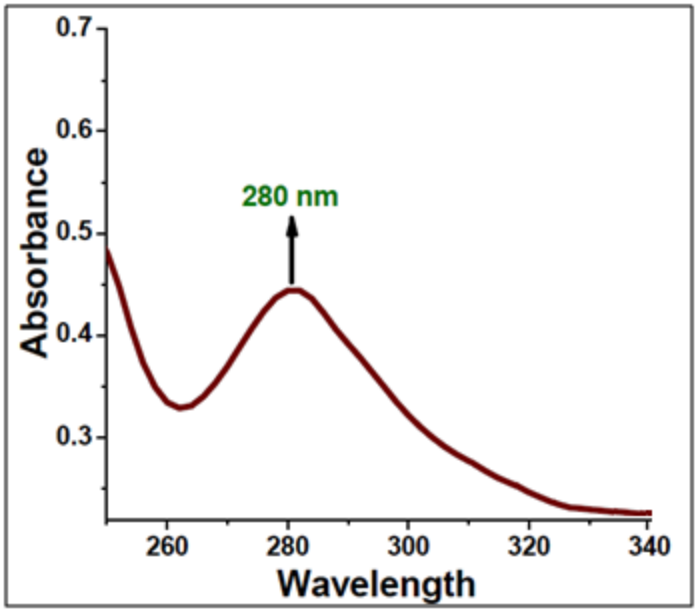


Figure S21: Characteristic UV-Vis spectrum of **[2]catenane** ($2X10^{-5}M$) in $CH_3CN:CH_3Cl$ (9:1) medium at 298 K

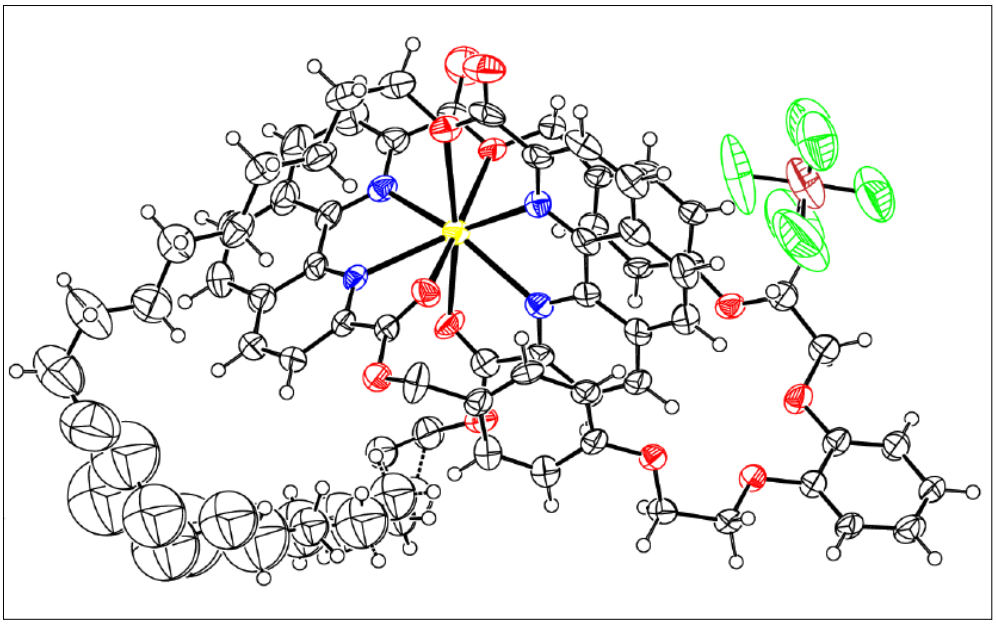


Figure S22: Single Crystal X-ray structure of **Na-Catenate** (ellipsoid model using platon version)

Table 2S: Crystallographic details of **Na-Catenate**

Compound reference	CATN
Chemical formula	$C_{72}H_{60}N_4NaO_{12}\bullet F_6P$
Formula Mass	1341.20
Crystal system	Triclinic
a/Å	9.036(5)
b/Å	18.365(10)
c/Å	21.014(12)
α/°	88.766(18)
β/°	85.77(2)
γ/°	87.085(19)
Unit cell volume/Å^3	3473(3)
Temperature/K	107.35
Space group	$P\bar{1}$
No. of formula units per unit cell, *Z*	2
No. of reflections measured	19831
No. of independent reflections	10288
R_{int}	0.1209
Final R_1 values ($I > 2\sigma(I)$)	0.1218
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.3045
Final R_1 values (all data)	0.2255
Final $wR(F^2)$ values (all data)	0.3667
Goodness of fit on F^2	1.024
CCDC number	1871207

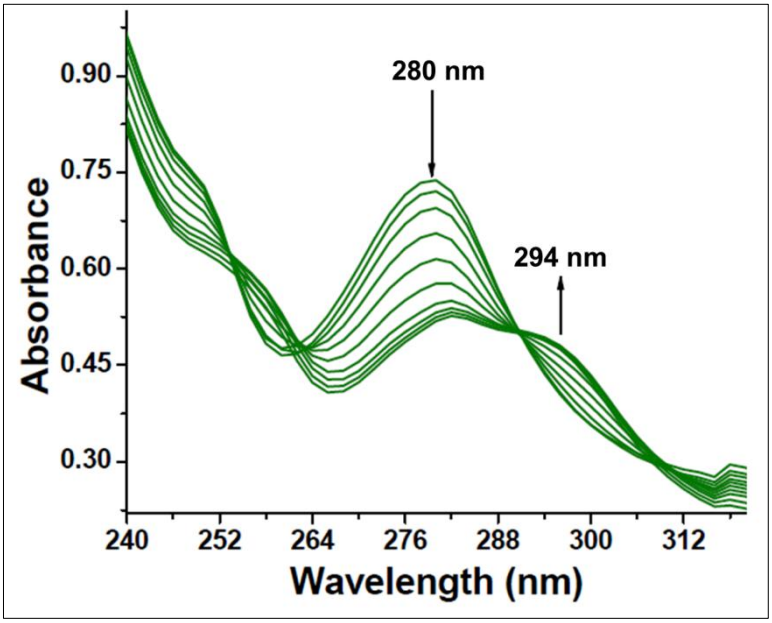


Figure S23: UV-Vis titration profile between **CATN** ($2x10^{-5}$M) and **Eu^{3+} (**$2x10^{-4}$M) in CH_3CN-$CHCl_3$ (9:1) at 298 K

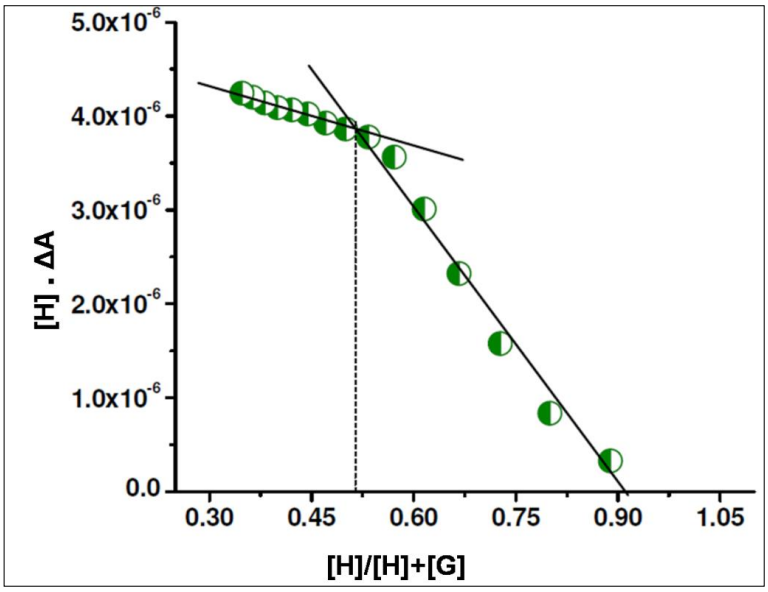


Figure S24: Molar ratio plot from UV-Vis titration experiment between **CATN** ($2x10^{-5}$M) and **Eu^{3+}** ($2x10^{-4}$M) in CH_3CN:CH_3Cl (9:1) medium at 298 K

