

Supporting Information

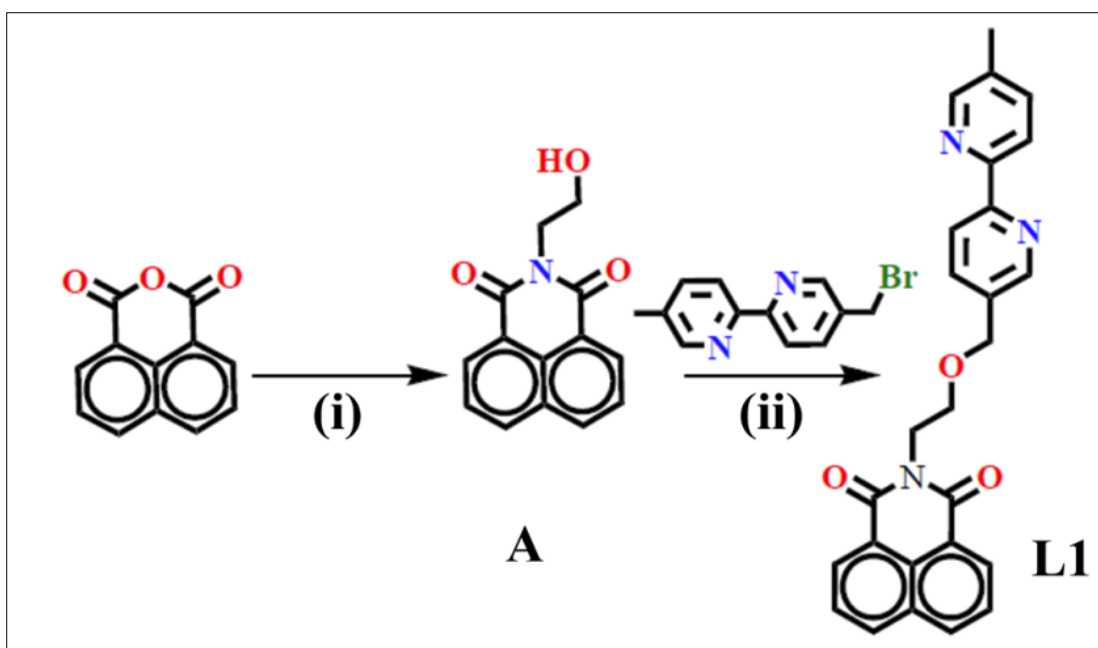
Development of fluorophoric [2]pseudorotaxanes and [2]rotaxane: Selective sensing of Zn(II)

Somnath Bej, Mandira Nandi and Pradyut Ghosh*

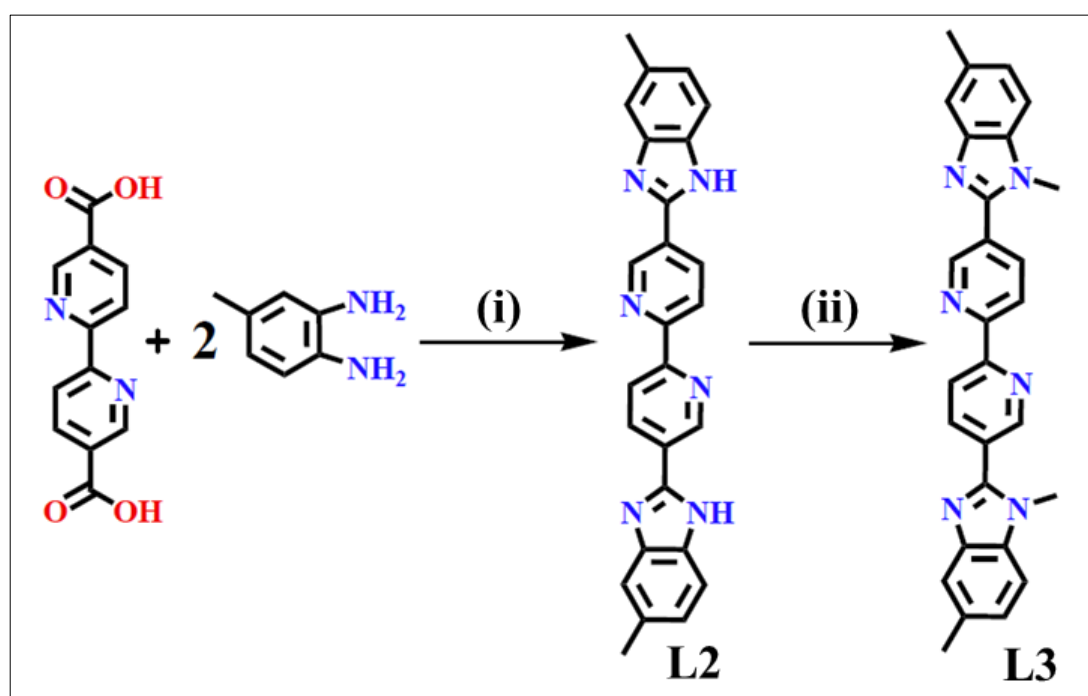
School of Chemical Sciences, Indian Association for the Cultivation of Science, 2A & 2B
Raja S. C. Mullick Road, Kolkata 700032, India. E-mail: icpg@iacs.res.in

List of contents

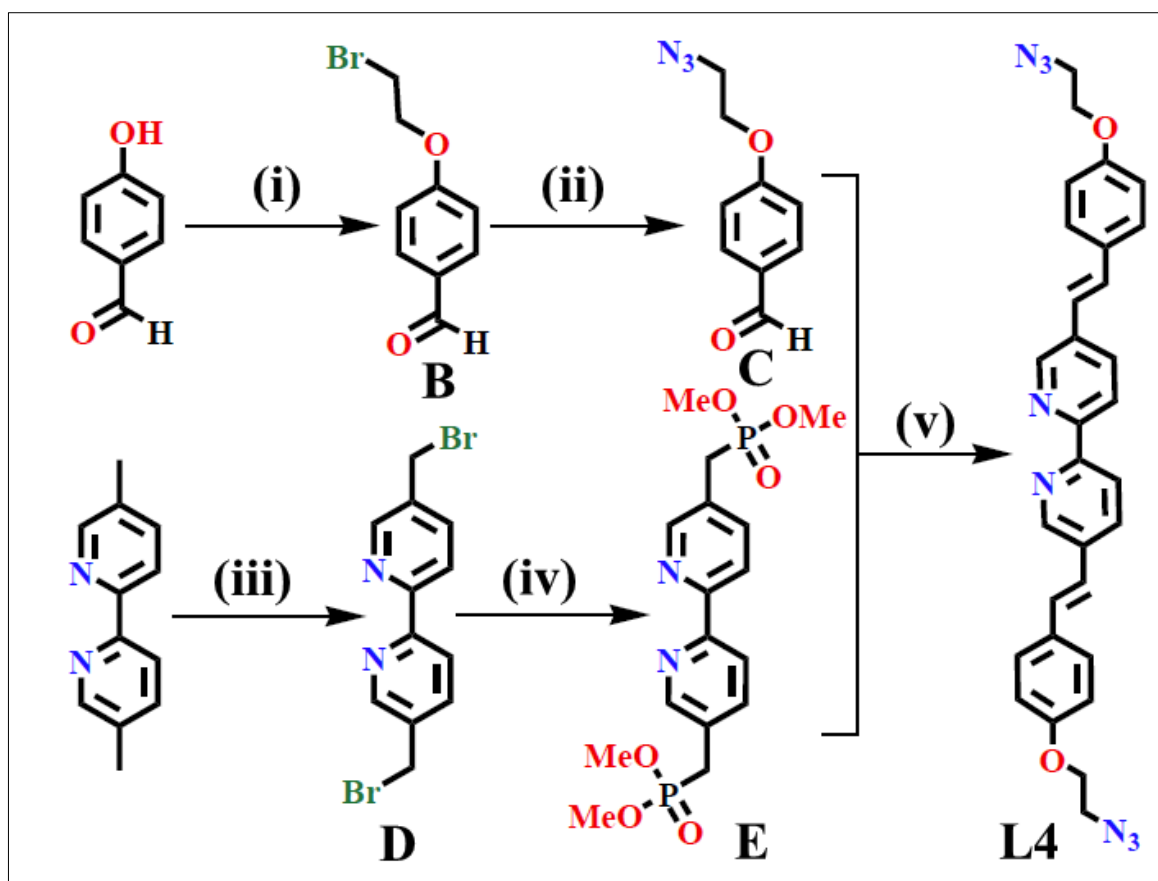
| | |
|---|---------|
| ❖ Synthetic scheme of L1-L4 (Scheme 1S-Scheme 3S) | S2-S3 |
| ❖ UV/Vis and Emission spectra of NaphMC (Figure 1S)..... | S3 |
| ❖ Characterization of compound A (Figure 2S- Figure 3S)..... | S4 |
| ❖ Characterization of L1 (Figure 4S- Figure 7S)..... | S5-S6 |
| ❖ Characterization of compound L2 (Figure 8S- Figure 10S)..... | S7-S8 |
| ❖ Characterization of L3 (Figure 11S- Figure 14S)..... | S8-S10 |
| ❖ Characterization of compound C (Figure 15S- Figure 16S)..... | S10-S11 |
| ❖ Characterization of L4 (Figure 17S- Figure 18S)..... | S11-S12 |
| ❖ Characteristic UV/Vis spectra of {NiPR1(ClO ₄) ₂ -NiPR4(ClO ₄) ₂ } (Figure 19S).... | S12 |
| ❖ PL spectra of {NiPR1(ClO ₄) ₂ -NiPR4(ClO ₄) ₂ } (Figure 20S- Figure 23S).... | S12-S13 |
| ❖ ESI-MS spectrum of [NiRTX(ClO ₄) ₂] (Figure 24S)..... | S14 |
| ❖ Stacked plot of ¹ H NMR spectra (Figure 25S)..... | S14 |
| ❖ ESI-MS spectrum of [RTX] (Figure 26S)..... | S15 |
| ❖ NMR spectrum of [NAPRTX] (Figure 27S- Figure 28S)..... | S15-S16 |
| ❖ UV and PL spectra of [NAPRTX] (Figure 29S- Figure 30S)..... | S16-S17 |
| ❖ Characterization of ConAx (Figure 31S- Figure 35S)..... | S17-S19 |
| ❖ Non-linear fitting plot from PL titration data (Figure 36S)..... | S20 |
| ❖ UV titration of NAPRTX with Zn(ClO ₄) ₂ in solvent mixture and Molar ratio plot. (Figure 37S). | S20 |
| ❖ PL titration of NAPRTX with Zn(ClO ₄) ₂ in solvent mixture and Molar ratio plot (Figure 38S) | S21 |



Scheme 1S. Synthetic path of **L1**: (i) 2-amino ethanol, CH₃CH₂OH, reflux, 14h; (ii) NaH, THF, stirring at 0 °C followed by stirring at RT for 12 h.



Scheme 2S. Synthetic path of **L2** and **L3**: (i) PPA, reflux, 18h; (ii) Methyl iodide, NaH, THF, stirring at 0°C followed by stirring at RT for 12 h.



Scheme 3S. Synthetic path of L4: (i) 1,2-dibromo ethane, CH_3CN , K_2CO_3 , reflux; (ii) NaN_3 , DMF, reflux, 8h; (iii) NBS, AIBN, CCl_4 , reflux; (iv) trimethyl phosphite, reflux; (v) potassium tertbutoxide, DMF, 0°C , stirring, 10 h.

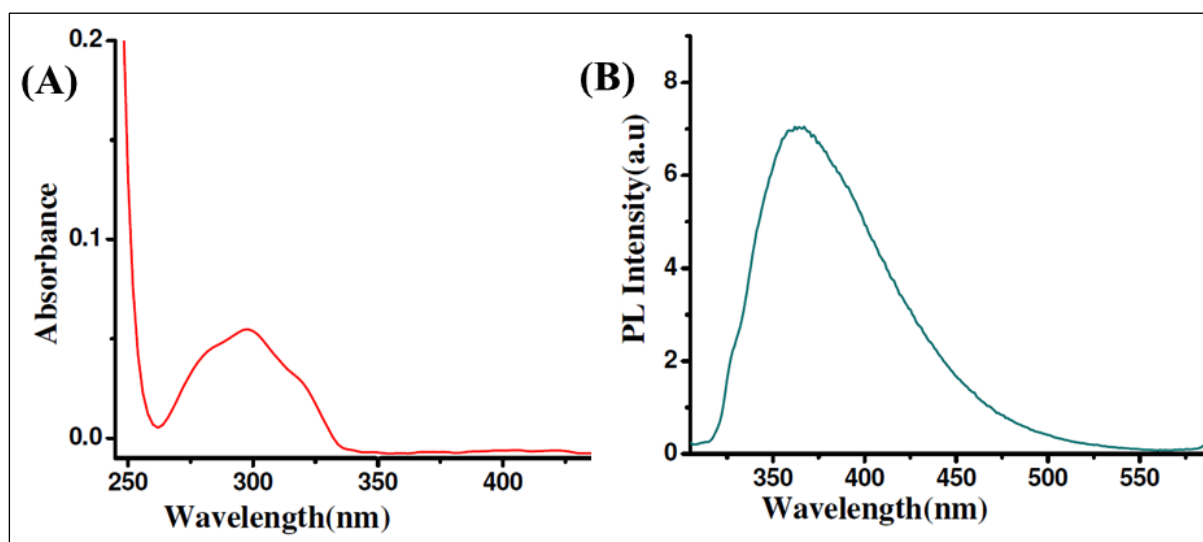


Figure 1S. (A) UV/Vis and (B) emission spectra of NaphMC at 298K.

