Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Coordination-Assembly for Quantitative Construction of Bis-Branched Molecular Shuttles

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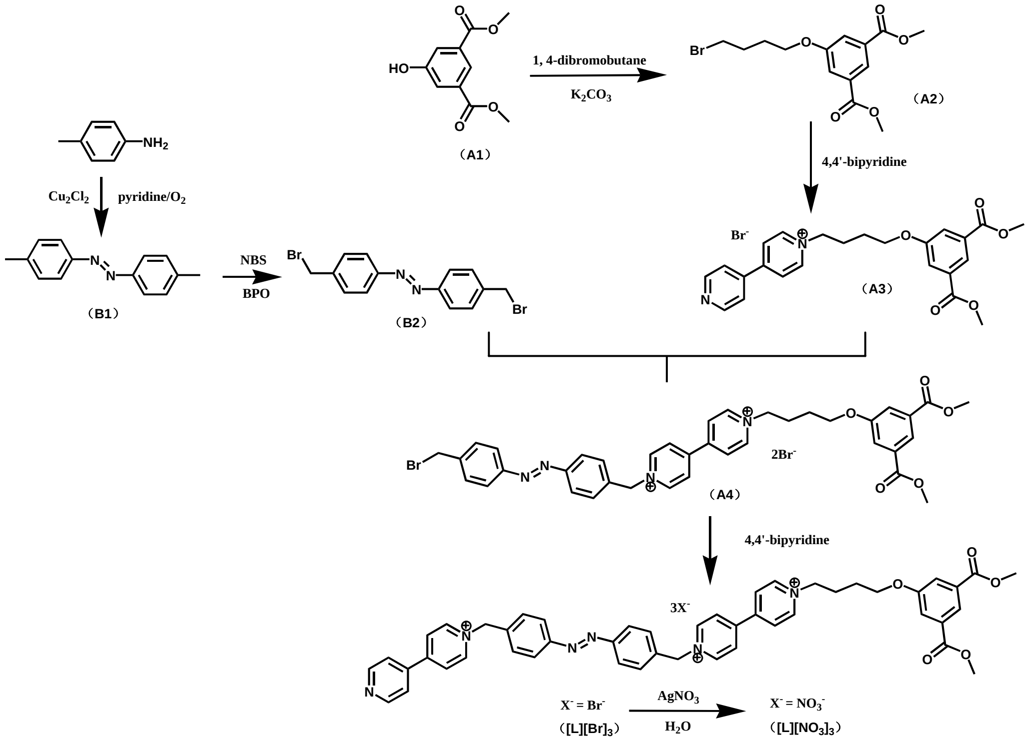
General: ^{1}H NMR spectra and the ^{13}C NMR were measured on a Brüker AV-400 or AV-500 spectrometer, and the 2D-NOESY NMR spectra were recorded on a Brüker AV-500 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a HP5989 mass spectrometer. Elemental analysis was performed on a vario EL III instrument. Absorption spectra were done on a Varian Cary 500 UV/Vis spectrophotometer (1-cm quartz cell used), while the ICD spectra were recorded on a Jasco J-815 CD spectrophotometer in a 1 mm quartz cell. The photoirradiation was carried on a CHF-XM 500-W high-pressure mercury lamp with a filter for 365 nm in a sealed Ar-saturated 1 cm quartz cell. The distance between the lamp and the sample cell was 20 cm. Melting points were determined by using an X-6 micro-melting point apparatus.

Materials: α-cyclodextrin (α-CD), 1, 4-dibromobutane, silver nitrate, cuprous chloride, *p*-toluidine, 4, 4'-bipyridine, N-bromosuccinimide (NBS), benzoyl peroxide

(BPO) and the inorganic reagents were commercially available and used as received. Ethylene diamine palladium chloride and ethylene diamine platinum chloride was purchased from Alfa Aesar and used as received. Acetone and pyridine were dried with anhydrous magnesium sulfate. Acetonitrile and DMF were dried by 4A molecular sieve and distilled under reduced pressure before used.