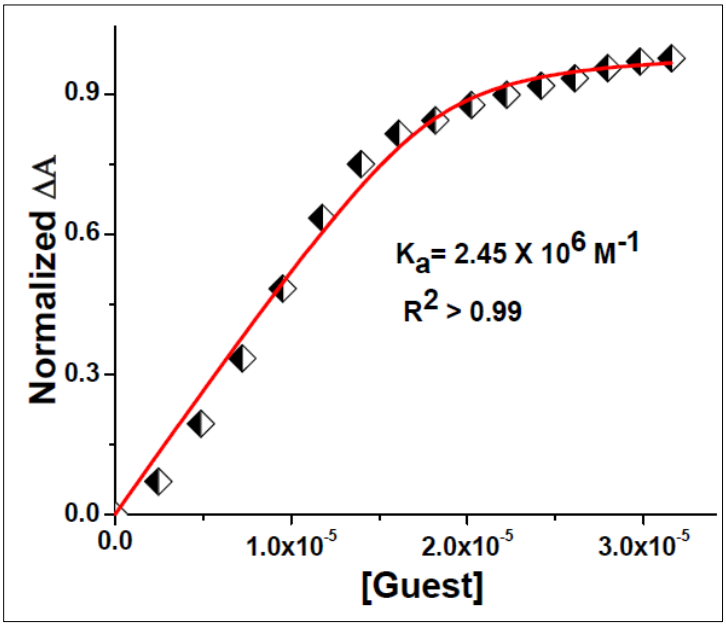


Figure S25: Non-linear 1:1 curve fitting plot to determine binding constant for the formation of **CATN** ($2x10^{-5}$M) **-Eu^{3+}** ($2x10^{-4}$M) complex in CH_3CN:CH_3Cl (9:1) medium from UV-Vis titration experiment at 298 K. (Some data points in the figure deviated very marginally from the fitting curve. However, the overall fitting of the data points was reasonably good as clearly evident from the R^2 value of >0.99.)

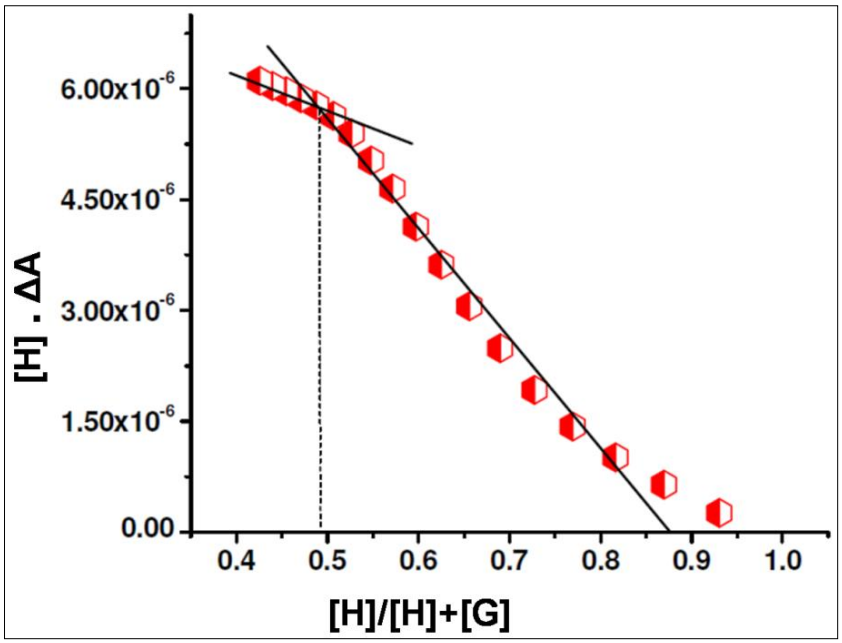


Figure S26: Molar ratio plot from UV-Vis titration experiment between **CATN** ($2x10^{-5}$M) and **Gd^{3+}** ($2x10^{-4}$M) in CH_3CN:CH_3Cl (9:1) medium at 298 K

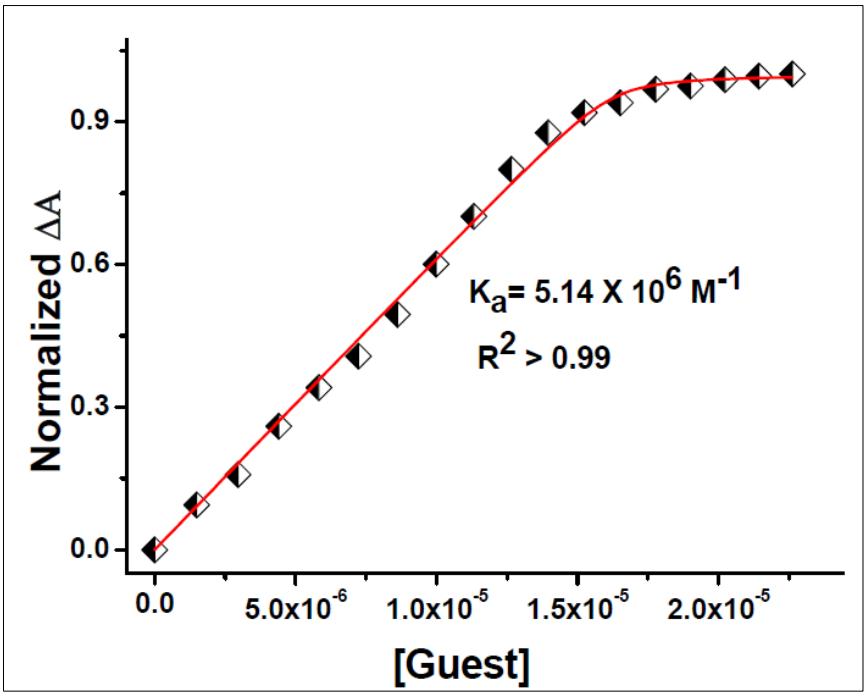


Figure S27: Non-linear 1:1 curve fitting plot from UV-Vis titration experiment to determine binding constant for the formation of **CATN** ($2x10^{-5}$M) **-Gd^{3+}** ($2x10^{-4}$M) complex in CH_3CN:CH_3Cl (9:1) medium at 298 K. (Some data points in the figure deviated very marginally from the fitting curve. However, the overall fitting of the data points was reasonably good as clearly evident from the R^2 value of >0.99.)