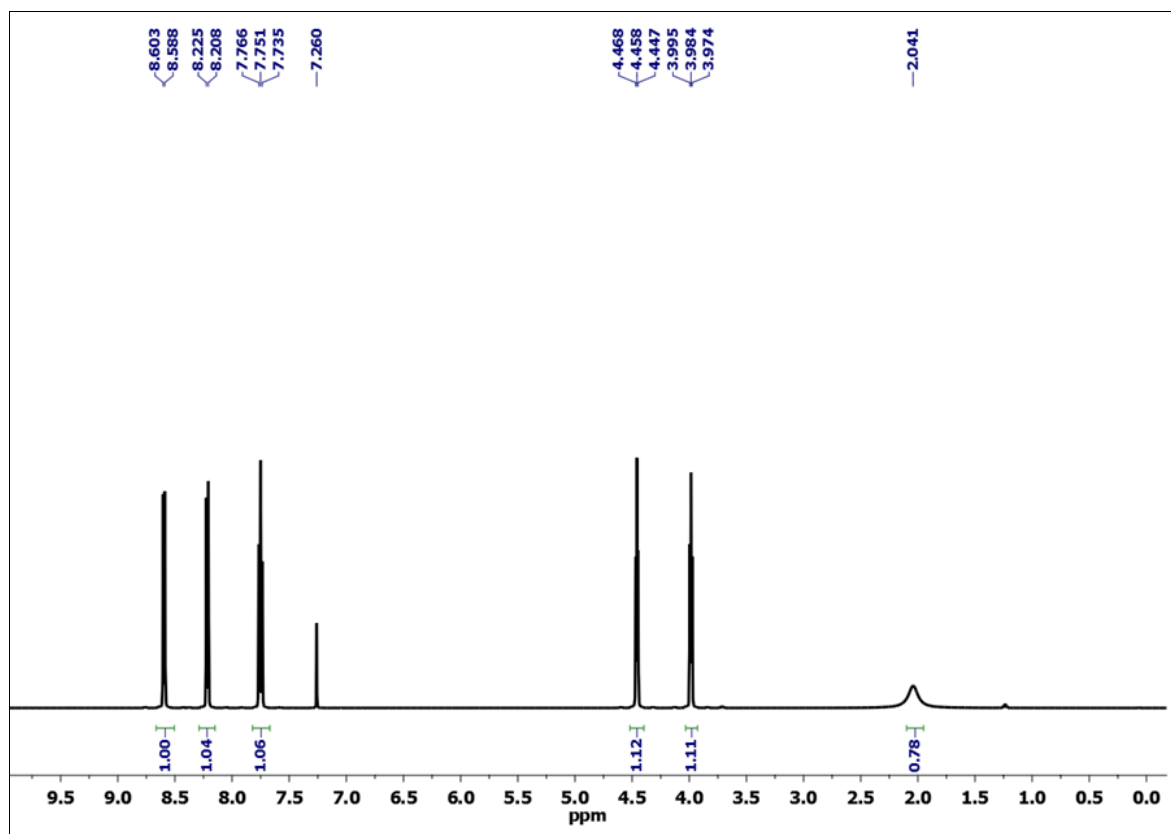


Figure 2S. ^1H -NMR spectrum of A in CDCl_3 in 500 MHz at 298K.

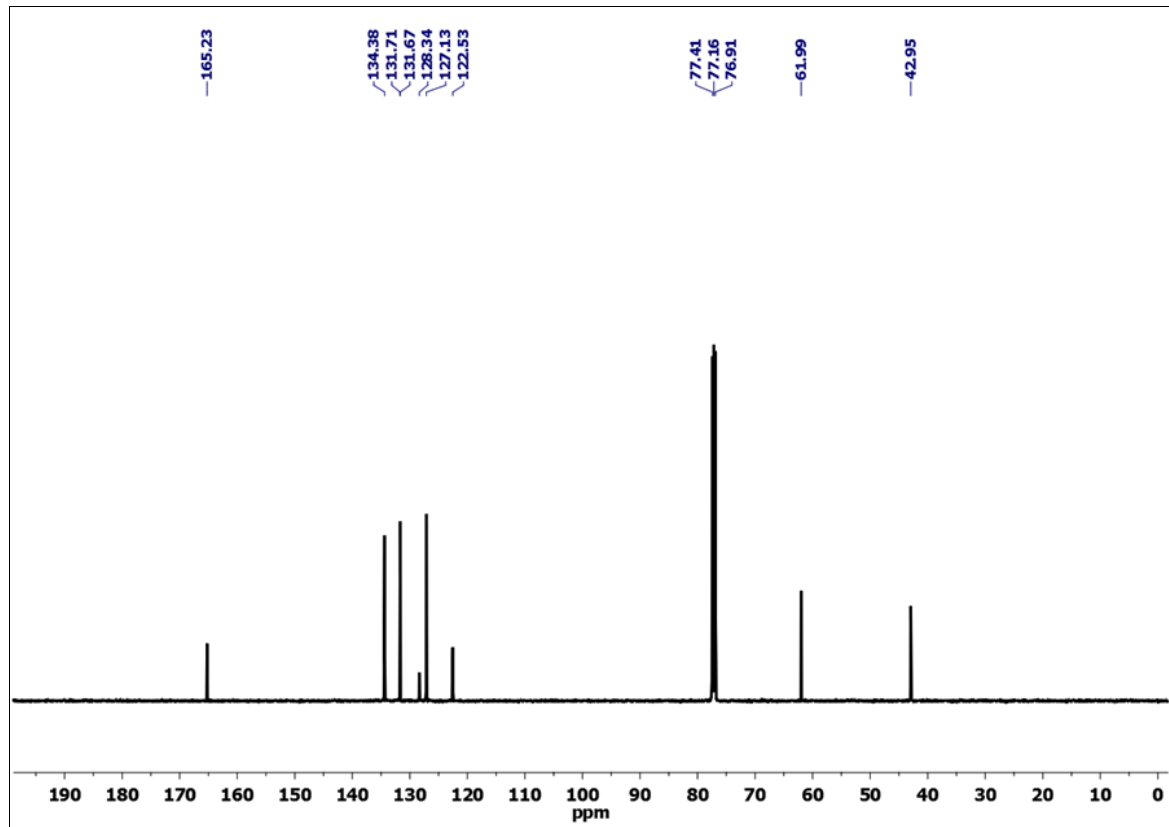


Figure 3S. ^{13}C -NMR spectrum of A in CDCl_3 in 125 MHz at 298K.

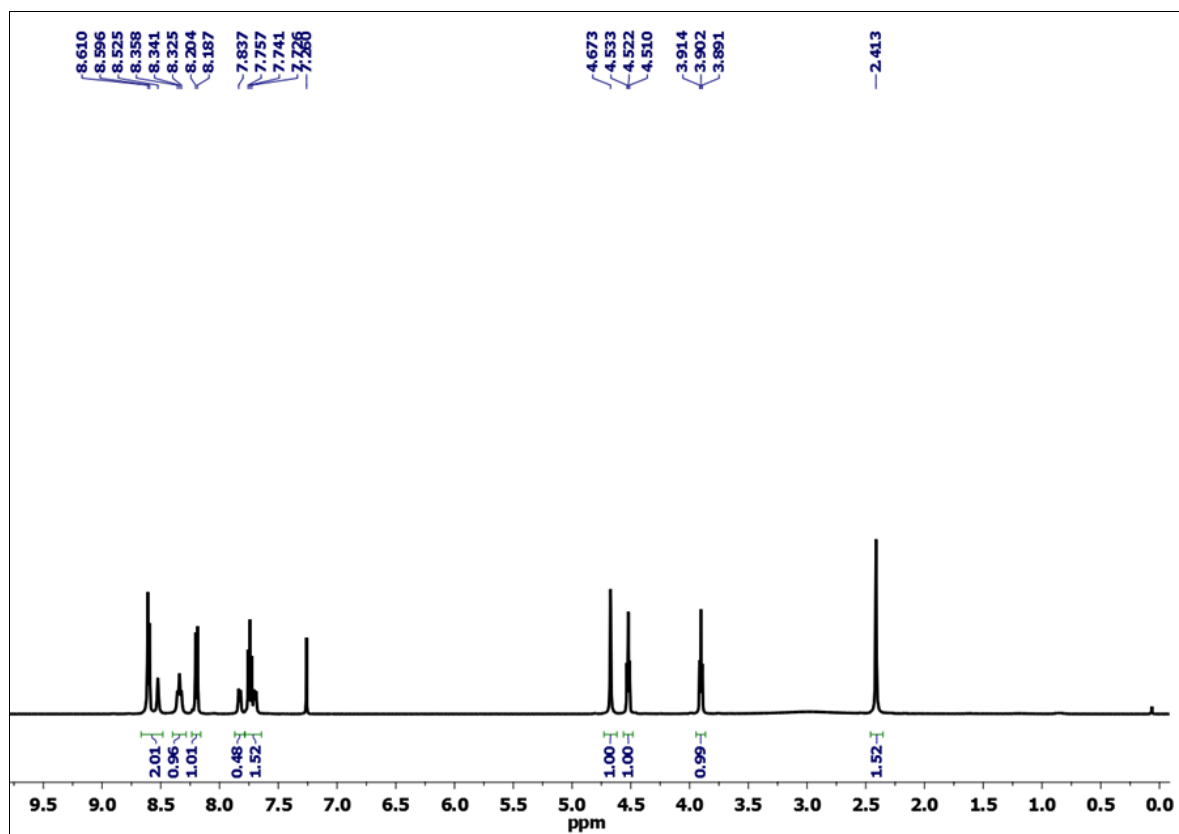


Figure 4S. ^1H -NMR spectrum of **L1** in CDCl_3 in 500 MHz at 298K.

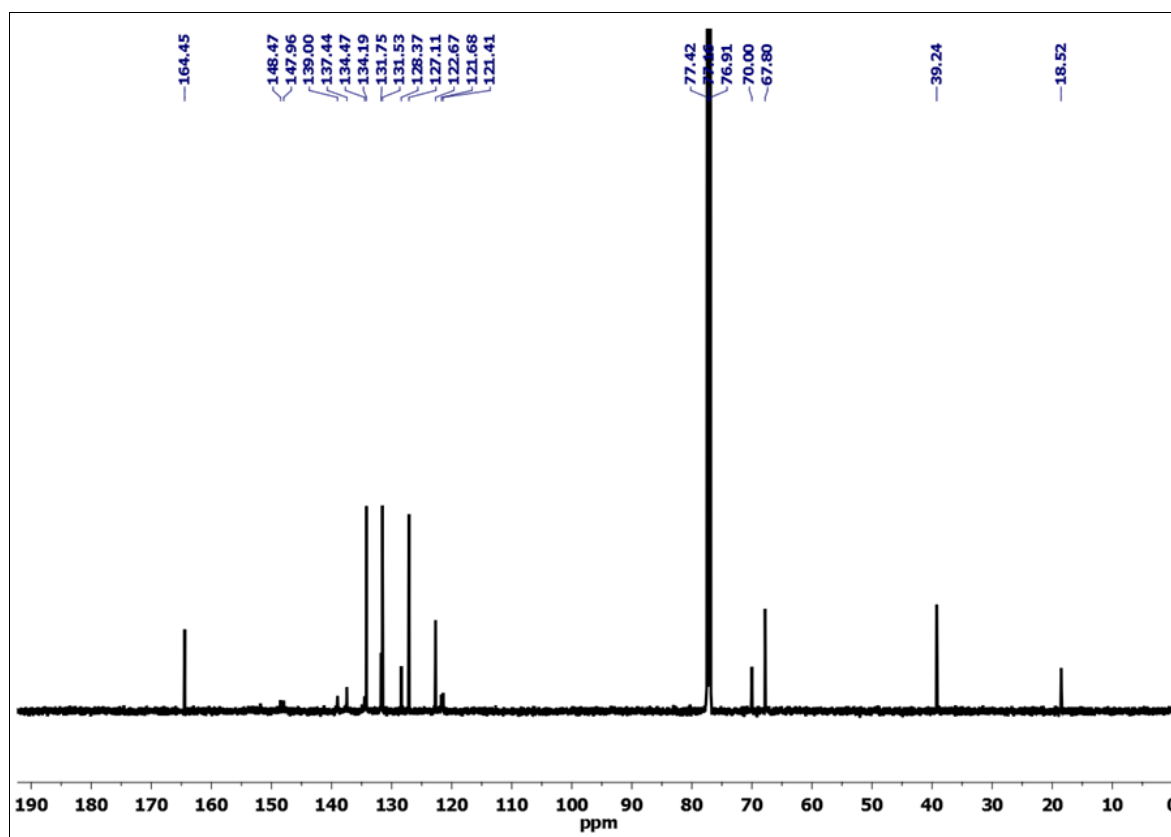


Figure 5S. ^{13}C -NMR spectrum of **L1** in CDCl_3 in 125 MHz at 298K.