Scheme S1. Synthetic route to the ligand [**L**][NO$_3$]$_3$

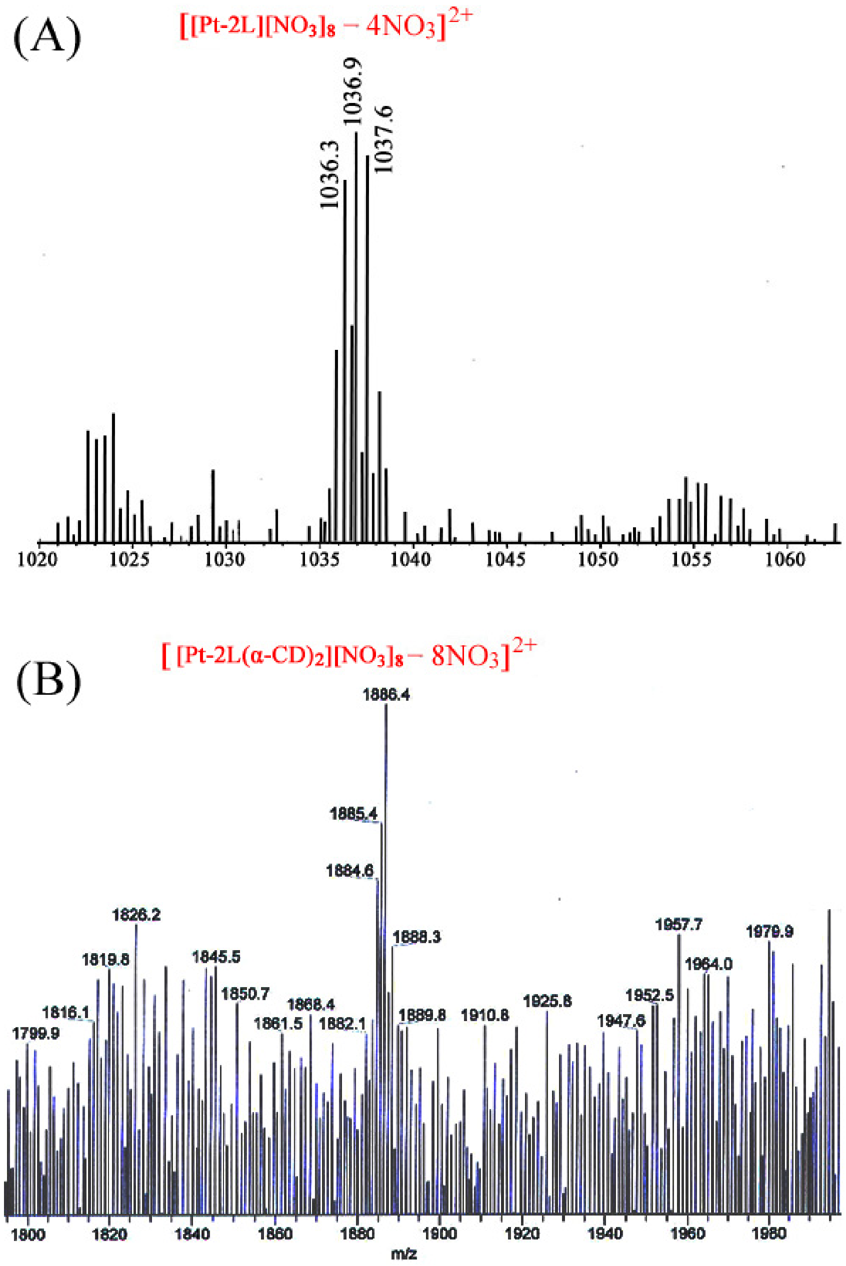


Fig. S1 ESI-MS spectra in aqueous solution of A) [**Pt-2L**][NO$_3$]$_8$ and B) [**Pt-2L**(α-CD)$_2$][NO$_3$]$_8$. It shows a standard Pt isotopic distribution around m/z = 1036.9 and 1886.4, respectively.

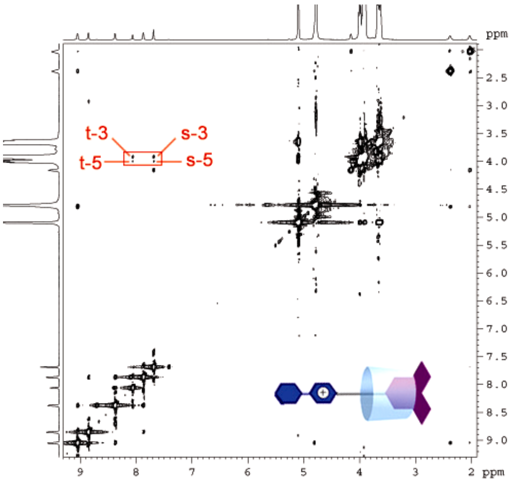


Fig. S2 The two-dimensional ^{1}H NOESY NMR spectra (500 MHz in D_2O at 298 K) of **A3** in D_2O after addition of 3 equiv. α-CD (**A3-CD**). The concentration of **A3** was maintained at 2.0×10^{-2} M.