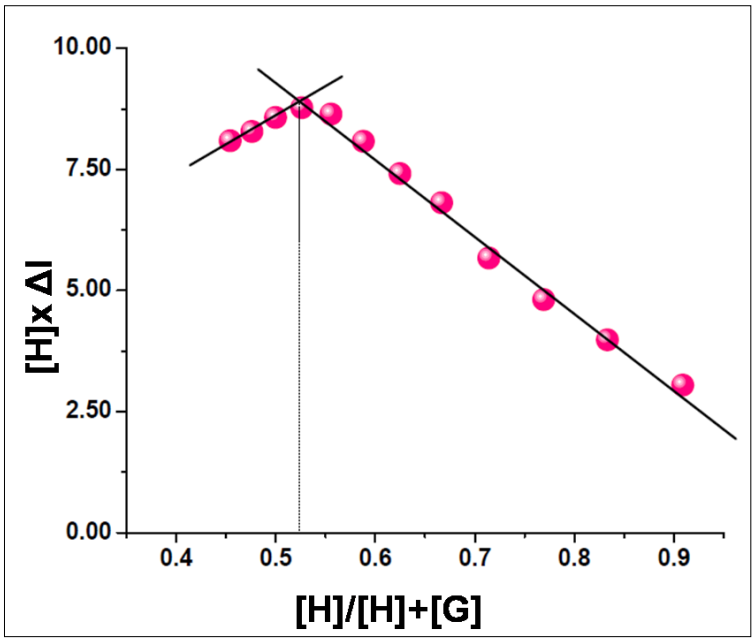


Figure S28: Molar ratio plot from PL titration experiment at 613 nm emission wavelength between **CATN** ($2x10^{-5}$M) and **Eu^{3+}** (**(**$2x10^{-4}$M) in CH_3CN:CH_3Cl (9:1) medium at 298 K

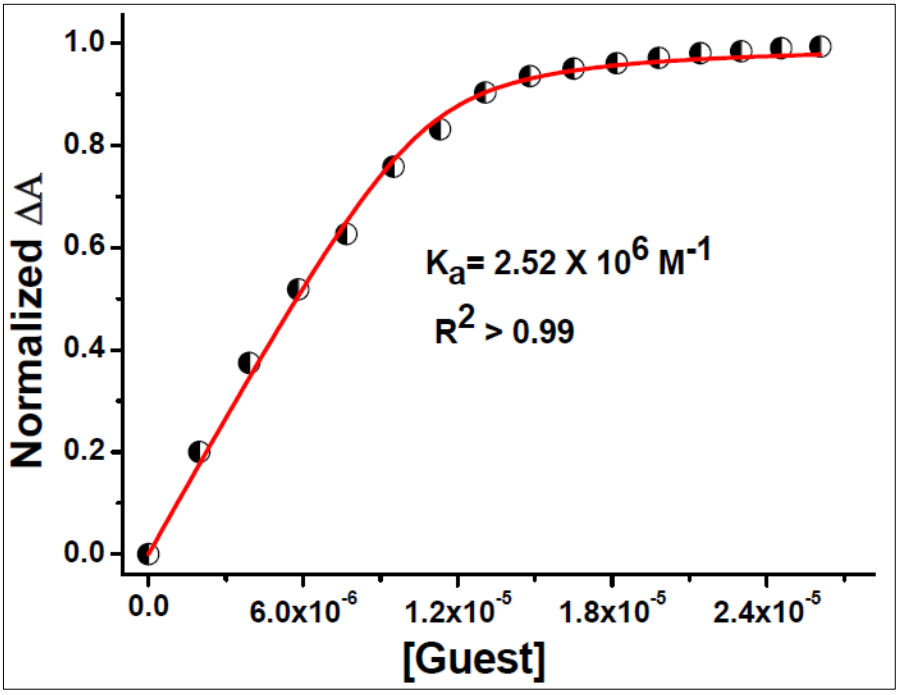


Figure S29: Non-linear 1:1 curve fitting plot from PL titration experiment to determine binding constant for the formation of **CATN** ($2x10^{-5}$M) **-Eu^{3+}** (**(**$2x10^{-4}$M) complex in CH_3CN:CH_3Cl (9:1) medium at 298 K. (Some data points in the figure deviated very marginally from the fitting curve. However, the overall fitting of the data points was reasonably good as clearly evident from the R^2 value of >0.99.)

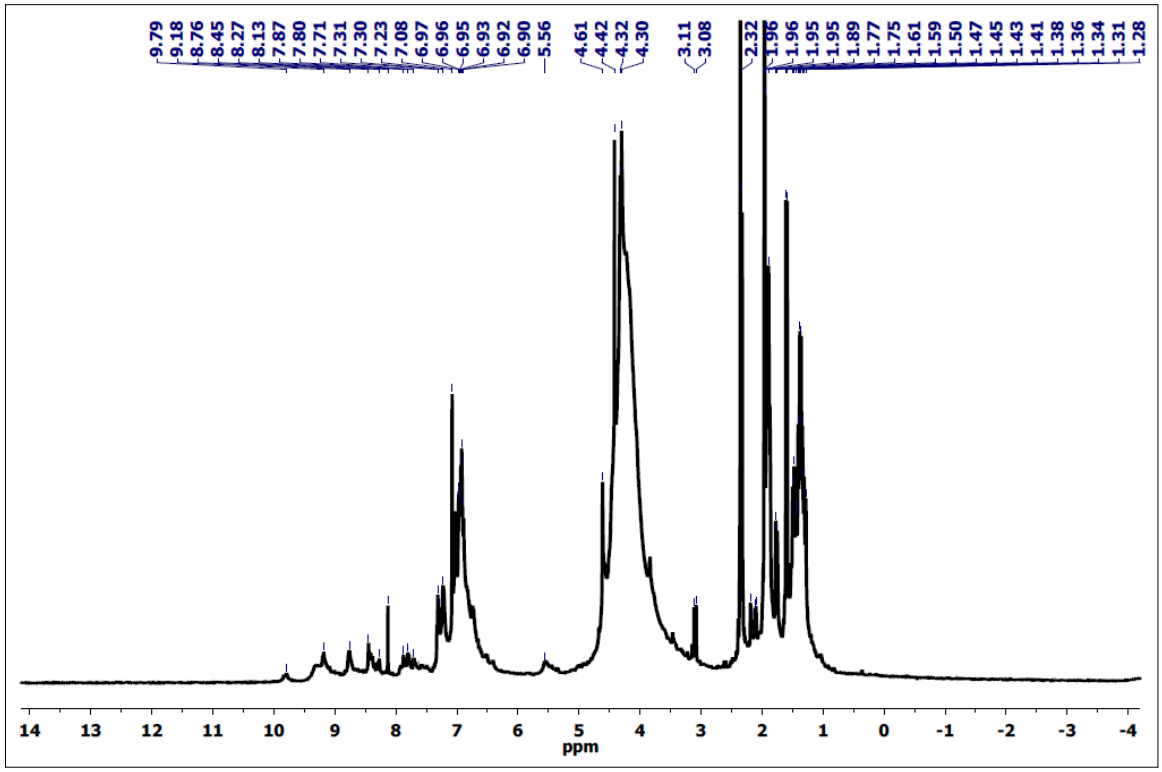


Figure S30: ^{1}H NMR spectrum of **CATN-Eu^{3+}** complex in CD_3CN (500 MHz) at 298 K