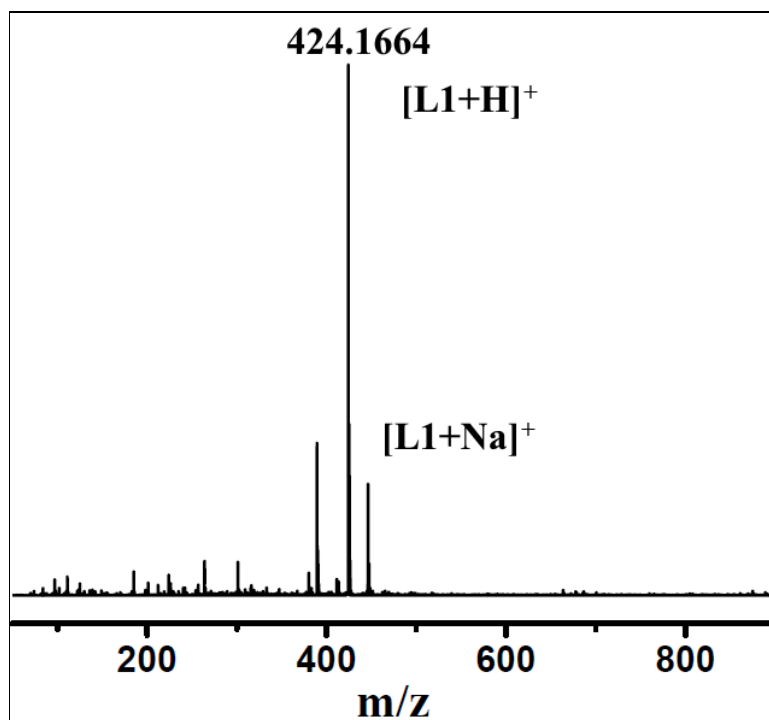


Figure 6S. ESI-MS (+ve) spectrum of L1 at 298K.

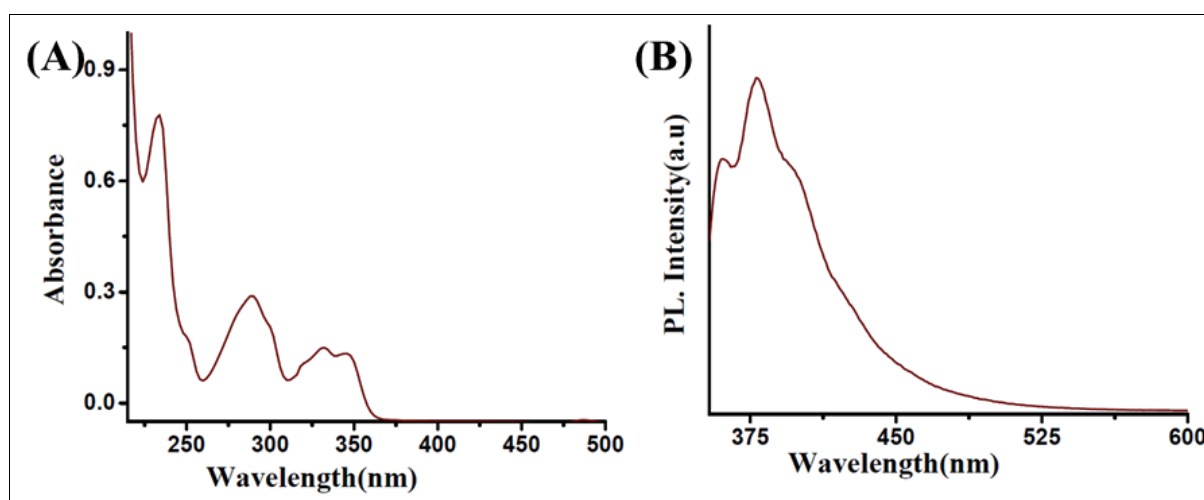


Figure 7S. (A) UV/Vis and (B) Emission spectra of L1 at 298K.

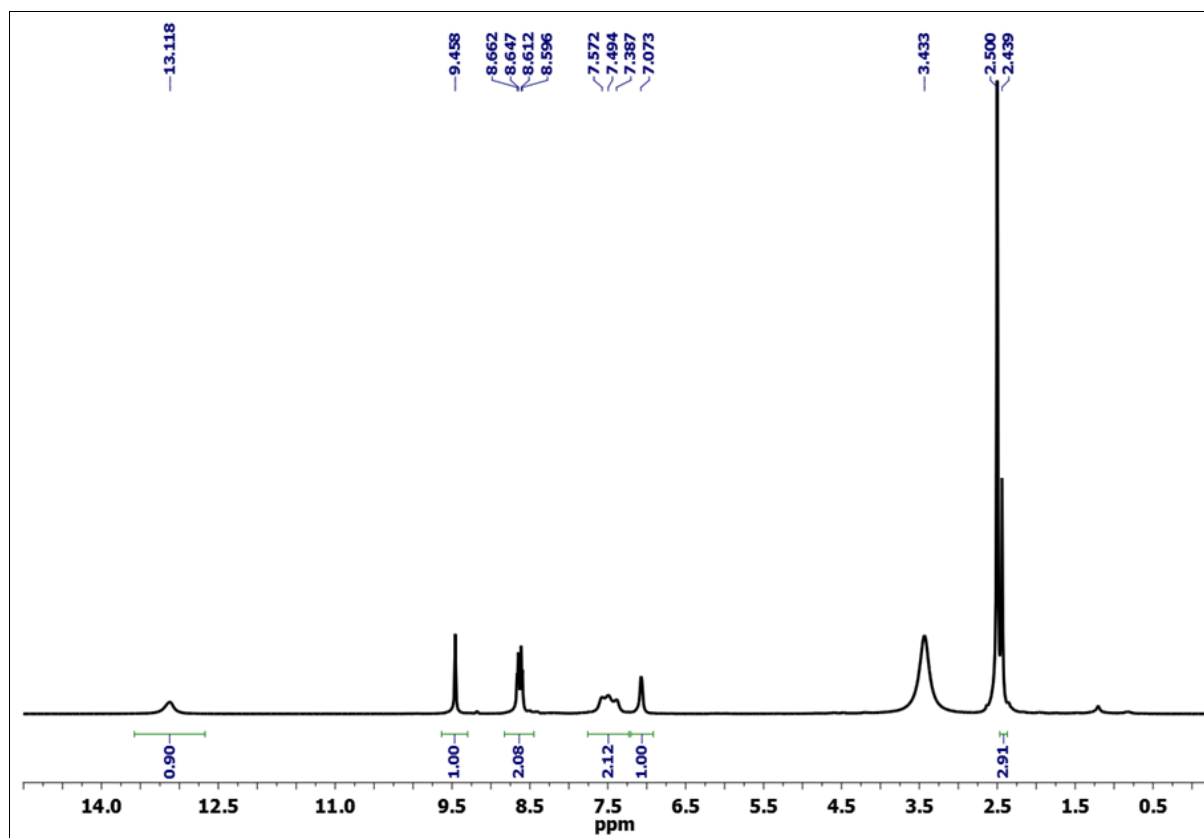


Figure 8S. $^1\text{H-NMR}$ spectrum of **L2** in DMSO-d_6 in 500 MHz at 298K.

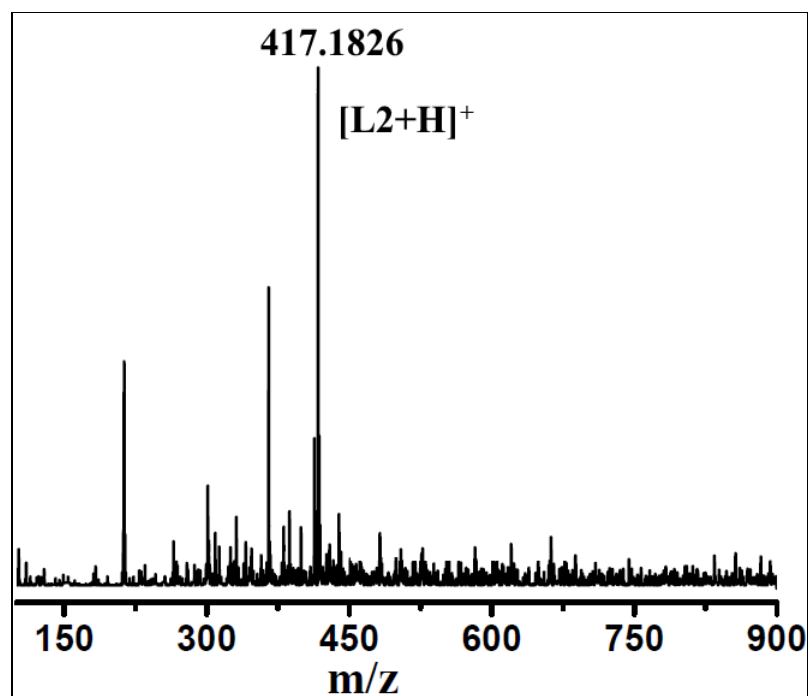


Figure 9S. ESI-MS (+ve) spectrum of **L2** at 298K.

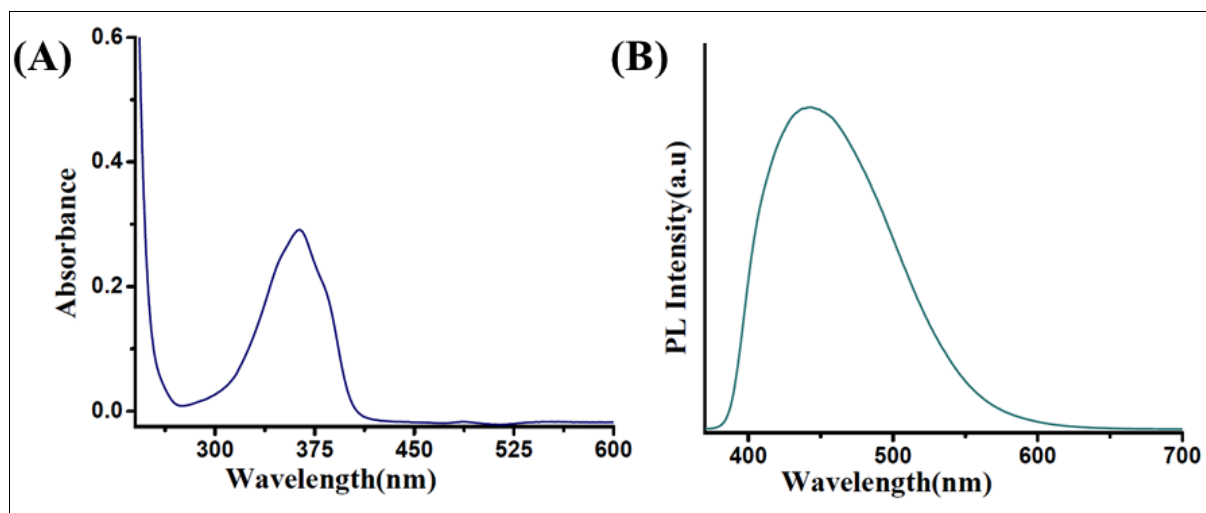


Figure 10S. (A) UV/Vis and (B) Emission spectra of **L2** ($\lambda_{\text{exc}} = 363 \text{ nm}$) at 298K.

