

Supplementary Information

Naphthalene containing amino-ether macrocycle based Cu(II) templated [2]pseudorotaxanes and OFF/ON fluorescence switching via axle substitution

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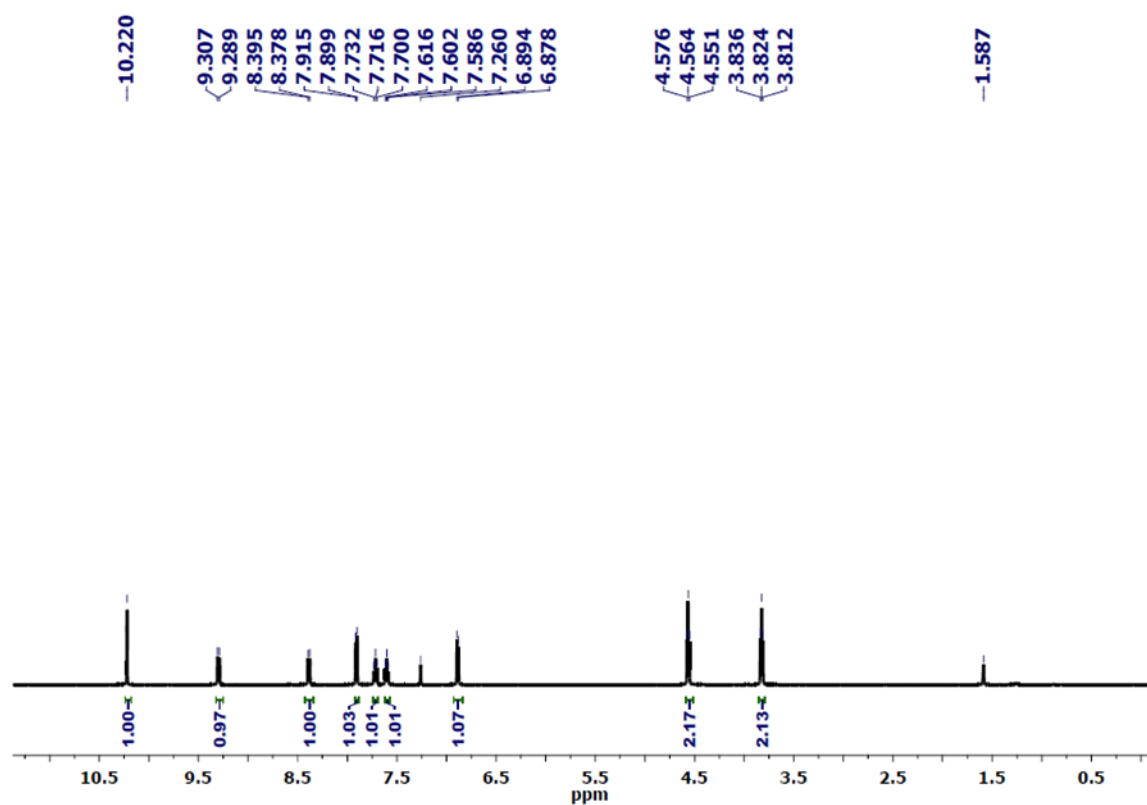


Figure 1S: ¹H-NMR spectrum of compound A in CDCl₃ (500 MHz) at 298 K.

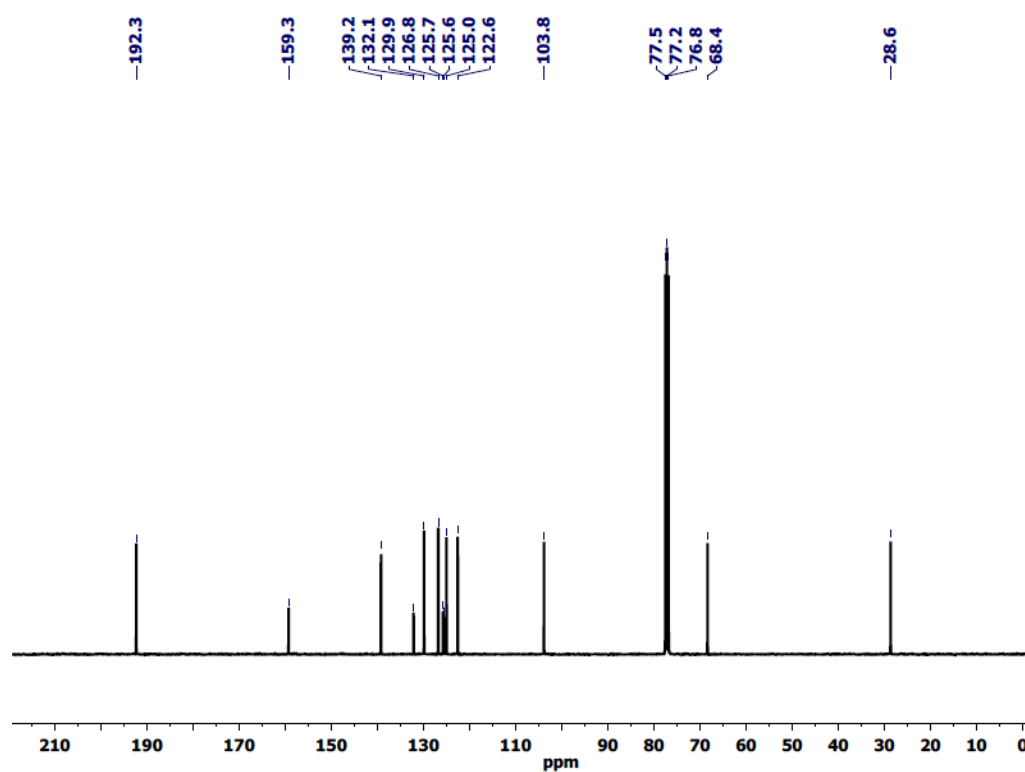


Figure 2S: ¹³C-NMR spectrum of compound A in CDCl₃ (100 MHz) at 298 K.

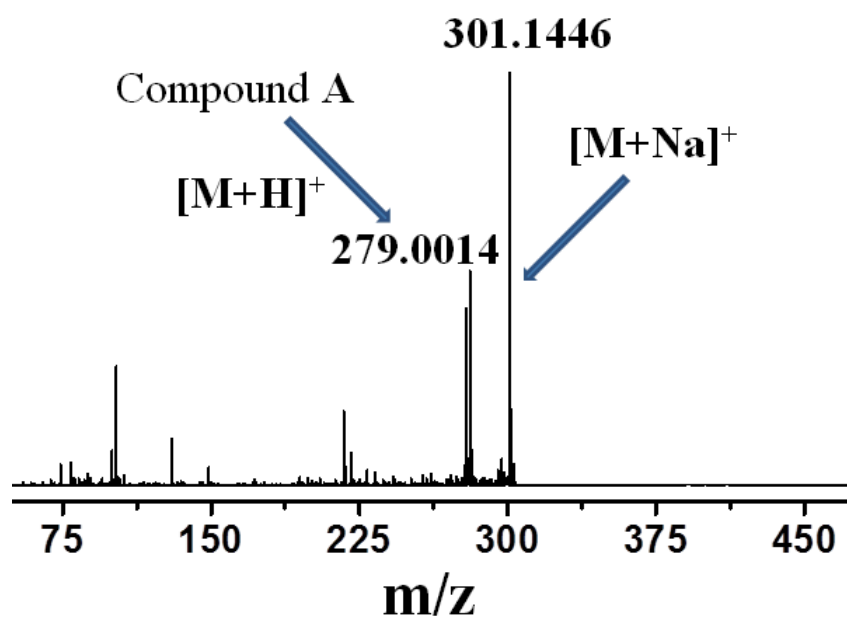


Figure 3S: ESI-MS(+ve) spectrum of compound A.

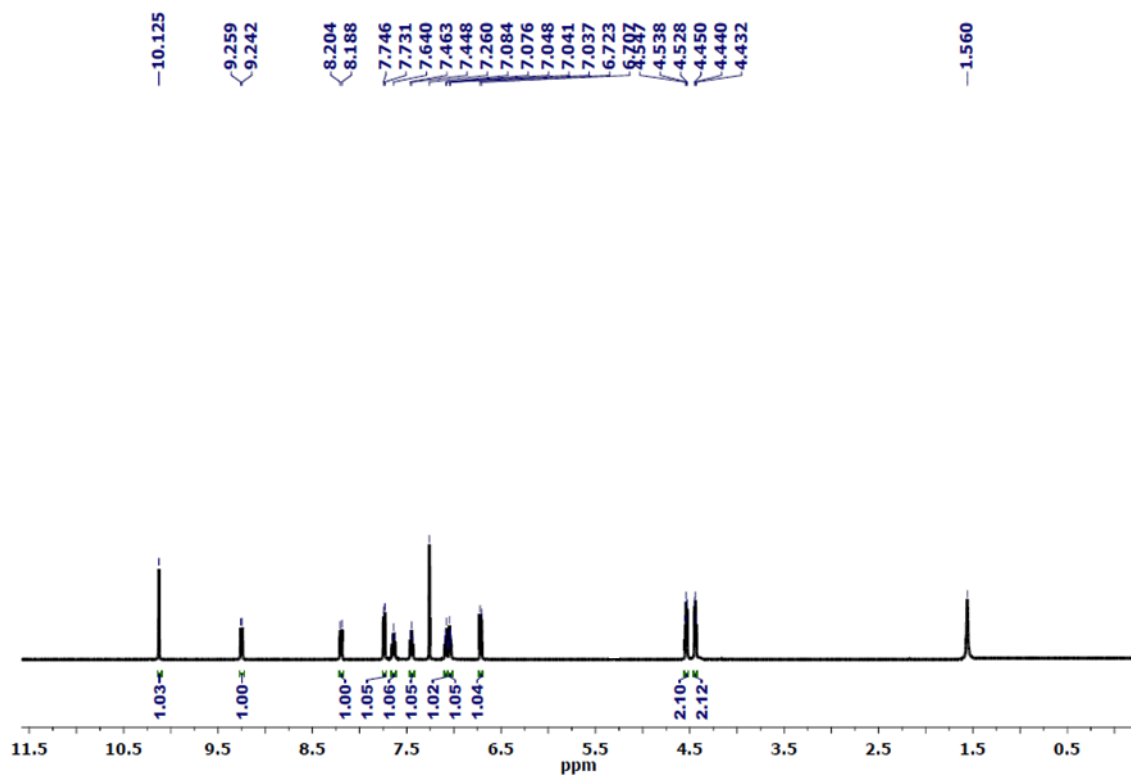


Figure 4S: ^1H -NMR spectrum of compound B in CDCl_3 (500 MHz) at 298 K.

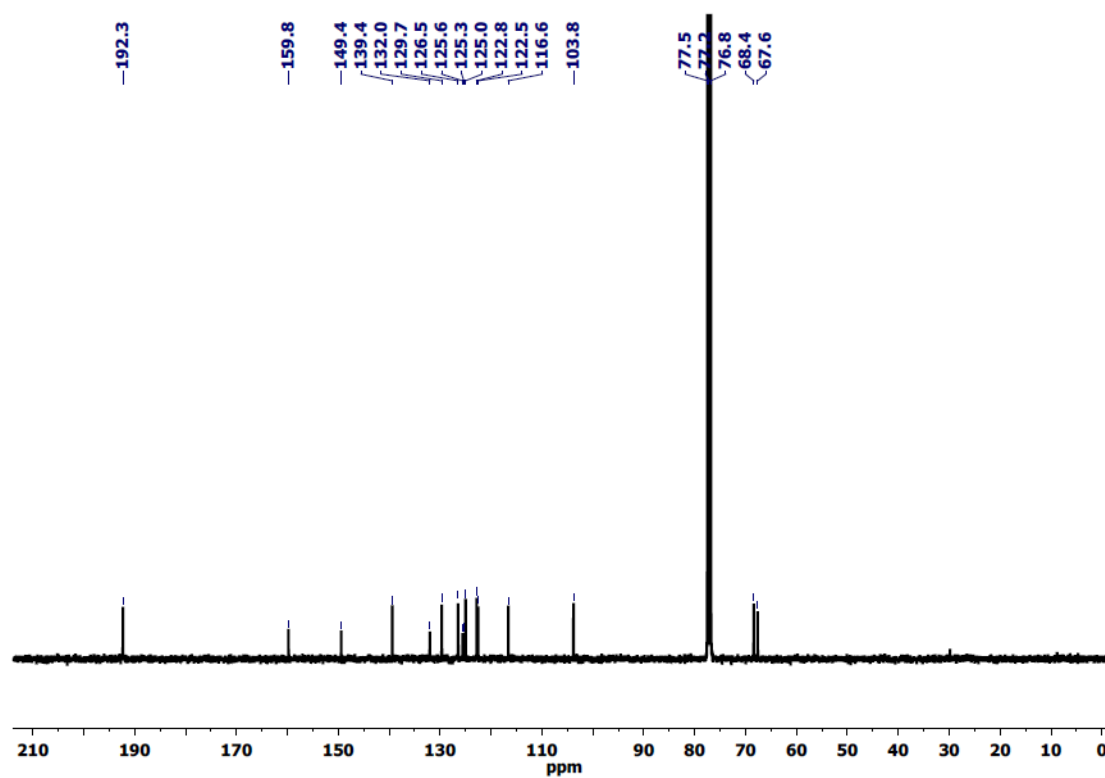


Figure 5S: ^{13}C -NMR spectrum of compound **B** in CDCl_3 (100 MHz) at 298 K.

