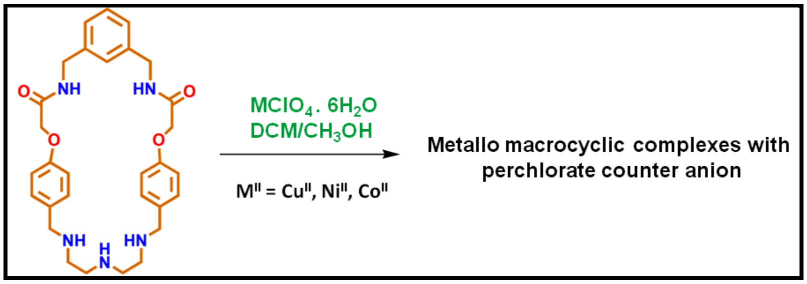
Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information

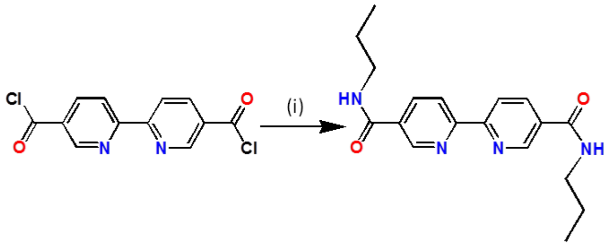
Syntheses of metallo-pseudorotaxanes, rotaxane and post-synthetically functionalized rotaxane: a comprehensive spectroscopic study and dynamic properties

Saikat Santra [a], Somnath Bej [a #], Mandira Nandi [a #], Partha Mondal [b] and Pradyut Ghosh [a]*

Contents



Scheme 1S. Synthetic route of metallo macrocyclic complexes (using perchlorate counter anion)



(i) n-propyl amine, Et_3N, 0°C, THF

Scheme 1S a. Synthetic route of **L3**

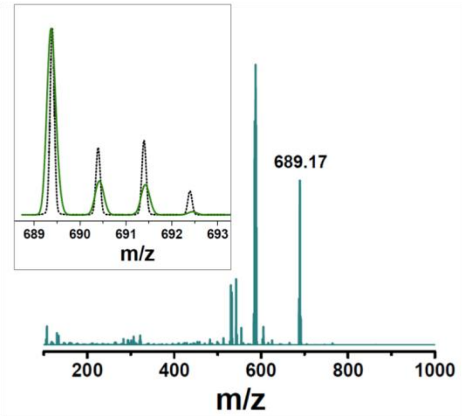


Fig. 1 *(a) ESI-MS spectrum of* ***MC****-Co^{II} complex, (b) inset picture shows exact matching of simulated (black) and experimental isotopic distribution pattern (green)*

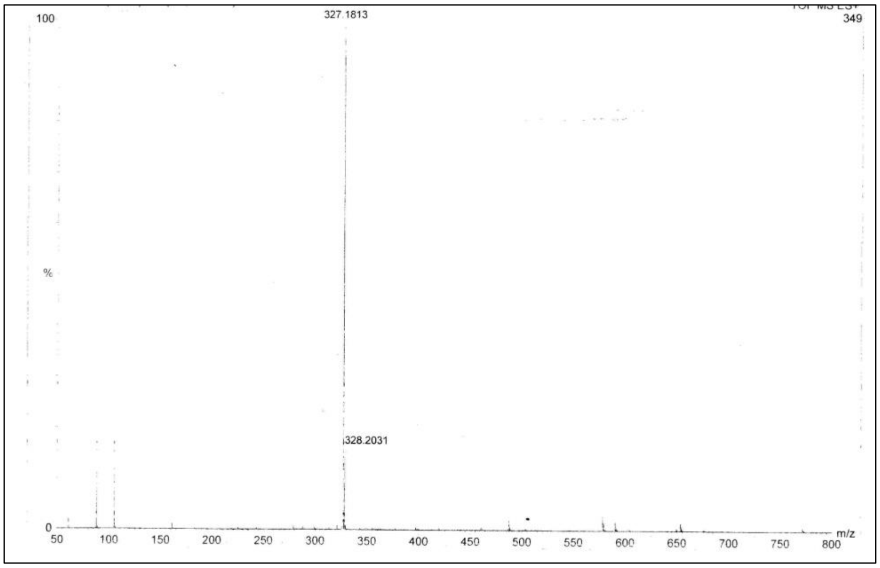


Fig. 2S *ESI-MS of* ***L3***

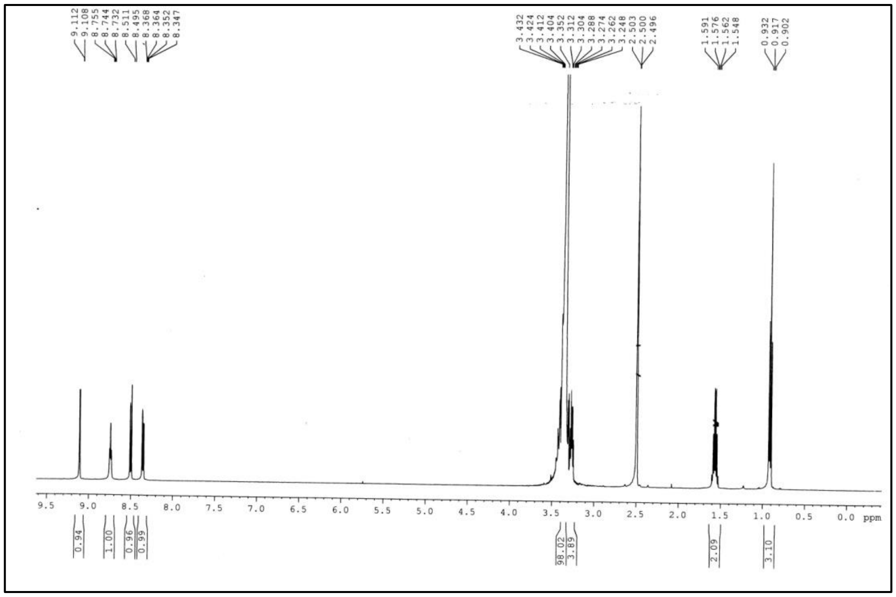


Fig. 3S *^{1}H-NMR of* ***L3*** *in DMSO-d_6 at 298K (500MHz)*

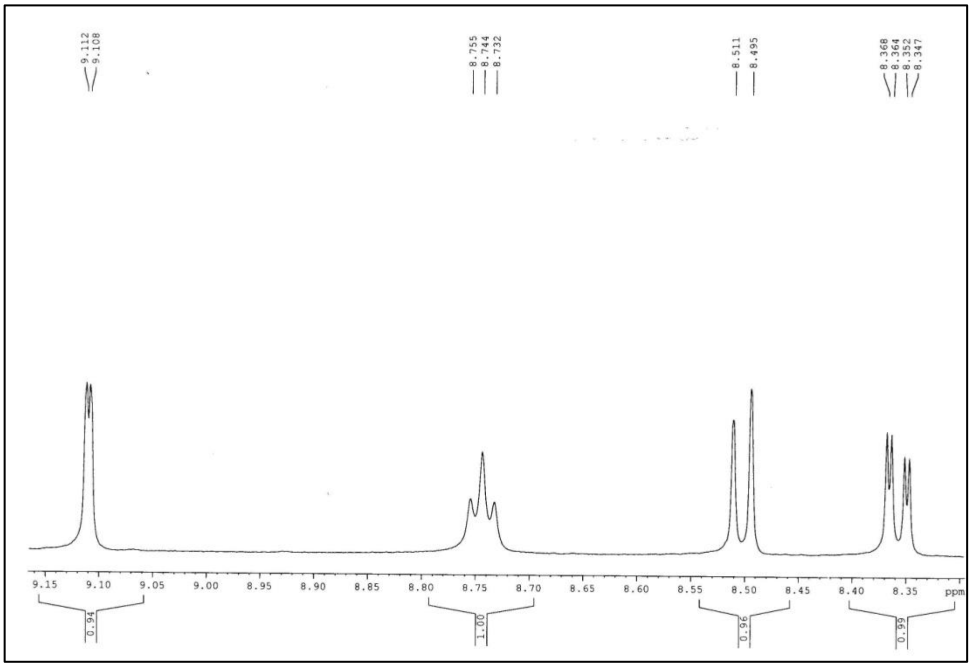


Fig. 3S *(a) Expanded ^{1}H-NMR of **L3** in DMSO-d_6 at 298K (500MHz)*

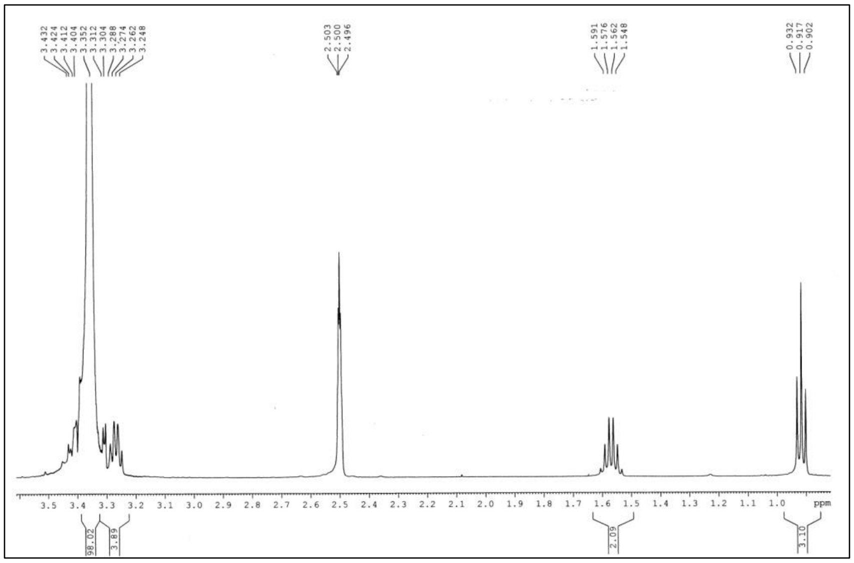


Fig. 3S *(b) Expanded ^{1}H-NMR of **L3** in DMSO-d_6 at 298K (500MHz)*

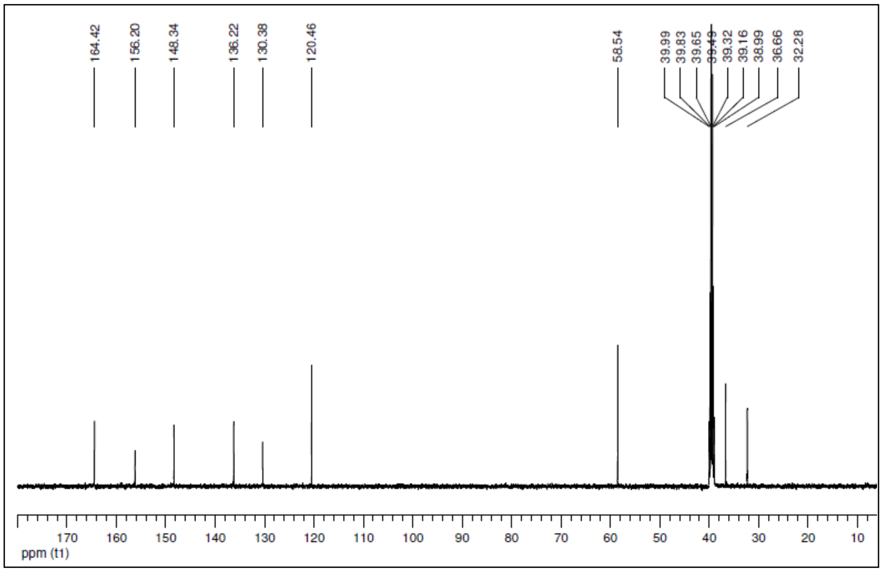


Fig. 4S *^{13}C-NMR spectrum of* ***L3*** *in DMSO-d_6 at 298K (500MHz)*

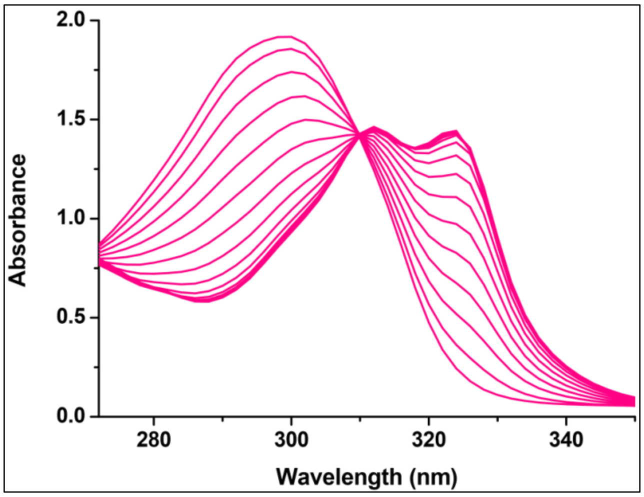


Fig.5S Absorption titration profile of **MC**-Ni^{II} (6 x 10^{-4} M) complex and **L2** (8 x 10^{-5} M)