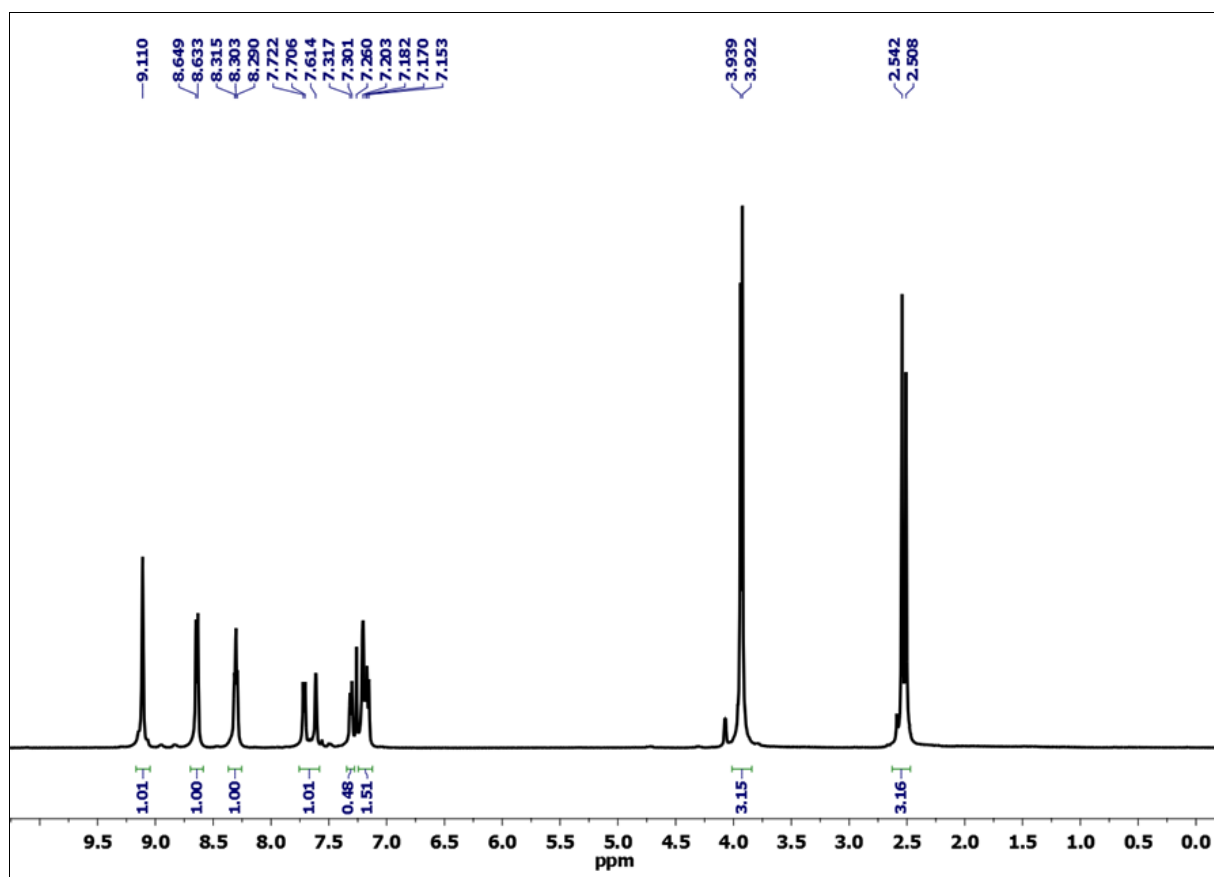


Figure 11S. $^1\text{H-NMR}$ spectrum of **L3** in CDCl_3 in 500 MHz at 298K.

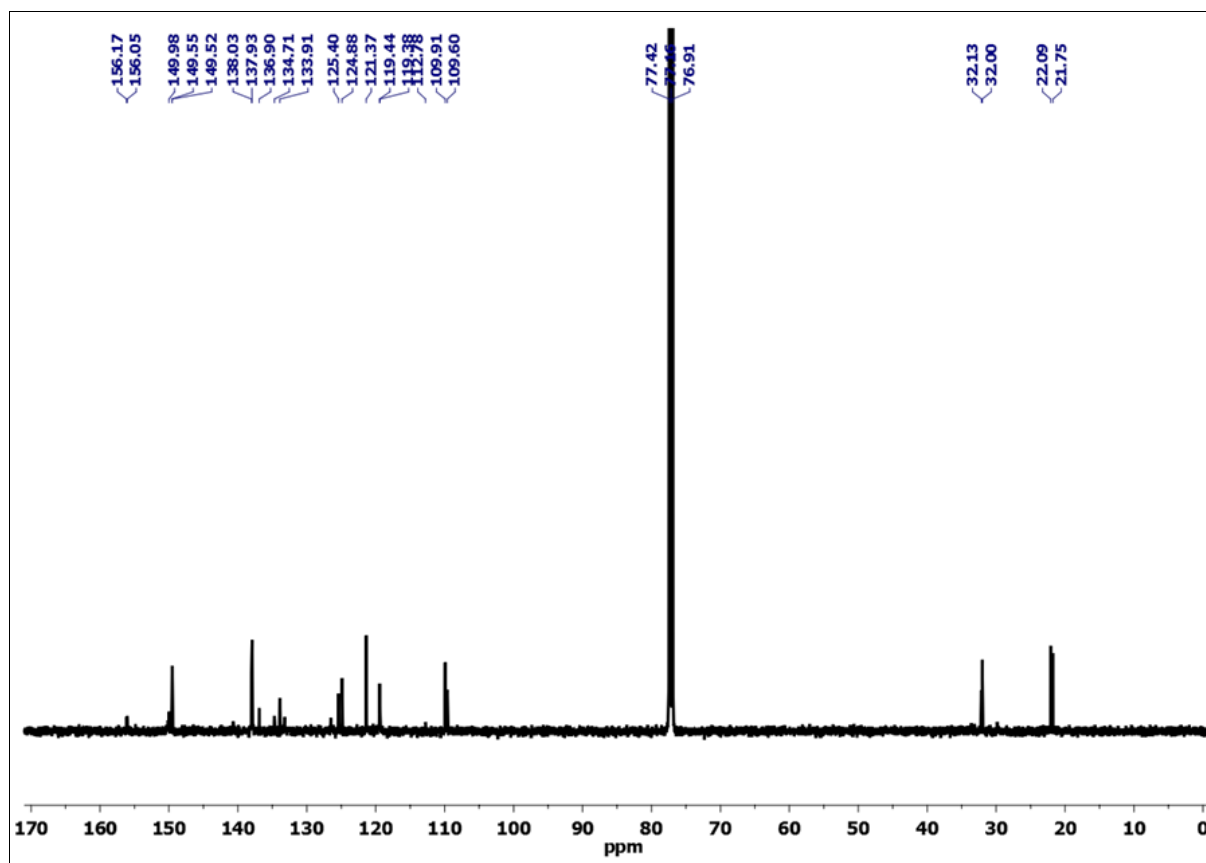


Figure 12S. ^{13}C -NMR spectrum of L3 in CDCl_3 in 500 MHz at 298K.

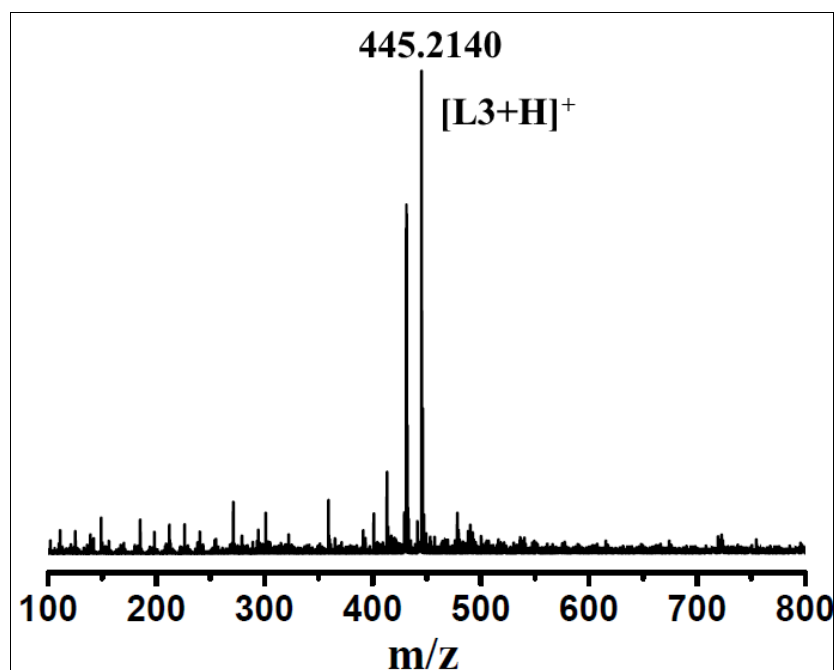


Figure 13S. ESI-MS (+ve) spectrum of L3 at 298K.

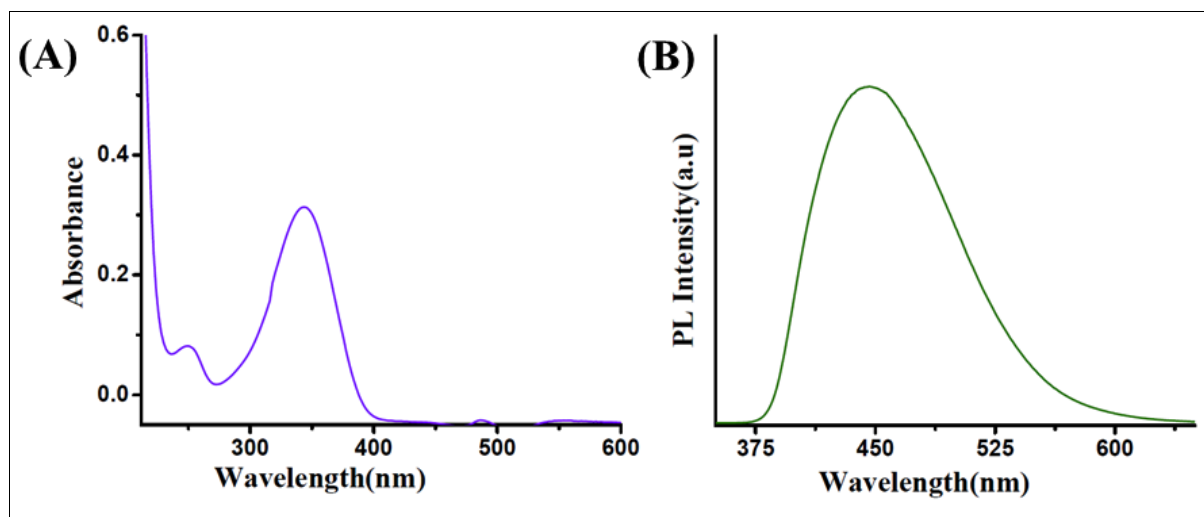


Figure 14S. (A) UV/Vis and (B) Emission spectra of **L3** ($\lambda_{exc} = 345$ nm) at 298K.

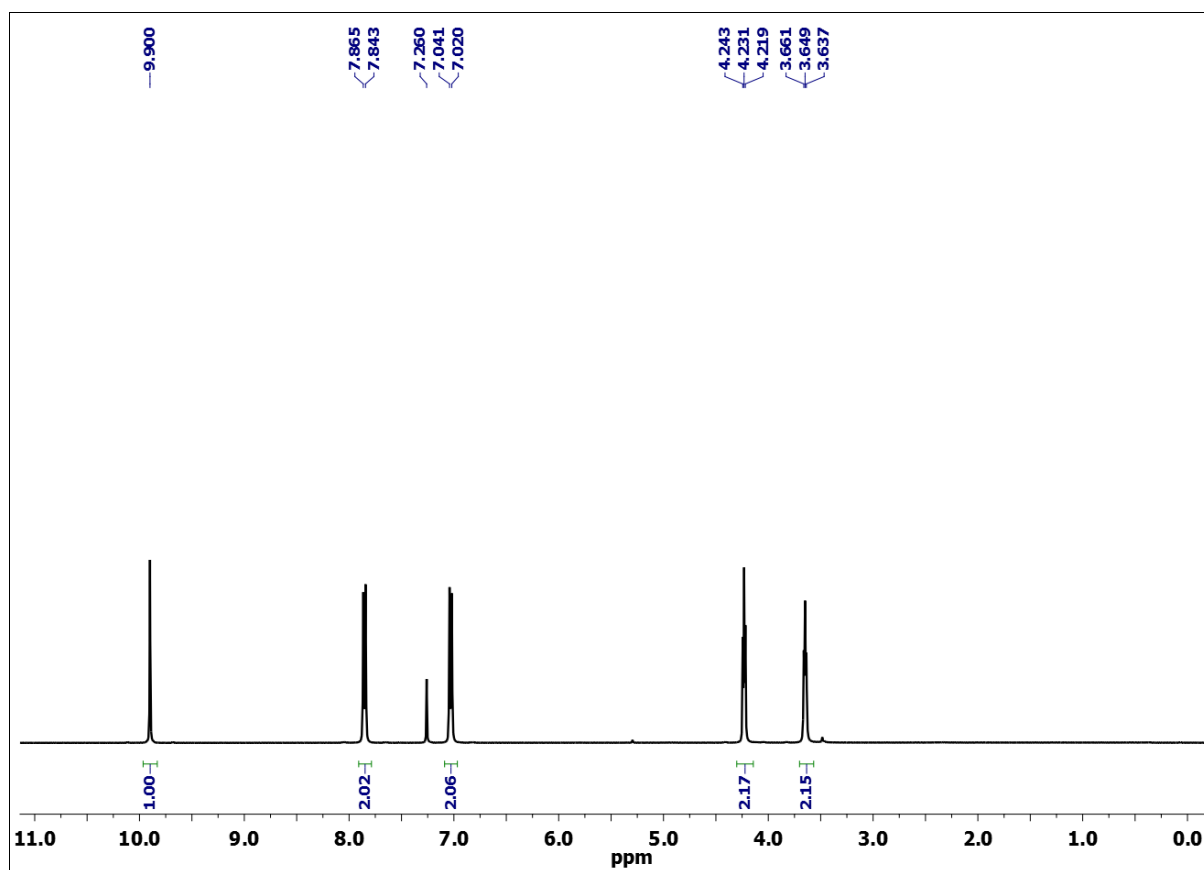


Figure 15S. $^1\text{H-NMR}$ spectrum of compound **C** in CDCl_3 in 400 MHz at 298K.