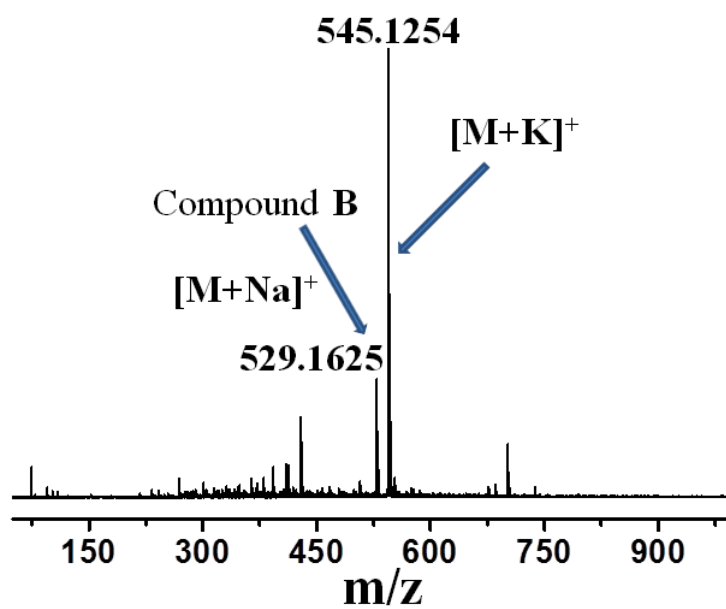


Figure 6S: ESI-MS (+ve) spectrum of compound **B**.

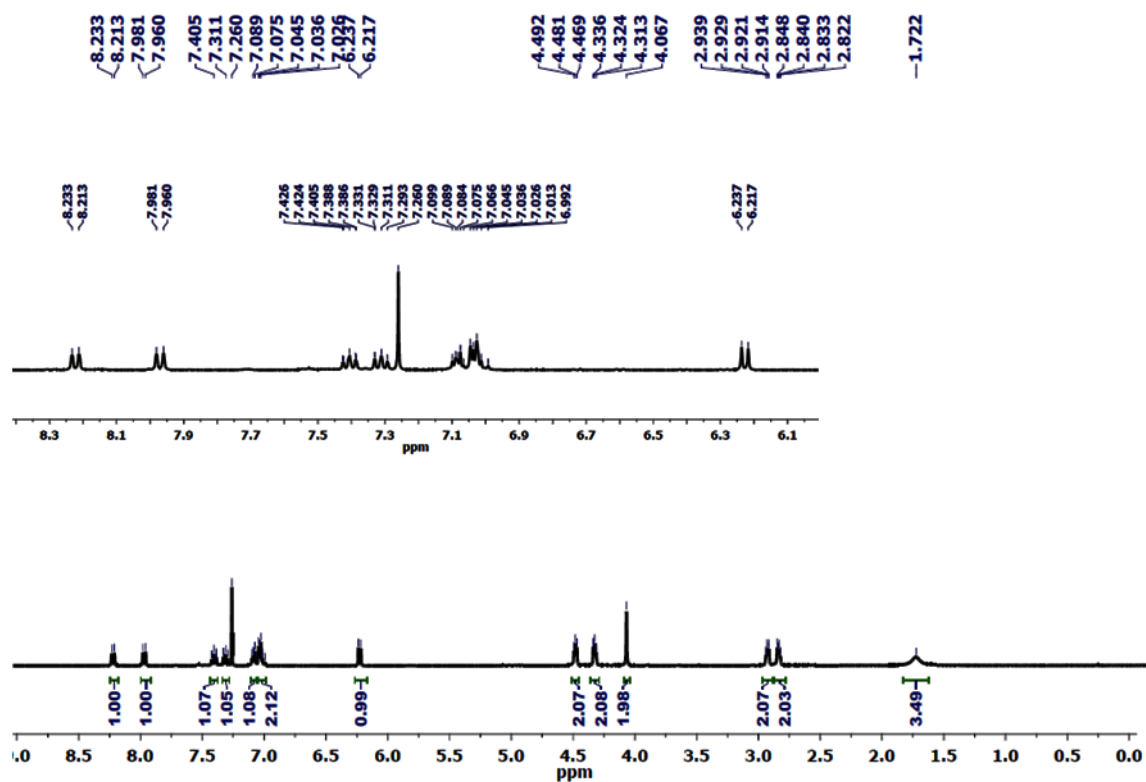


Figure 7S: ^1H -NMR spectrum of NaphMC in CDCl_3 (400 MHz) at 298 K.

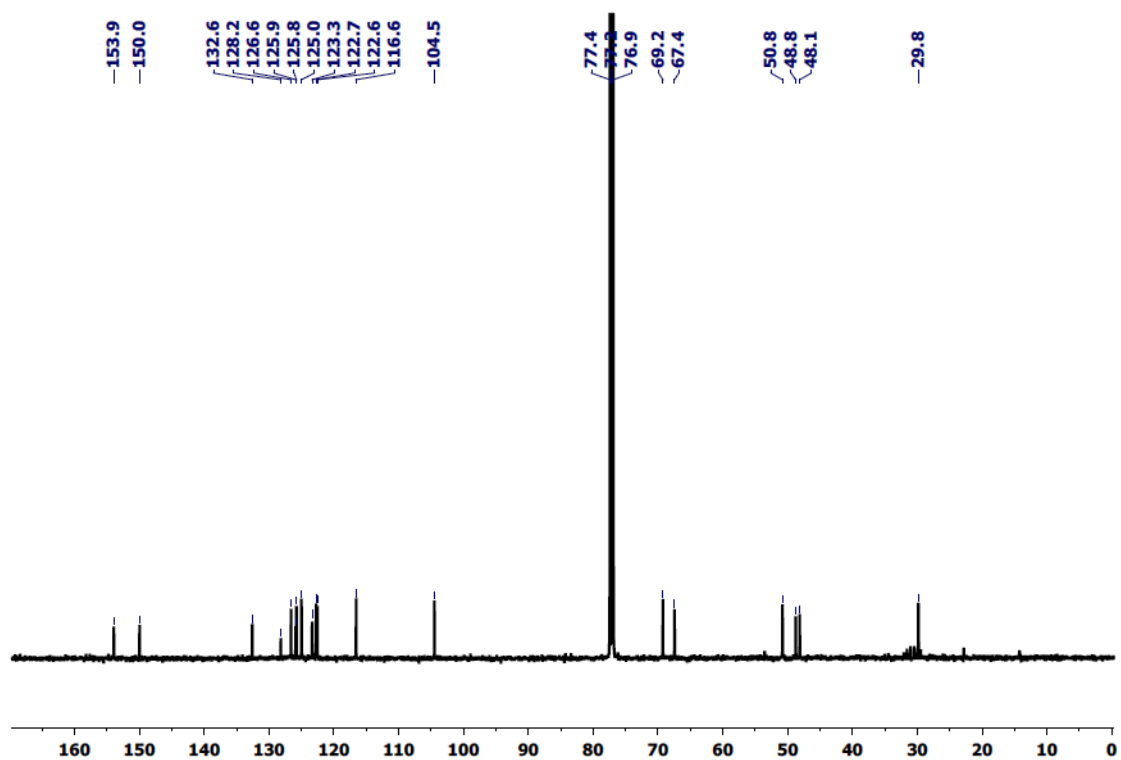


Figure 8S: ^{13}C -NMR spectrum of NaphMC in CDCl_3 (125 MHz) at 298 K.

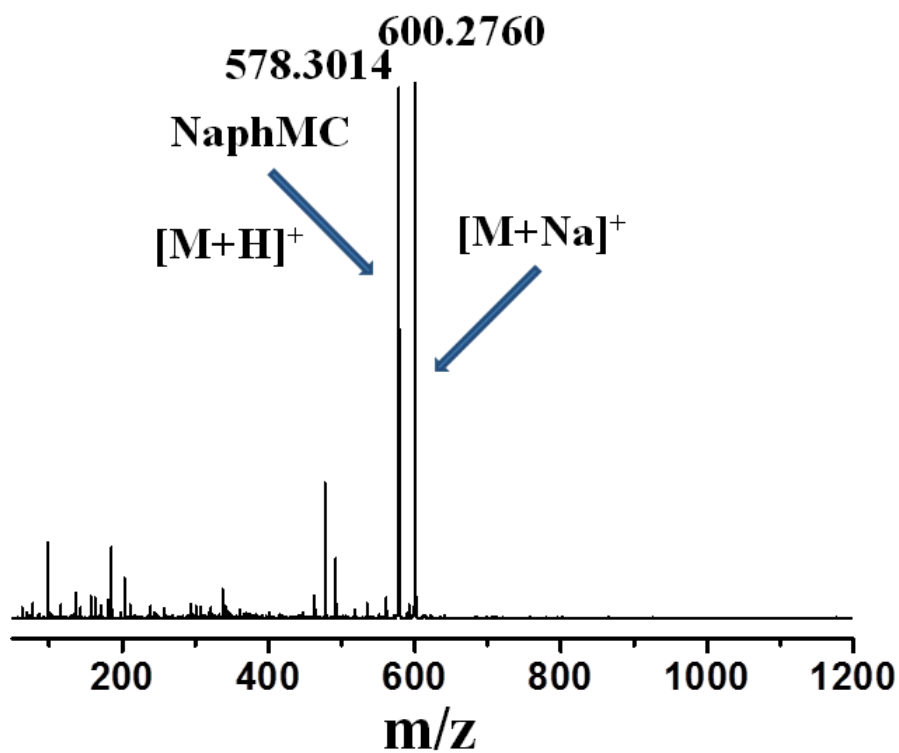


Figure 9S: ESI-MS(+ve) spectrum of NaphMC.

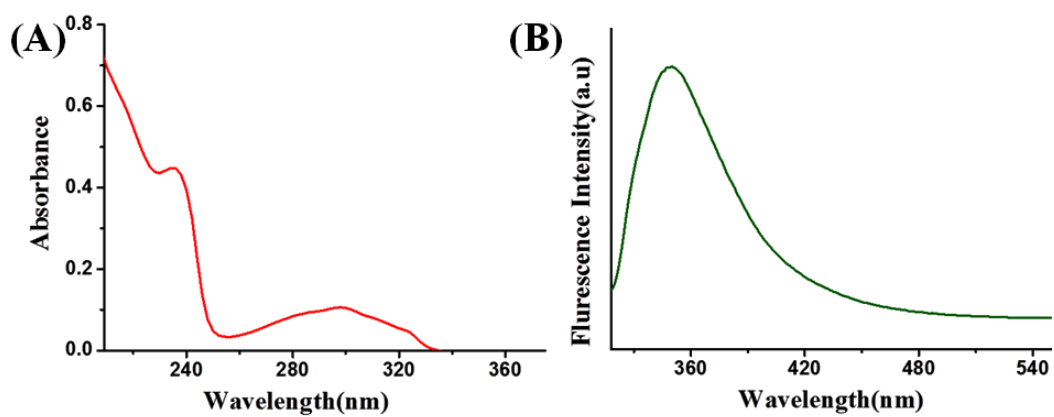


Figure 10S: (A) UV/Vis and (B) emission spectra of NaphMC(1×10^{-5} M) in dry THF at 298 K, $\lambda_{\text{exc}} = 300$ nm.