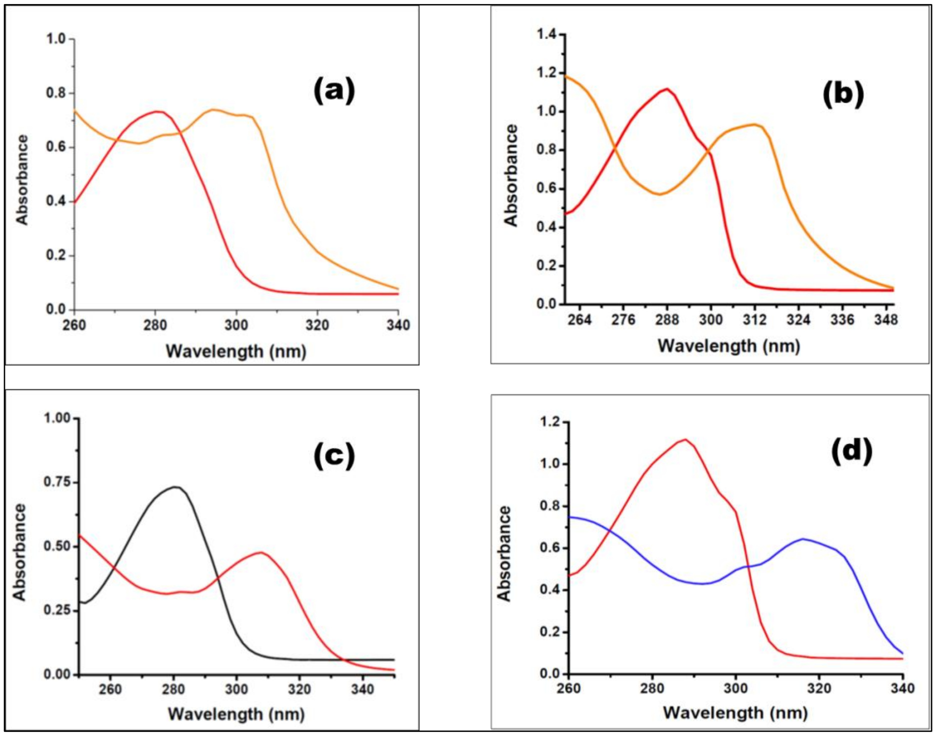


Fig. 6S(a). Absorption spectra of **L1@MC-Co^{II}** (yellow) and **L1** (red); (b) **L2@MC-Co^{II}** (yellow) and **L2** (red); (c) **L3@MC-Co^{II}** (red) and **L3** (black); (d) **L4@MC-Co^{II}** (blue) and **L4** (red)

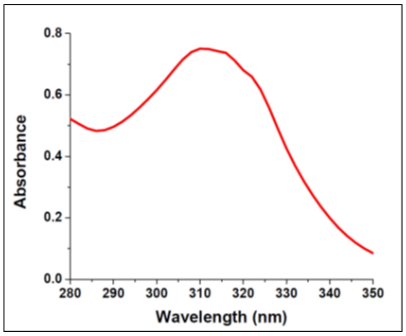


Fig. 6S (e). Absorption spectra of **L5@MC-Co^{II}**

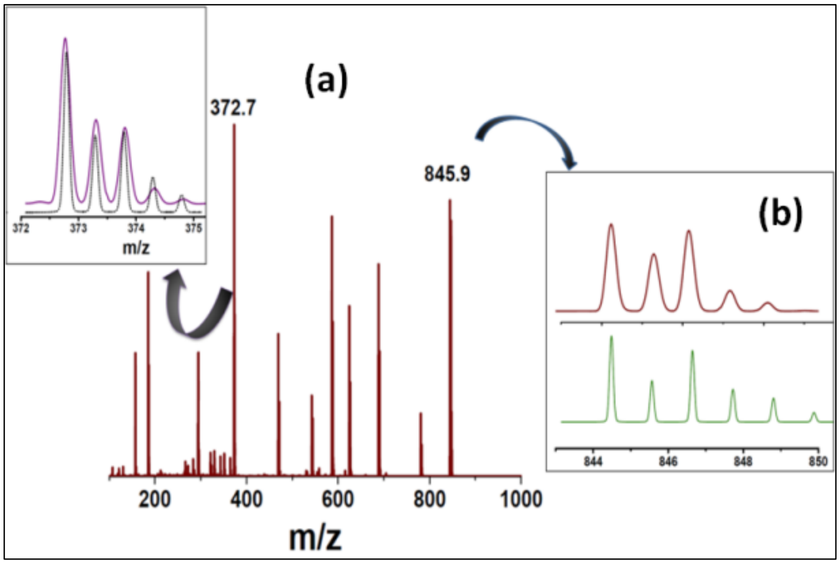


Fig. 7S *[A] ESI-MS spectrum of (a)* ***L1****@[***MC****.Ni.*ClO_4^-*]*$^+$*;(b) simulated (green) and experimental (brown) distribution pattern of desired peak*

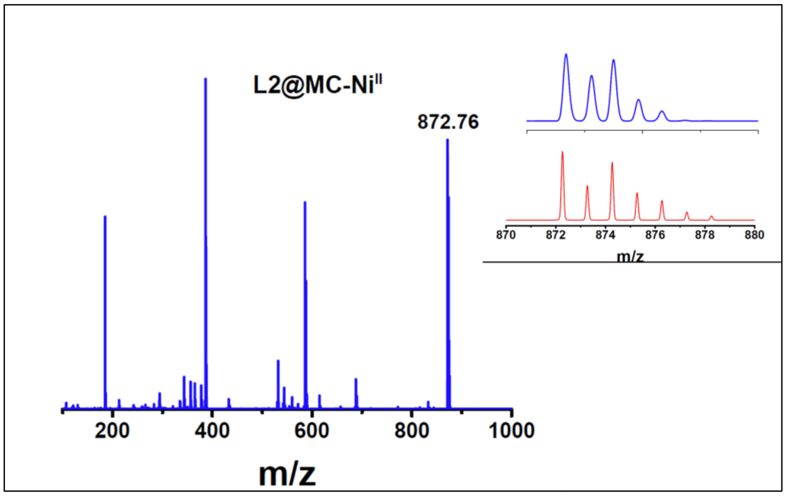


Fig. 7S*. [B] ESI-MS spectrum of* ***L2****@[***MC****.Ni.*ClO_4^-*]*$^+$*;inset picture shows simulated (red) and experimental (blue) distribution pattern of desired peak*

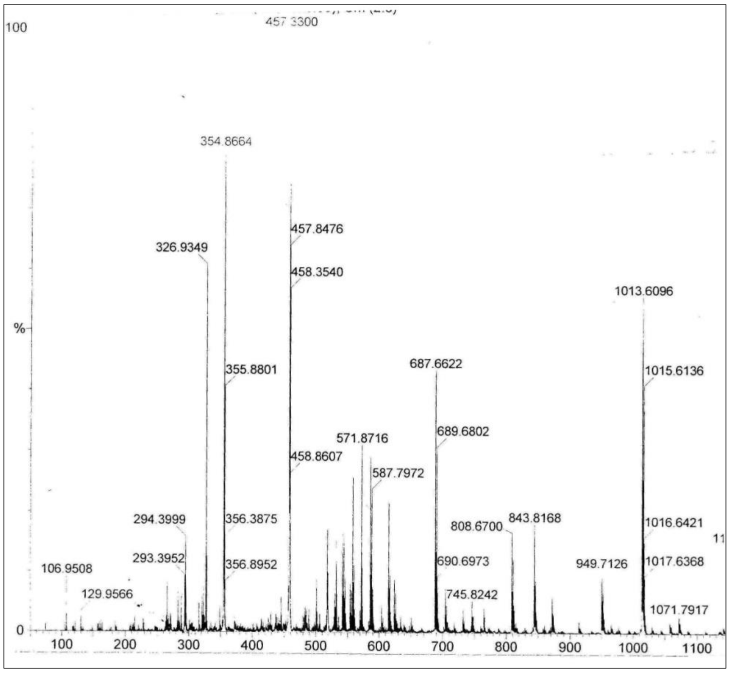


Fig. 7S *[C] ESI-MS spectrum of* ***L3****@[****MC****.Ni.ClO$_4^-$]$^+$*

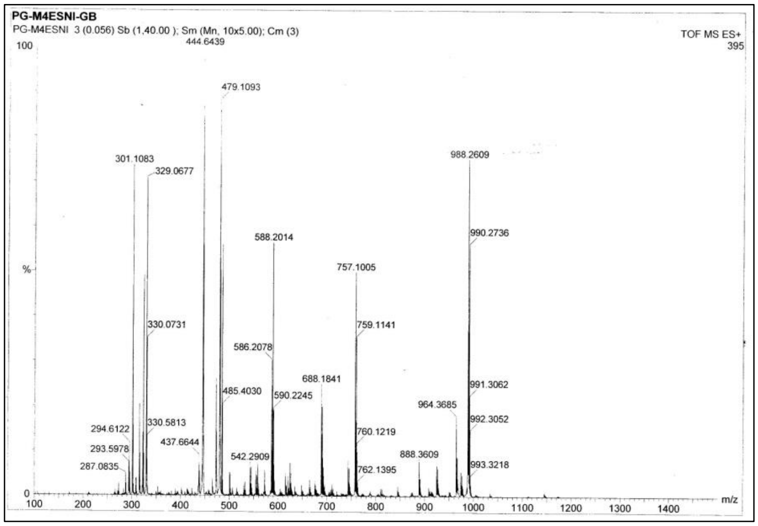


Fig. 7S *[D] ESI-MS spectrum of* ***L4****@[****MC****.Ni.ClO$_4^-$]$^+$*

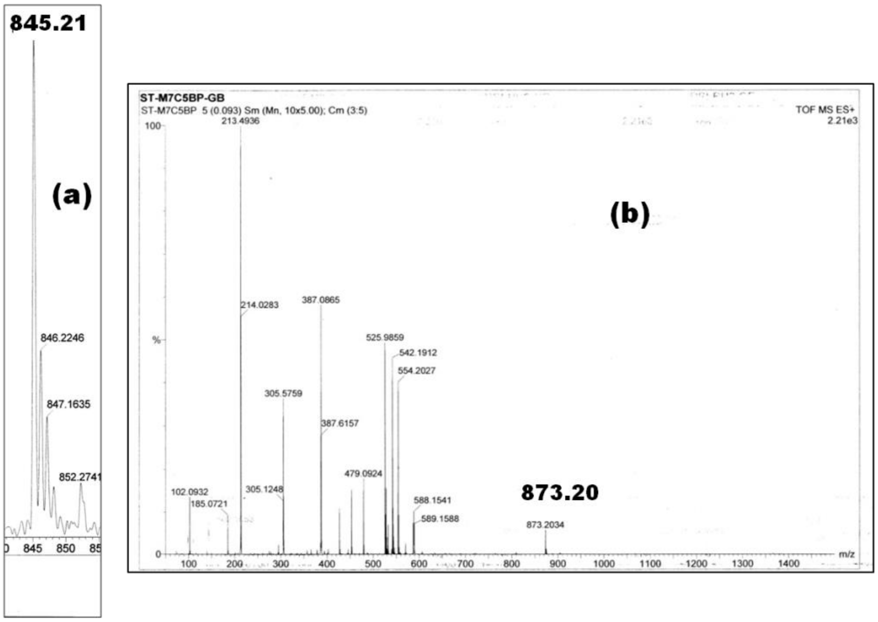


Fig. 8S *ESI-MS spectrum of [a]* ***L1****@[****MC****.Co.ClO$_4^-$]$^+$ and (b)* ***L2****@[****MC****.Co.ClO$_4^-$]$^+$*