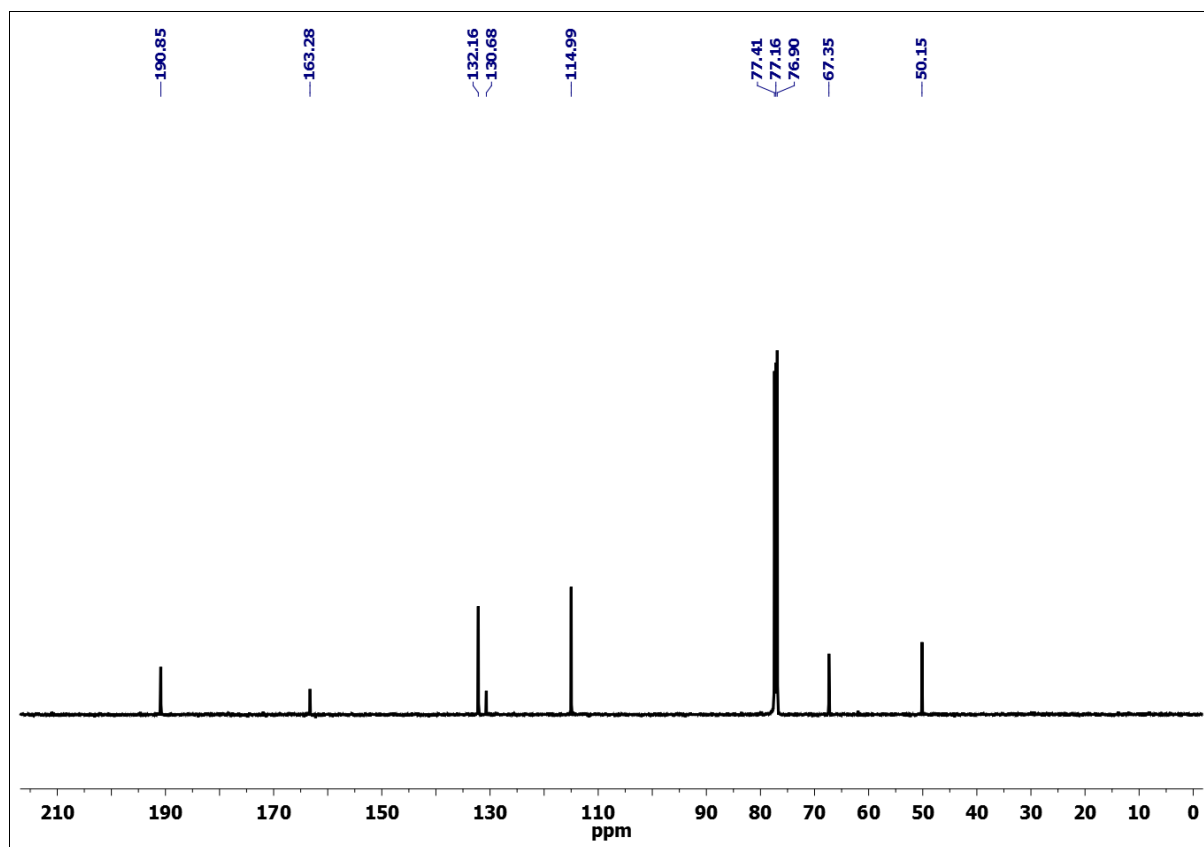


Figure 16S. ^{13}C -NMR spectrum of compound **C** in CDCl_3 in 125 MHz at 298K.

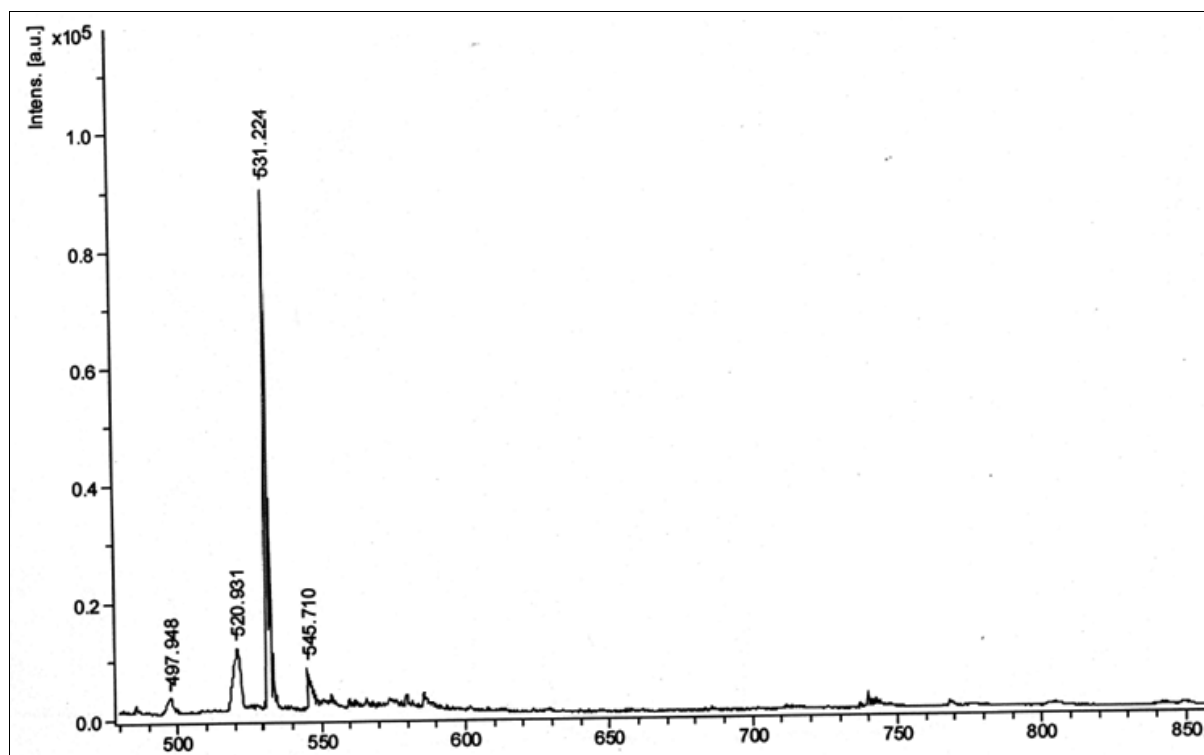


Figure 17S. MALDI-mass (+ve) spectrum of compound **L4** at 298K.

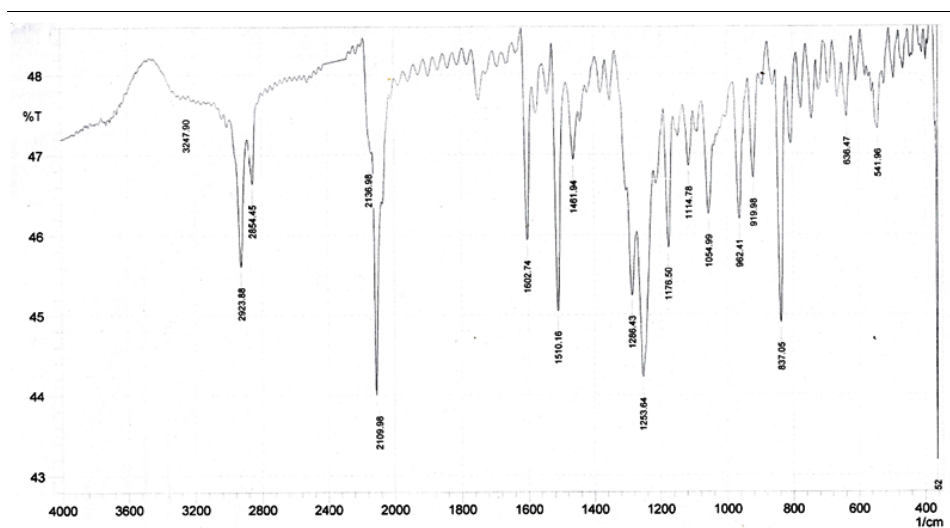


Figure 18S. IR spectrum of compound L4.

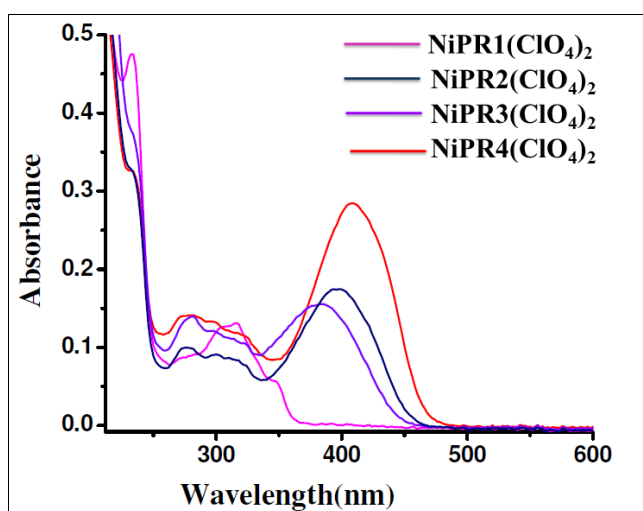


Figure 19S. Characteristic UV/Vis spectra of ternary complexes $\{\text{NiPR1}(\text{ClO}_4)_2\text{-NiPR4}(\text{ClO}_4)_2\}$ in CH_3CN at 298K.

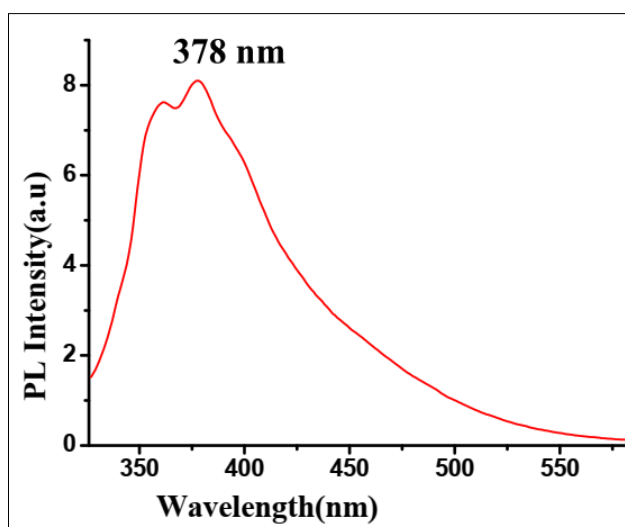


Figure 20S. Emission spectrum of $\text{NiPR1}(\text{ClO}_4)_2$ in CH_3CN at 298K ($\lambda_{\text{exc}} = 317 \text{ nm}$).

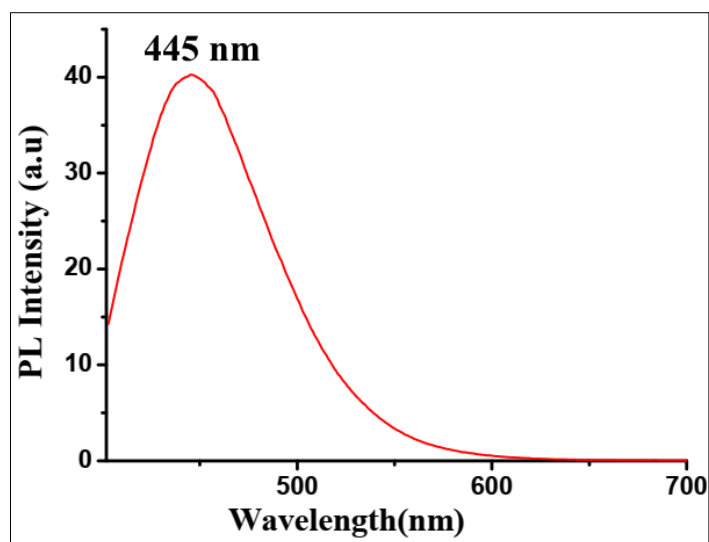


Figure 21S. Emission spectrum of NiPR2(ClO₄)₂ in CH₃CN at 298K (λ_{exc} = 396 nm).