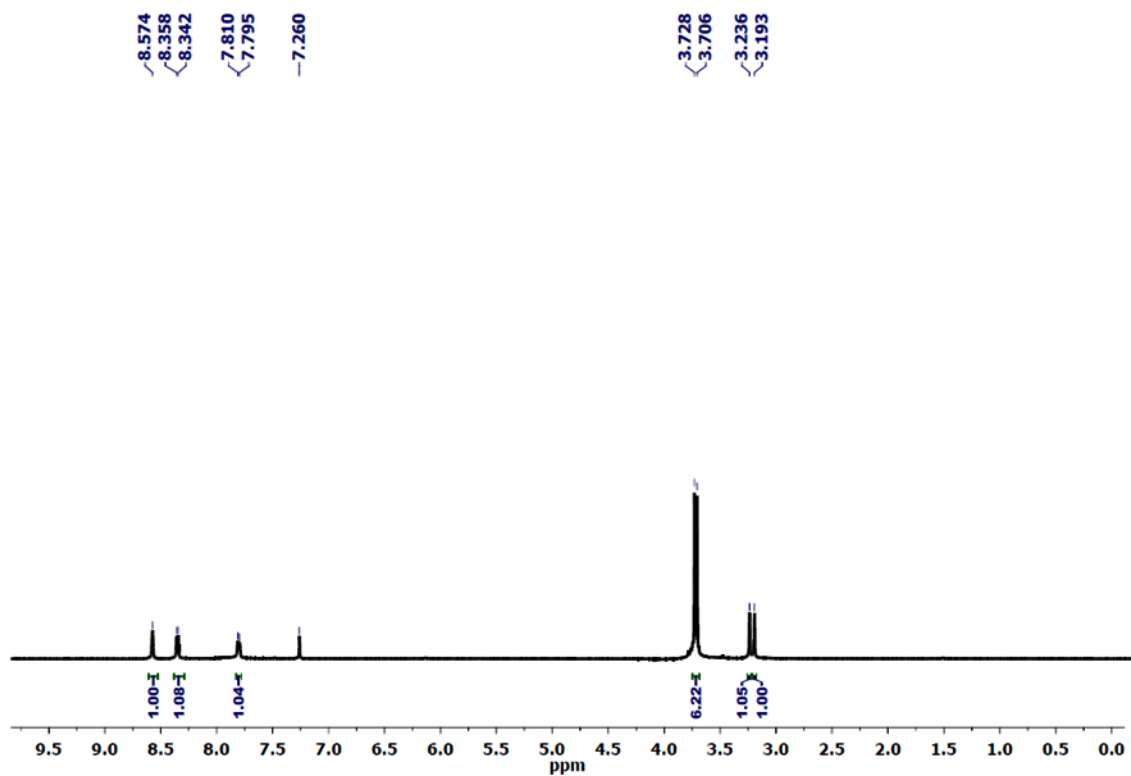


Figure 11S: ¹H-NMR spectrum of compound **D** in CDCl₃ (500 MHz) at 298 K.

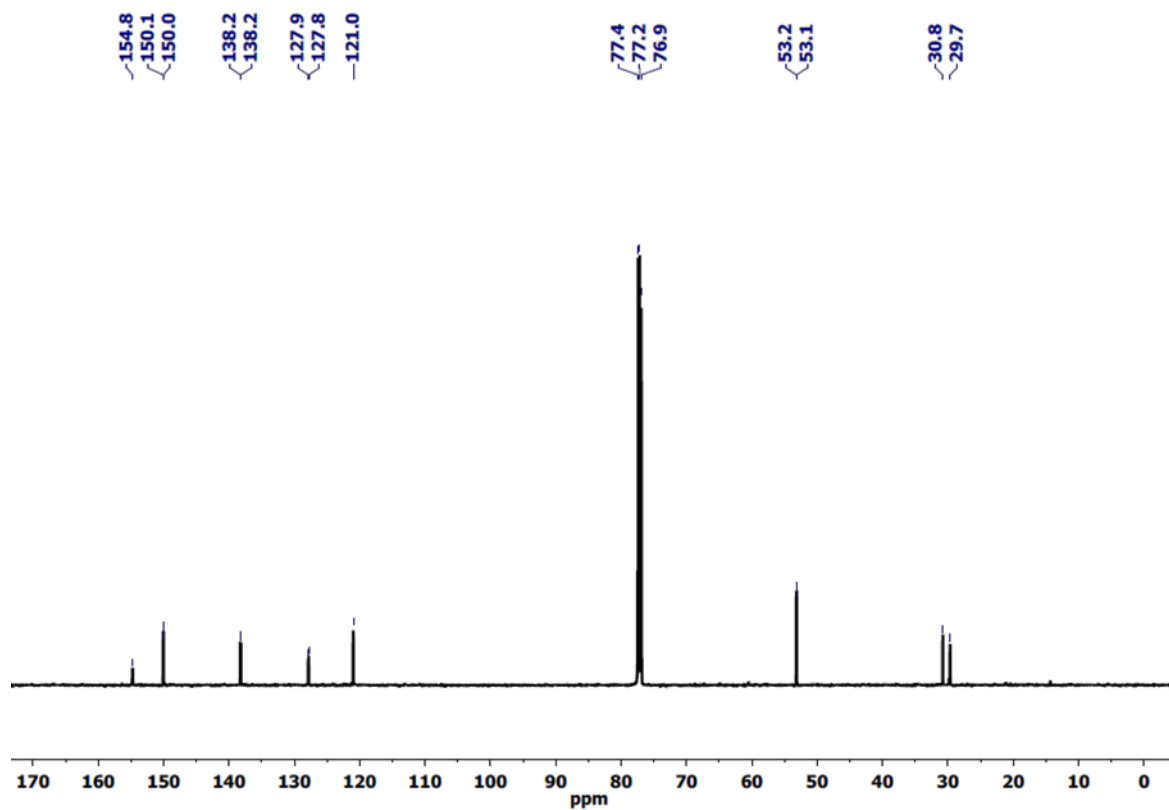


Figure 12S: ¹³C-NMR spectrum of compound **D** in CDCl₃ (125 MHz) at 298 K.

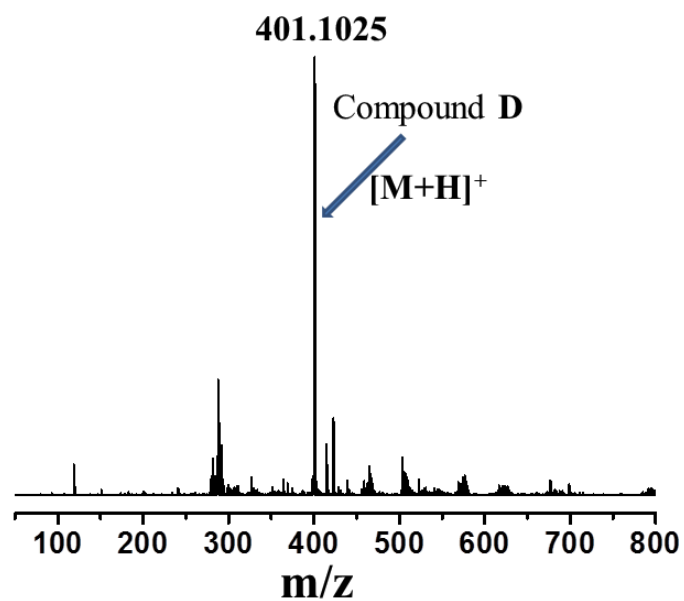


Figure 13S: ESI-MS(+ve) spectrum of compound D.

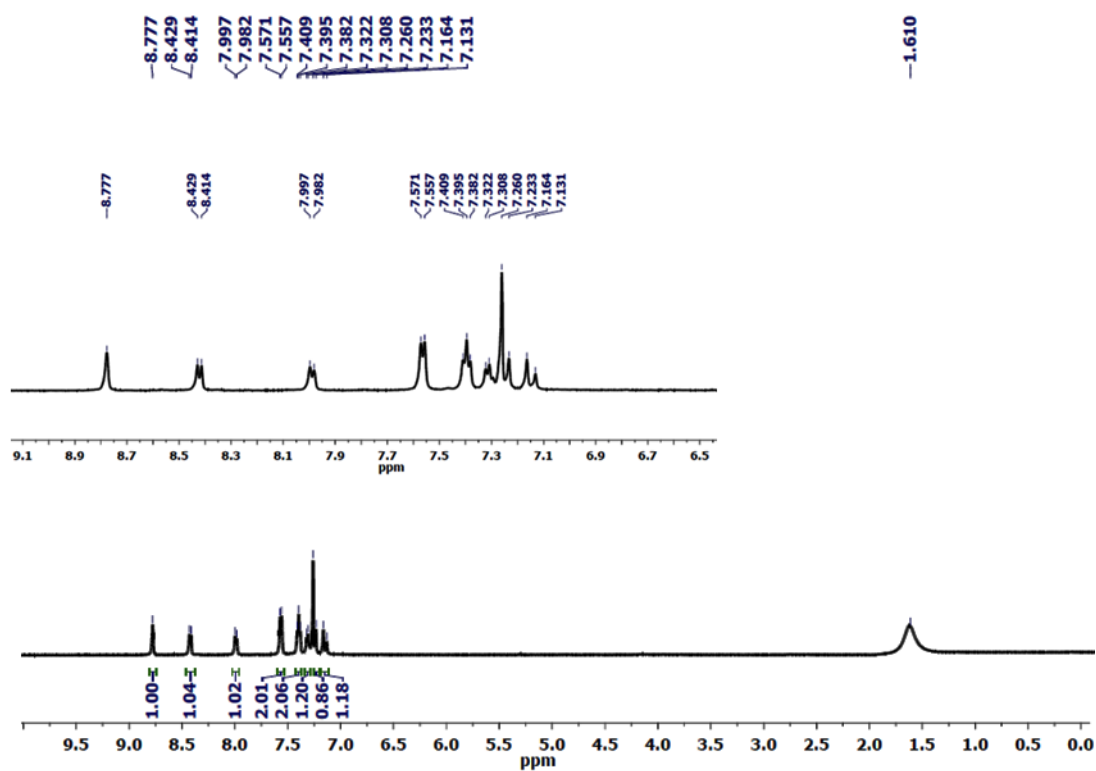


Figure 14S: 1H -NMR spectrum of L3 in $CDCl_3$ (500 MHz) at 298 K.

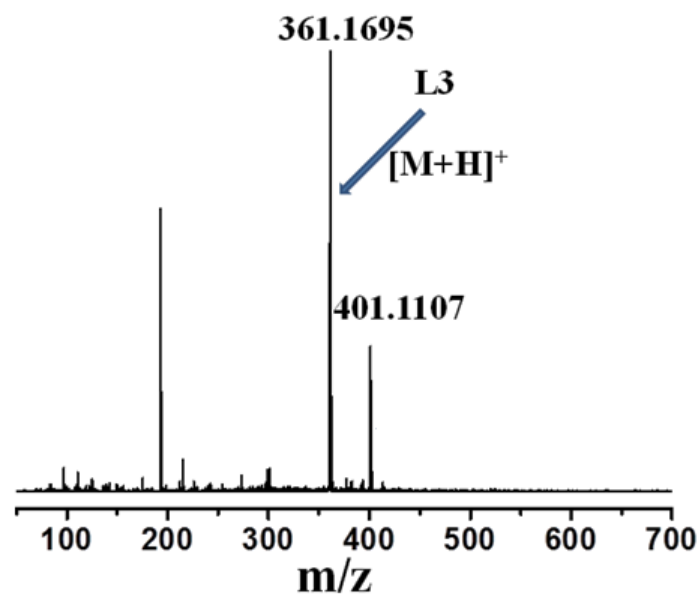


Figure 15S: ESI-MS(+ve) spectrum of L3.