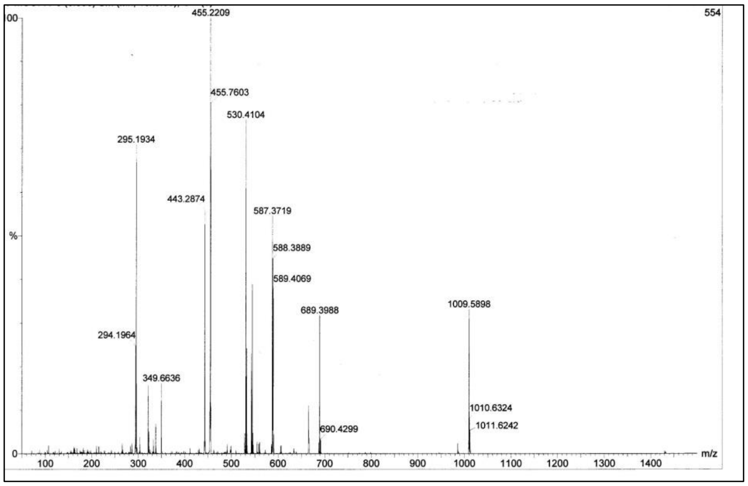


Fig. 8S *[c] ESI-MS spectrum of* ***L3****@[****MC****.Co.ClO$_4^-$]$^+$*

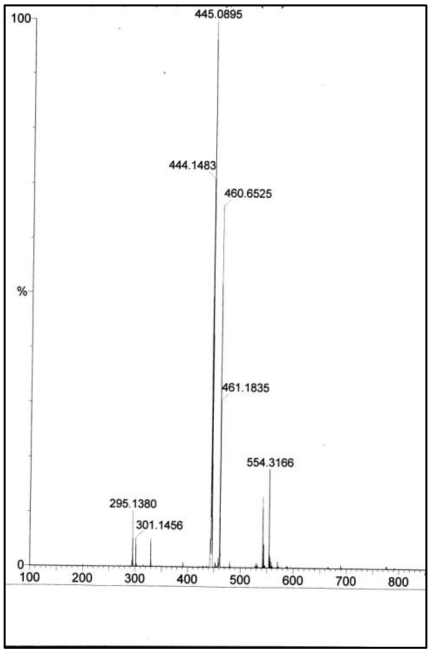


Fig. 8S *[d] ESI-MS spectrum of* ***L4****@[****MC****.Co.]*$^{+2}$

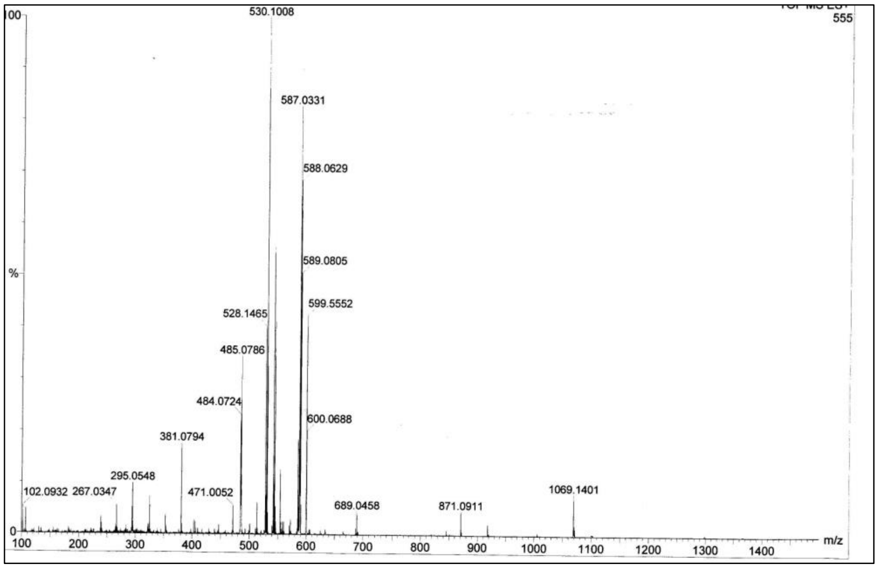


Fig. 8S *[e] ESI-MS spectrum of* ***L5****@[****MC****.Co.ClO*$_4^-$*]*$^+$

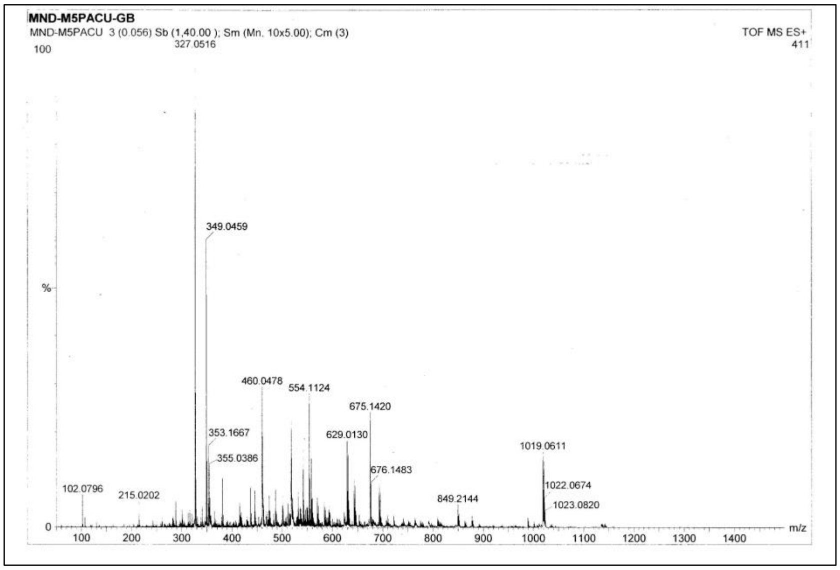


Fig. 9S *(a) ESI-MS (+ve) of* ***L3****@[****MC****.Cu.*ClO_4^-*]*$^+$

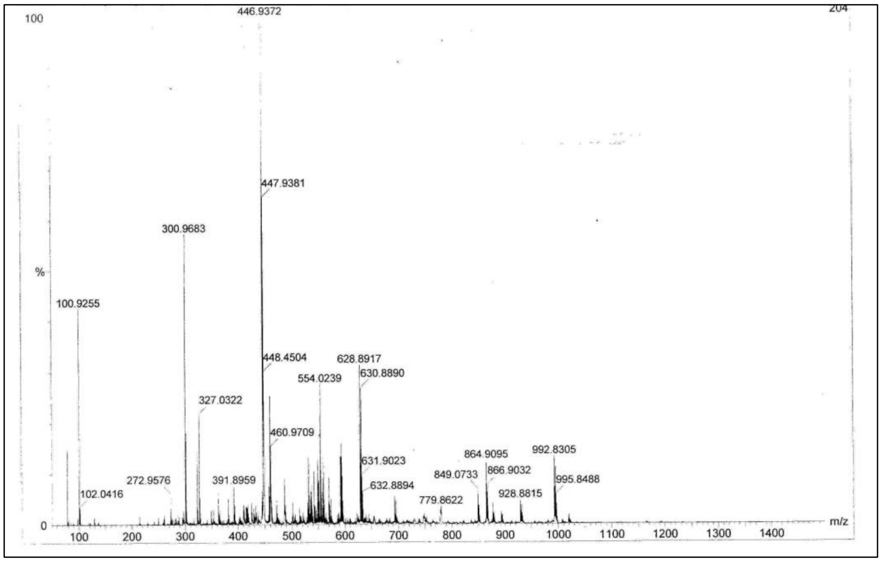


Fig. 9S *(b)* *ESI-MS (+ve) of* ***L4****@[****MC****.Cu.*ClO_4^-*]*$^+$

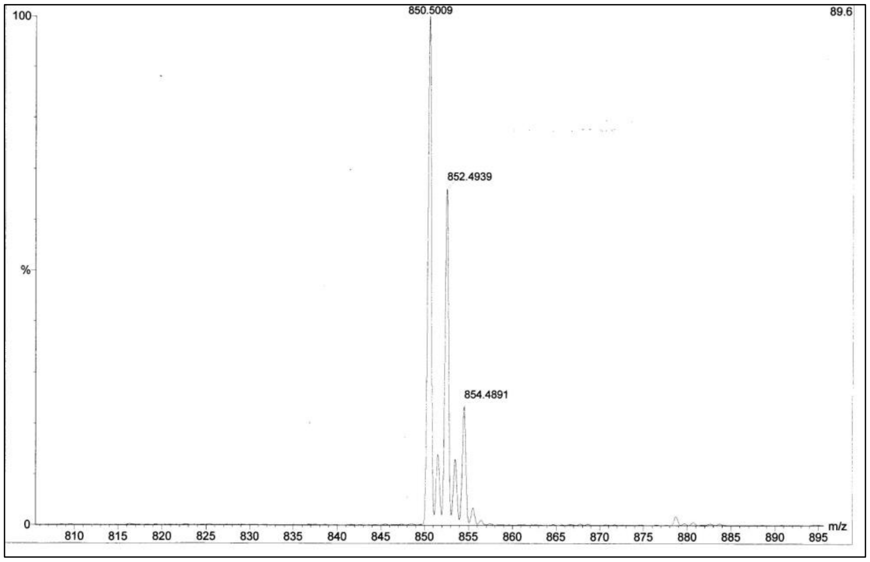


***Fig. 10S** (a)* *ESI-MS (+ve) of **L1**@[**MC**.Zn.ClO_4^-]$^+$*

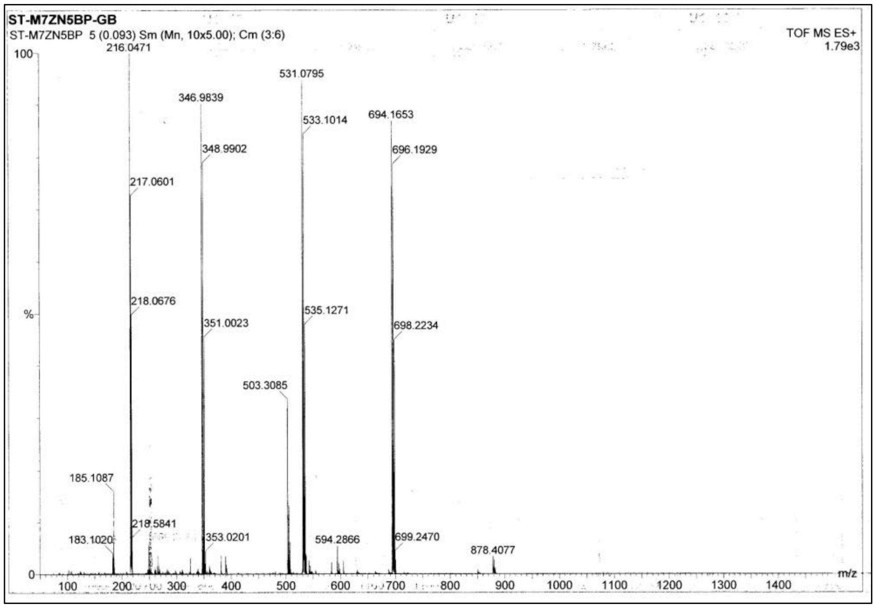


***Fig. 10S** (b)* *ESI-MS (+ve) of **L2**@[**MC**.Zn.ClO_4^-]$^+$*

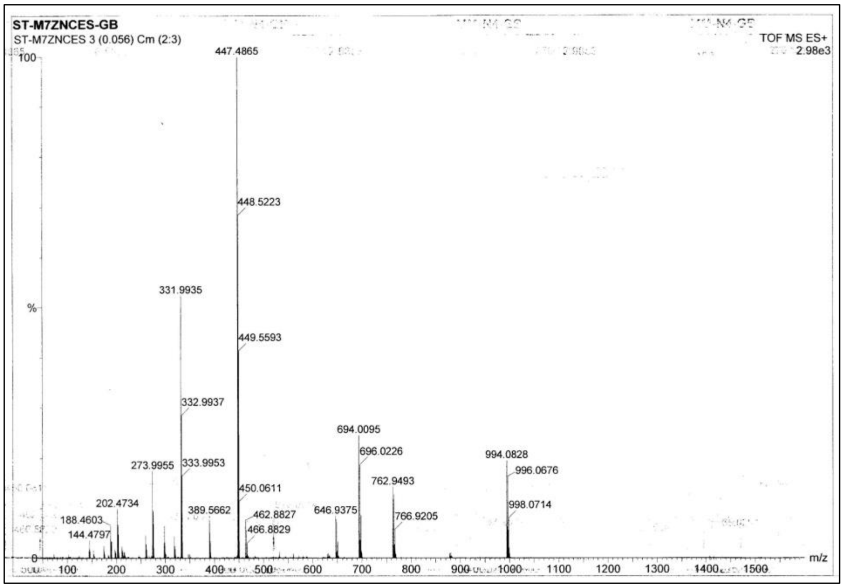


Fig. 10S (c) *ESI-MS (+ve) of* ***L4***@[***MC***.Zn.ClO_4^-]$^+$

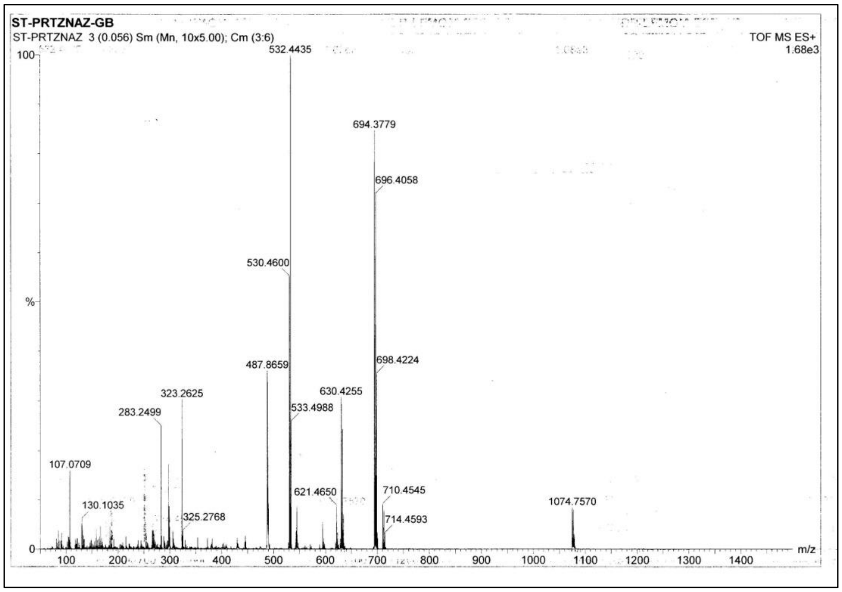


Fig. 10S (c) *ESI-MS (+ve) of* ***L5***@[***MC***.Zn.ClO_4^-]$^+$

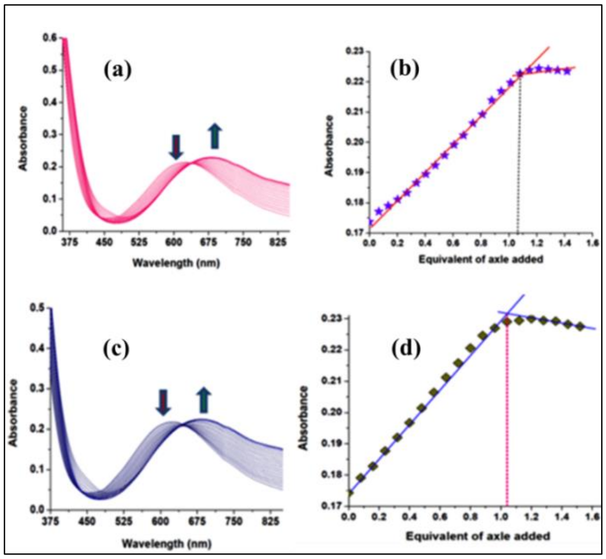