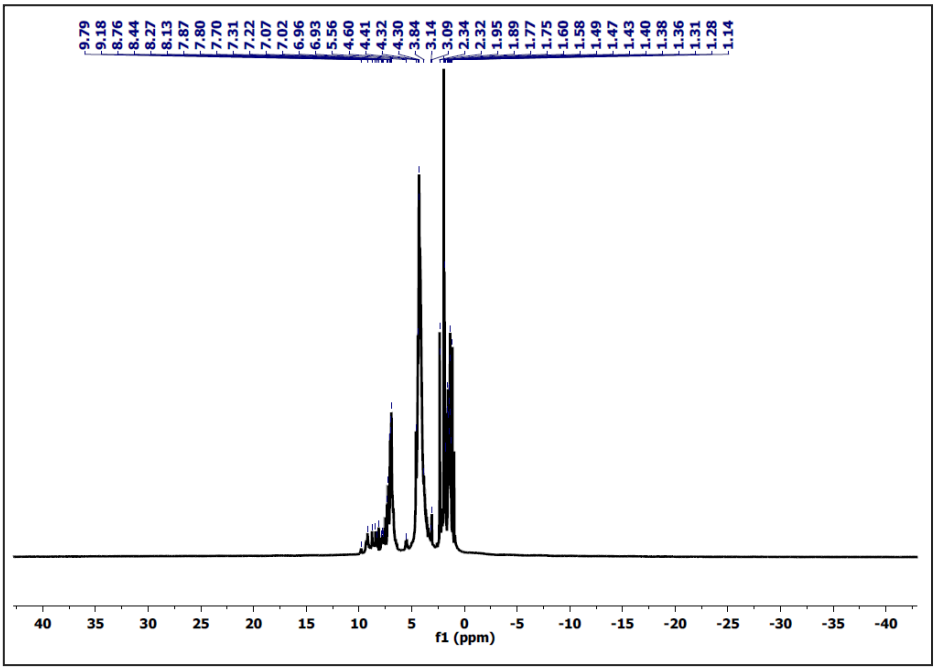


Figure S30a: ^{1}H NMR spectrum of **CATN-Eu^{3+}** complex in CD_3CN (500 MHz) at 298 K in a wide range chemical shift

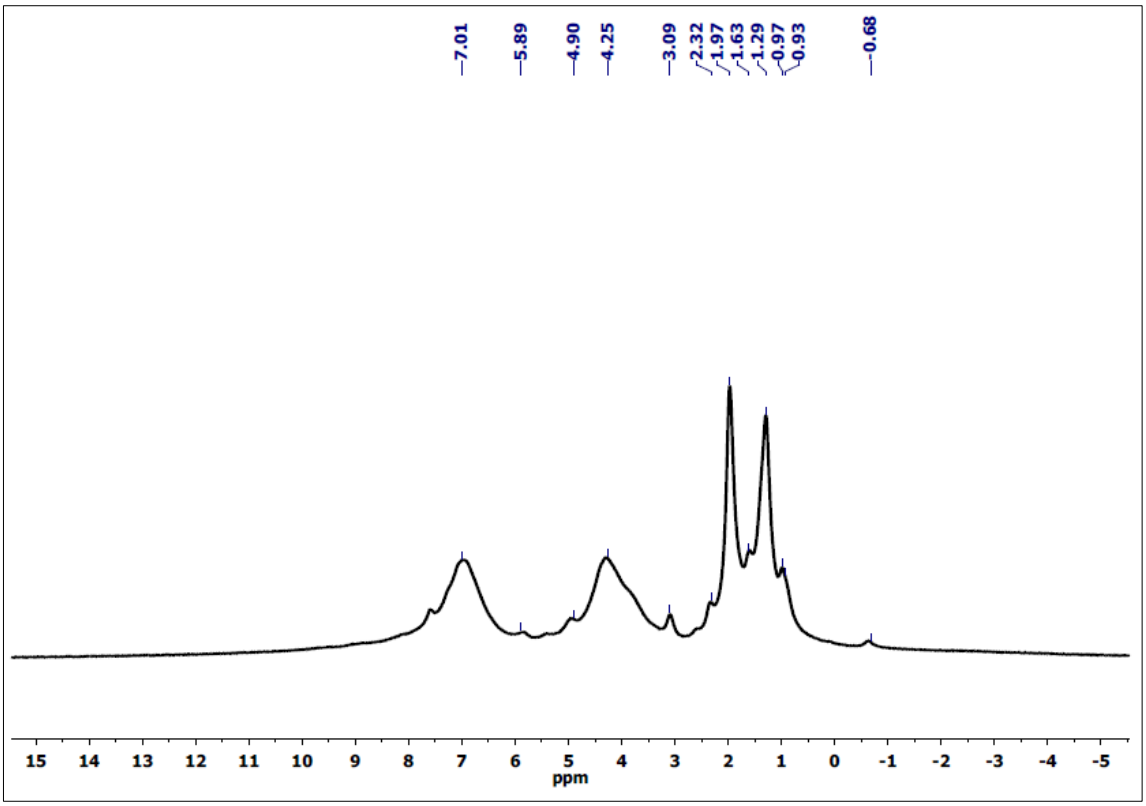


Figure S31: ^{1}H NMR spectrum of **CATN-Gd^{3+}** complex in CD_3CN (500 MHz) at 298 K