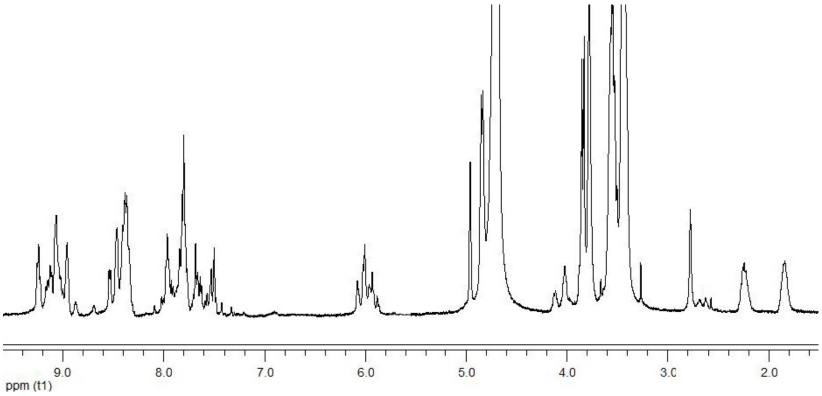


Figure S3. ^{1}H NMR spectra (400 MHz in D_2O at 298 K) of **[Pt-2L**(α-CD)$_2$][NO$_3$]$_8$, irradiation back from its photostationary state by visible light for 4 h. All the peaks