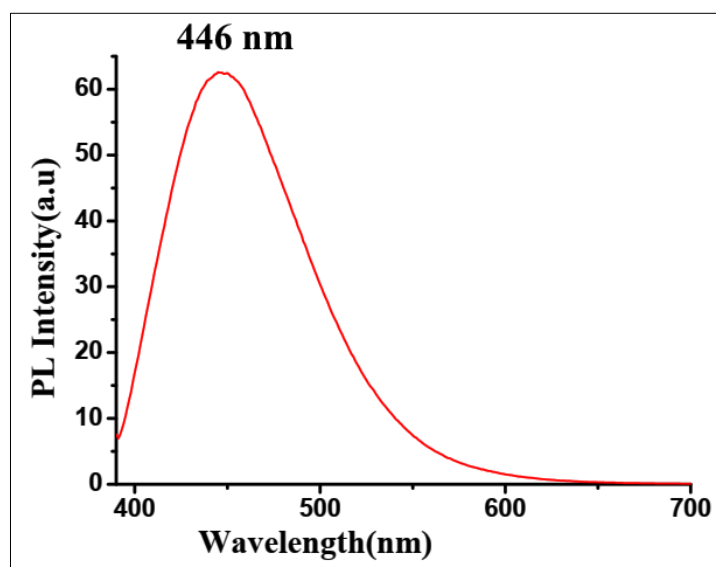


Figure 22S. Emission spectrum of NiPR3(ClO₄)₂ in CH₃CN at 298K (λ_{exc} = 385 nm).

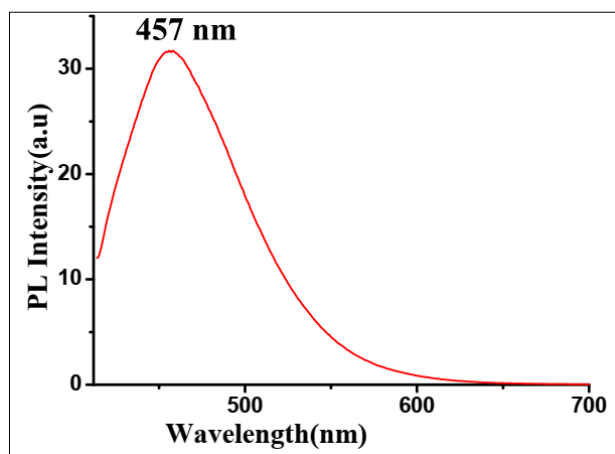


Figure 23S. Emission spectrum of NiPR4(ClO₄)₂ in CH₃CN at 298K (λ_{exc} = 408 nm).

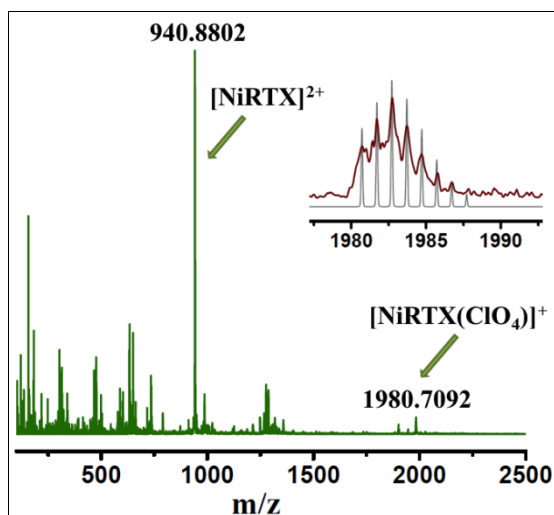


Figure 24S. ESI-MS (+ve) spectrum of Ni(II) templated rotaxane $[\text{NiRTX}(\text{ClO}_4)_2]$ at 298K.

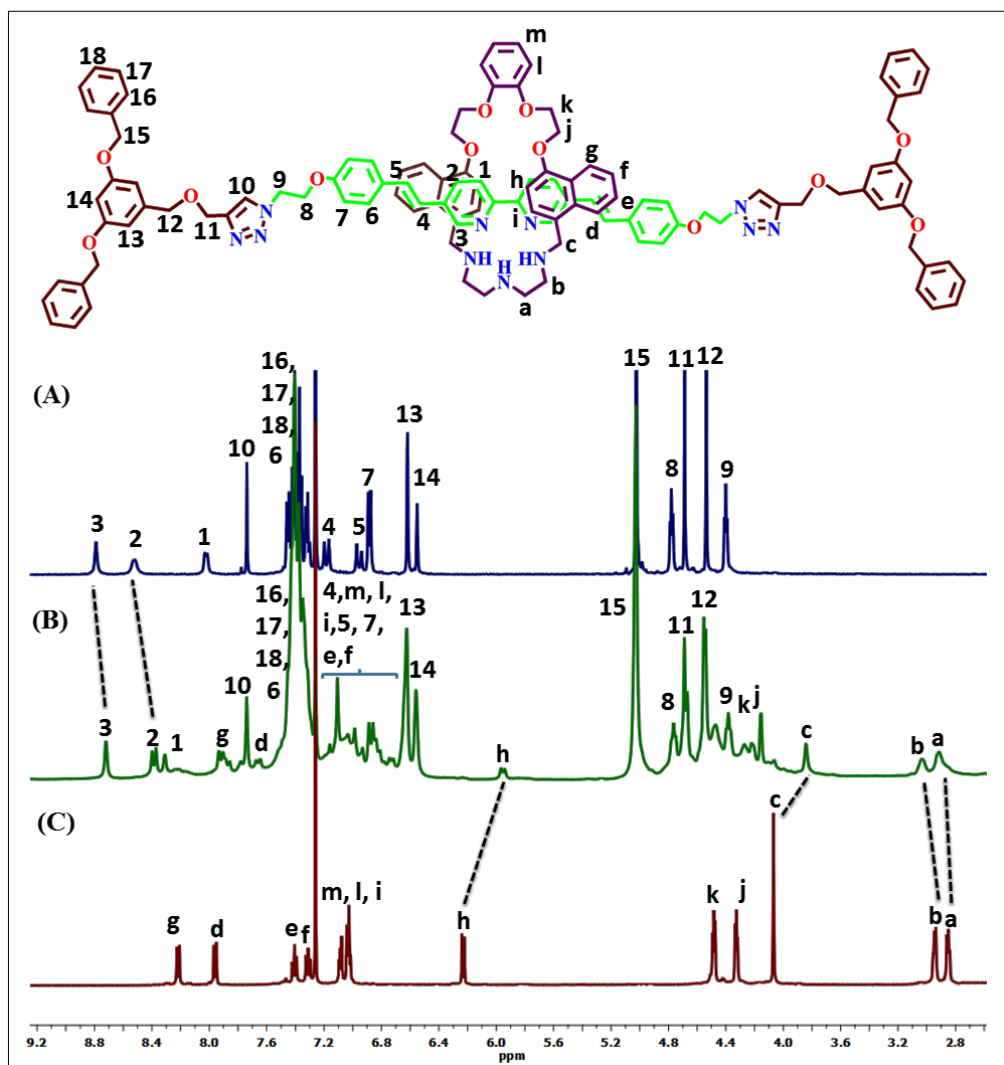


Figure 25S. Stacked ^1H NMR spectra of (A) ConAx, (B) RTX, and (C) NaphMC in CDCl_3 at 298 K. The labels of protons are shown correspond to NaphMC and ConAx in RTX in the above mentioned structure.

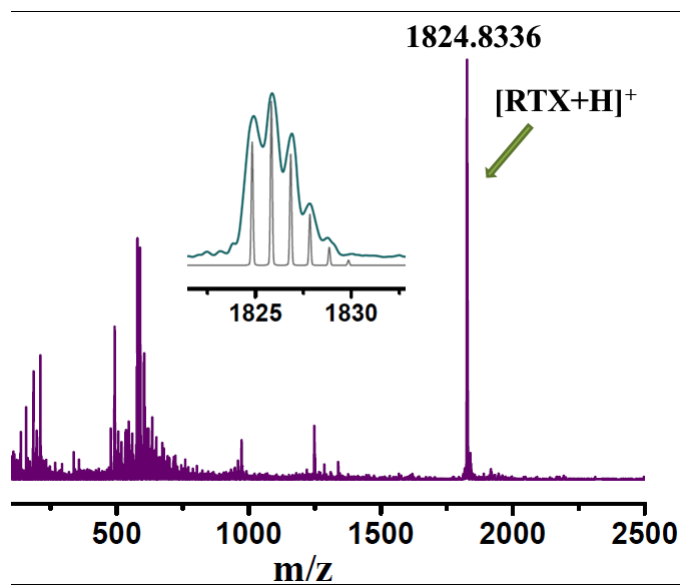


Figure 26S. ESI-MS (+ve) spectrum of metal free rotaxane [RTX] at 298K.

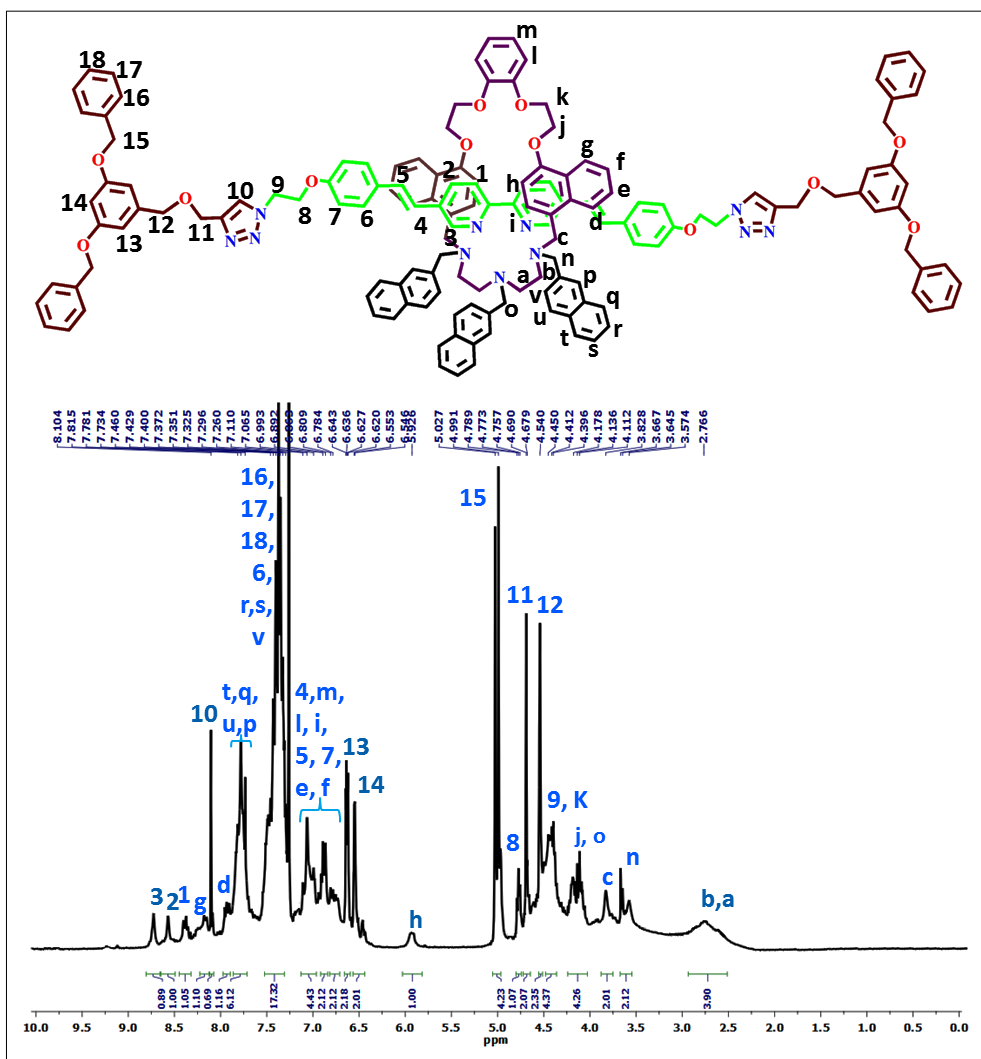


Figure 27S. ¹H-NMR spectrum of NAPRTX in CDCl₃ in 300 MHz at RT.