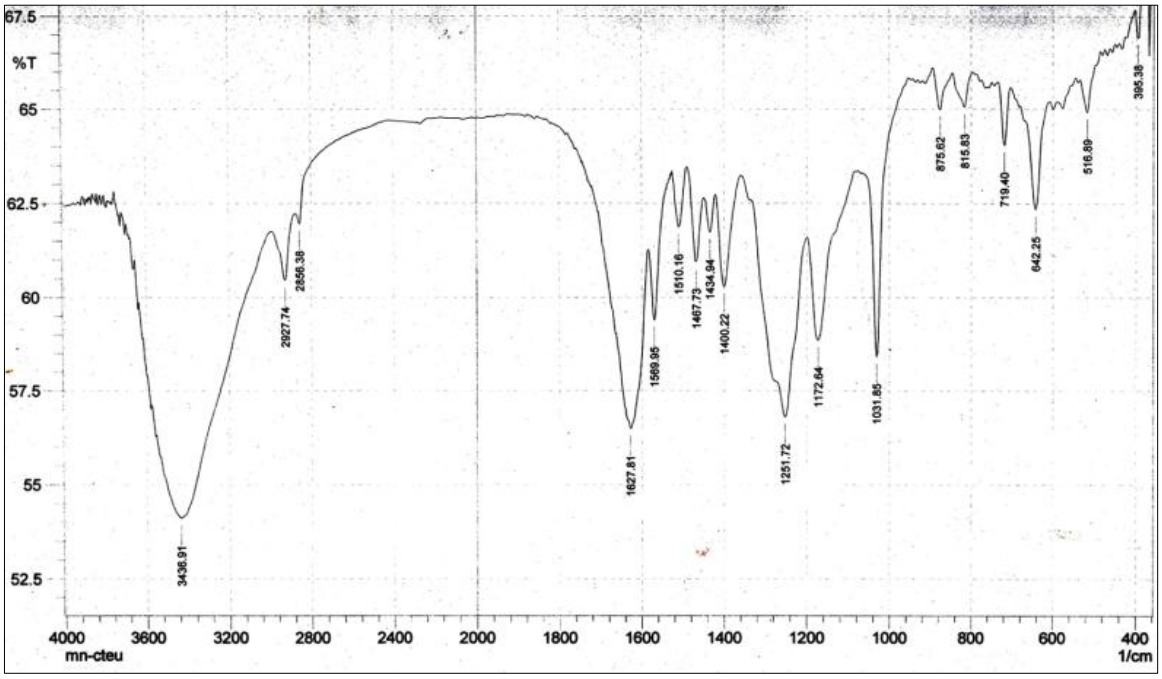


Figure S32: FTIR (KBr, ν cm^{-1}) spectrum of **CATN-Eu^{3+}** complex

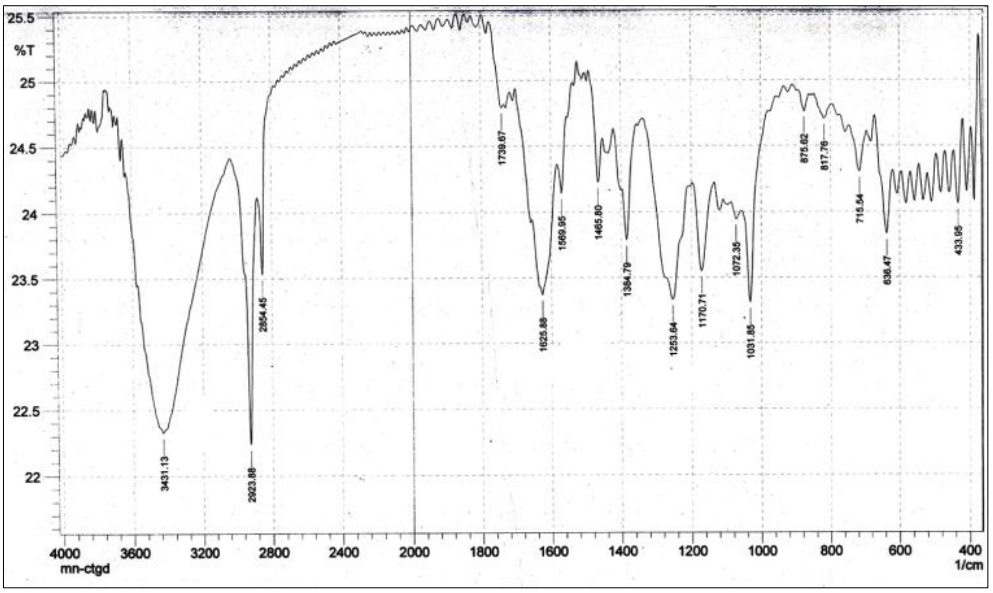


Figure S33: FTIR (KBr, ν cm^{-1}) spectrum of **CATN-Gd^{3+}** complex

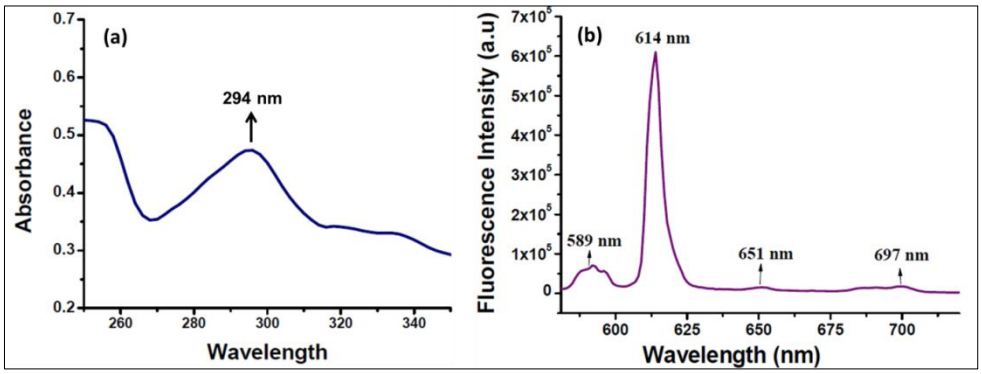


Figure S34: Characteristic (a) UV-Vis spectrum and (b) PL spectrum of **CATN-Eu^{3+}** ($2X10^{-5}$M) in CH_3CN medium at 298 K

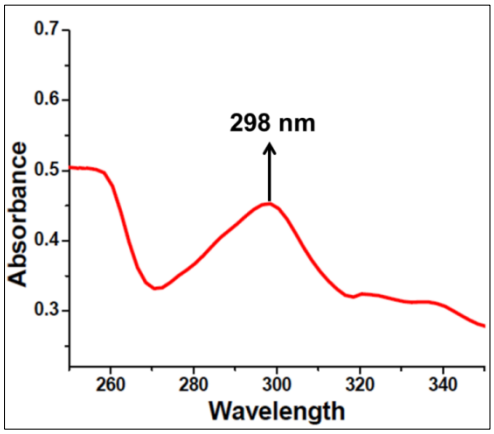


Figure S35: Characteristic UV-Vis spectrum of **CATN-Gd^{3+}** ($2X10^{-5}$M) in CH_3CN: CH_3Cl (9:1) medium at 298 K

CATN-Y^{3+} complex: By following the general procedure CATN-Y^{3+} complex has been prepared and off white solid Y-catenate was isolated in 52% yield.

CATN-Y^{3+} complex ($C_{75}H_{74}F_9N_4O_{21}S_3Y$, M_w=1723.49). Anal.calcd for $C_{75}H_{74}F_9N_4O_{21}S_3Y$: C, 52.27; H, 4.33; N, 3.25. Found C, 51.01; H, 4.52; N, 3.49. HRMS (ESI-MS): $C_{73}H_{74}F_3N_4O_{15}SY$ [M- $2CF_3SO_3^-]^{2+}$: calcd, m/z 712.1936; found, 712.1929. Characteristic λ_{max} = 292 nm in (2 x 10^{-5}) M CH_3CN and molar extinction coefficient value (ε) = 2.20 × 10^4 M^{-1} cm^{-1}. ^1H NMR (400 MHz, CD_3CN): δ (ppm) 1.25-1.41 (m), 2.31 (d), 3.81 (s), 4.04-4.30 (m), 4.86 (d), 5.29-5.32 (m), 6.71 (d), 6.79 (d), 6.86-7.05 (m), 7.16-7.45 (m), 8.33 (d), 8.43 (s), 8.75 (d), 8.96-9.00 (m), 9.17 (d), 9.25 (bs). IR (KBr, ν cm^{-1}): 362.59, 426.24, 516.89, 646.11, 719.40, 765.69, 1047.27, 1174.57, 1234.36, 1261.36, 1400.22, 1467.73, 1508.23, 1573.81, 1620.09, 2927.74, 3394.48.