Fig.11S *Electronic spectra for titration experiment among bidentate chelating ligand as axles, (a)* ***L3****(7.8 x* 10^{-3} *M), (c)* ***L4*** *(8.2 x* 10^{-3} *M), and* ***MC****-*Cu^{II} *(1.0 x* 10^{-3} *M)complex, (b) and (d) indicate equivalent plot between* ***MC****-*Cu^{II} *complex and respective axles*

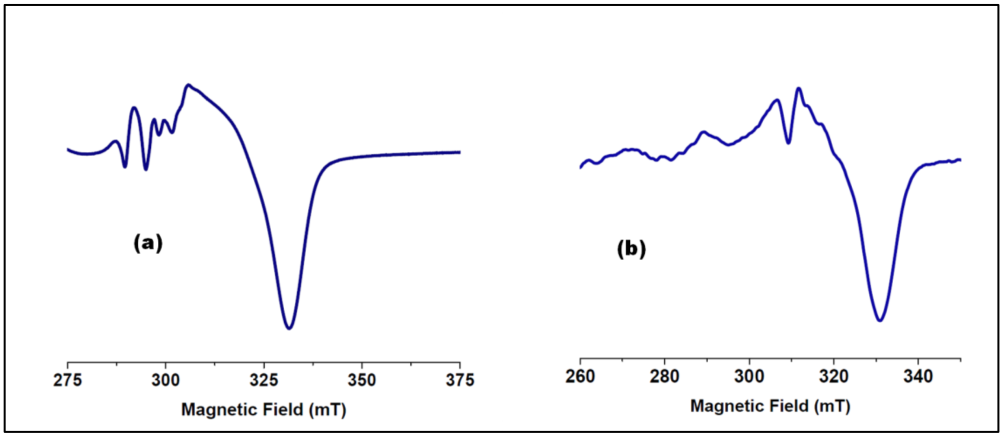


Fig. 12S *EPR spectra of (a)* ***L3*** [$g_{\|}$ = 2.1871, $g_{\perp}$ = 2.02689] *and (b)* ***L4*** [$g_{\|}$ = 2.2076, $g_{\perp}$ = 2.02573] *threaded* Cu^{II} *templated pseudorotaxane*

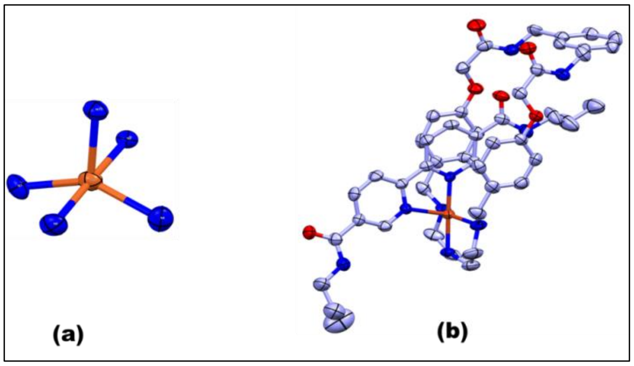


Fig. 13S *[A]:* ***(a)*** *Geometry around the metal centre of* ***L3@MC-Cu^{II};(b)*** *ORTEP dagram of* ***L3@MC-Cu^{II}***

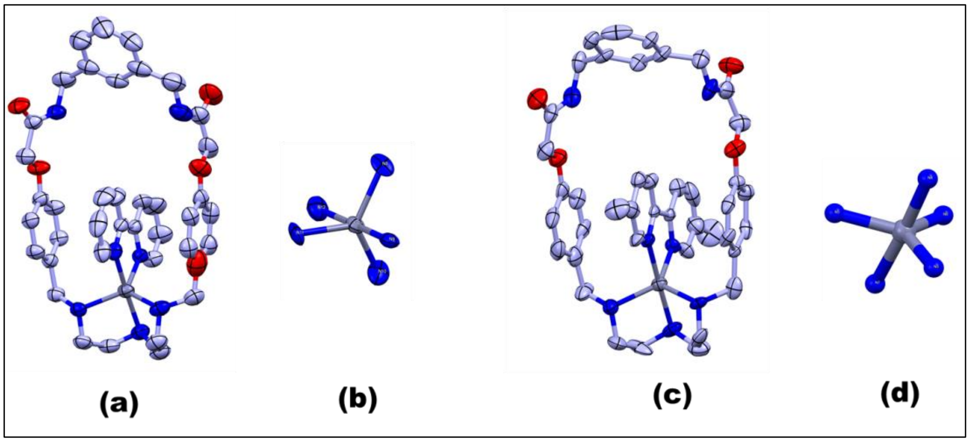


Fig. 13S *[B]: ORTEP dagram of (a)* ***L1@MC-Zn^{II}****;(c)* ***L2@MC-Cu^{II}*** *and geometry around the metal centre (b), (d). H-atoms are omitted for clarity*

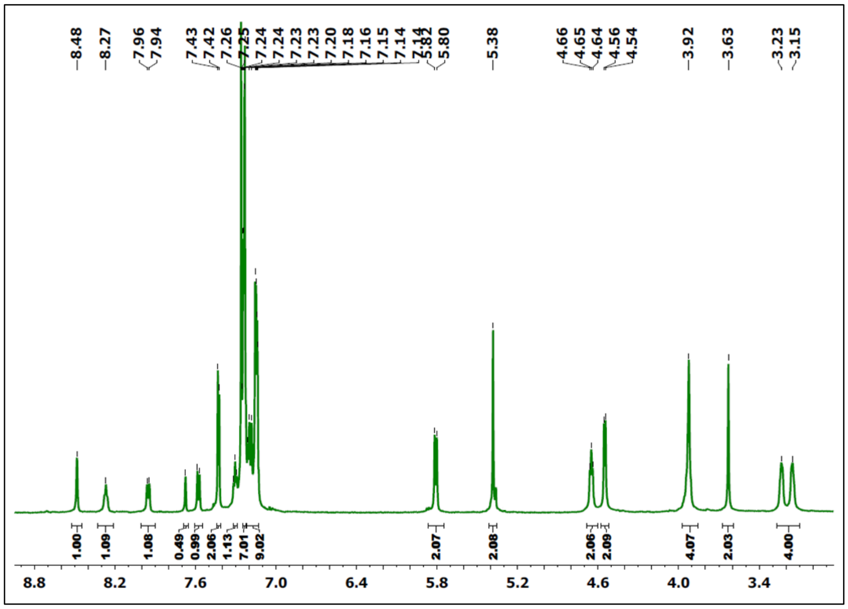


Fig. 14S a *^{1}H-NMR spectrum of metal free [2]rotaxane,* ***ROT*** *in CDCl$_3$*

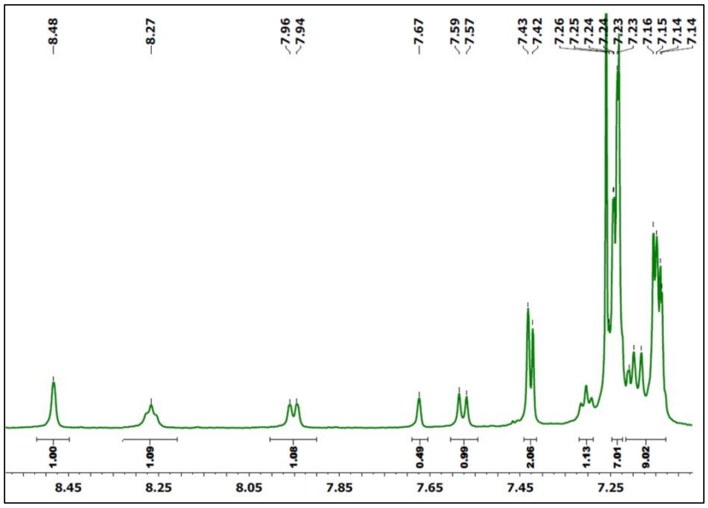


Fig. 15S *Expanded ^{1}H-NMR spectrum of metal free [2]rotaxane,* ***ROT*** *in CDCl$_3$*

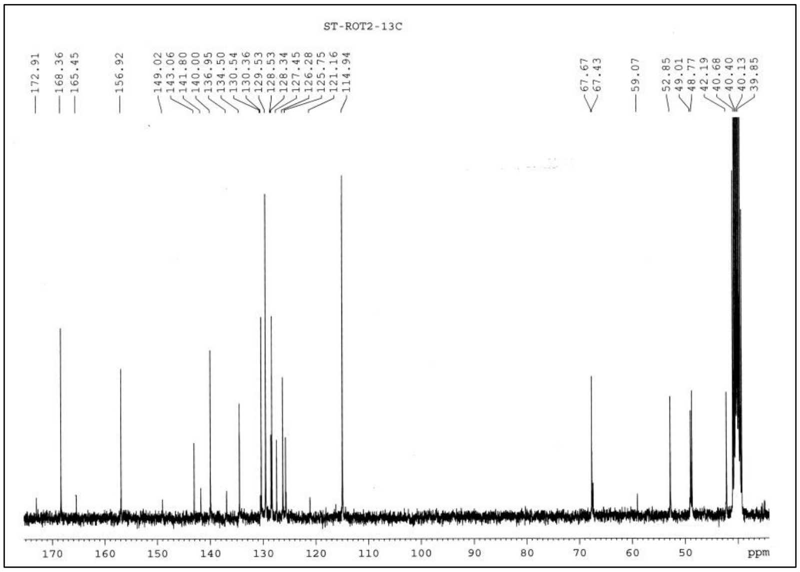


Fig. 16S ^{13}C-NMR (75 MHz) spectrum of **ROT** in DMSO-d_6 at 298K

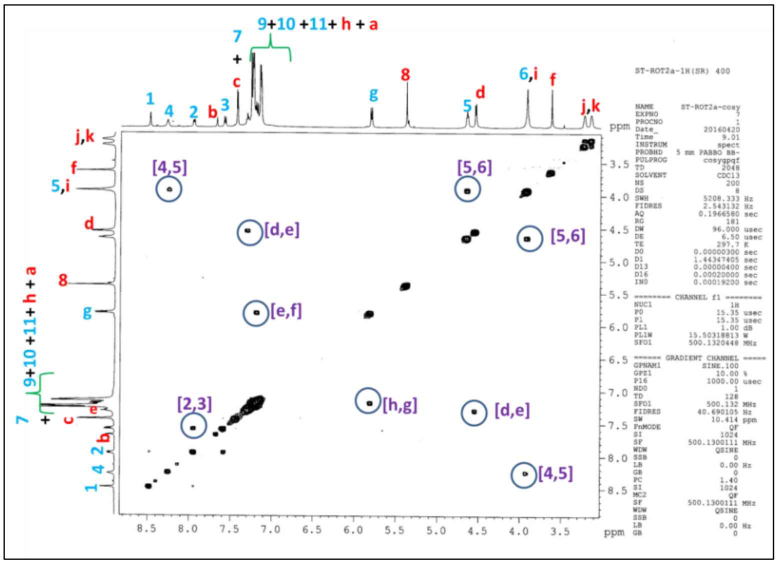
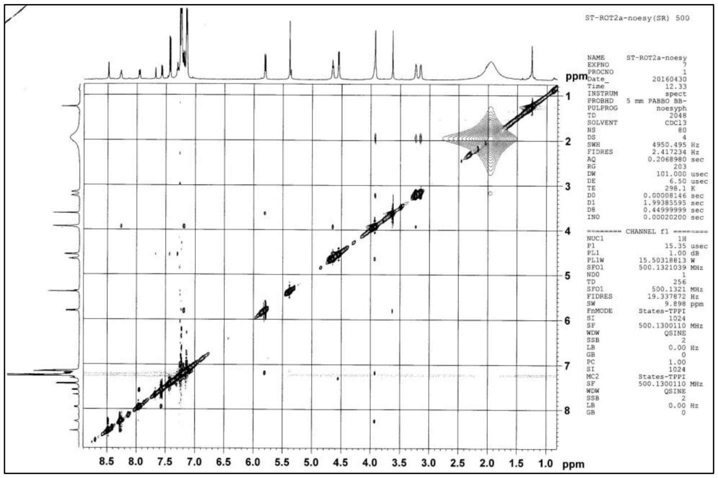