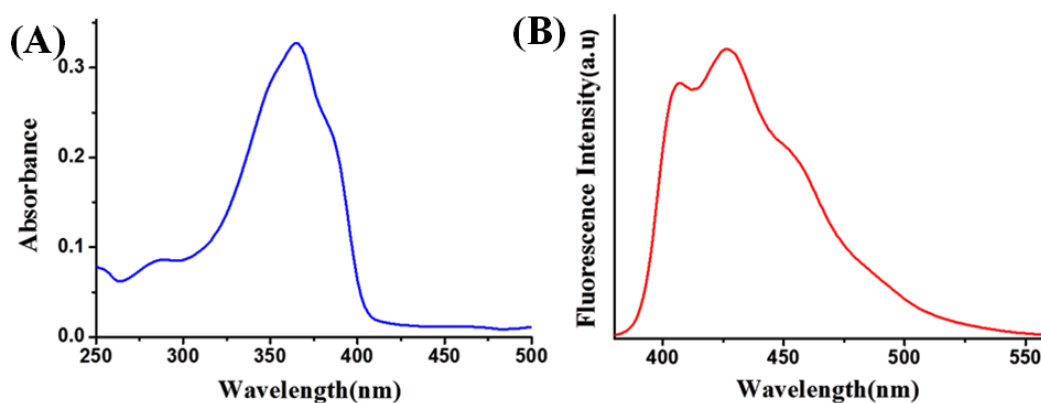
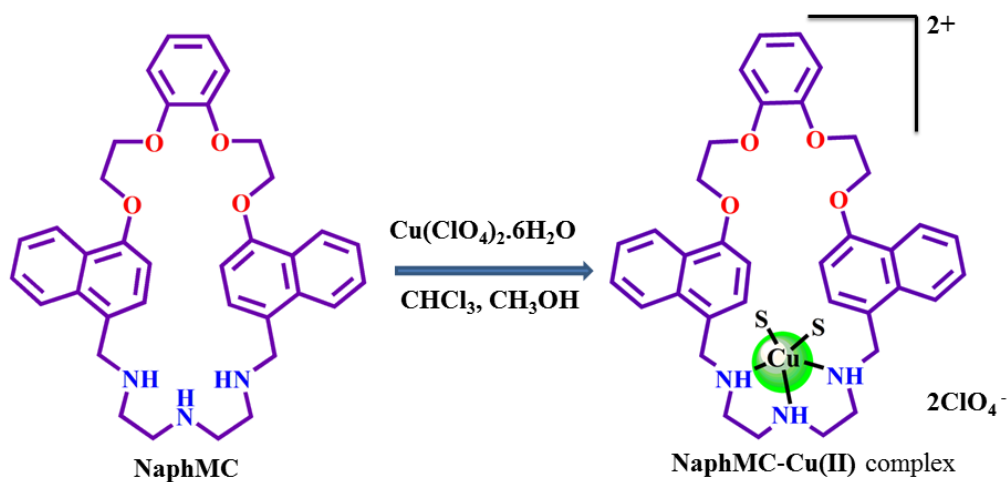


Figure 16S: (A) UV/Vis and (B) emission spectra of L3 (1×10^{-5} M) in dry THF at 298 K, $\lambda_{\text{exc}} = 362$ nm.



Scheme 1S. Synthetic route of the NaphMC- Cu^{II} complex [S= solvent molecule].

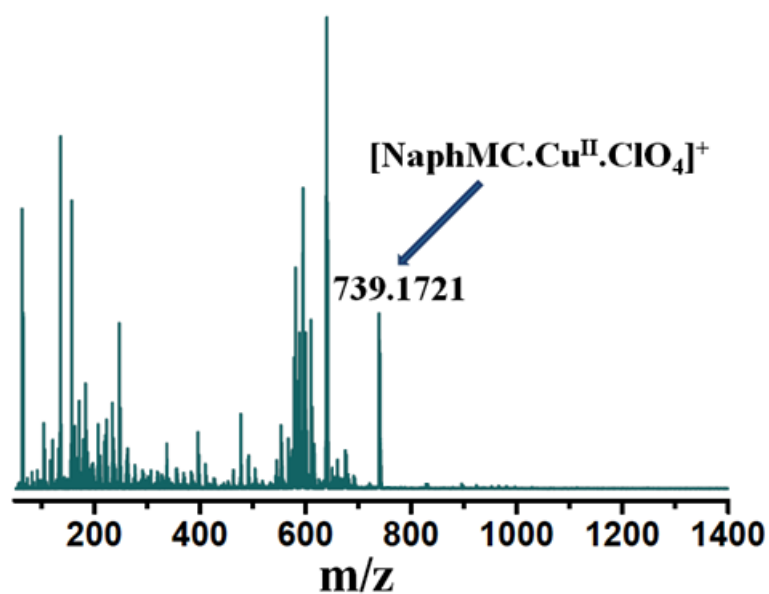


Figure 17S: ESI-MS(+ve) spectrum of **NaphMC-Cu^{II}** complex.

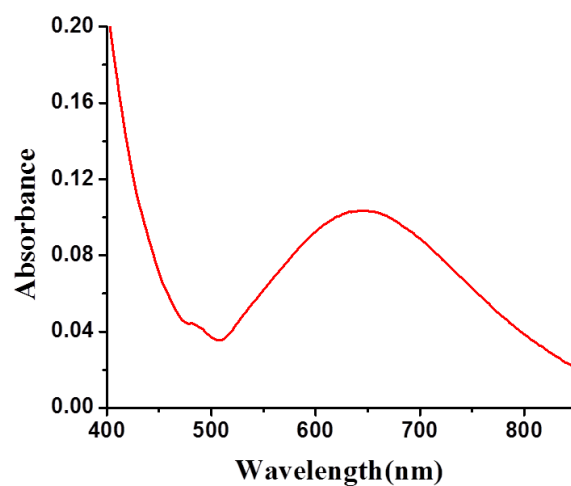


Figure 18S: Characteristic UV/Vis spectrum of **NaphMC-Cu^{II}** complex in CH_3OH at 298K.

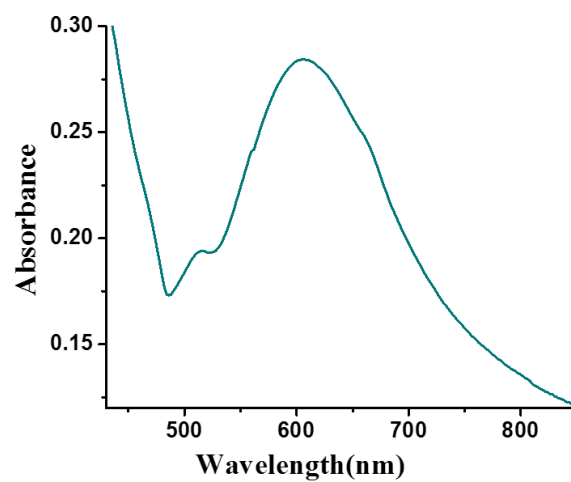


Figure 19S: Characteristic UV/Vis spectrum of **NaphMC-Cu^{II}** complex in CH_3CN at 298 K.

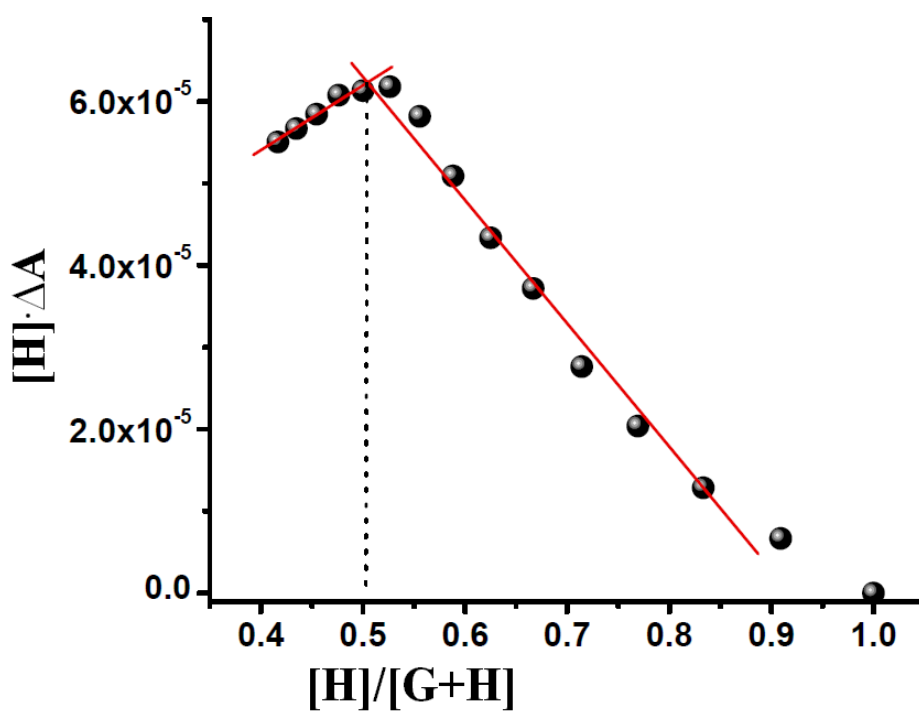


Figure 20S: Molar ratio plot from UV/Vis titration experiment between **NaphMC** with $\text{Cu}(\text{ClO}_4)_2$.

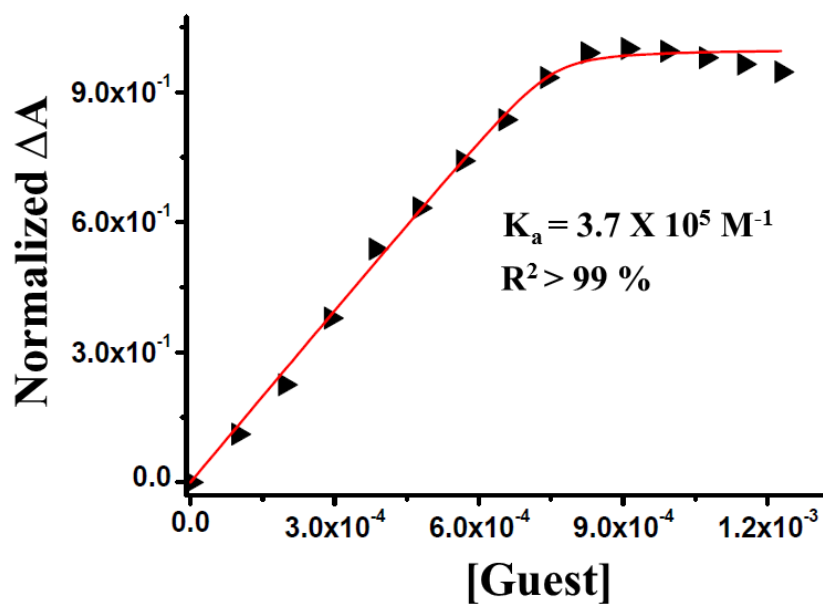
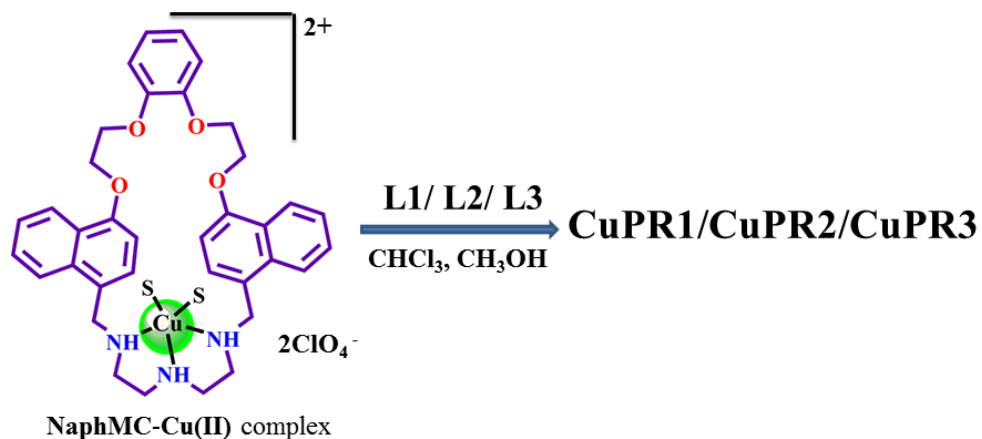


Figure 21S: Nonlinear 1:1 curve fitting to determine binding constant for **NaphMC-Cu^{II}** complex from UV/Vis titration experiment in MeOH.



Scheme2S. Synthetic route of [2]pseudorotaxanes, **CuPR1- CuPR3**.