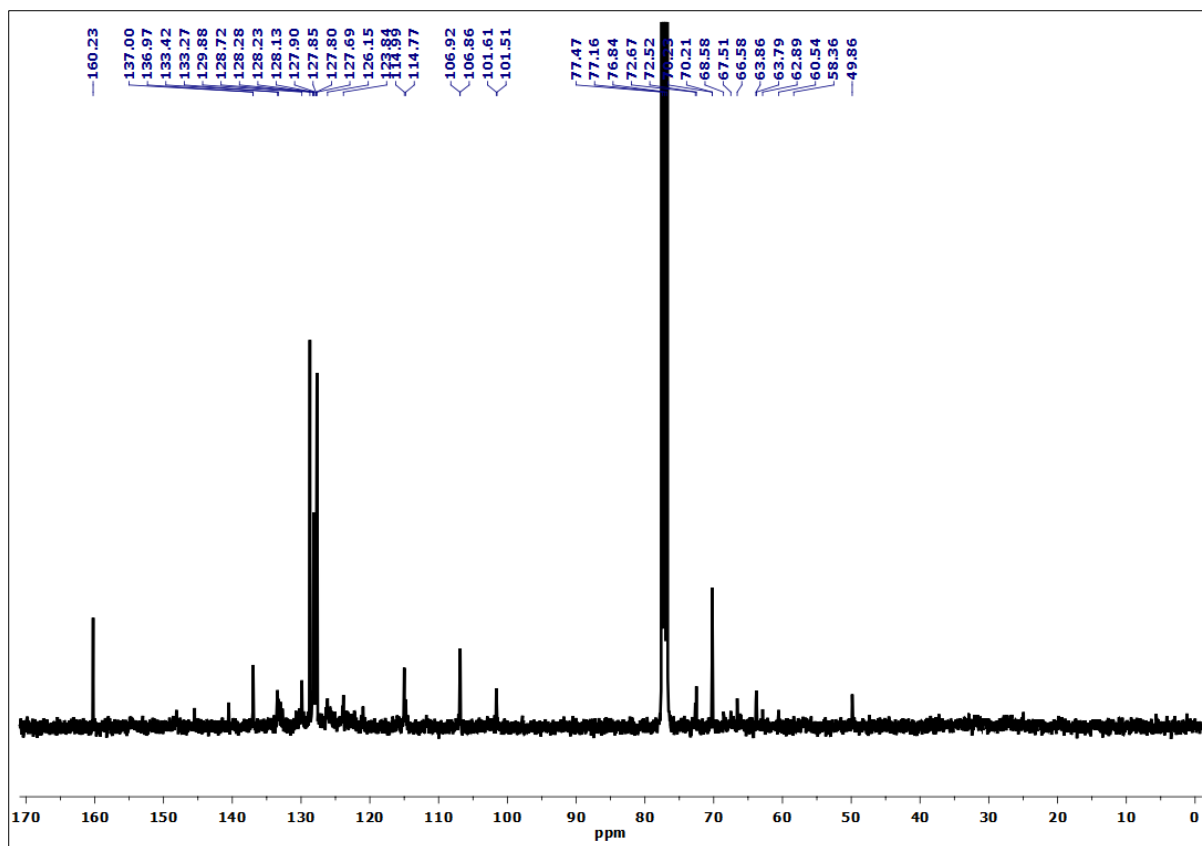


Figure 28S. ¹³C-NMR spectrum of NAPRTX in CDCl₃ in 300 MHz at RT.

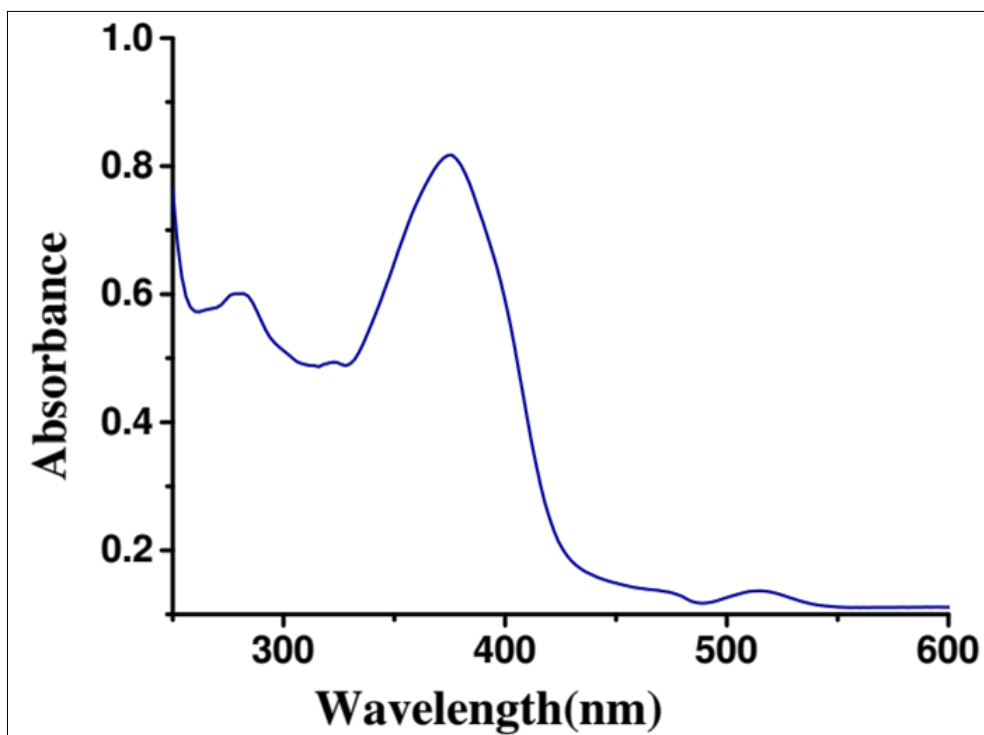


Figure 29S. UV/Vis spectrum of NAPRTX at 298K.

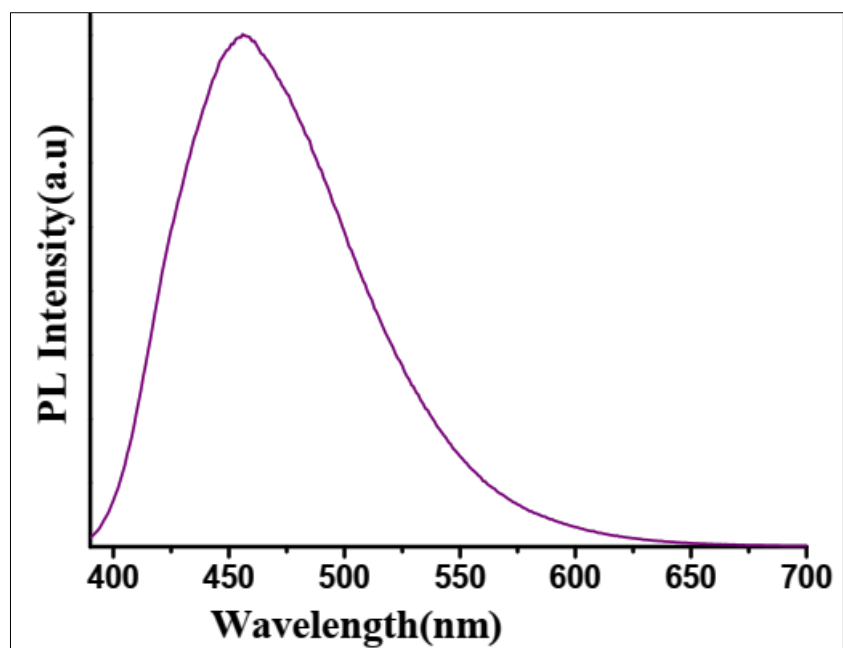


Figure 30S. Emission spectrum of NAPRTX exc at 375 nm at 298K.

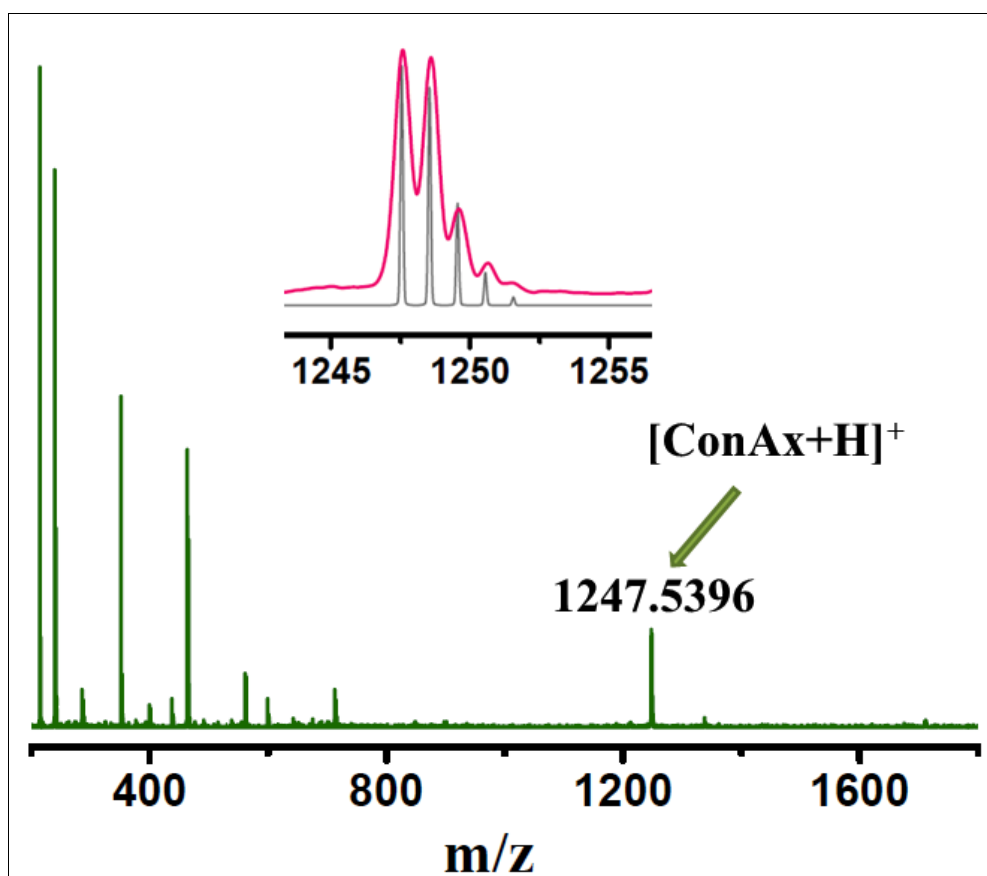


Figure 31S. ESI-MS (+ve) spectrum of ConAx at 298K.

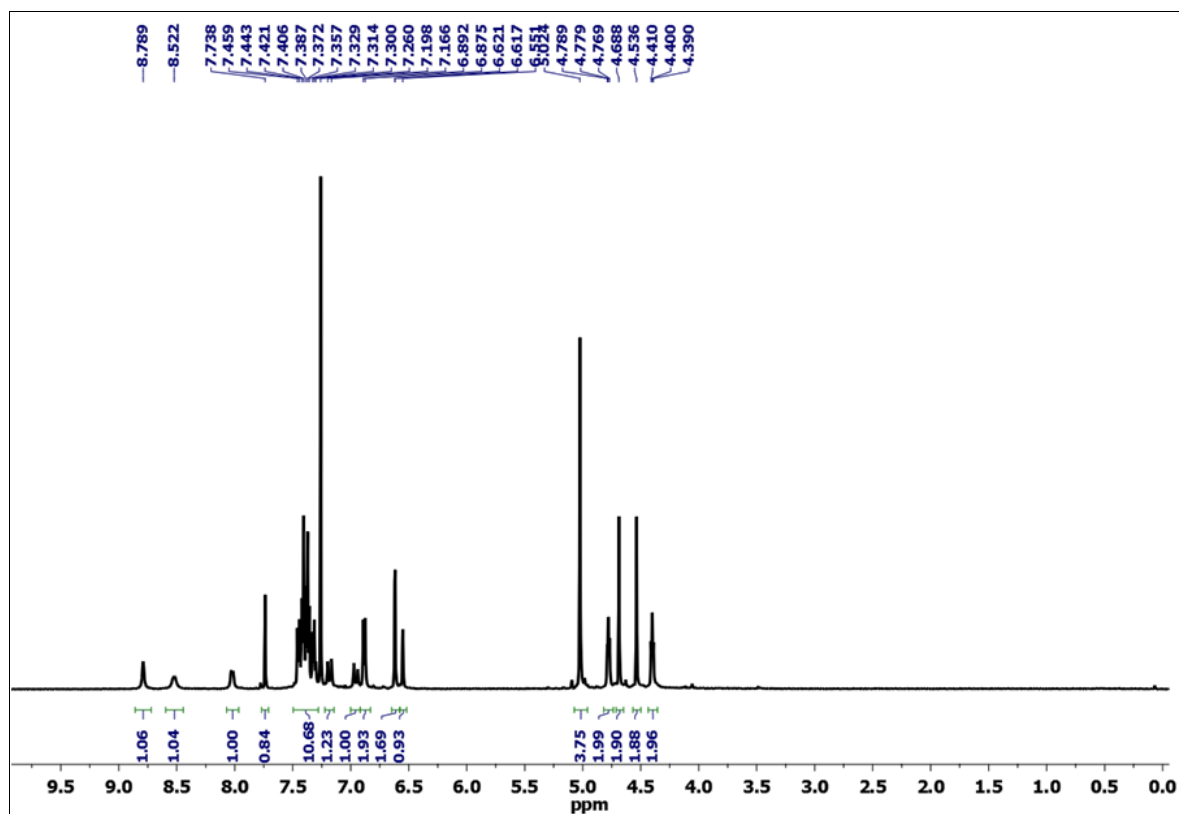


Figure 32S. ^1H -NMR spectrum of **ConAx** in CDCl_3 in 500 MHz at 298K.