are more or less the same as the ones in the initial state of **[Pt-2L**(α-CD)$_2$][NO$_3$]$_8$.

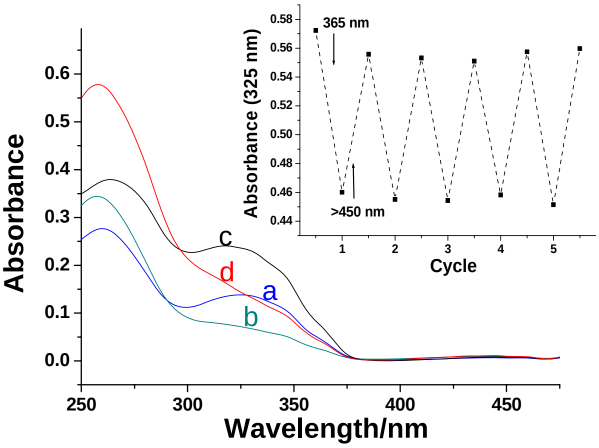
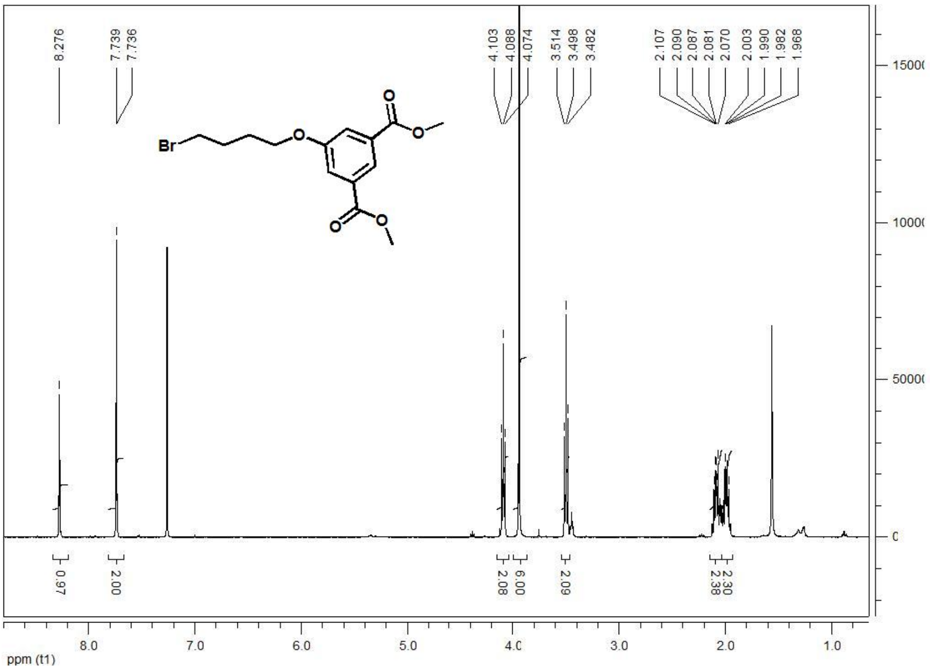
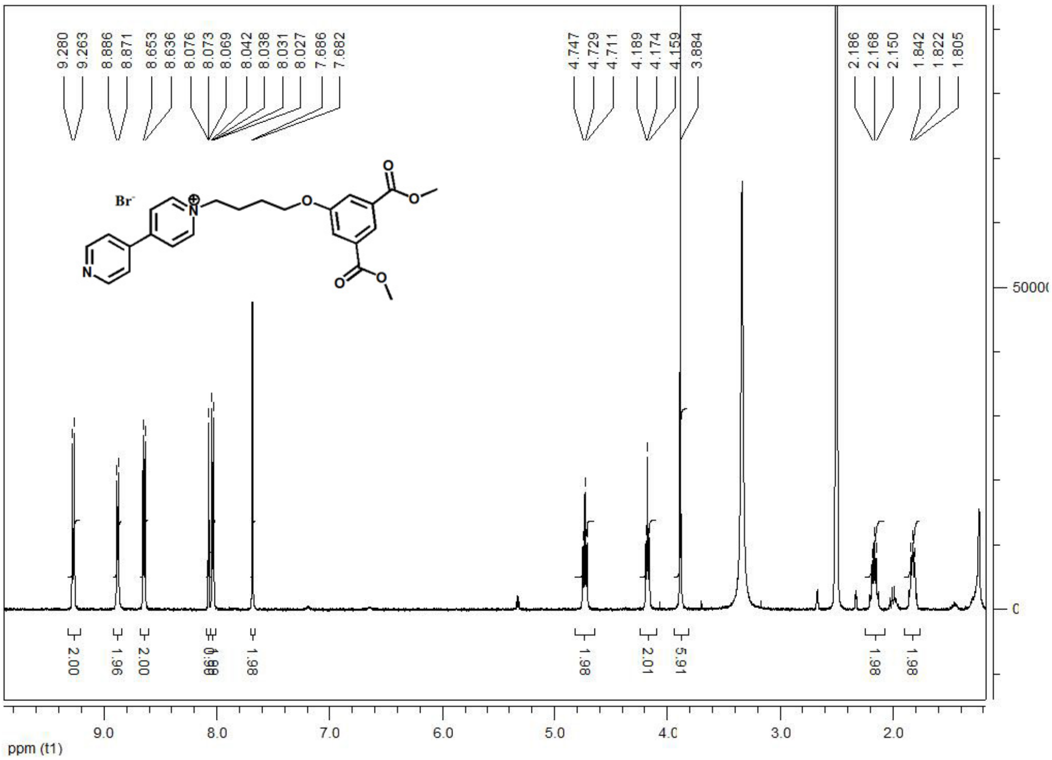