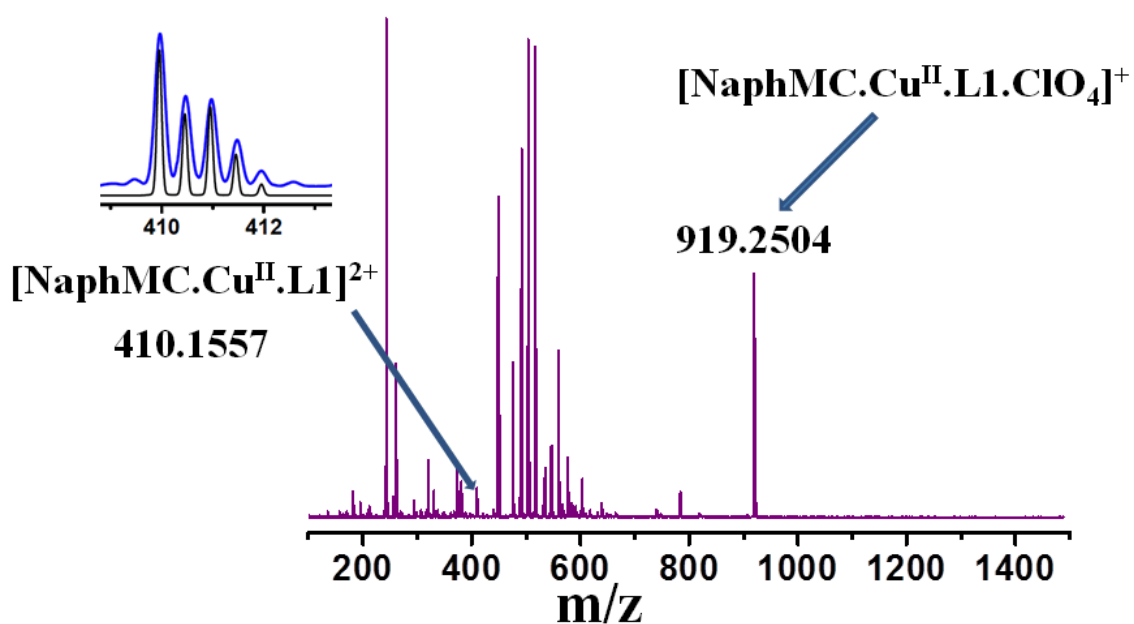


Figure22S: ESI-MS (+ve) spectrum of [2]pseudorotaxane **CuPR1** (inset shows the isotopic distribution pattern corresponding to $[\text{NaphMC.Cu}^{\text{II}}.\text{L1}]^{2+}$ with blue line for the experimental and black line for calculated pattern).

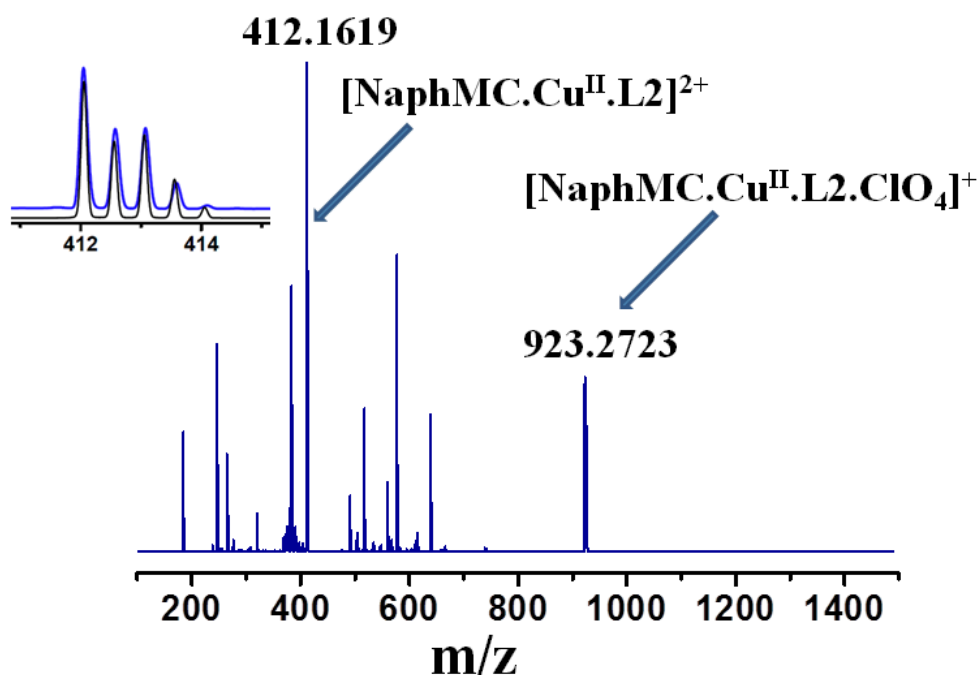


Figure 23S: ESI-MS (+ve) spectrum of [2]pseudorotaxane **CuPR2** (inset shows the isotopic distribution pattern corresponding to $[\text{NaphMC.Cu}^{\text{II}}.\text{L2}]^{2+}$ with blue line for the experimental and black line for calculated pattern).

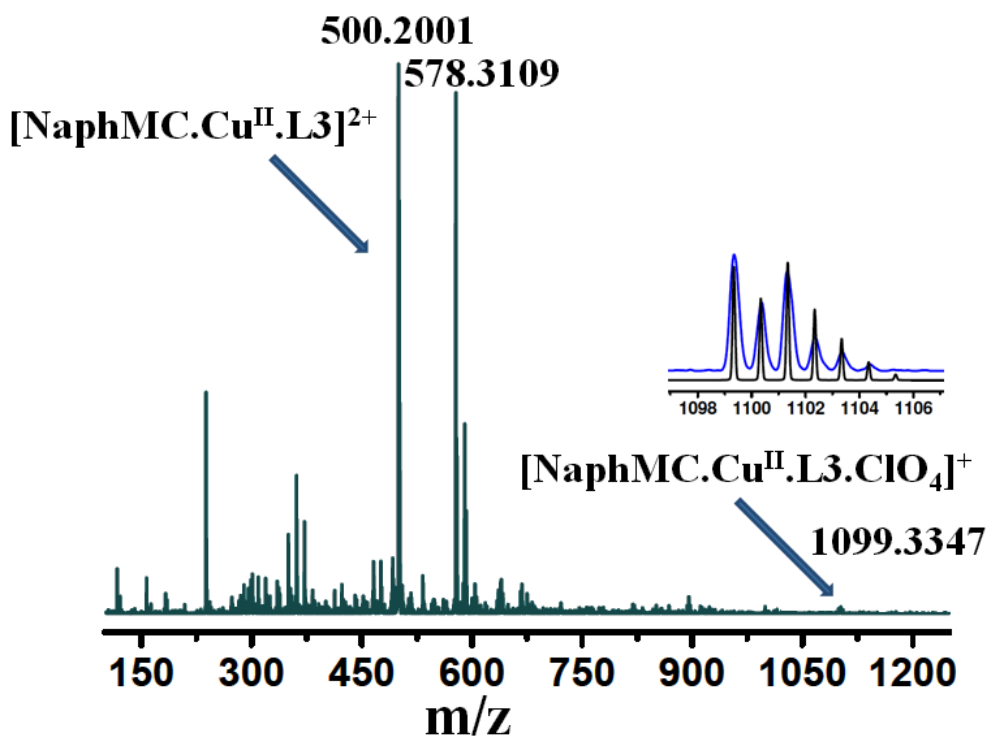


Figure 24S: ESI-MS (+ve) spectrum of [2]pseudorotaxane **CuPR3** (inset shows the isotopic distribution pattern corresponding to $[\text{NaphMC.Cu}^{\text{II}}.\text{L3}.\text{ClO}_4]^+$ with blue line for the experimental and black line for calculated pattern).

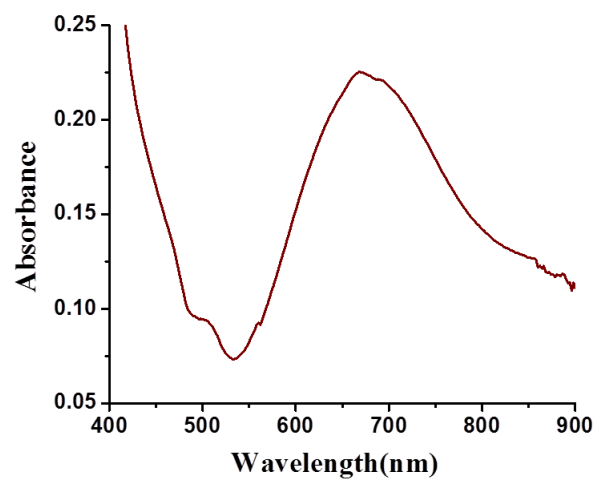


Figure 25S: Characteristic UV/Vis spectrum of **CuPR1** in CH₃CN at 298 K.

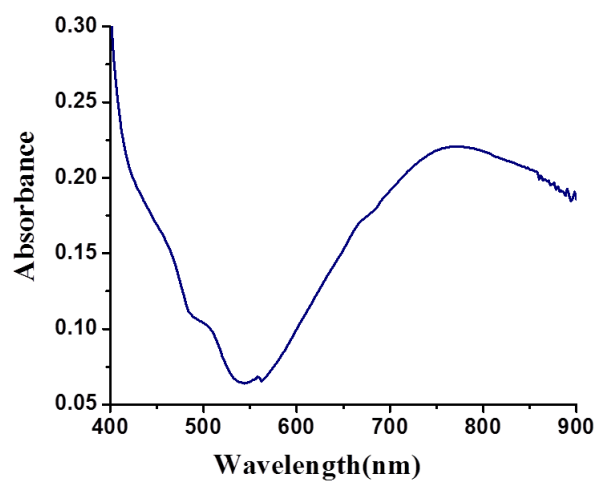


Figure 26S: Characteristic UV/Vis spectrum of **CuPR2** in CH₃CN at 298 K.

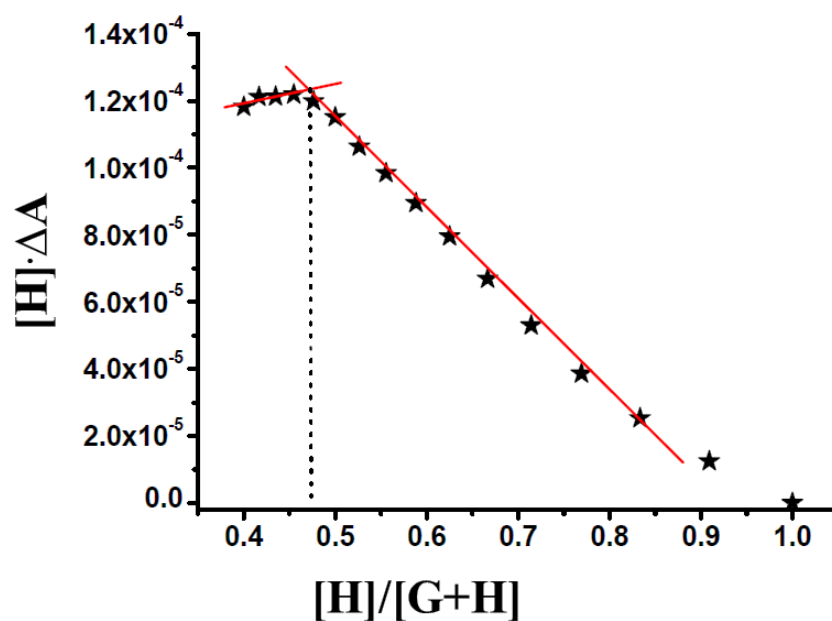


Figure 27S: Molar ratio plot from UV/Vis titration experiment between **NaphMC-Cu^{II}** with **L1**.

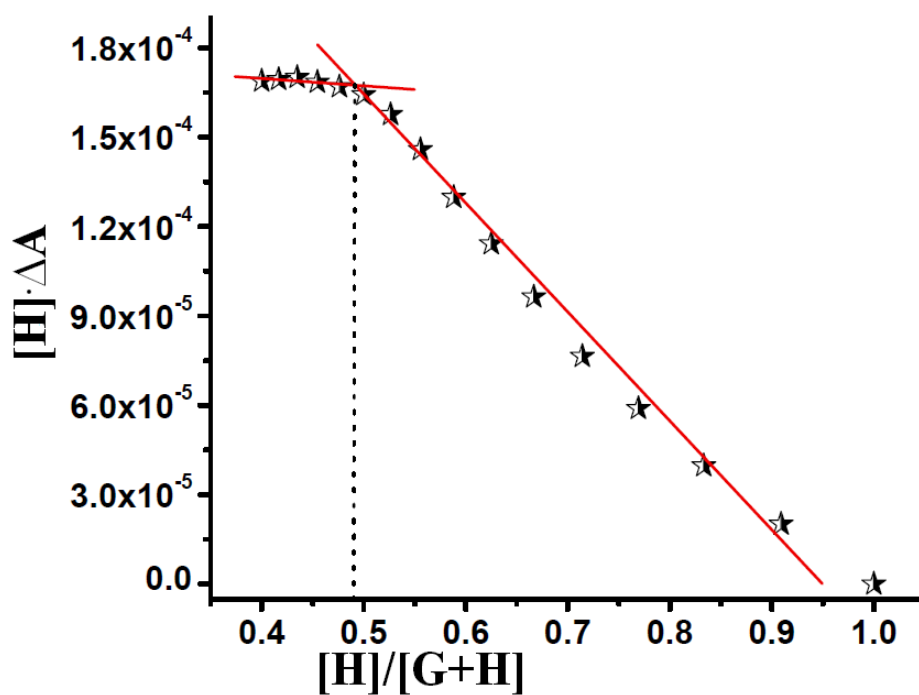


Figure 28S: Molar ratio plot from UV/Vis titration experiment between **NaphMC-Cu^{II}** with **L2**.