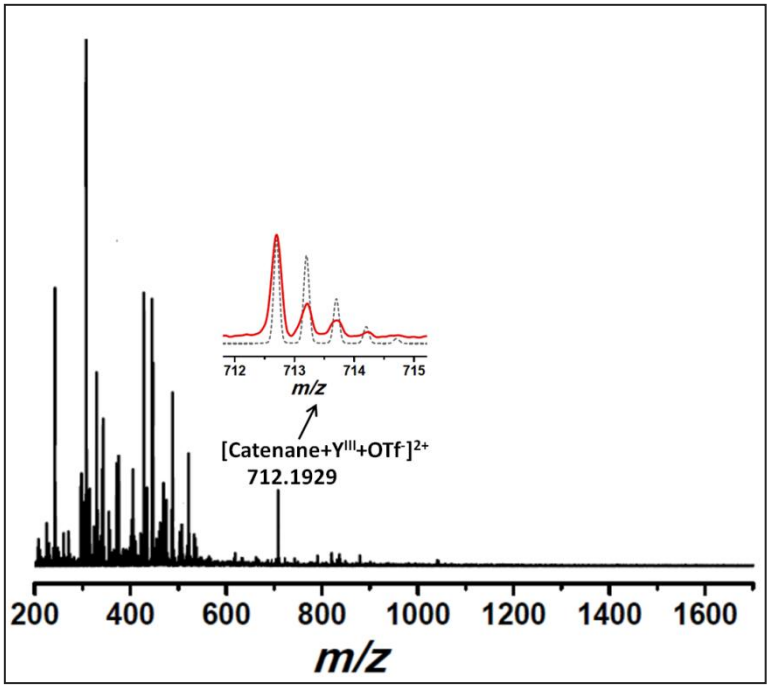


Figure S36: ESI-MS of **CATN-Y^{3+}** complex

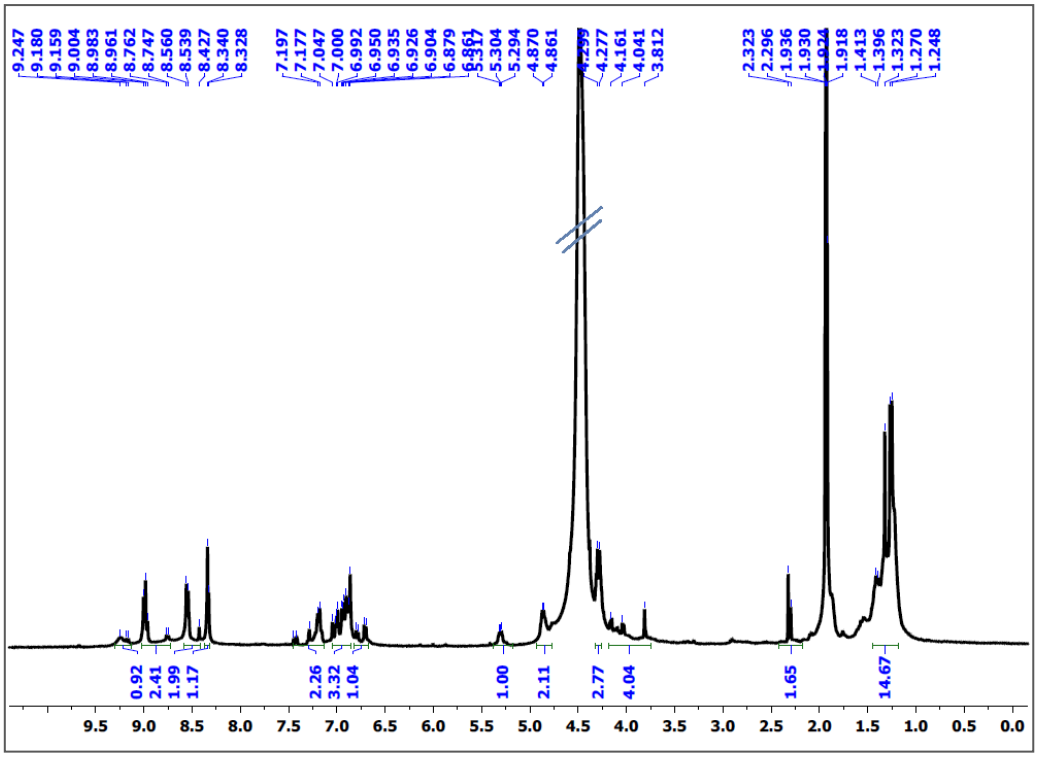


Figure S37: ^{1}H NMR spectrum of **CATN-Y^{3+}** complex in CD_3CN (400 MHz) at 298 K

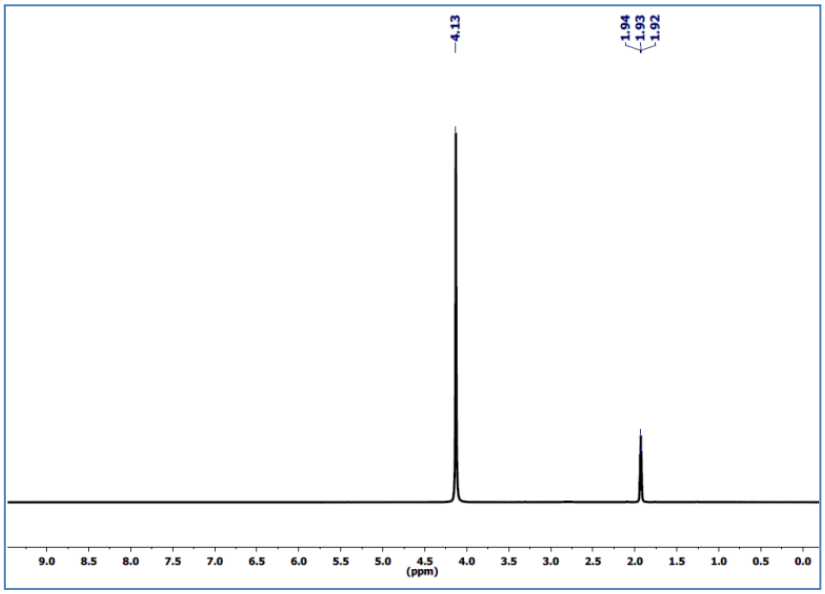


Figure S37a: ^{1}H NMR spectrum of **Y(OTf)$_3$** in CD_3CN (400 MHz) at 298K (broad singlet peak appeared at 4.13 ppm may be due to the hygroscopic nature of the salt)

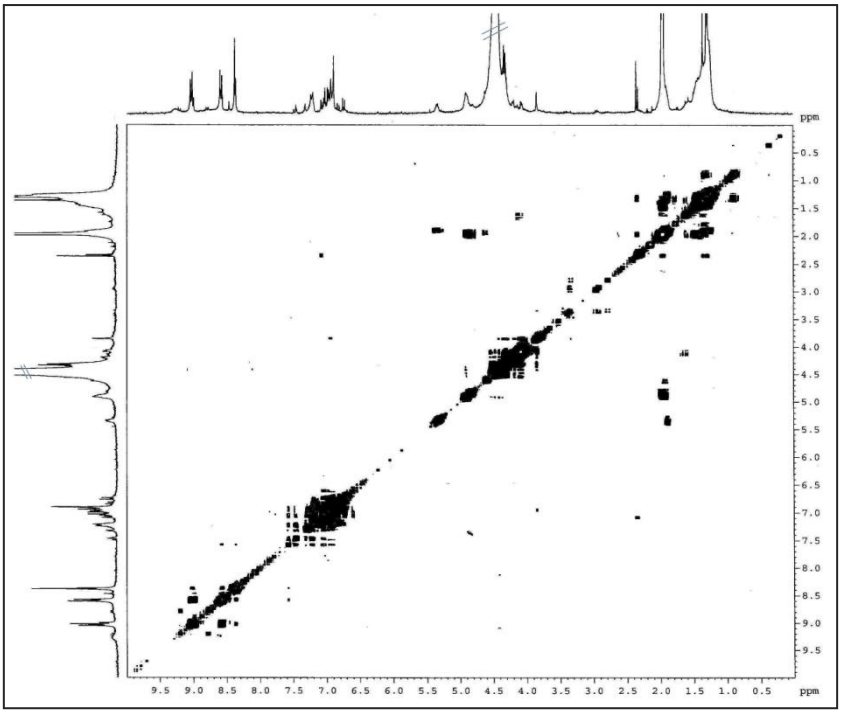


Figure S38: ^{1}H-^{1}H COSY spectrum of **CATN-Y^{3+}** complex in CD_3CN (300 MHz) at 298 K