Fig. 17S ^{1}*H-*^{1}*H COSY NMR spectrum of metal free [2]rotaxane,* ***ROT*** *in CDCl*$_3$ *at 298K in 400MHz*



```
NAME      ST-ROT2a-noesy
EXPNO                  7
PROCNO                 1
Date_           20160430
Time               12.33
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          noesyph
TD                  2048
SOLVENT            CDCl3
NS                    80
DS                     4
SWH             4950.495 Hz
FIDRES          2.417234 Hz
AQ             0.2068980 sec
RG                   203
DW               101.000 usec
DE                  6.50 usec
TE                 298.1 K
D0            0.00008146 sec
D1            1.99385595 sec
D8            0.44999999 sec
IN0           0.00020200 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.35 usec
PL1                 1.00 dB
PL1W         15.50318813 W
SFO1         500.1321039 MHz
ND0                    1
TD                   256
SFO1            500.1321 MHz
FIDRES         19.337872 Hz
SW                 9.898 ppm
FnMODE       States-TPPI
SI                  1024
SF           500.1300110 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  1.00
SI                  1024
MC2          States-TPPI
SF           500.1300110 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```

Fig. 18S *^{1}H-^{1}H- NOESY NMR spectrum of metal free [2]rotaxane,* ***ROT*** *in CDCl$_3$ at 298 K in 500 MHz*

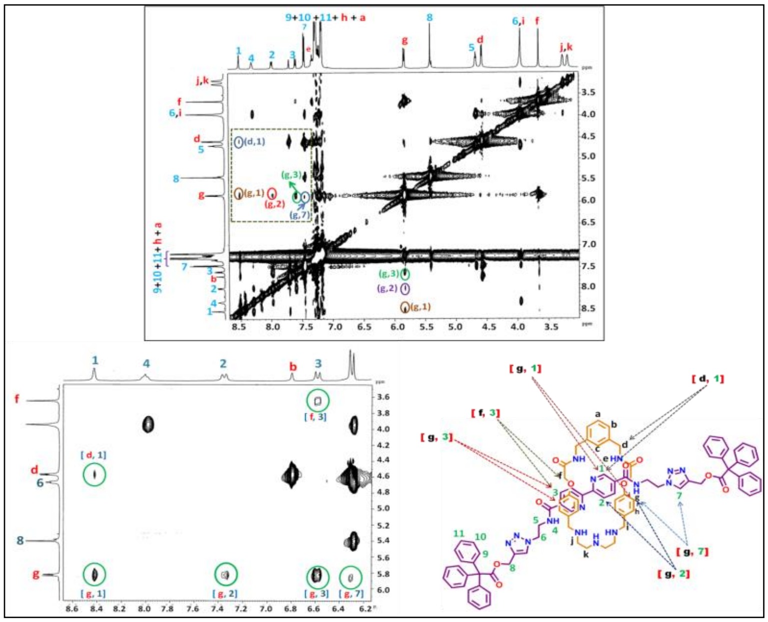


Fig. 19S *^{1}H-^{1}H ROESY NMR spectrum of metal free [2]rotaxane,* ***ROT*** *in CDCl$_3$ at 298K in 500 MHz*

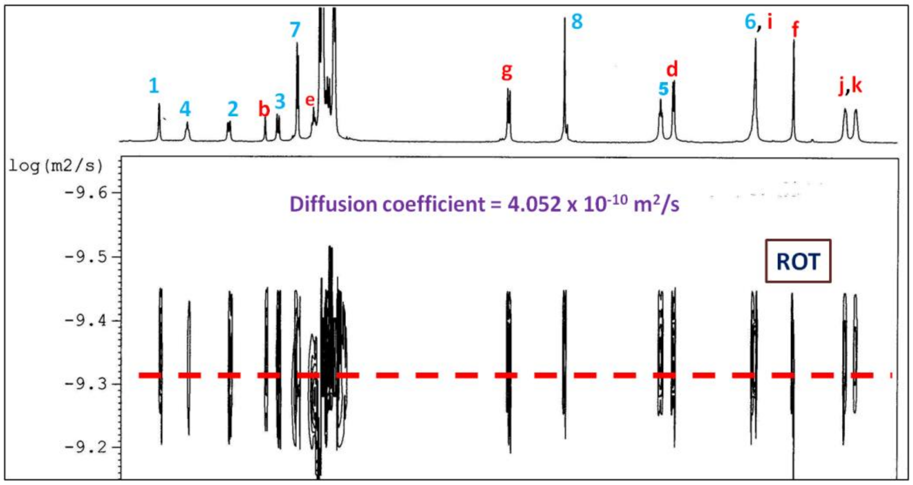


Fig. 20S *DOSY-NMR spectrum of* ***ROT*** *in* $CDCl_3$ *at 298K (500 MHz)*

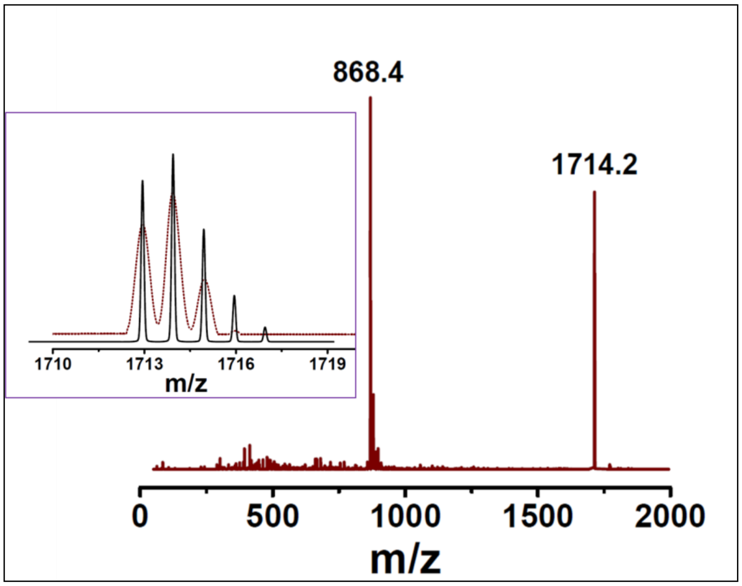


Fig. 21S *ESI-MS (+ve mode) of* ***AcROT****, inset picture shows that the isotopic distribution pattern of* ***AcROT*** *(brown, bold) matches well with simulated data (black)*

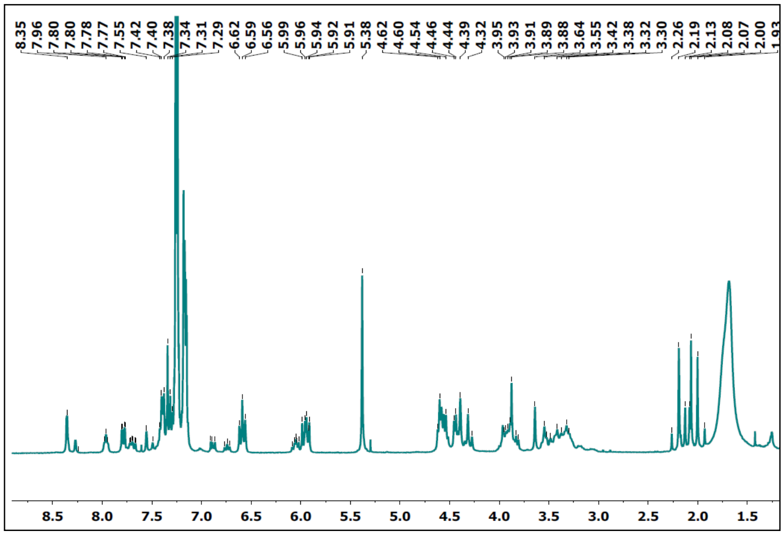


Fig. 22S *^{1}H-NMR spectrum of* ***AcROT*** *in CDCl$_3$ at 298K in 500 MHz*

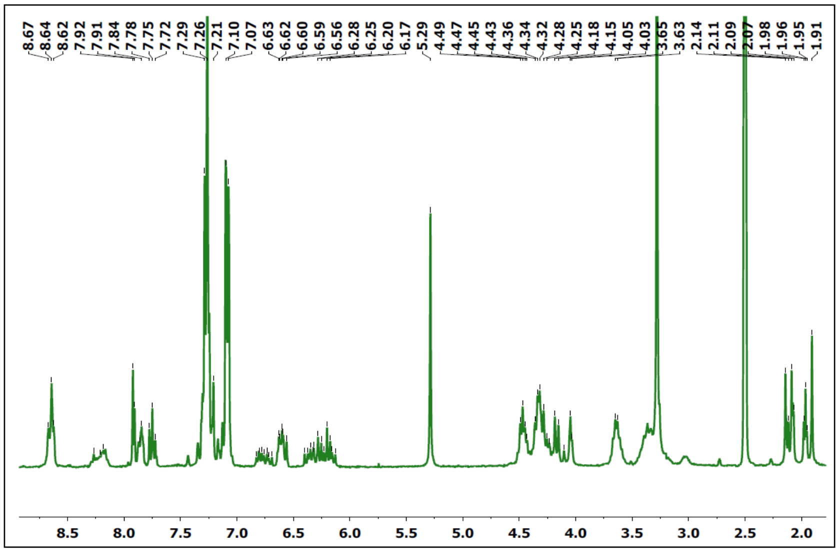


Fig. 23S *^{1}H-NMR spectrum of* ***AcROT*** *in DMSO-d$_6$ at 298K in 300 MHz*

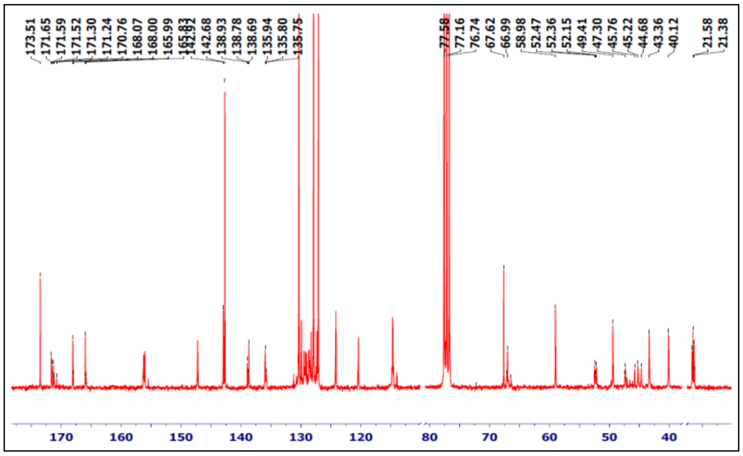


Fig. 24S a *^{13}C-NMR spectrum of* ***AcROT*** *in CDCl$_3$ (75MHz) at 298K*

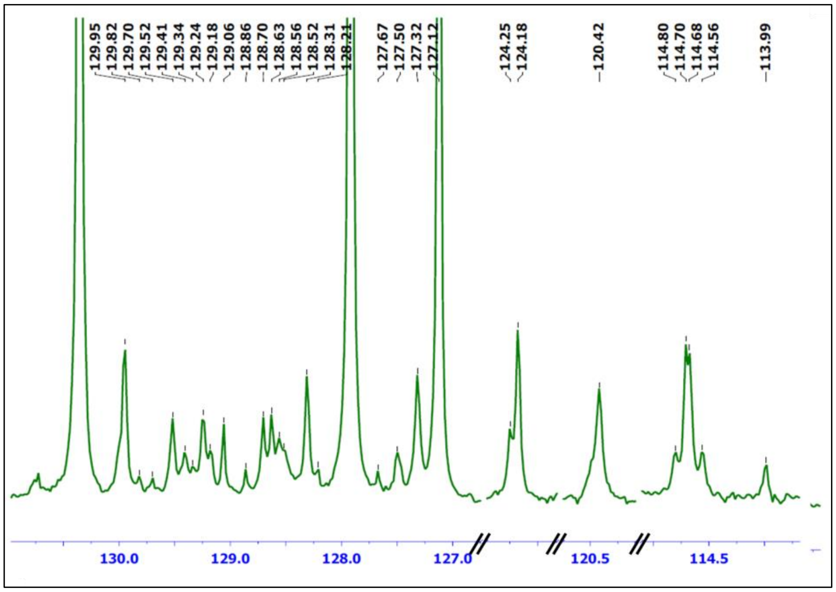


Fig. 24S b *Expanded ^{13}C-NMR spectrum of* ***AcROT*** *in CDCl$_3$ (75MHz) at 298K*

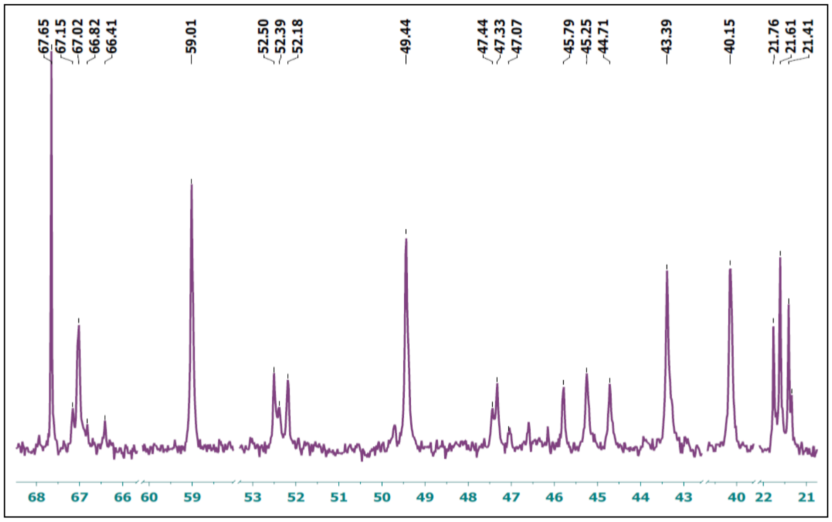


***Fig. 24S c** Expanded ^{13}C-NMR spectrum of **AcROT** in $CDCl_3$ (75MHz) at 298K*

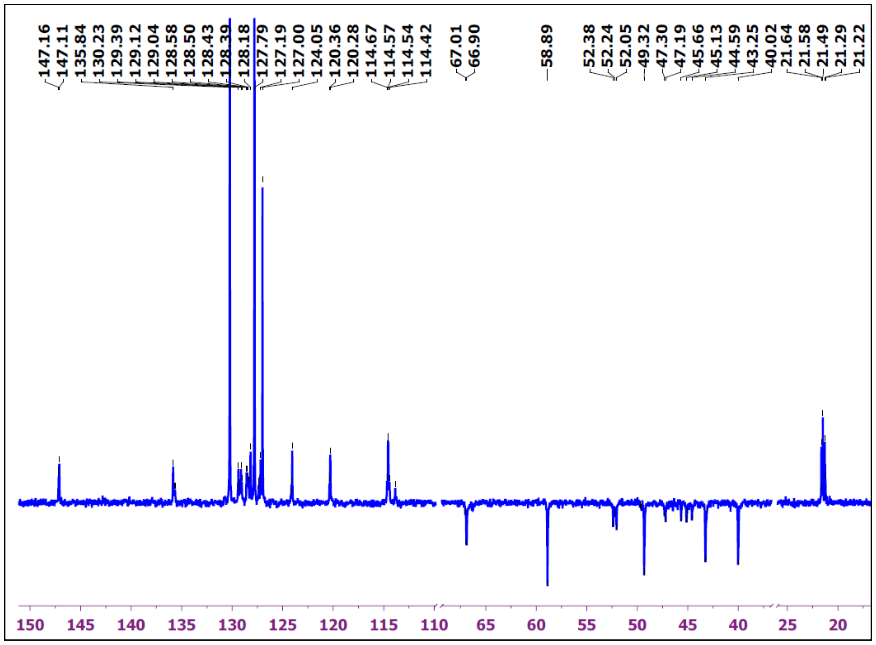


***Fig. 25S a.** DEPT-135 spectrum of **AcROT** in $CDCl_3$*

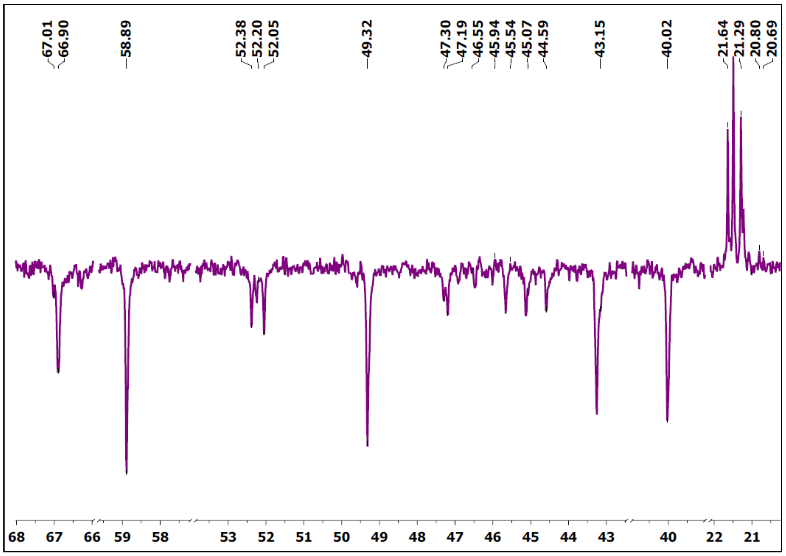


***Fig. 25S b** Expanded DEPT-135 spectrum of **AcROT** in $CDCl_3$*

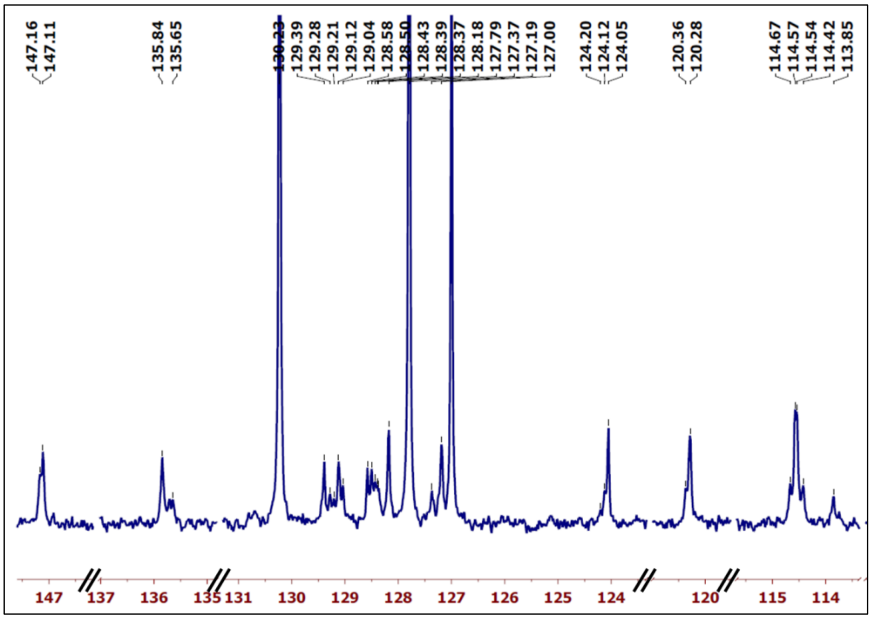
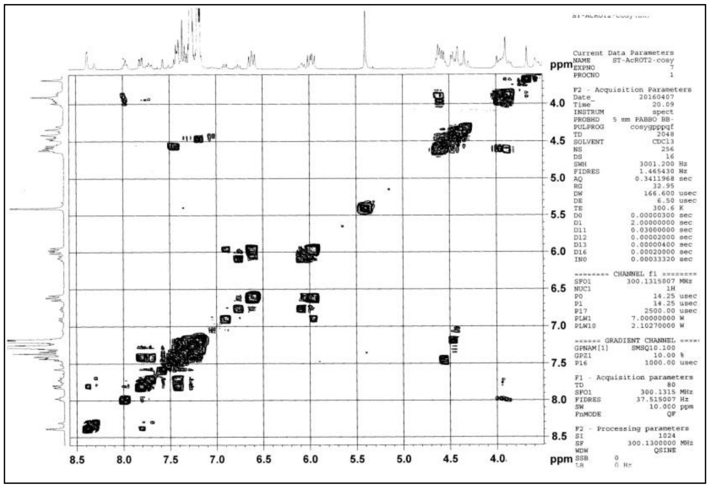
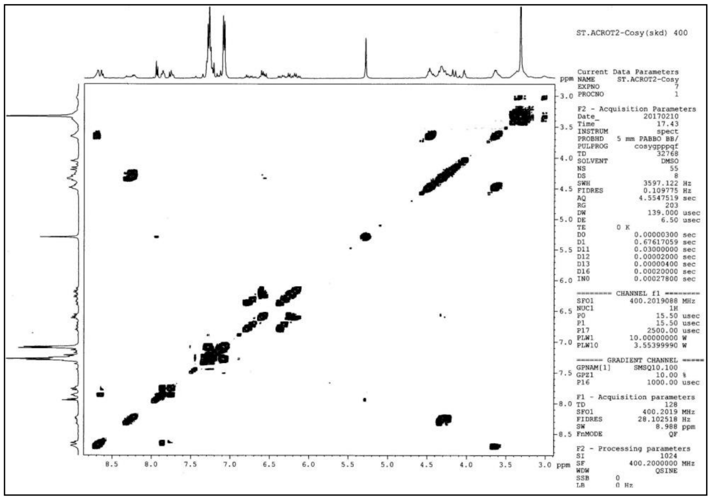


***Fig. 25S c.** Expanded DEPT-135 spectrum of **AcROT** in $CDCl_3$*