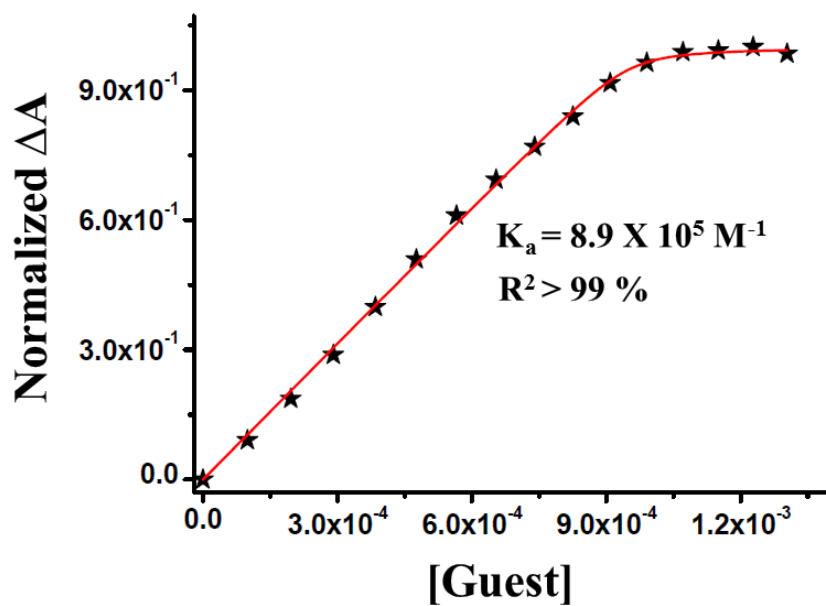


Figure 29S: Nonlinear 1:1 curve fitting plot of formation of **CuPR1** complex from UV/Vis titration experiment.

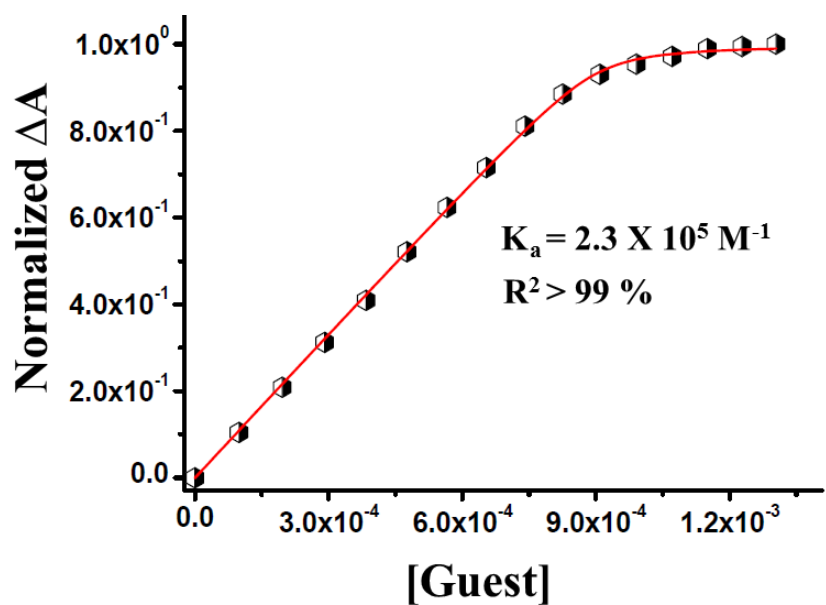


Figure 30S: Nonlinear 1:1 curve fitting plot of formation of **CuPR2** complex from UV/Vis titration experiment.

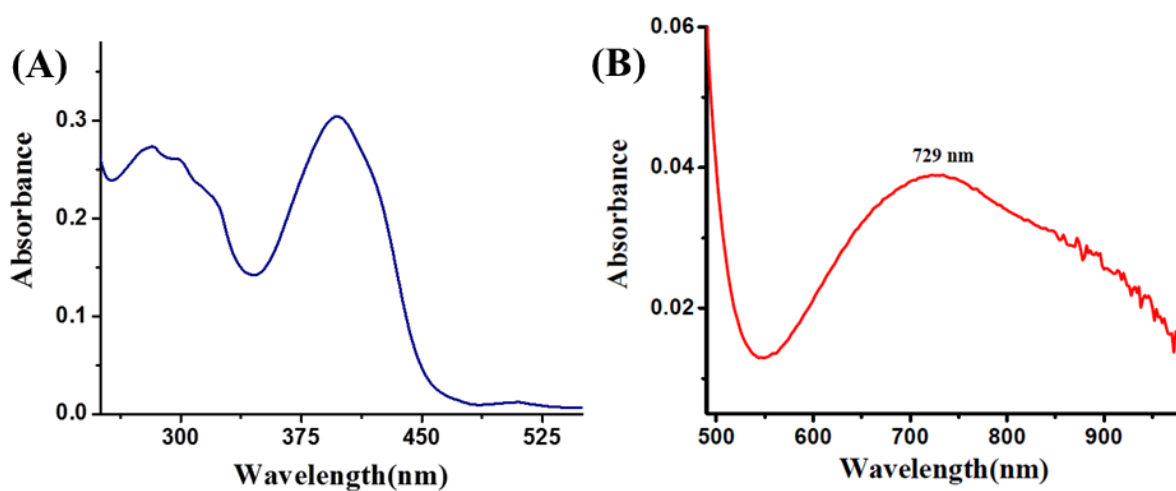


Figure 31S: Characteristic UV/Vis spectrum at 298 K (A) **CuPR3** in THF at UV region, (B) **CuPR3** at Visible region in THF.

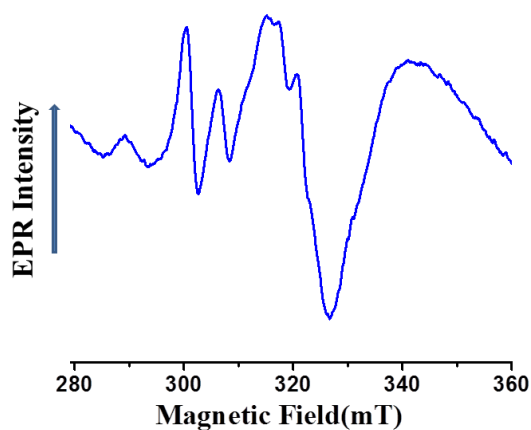


Figure 32S: EPR spectrum of **CuPR1** in DMF at 80K.

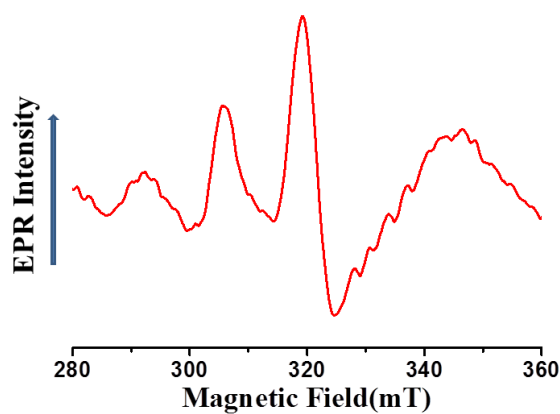


Figure 33S: EPR spectrum of **CuPR2** in DMF at 80K.

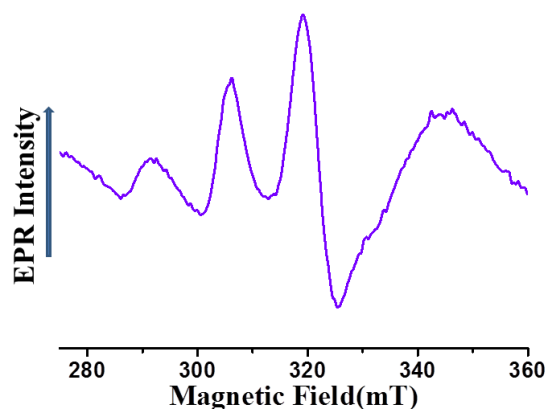


Figure 34S: EPR spectrum of **CuPR3** in DMF at 80K.

Table 1S. $g_{||} > g_{\perp}$ values^a of **CuPR1-CuPR3** from EPR spectra in DMF

[2]pseudorotaxane	$g_{ }$	$g_{\perp}$
CuPR1	2.09	1.99
CuPR2	2.17	2.02
CuPR3	2.15	2.02

^a $g_{||}$ and $g_{\perp}$ values^{2,3} from the EPR spectrum analyzed by the following equation¹:

$$h\nu = g\beta B,$$

$$g = 71.4484\nu \text{ (in GHz)} / B \text{ (in mT)}$$

[where, ν = Microwave frequency, B = Magnetic field, β = Bohr magneton constant, h = Planck's constant].

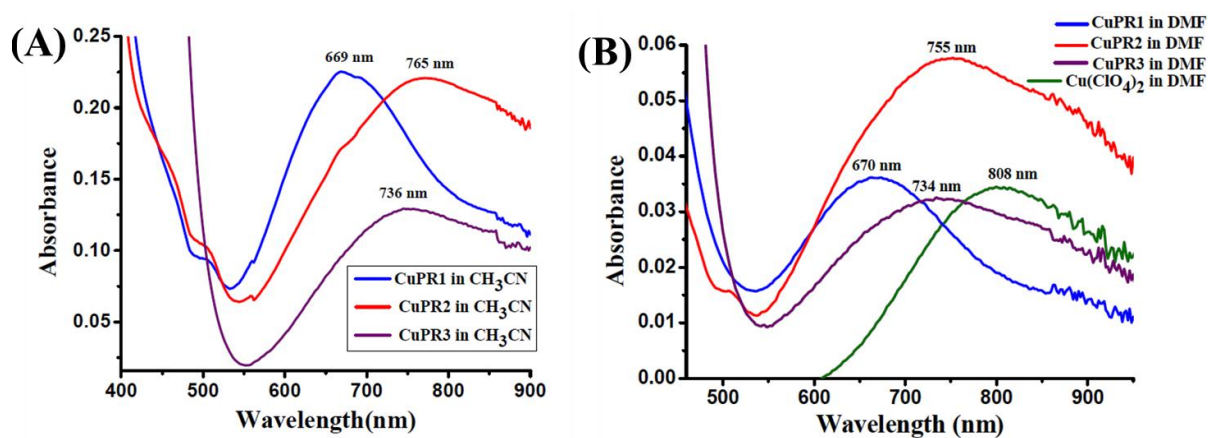


Figure 35S: Characteristic UV/Vis spectra of (A) **CuPR1**, **CuPR2** and **CuPR3** in CH_3CN and (B) **CuPR1**, **CuPR2**, **CuPR3** and **$\text{Cu}(\text{ClO}_4)_2$** in DMF medium at 298 K.

Crystallographic details of **CuPR1** and **CuPR2**

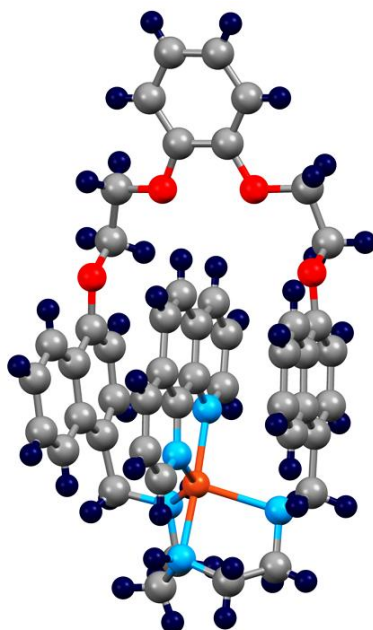


Figure 36S: Single Crystal X-ray structure of **CuPR1** (Ball and stick model).