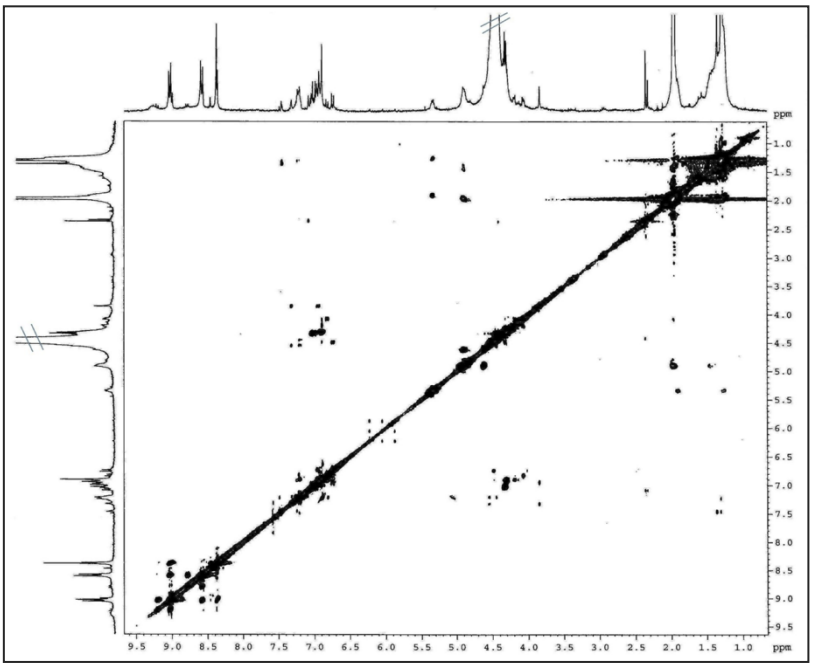


Figure S39: ^{1}H-^{1}H ROESY spectrum of **CATN-Y^{3+}** complex in CD_3CN (300 MHz) at 298 K.

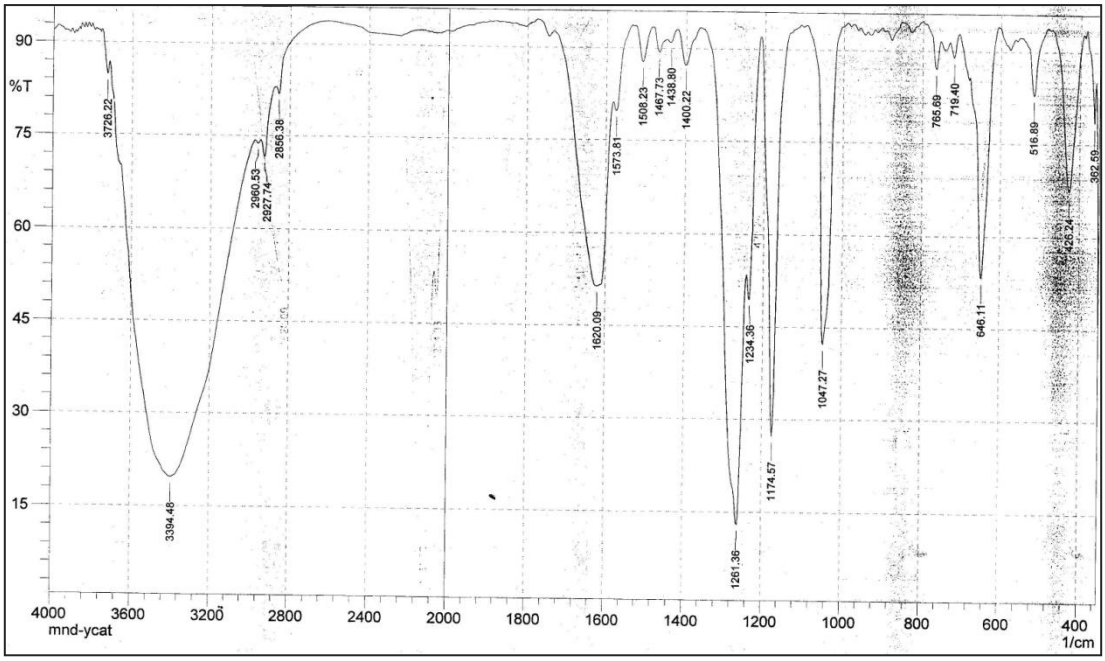


Figure S40: FTIR (KBr, ν cm^{-1}) spectrum of **CATN-Y^{3+}**complex

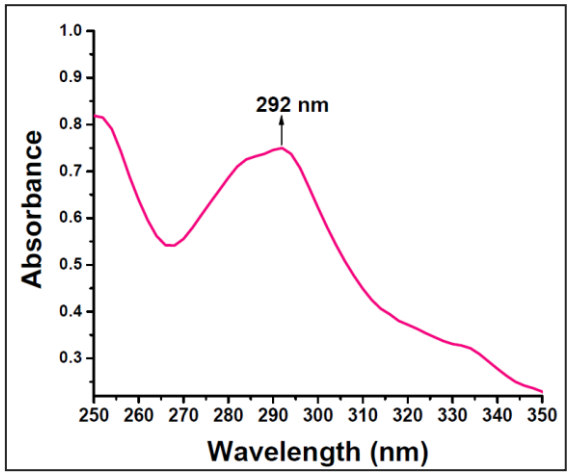


Figure S41: Characteristic UV-Vis spectrum of **CATN-Y^{3+}** ($2X10^{-5}$M) in CH_3CN: CH_3Cl (9:1) medium at 298 K