```
Current Data Parameters
NAME        ST-AcROT2-cosy
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160407
Time                 20.09
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG         cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                     256
DS                      16
SWH               3001.200 Hz
FIDRES            1.465430 Hz
AQ               0.3411968 sec
RG                   32.95
DW                 166.600 usec
DE                    6.50 usec
TE                   300.6 K
D0              0.00000300 sec
D1              2.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00033320 sec

======== CHANNEL f1 ========
SFO1           300.1315007 MHz
NUC1                    1H
P0                   14.25 usec
P1                   14.25 usec
P17                2500.00 usec
PLW1            7.00000000 W
PLW10           2.10270000 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                      80
SFO1              300.1315 MHz
FIDRES           37.515007 Hz
SW                  10.000 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             300.1300000 MHz
WDW                  QSINE
SSB        0
LB         0 Hz
```

Fig. 26S *^{1}H-^{1}H COSY NMR spectrum of **AcROT** at 298K in $CDCl_3$ at 300MHz*



```
ST.ACROT2-Cosy(skd) 400

Current Data Parameters
NAME        ST.ACROT2-Cosy
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170210
Time                 17.43
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG         cosygpppqf
TD                   32768
SOLVENT               DMSO
NS                      55
DS                       8
SWH               3597.122 Hz
FIDRES            0.109775 Hz
AQ               4.5547519 sec
RG                     203
DW                 139.000 usec
DE                    6.50 usec
TE         0 K
D0              0.00000300 sec
D1              0.67617059 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00027800 sec