Figure 37S: Geometry of the Cu^{II} center of **CuPR1** ($\tau = 0.516$).

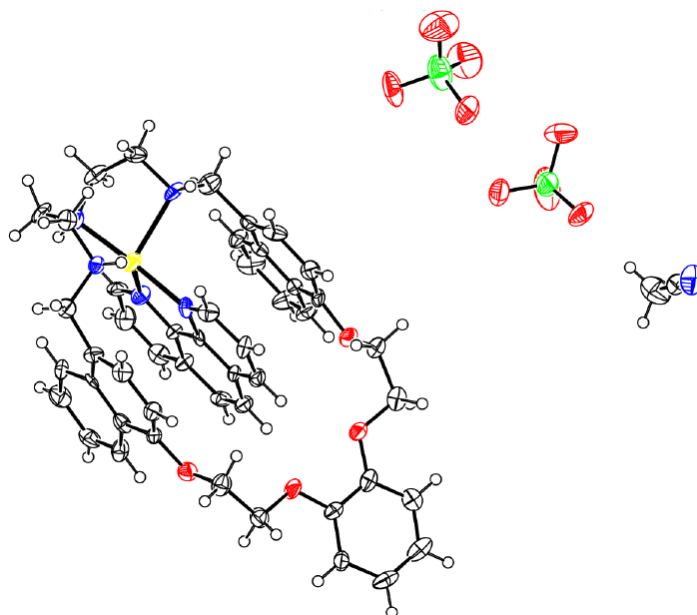


Figure 38S: Single Crystal X-ray structure of **CuPR1** (ellipsoid model using platon version).

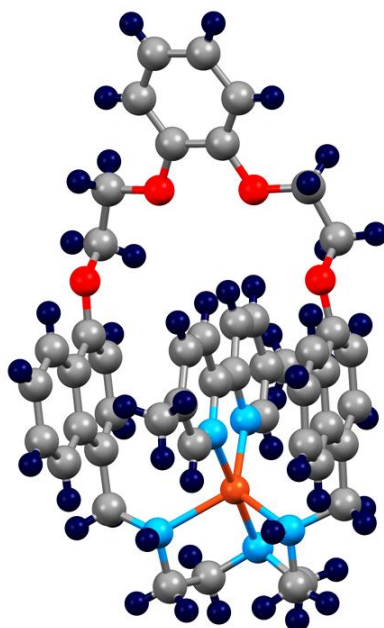


Figure 39S: Single Crystal X-ray structure of **CuPR2** (Ball and stick model).

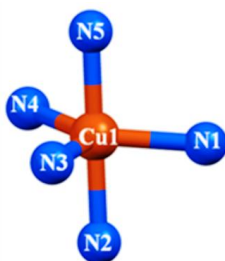


Figure 40S: Geometry of the Cu^{II} centre of **CuPR2** ($\tau = 0.821$).

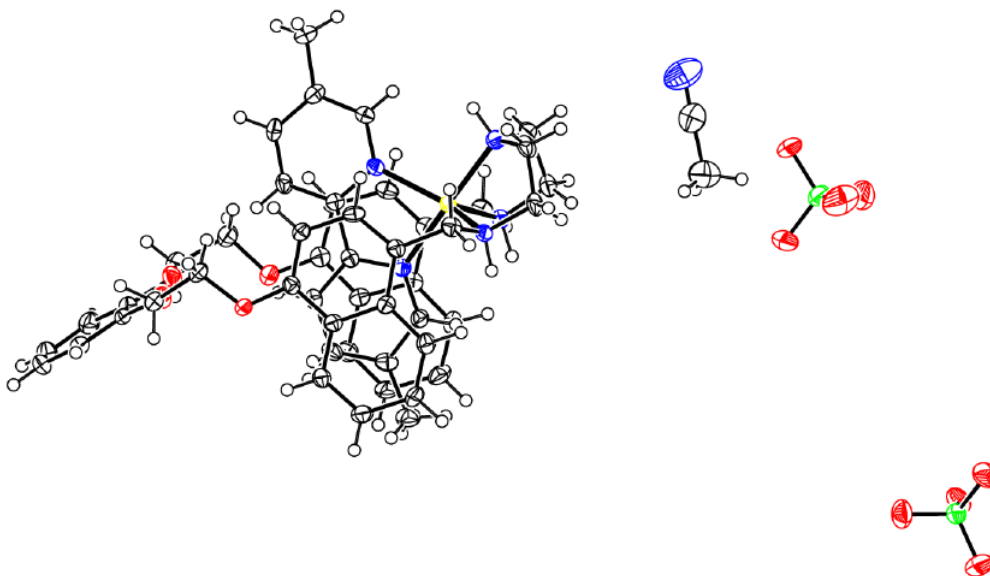


Figure 41S: Single Crystal X-ray structure of **CuPR2** (ellipsoid model using platon version).

Table 2S. N-Cu-N bond angle of CuPR1 and CuPR2

CuPR1				CuPR2			
N1	-Cu1	-N2	81.6(3)	N1	-Cu1	-N2	84.07(11)
N1	-Cu1	-N3	95.7(3)	N1	-Cu1	-N3	109.27(11)
N1	-Cu1	-N4	105.7(3)	N1	-Cu1	-N4	130.09(11)
N1	-Cu1	-N5	145.3(3)	N1	-Cu1	-N5	95.45(11)
N2	-Cu1	-N3	176.3(3)	N2	-Cu1	-N3	83.86(11)
N2	-Cu1	-N4	99.7(3)	N2	-Cu1	-N4	100.42(11)
N2	-Cu1	-N5	96.5(3)	N2	-Cu1	-N5	179.06(12)
N3	-Cu1	-N4	83.4(3)	N3	-Cu1	-N4	120.64(10)
N3	-Cu1	-N5	84.3(3)	N3	-Cu1	-N5	95.55(11)
N4	-Cu1	-N5	108.7(3)	N4	-Cu1	-N5	80.51(11)

Table 3S. N-C-C-N torsional angle of CuPR1 and CuPR2

CuPR1					CuPR2				
N3	-C31	-C32	-N4	57.4(9)	N1	-C20	-C21	-N2	-48.0(4)
N3	-C33	-C34	-N5	-46.6(10)	N2	-C22	-C23	-N3	55.2(4)
N1	-C41	-C42	-N2	2.1(13)	N4	-C41	-C42	-N5	-1.8(4)

Table 4S. Cu-N bond distance of CuPR1 and CuPR2

CuPR1			CuPR2		
Cu1	-N1	2.067(9)	Cu1	-N1	2.111(3)
Cu1	-N2	2.018(7)	Cu1	-N2	2.044(3)
Cu1	-N3	2.027(8)	Cu1	-N3	2.180(3)
Cu1	-N4	2.282(8)	Cu1	-N4	2.072(3)
Cu1	-N5	2.091(8)	Cu1	-N5	1.997(3)

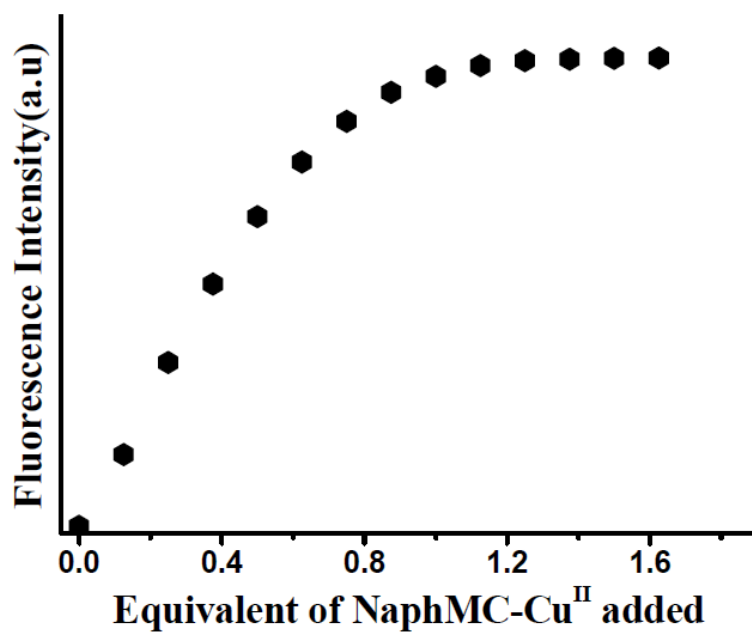


Figure 42S: Equivalence plot between **L3** and **NaphMC-Cu^{II}** (from emission titration experiment).

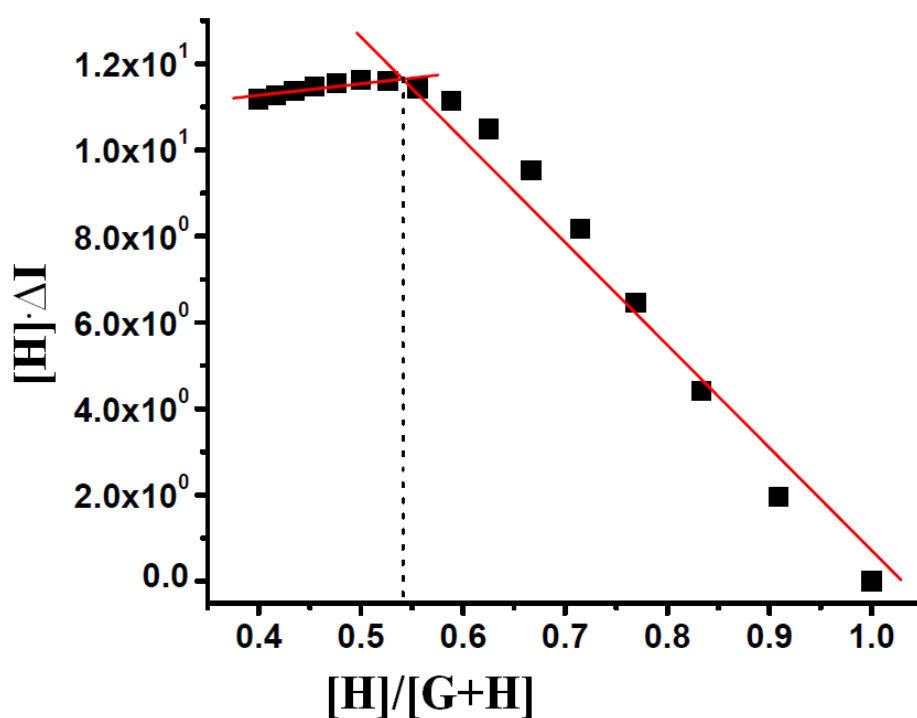


Figure 43S: Molar ratio plot of titration between **NaphMC-Cu^{II}** with **L3** (from emission titration experiment).

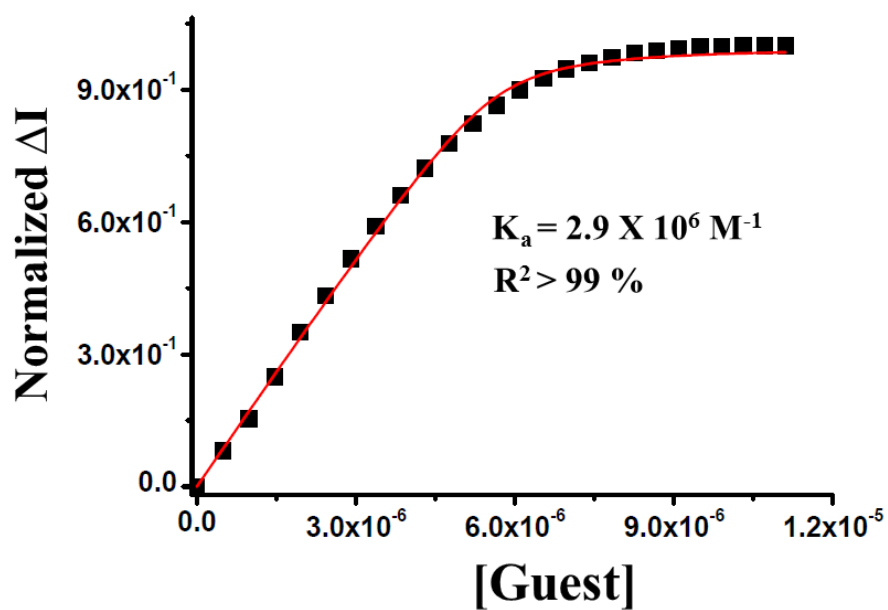


Figure 44S: Nonlinear 1:1 curve fitting plot of formation of CuPR3 complex from emission titration experiment.