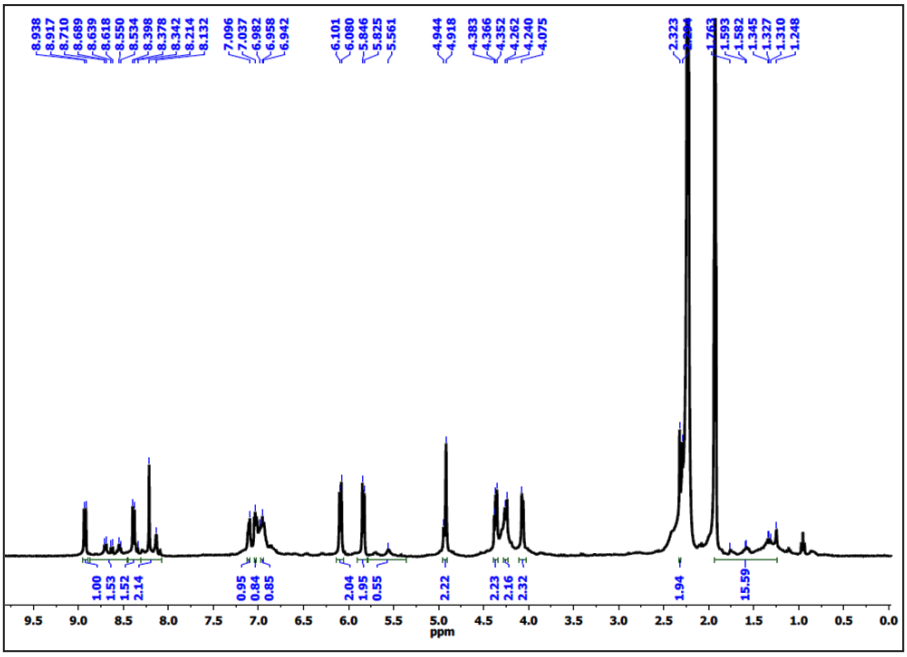


Figure S42: ^{1}H NMR spectrum of **Na-catenate** in CD_3CN (400 MHz) at 298 K

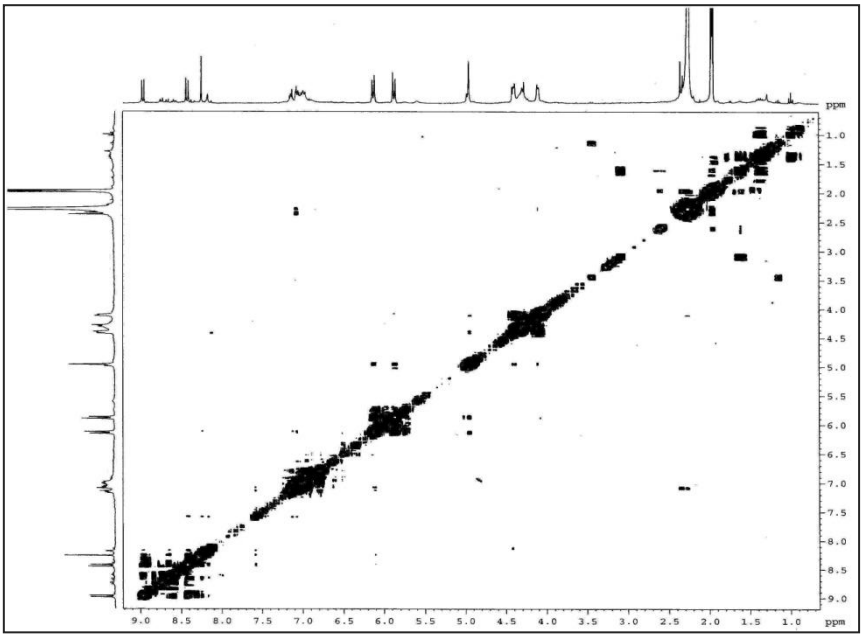


Figure S43: ^{1}H-^{1}H COSY spectrum of **Na-catenate** complex in CD_3CN (300 MHz) at 298 K

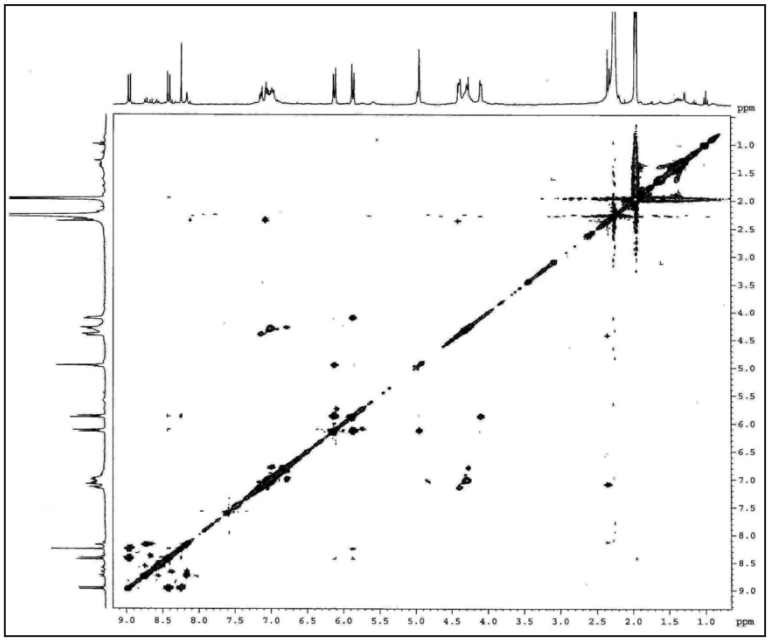


Figure S44: ^{1}H-^{1}H ROESY spectrum of **Na-catenate** complex in CD_3CN (300 MHz) at 298 K.

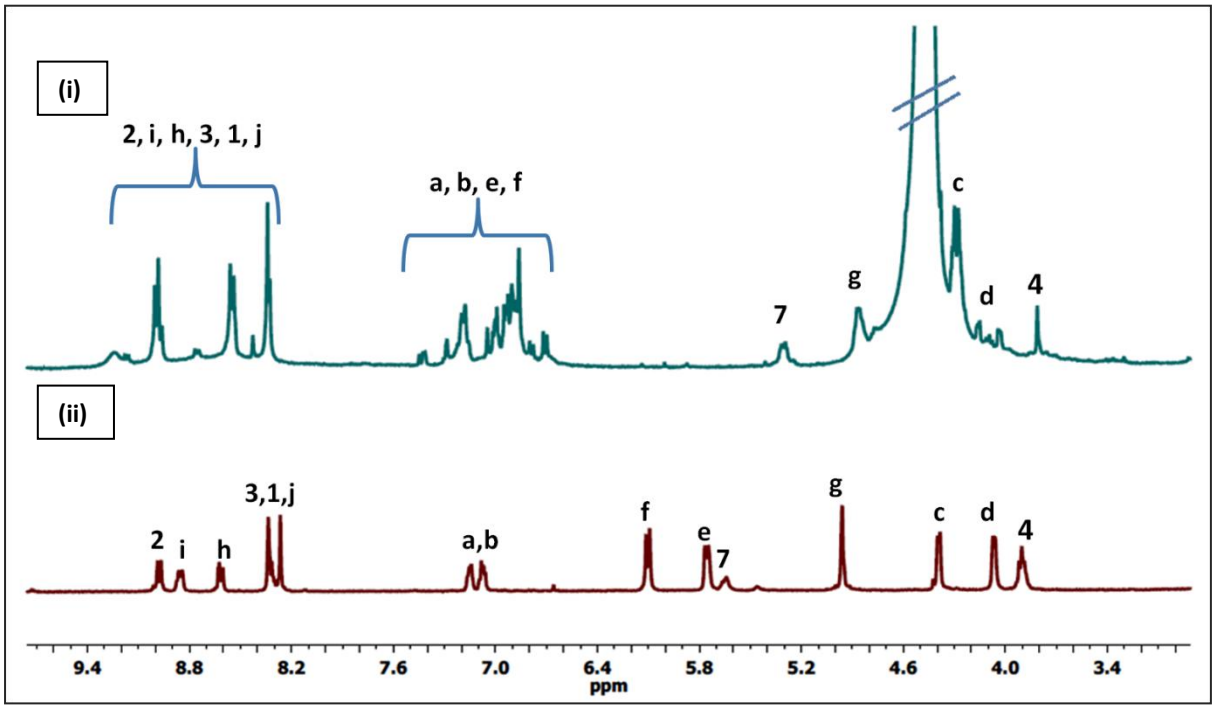


Figure S45: Comparative ^{1}H NMR analysis between (i) Y-catenate and (ii) [2]catenane in CD_3CN (400 MHz) at 298 K.

References

1. S. Santra, S. Mukherjee, S. Bej, S. Saha and P. Ghosh, *Dalton Trans.*, 2015, **44**, 15198.
2. J. Dehaudt, N. J. Williams, I. A. Shkrob, H. Luo and S. Dai, *Dalton Trans.*, 2016, **45**, 11624.
3. M. Nandi, S. Santra, B. Akhuli and P. Ghosh, *Dalton Trans*., 2017, **46**, 7421.
4. G. M. Sheldrick, *SAINT and XPREP, version 5.1*, Siemens Industrial Automation Inc., Madison, WI, 1995.
5. G. M. Sheldrick, *SHELXS97. Program for Crystal Structure Solution and Refinement*, University of Göttingen, Göttingen, 1997.
6. G. M. Sheldrick, *SHELXL v. 2014, Program for Crystal Structure Refinement*, University of Göttingen, 2014.
7. G. M. Sheldrick, *SADABS*, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997.
8. A. L. Spek, *PLATON-97*, University of Utrecht, Utrecht, the Netherlands, 1997.
9. Mercury, *version 3.7, supplied with Cambridge Structural Database,* CCDC, Cambridge, U.K., 2003–2004.