======== CHANNEL f1 ========
SFO1           400.2019088 MHz
NUC1                    1H
P0                   15.50 usec
P1                   15.50 usec
P17                2500.00 usec
PLW1           10.00000000 W
PLW10           3.55399990 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     128
SFO1              400.2019 MHz
FIDRES           28.102518 Hz
SW                   8.988 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             400.2000000 MHz
WDW                  QSINE
SSB        0
LB         0 Hz
```

Fig. 27S *^{1}H-^{1}H COSY NMR spectrum of **AcROT** at 298K in DMSO-d_6 at 400MHz*

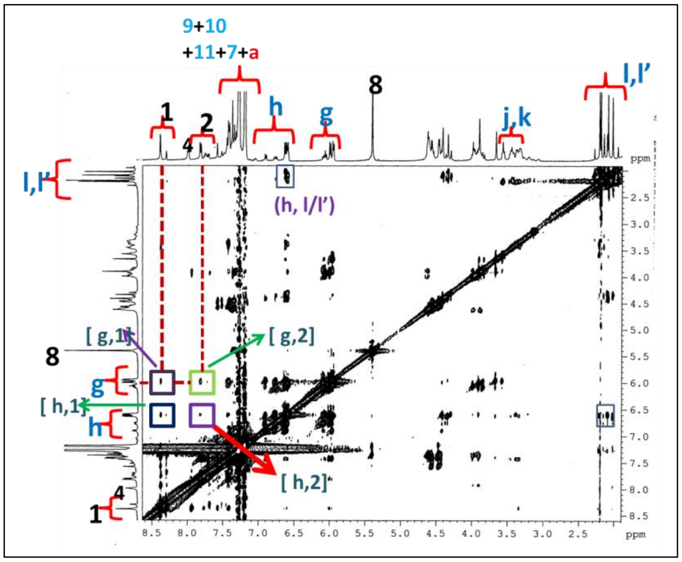


Fig. 28S.a . *^{1}H-^{1}H-ROESY NMR spectrum of* ***AcROT*** *at 298K in CDCl$_3$ at 500MHz*

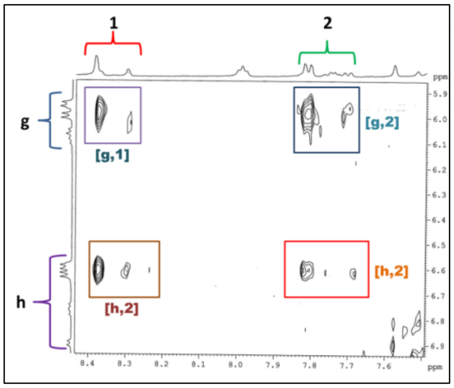
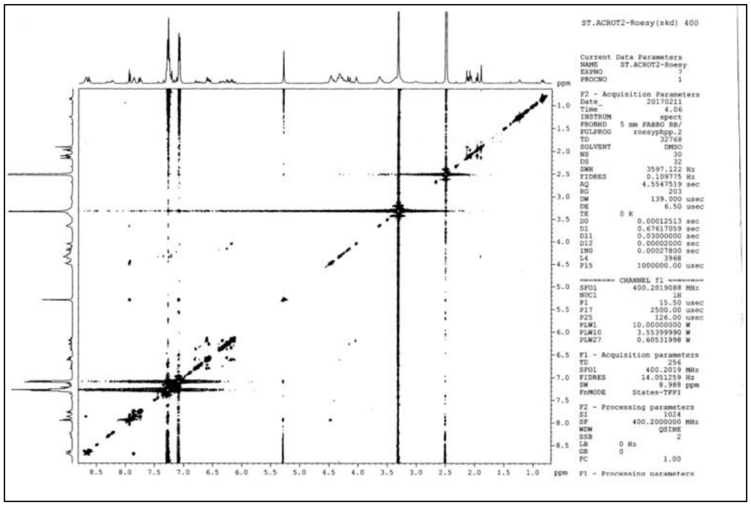


Fig. 28S.b *^{1}H-^{1}H-ROESY NMR spectrum of* ***AcROT*** *at 298K in CDCl$_3$ at 500MHz*



```
ST.ACROT2-Roesy(skd) 400

Current Data Parameters
NAME      ST.ACROT2-Roesy
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170211
Time                 4.06
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG      roesyphpp.2
TD                  32768
SOLVENT              DMSO
NS                     30
DS                     32
SWH              3597.122 Hz
FIDRES           0.109775 Hz
AQ              4.5547519 sec
RG                    203
DW                139.000 usec
DE                   6.50 usec
TE        0 K
DO             0.00012513 sec
D1             0.67617059 sec
D11            0.03000000 sec
D12            0.00002000 sec
IN0            0.00027800 sec
L4                   3968
P15            1000000.00 usec

======== CHANNEL f1 ========
SFO1          400.2019088 MHz
NUC1                   1H
P1                  15.50 usec
P17               2500.00 usec
P25                126.00 usec
PLW1          10.00000000 W
PLW10          3.55399990 W
PLW27          0.60531998 W

F1 - Acquisition parameters
TD                    256
SFO1             400.2019 MHz
FIDRES          14.051259 Hz
SW                  8.988 ppm
FnMODE        States-TPPI

F2 - Processing parameters
SI                   1024
SF            400.2000000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                   1.00