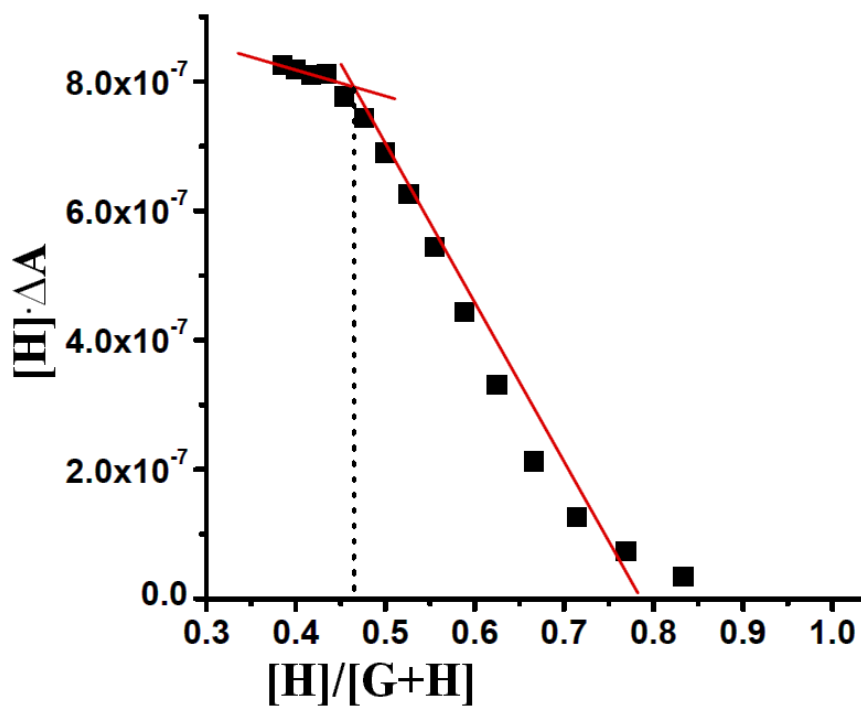


Figure 45S: Molar ratio plot of titration (UV/Vis study) between CuPR3 with L1.

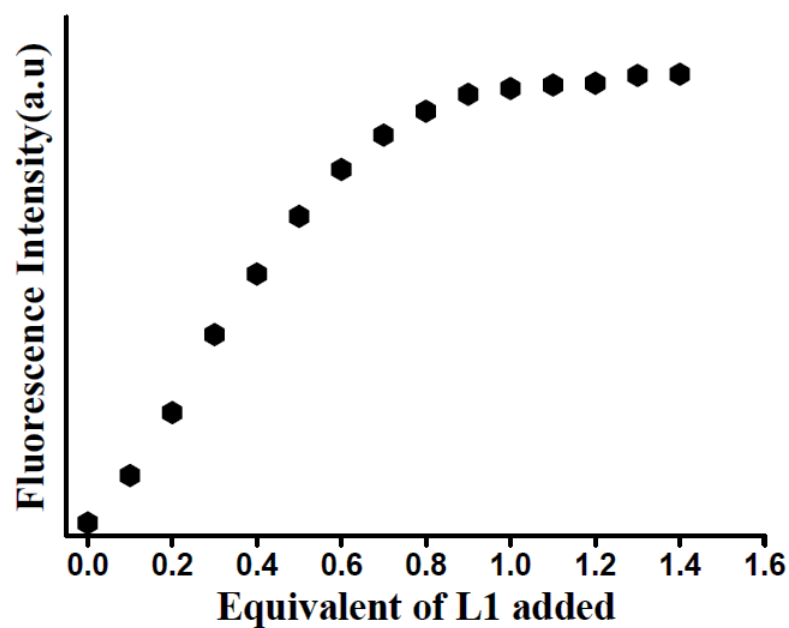


Figure 46S: Equivalence plot from emission titration experiment between **CuPR3** with **L1** in dry THF.

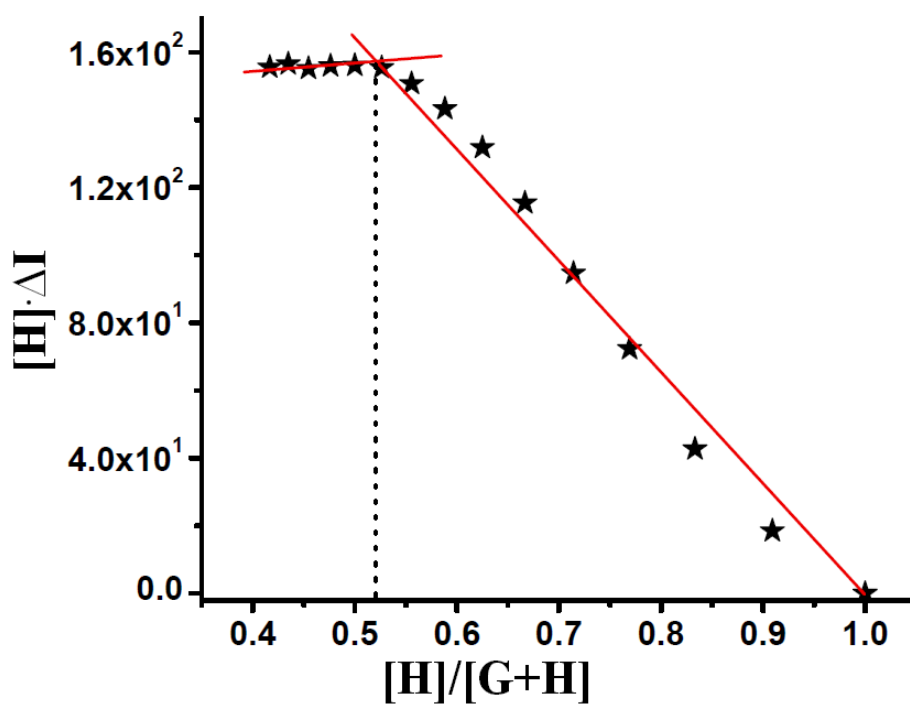


Figure 47S: Molar ratio plot of titration (PL study) between **CuPR3** with **L1**.

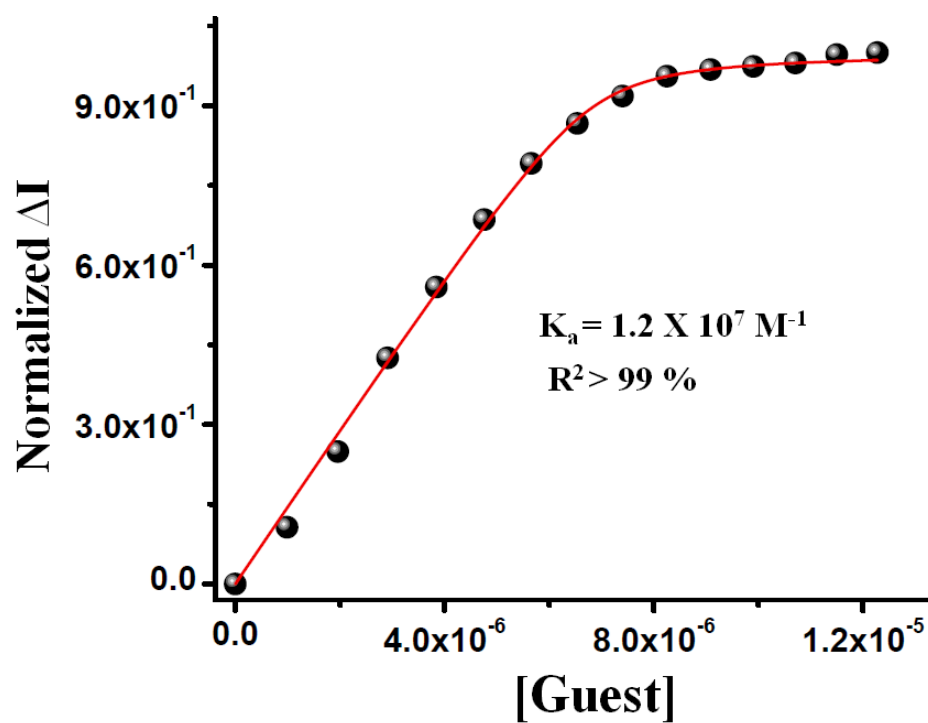


Figure 48S: Nonlinear 1:1 curve fitting from emission titration experiment between **CuPR3** with **L1** in dry THF.

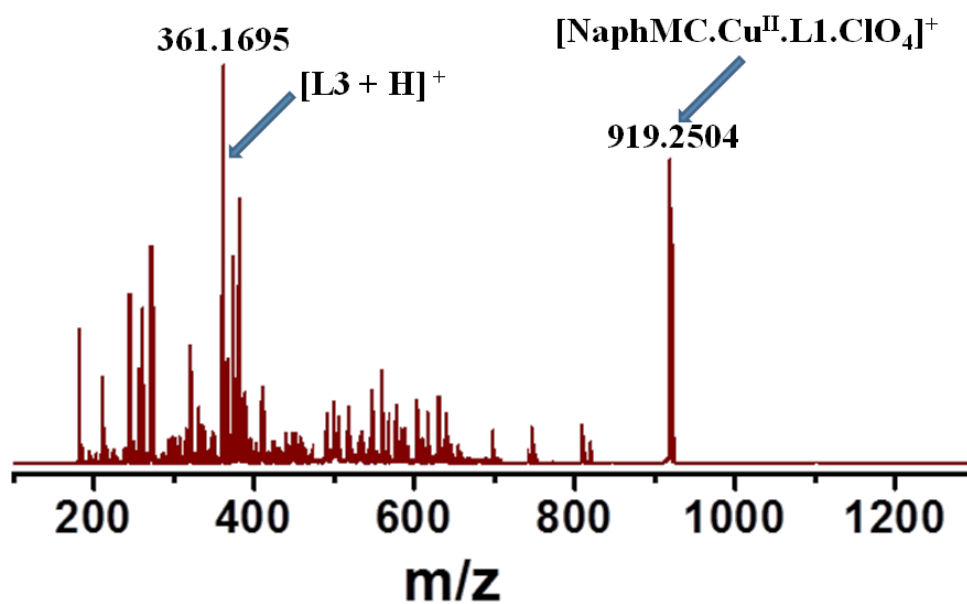


Figure 49S: ESI-MS (+ve) spectrum of resultant titrated solution from titration between **CuPR3** with **L1**.

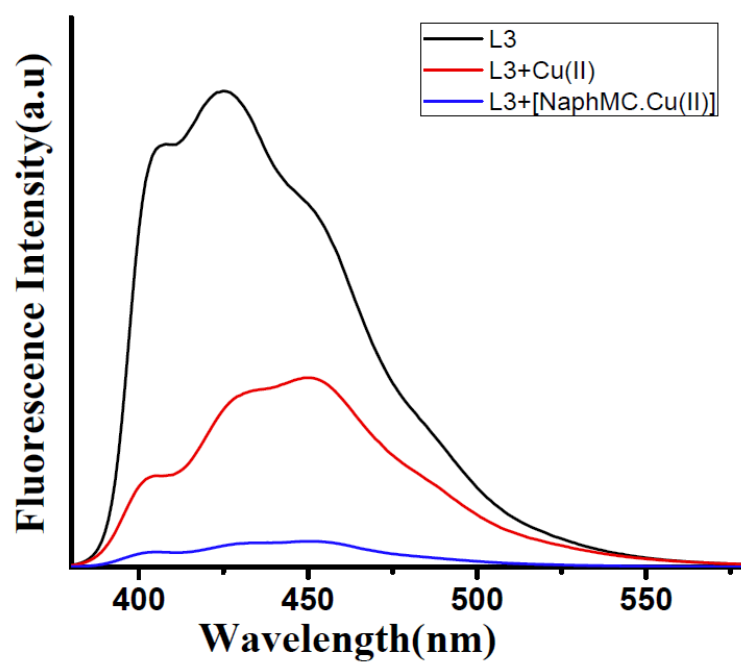


Figure50S: Comparable emission studies of **L3**, [**L3**+ Cu(II)] and [**L3**+**NaphMC**.Cu(II) complex].

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1. W. R. Hagen, *Dalton Trans.*, 2006, 4415–443,
2. S. Gilch, O. Meyer, I. Schmidt, *Biometals* .,2010, **23**,613–622,
3. L. Husarikova, Z. Repicka, J. Moncol, D. Valigura, M. Valko, M. Mazur., *Appl Magn Reson*, 2013, **44**,571–582.