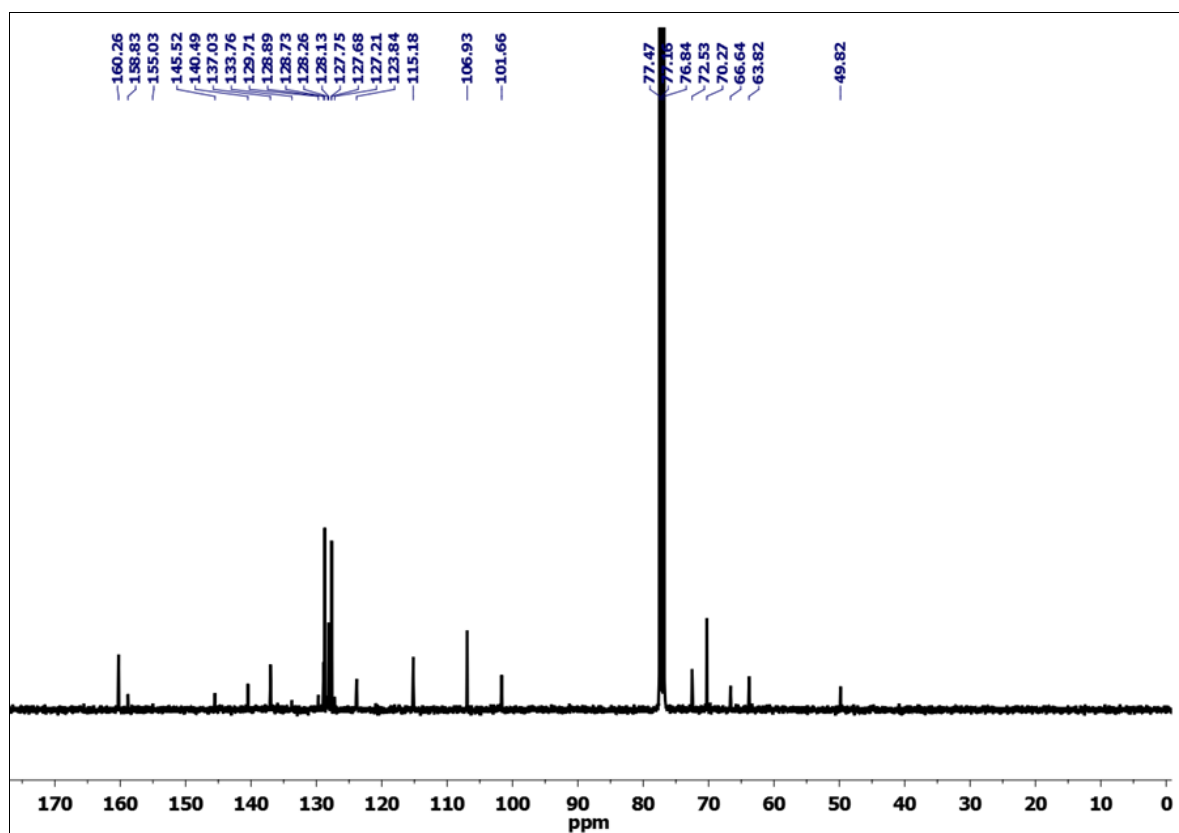


Figure 33S. ^{13}C -NMR spectrum of **ConAx** in CDCl_3 in 100 MHz at 298K.

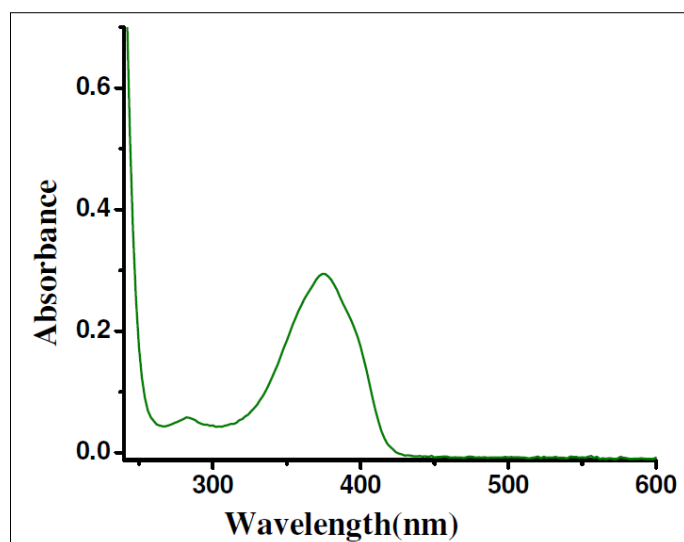


Figure 34S. UV/Vis spectrum of **ConAx** in DMF-CH₃CN (2:8) at 298K.

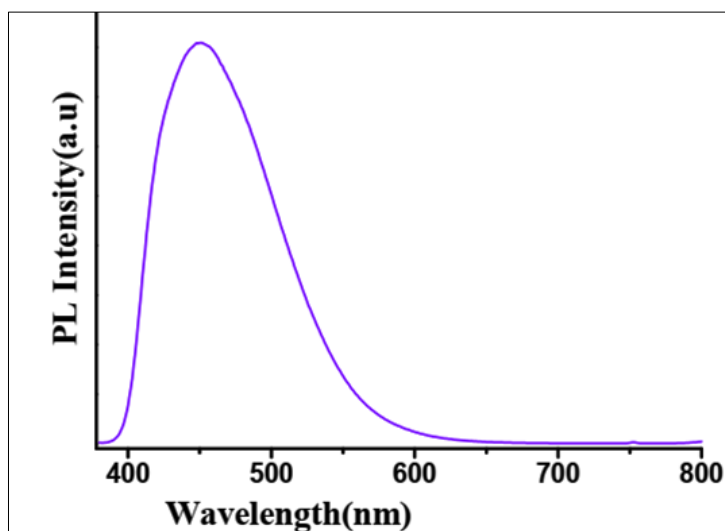


Figure 35S. Emission spectrum of **ConAx** (5×10^{-6} M) in DMF-CH₃CN (2:8) exc at 375 nm at 298K.

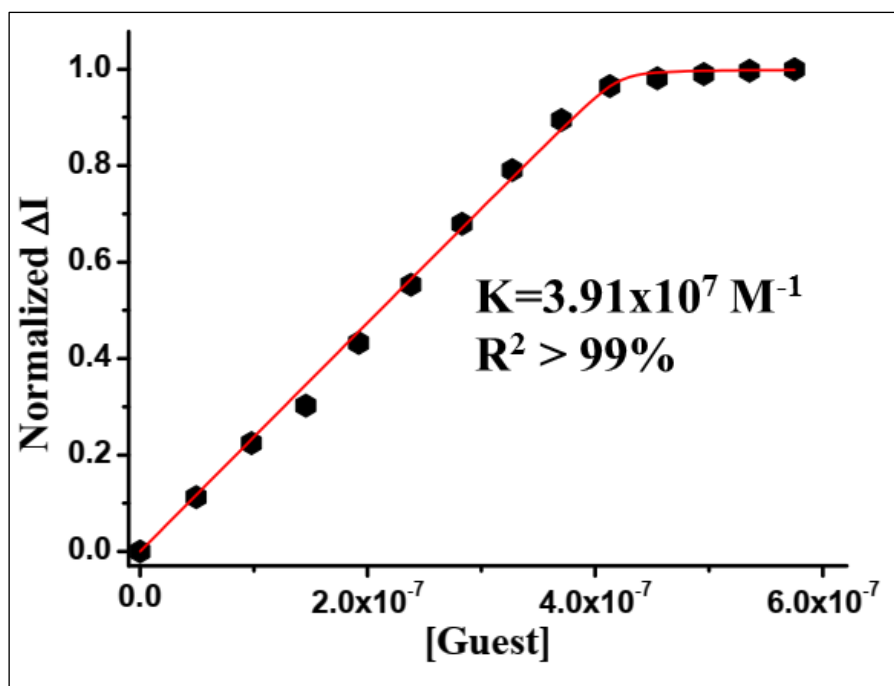


Figure 36S. Non-linear 1 : 1 curve fitting plot from PL titration data between NAPRTX and Zn^{2+} ion at 298 K, $\lambda_{\text{exc}} = 375 \text{ nm}$.

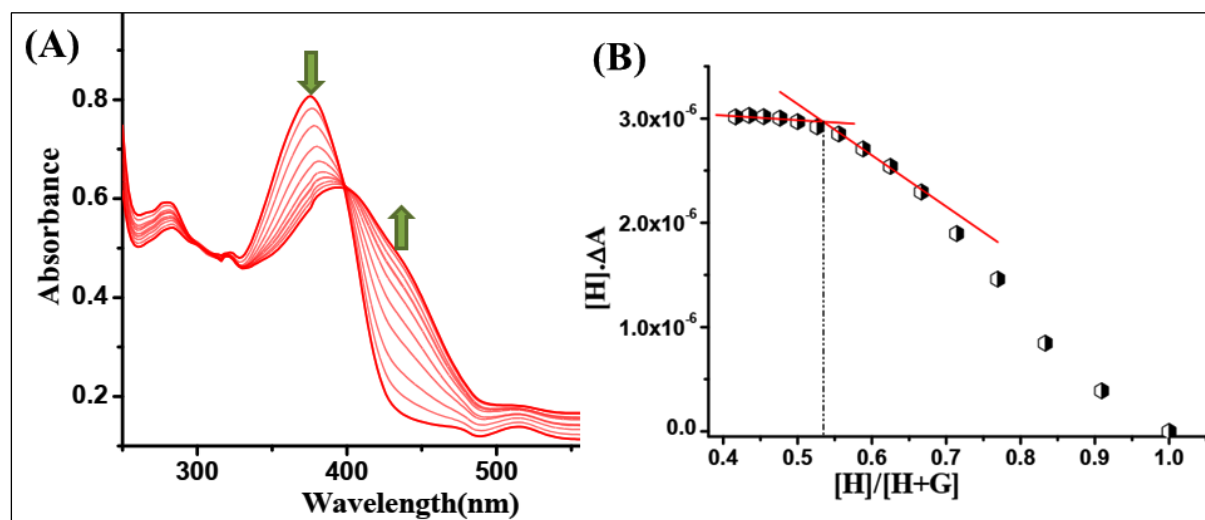


Figure 37S. (A) UV titration of NAPRTX with $\text{Zn}(\text{ClO}_4)_2$ in solvent mixture {3% water in mixture of solvent} at 298 K. (B) Molar ratio plot.

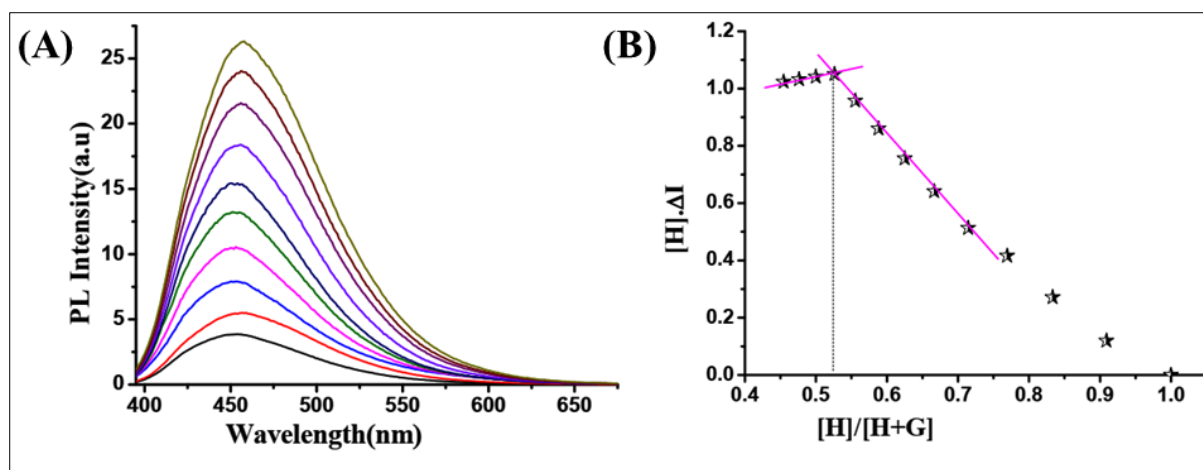


Figure 38S. (A) PL titration of NAPRTX with $Zn(ClO_4)_2$ in solvent mixture {3% water in mixture of solvent} at 298 K. (B) Molar ratio plot.