F1 - Processing parameters
```

Fig. 29S *^{1}H-^{1}H ROESY NMR spectrum of* ***AcROT*** *at 298K in DMSO-d_6 at 300MHz*

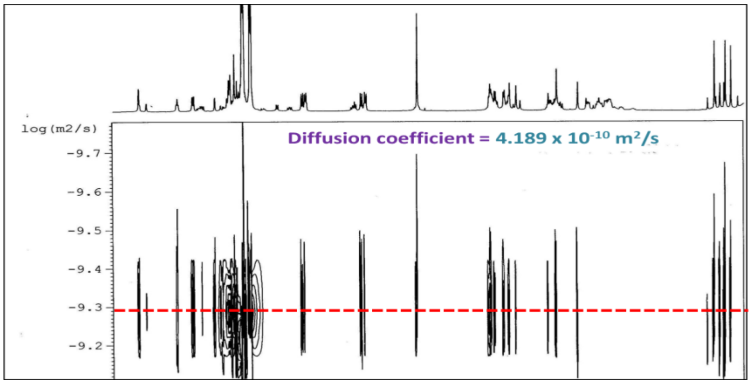


Fig. 30S *DOSY NMR spectrum of* ***AcROT*** *at 298K in $CDCl_3$ (500 MHz)*

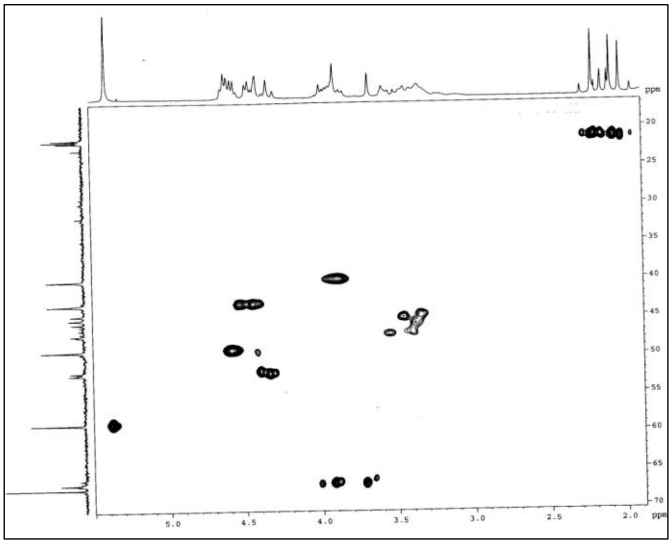


Fig. 31S a *HSQC NMR spectrum of* ***AcROT*** *at 298K in* $CDCl_3$ *(300 MHz)*

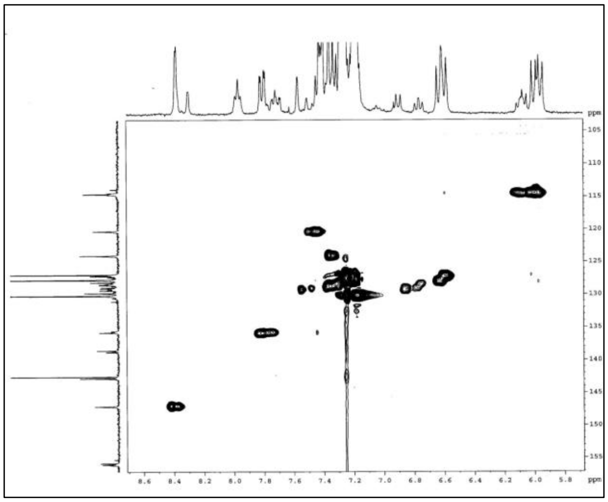


Fig. 31A b. *HSQC NMR spectrum of* ***AcROT*** *at 298K in* $CDCl_3$ *(300 MHz)*

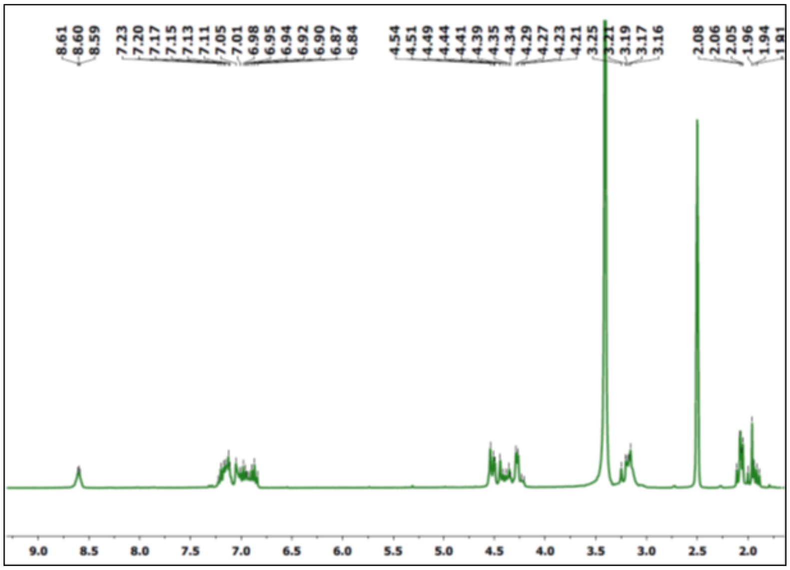


Fig. 32S. *^{1}H-NMR of AcMC in DMSO-d_6 recorded in 300 MHz at 298K*

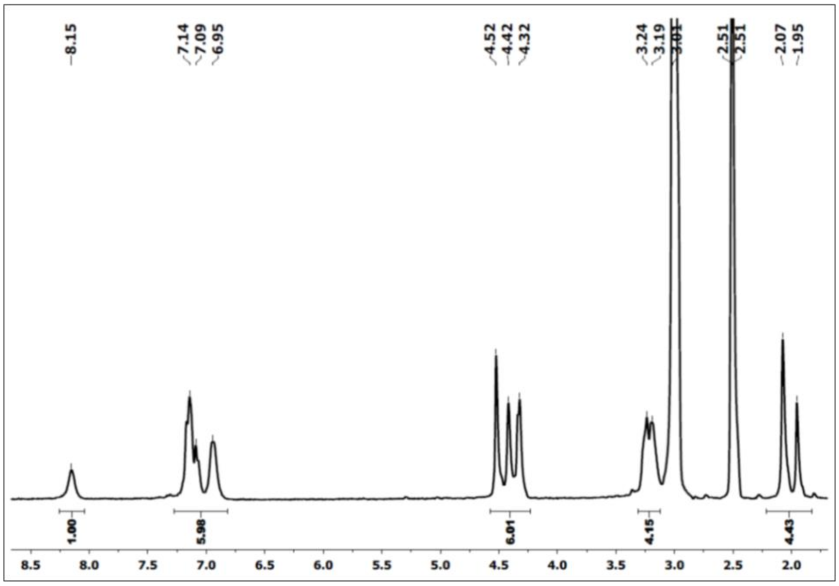


Fig. 32S *^{1}H-NMR of AcMC in DMSO-d_6 recorded in 300 MHz at 380K*

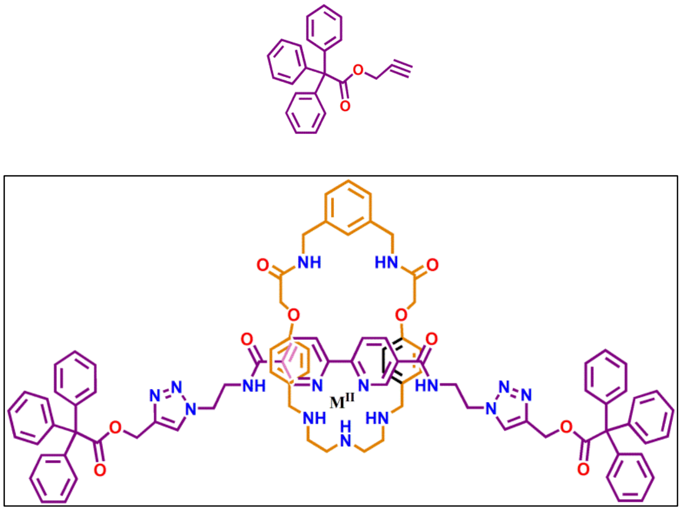


Chart 1S *Chemical diagram of stopper (STP, Top) and metallated rotaxane (bottom)*

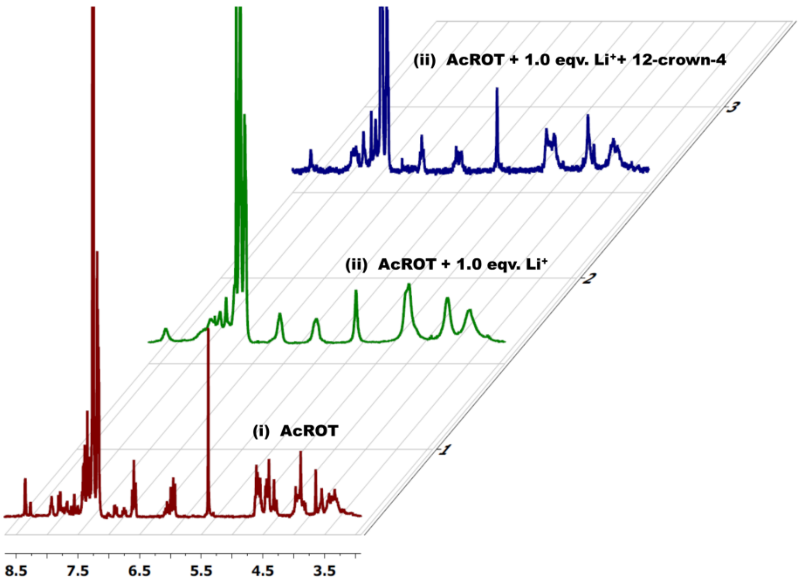


Fig.34S *(i) ^{1}H-NMR of **AcROT**; (ii) **AcROT** + Li$^+$; (iii) **AcROT** + Li$^+$+ 12-crown-4 in 9:1 CDCl$_3$:CD$_3$CN solvent mixture*

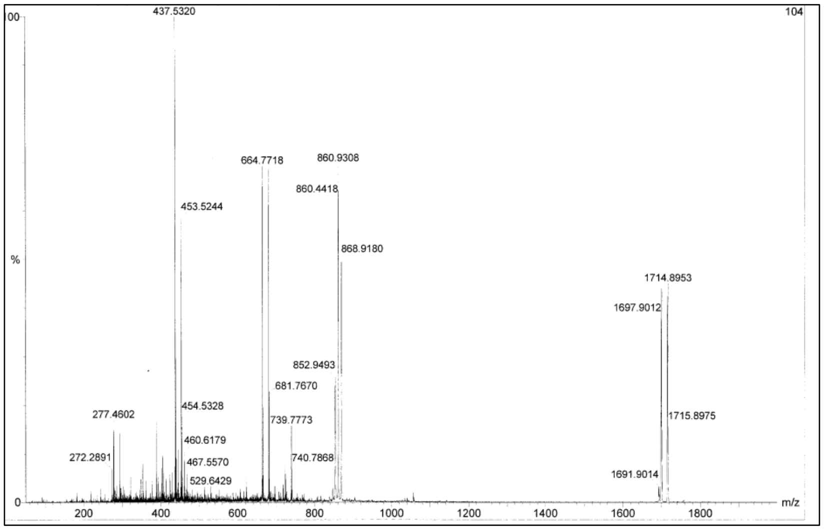


Fig. 35S *ESI-MS (+ve mode) of* ***AcROT*** *in presence of* Li^+

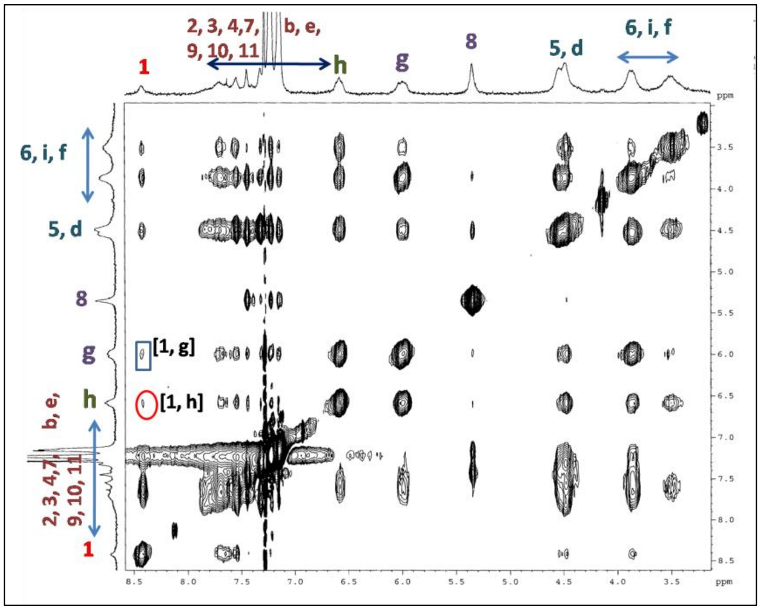


Fig.36S *NOESY-NMR spectrum of Ac****ROT*** *in presence of 1.0 eqv of Li+*

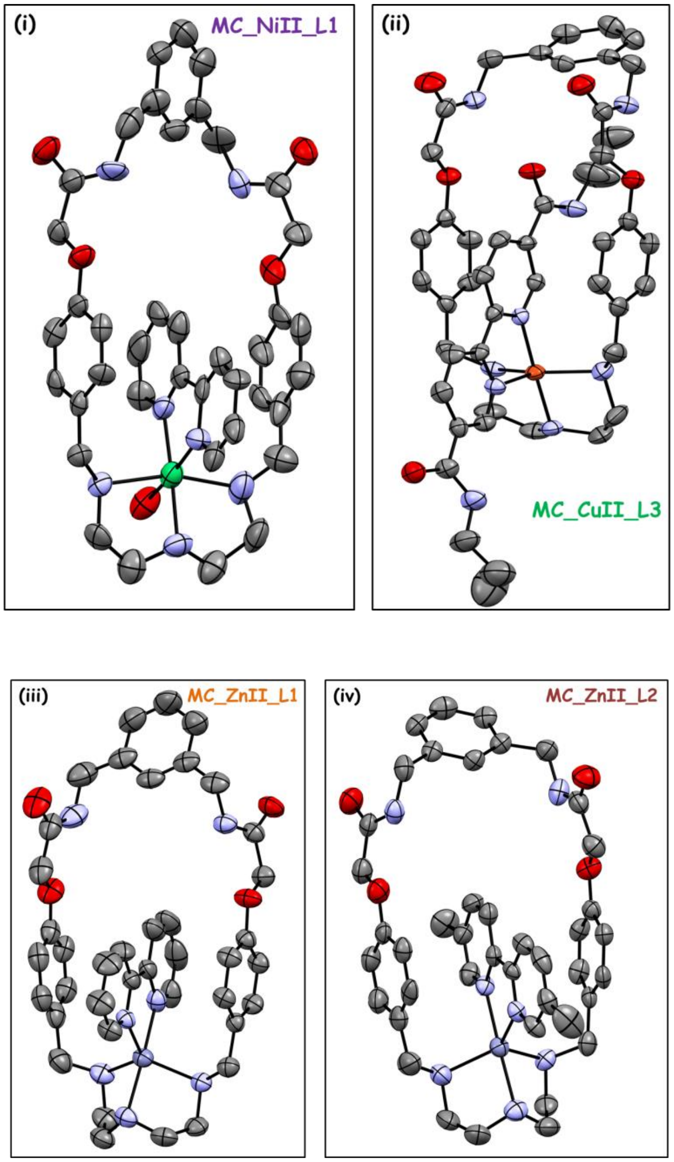


Fig.37S *ORTEP diagrams of ternary complexes having ellipsoids of 50% probability level. H-atoms, solvent molecules and counter anions are omitted for clarity: (i) MC_NiII_L1, (ii) MC_CuII_L3, (iii) MC_ZnII_L1, (iv)MC_ZnII_L2.*

Table 1S Crystallographic Information Table for MC_NiII_L1

Compound reference	MC_NiII_L1
Chemical formula	$C_{42}H_{57}Cl_2N_7NiO_{16}$
Formula Mass	1045.55
Crystal system	Orthorhombic
a/Å	13.4733(8)
b/Å	18.3502(10)
c/Å	19.0508(11)
α/°	90
β/°	90
γ/°	90
Unit cell volume/Å^3	4710.1(5)
Temperature/K	150(2)
Space group	*P*212121
No. of formula units per unit cell, *Z*	4
No. of reflections measured	37485
No. of independent reflections	4883
R_{int}	0.0983
Final R_1 values ($I > 2\sigma(I)$)	0.0774
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1962
Final R_1 values (all data)	0.0992
Final $wR(F^2)$ values (all data)	0.2168
CCDC number	1562608

Table 2S Crystallographic Information Table for MC_CuII_L3

Compound reference	MC_CuII_L3
Chemical formula	$C_{48}H_{63}Cl_2CuN_9O_{16}$
Formula Mass	1156.51
Crystal system	Triclinic
a/Å	11.4266(13)
b/Å	13.2646(15)
c/Å	18.043(2)
α/°	95.793(3)
β/°	100.492(3)
γ/°	100.063(3)
Unit cell volume/Å^3	2622.6(5)
Temperature/K	150(2)
Space group	$P\bar{1}$
No. of formula units per unit cell, Z	2
No. of reflections measured	27801
No. of independent reflections	10602
R_{int}	0.0449
Final R_1 values ($I > 2\sigma(I)$)	0.0534
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1379
Final R_1 values (all data)	0.0868
Final $wR(F^2)$ values (all data)	0.1579
CCDC number	1562607

Table 3S Crystallographic Information Table for MC_ZnII_L1

Compound reference	MC_ZnII_L1
Chemical formula	$C_{80} H_{100} Cl_4 N_{14} O_{29} Zn_2$
Formula Mass	1994.19
Crystal system	Monoclinic
a/Å	18.714(5)
b/Å	12.905(5)
c/Å	20.081(5)
α/°	90
β/°	108.561(5)
γ/°	90
Unit cell volume/Å^3	4597(2)
Temperature/K	150(2)
Space group	*P*21/*n*
No. of formula units per unit cell, *Z*	2
No. of reflections measured	45297
No. of independent reflections	8571
R_{int}	0.1669
Final R_1 values ($I > 2\sigma(I)$)	0.0648
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1902
Final R_1 values (all data)	0.0878
Final $wR(F^2)$ values (all data)	0.2086
CCDC number	1562609

Table 4S Crystallographic Information Table for MC_ZnII_L2

Compound reference	MC_ZnII_L2
Chemical formula	$C_{42}H_{55}Cl_2N_7O_{15}Zn$
Formula Mass	1034.20
Crystal system	Orthorhombic
a/Å	15.565(3)
b/Å	19.148(3)
c/Å	31.764(5)
α/°	90
β/°	90
γ/°	90
Unit cell volume/Å^3	9467(3)
Temperature/K	150(2)
Space group	*Pbca*
No. of formula units per unit cell, Z	8
No. of reflections measured	109156
No. of independent reflections	8443
R_{int}	0.0967
Final R_1 values ($I > 2\sigma(I)$)	0.0643
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1769
Final R_1 values (all data)	0.0937
Final $wR(F^2)$ values (all data)	0.2001
CCDC number	1562610

For all the ternary complexes, the non-hydrogen atoms are refined with anisotropic displacement co-efficient (except some case which has been discussed later) and all hydrogen atoms were tried to fix geometrically at idealized positions. However, for most of the solvent molecules we are unsuccessful to fix H-atoms geometrically in proper position. We have tried our best to fix the H-atoms on the solvent molecules via SHELXL as well as OLEX2 software but unable to do so. Since H-atoms of the solvent molecules cannot be located at the difference Fourier map, we are unable to add them properly in most of the cases.

For the crystal structure of Ni^{II} *templated ternary complex, two methanol and one water solvent molecules are present. For methanol, we are not successful to place H-atoms on the methoxy groups. The moiety formula has written in calculated Check CIF as "*C_{40} H_{47} N_7 *Ni* O_5*,* 2(ClO_4)*,* 2(CH_3O)*,* H_2O*. The* CH_3O*, mentioned in the formula is not representing the methoxide ions. Instead they are the methanol solvents and the charge of metal ion is +2 which is counter balanced by two perchlorate anions.*

Likewise, for Cu^{II} template structure, two water molecules are present in the crystal lattice. In this case also we are unable to fix H-atoms on two water molecules and thus it remains apparently as two oxide ions. But actually these are not oxides. Although, the moiety formula is written as "$C_{48}H_{59}$ Cu N_9 O_6, 2(ClO_4), 2(O)" in the in calculated Check CIF, the naked O-atoms written within the parenthesis does not indicate the presence of two oxide ions. These are actually two water molecules. The metal ion is present in the +2 oxidation state, where the two perchlorate counter anions are balancing the di positive charge.

L1 threaded Zn^{II} templated pseudorotaxane crystal structure shows that it has three solvent water molecules. Two of them are disordered in two positions having occupancy of 0.33458 and 0.66542. The disordered atoms are isotropically refined using the FVAR command of the SHELXTL program.

We are unsuccessful to fix the H-atoms geometrically with the solvent molecules of L1 threaded Zn^{II} templated pseudorotaxane after repeated effort. The moiety formula written in in calculated Check CIF as in Table 3S, as 2(C_{40} H_{45} N_7 O_4 Zn),2($O_{0.84}$), 4(ClO_4), 3.33(O). The naked O-atoms written within the parenthesis do not indicate the presence of oxide ions. These are indeed solvent water molecules. Metal ion present here is in +2 oxidation state where two perchlorate counter anions are balancing the di-positive charges.

Similarly, L2 threaded ternary complex of Zn^{II} consist of three water molecules. Here also we are unable to fix H-atoms properly. The moiety formula is written in crystallographic information table (Table 4S) and in CIF file as C_{42} H_{49} N_7O_4 Zn, 2(ClO_4), 3(O). These naked O-atoms are not the oxide ions. These are solvent water molecules. The anchoring metal ion is doubly charged which is balanced by two perchlorate counter anions.

However, according to reviewer's suggestion we have tried to adjust the moiety formula and sum formula in the CIF and re-refined the structure and the results obtained are tabulated in Table 1S - 4S .

The above discussion section is mentioned in the main text. However, for clarity and better understanding, we have again placed it here and the section is exactly same as in the main text.