Figure S4. Absorption spectra in water at 298K of $[\mathbf{L}(\alpha\text{-}\mathbf{CD})][\mathrm{NO}_3]_3$ a) in the initial state, b) after irradiation at 365 nm for 30 min and of $[\mathbf{Pt\text{-}2L}(\alpha\text{-CD})_2][\mathrm{NO}_3]_8$ c) in the initial state, d) after irradiation at 365 nm for 30 min. $[\mathbf{L}(\alpha\text{-}\mathbf{CD})][\mathrm{NO}_3]_3$ and $[\mathbf{Pt\text{-}2L}(\alpha\text{-CD})_2][\mathrm{NO}_3]_8$ were maintained at the same concentration of 1.25×10^{-5} M. Inset: changes in the absorbance at 325 nm of $[\mathbf{Pt\text{-}2L}(\alpha\text{-CD})_2][\mathrm{NO}_3]_8$ for several cycles. In one cycle, 365-nm UV light and visible light irradiation was used to isomerize the azobenzene unit.

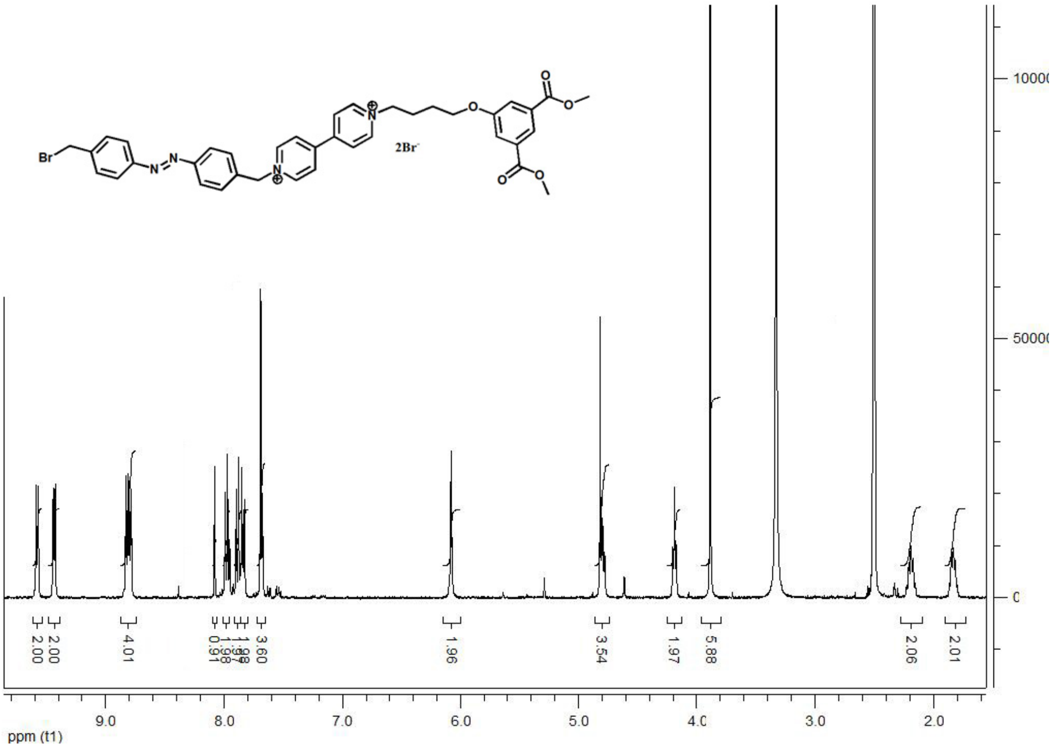
^{1}H NMR spectrum of **A2** in $CDCl_3$ (400MHz)



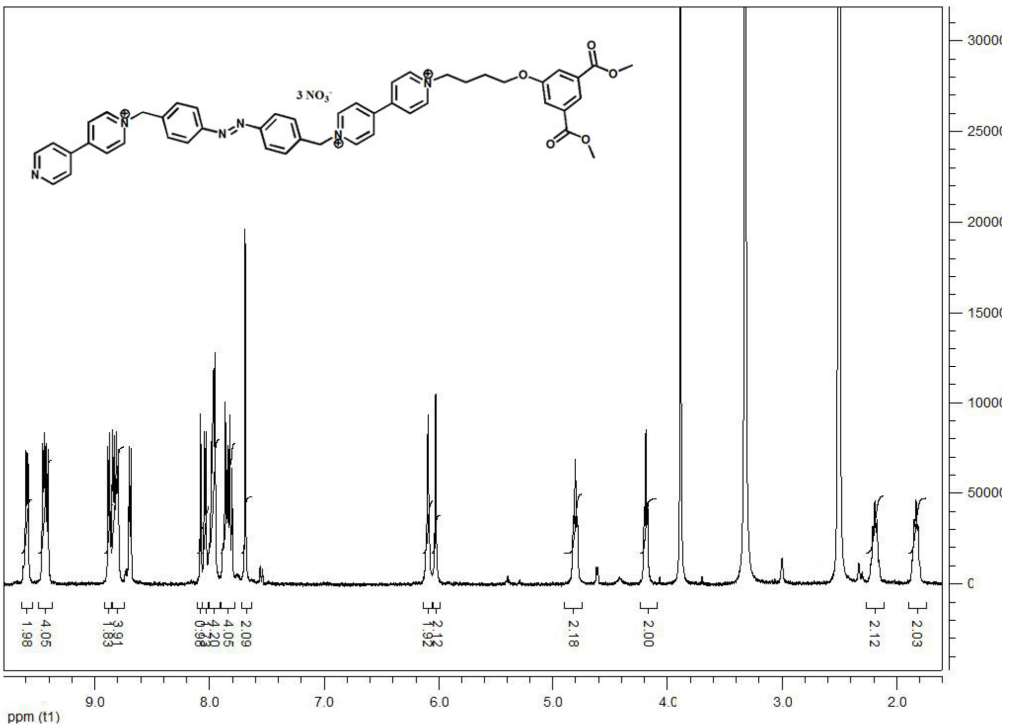
^{1}H NMR spectrum of **A3** in DMSO-d_6 (400MHz)



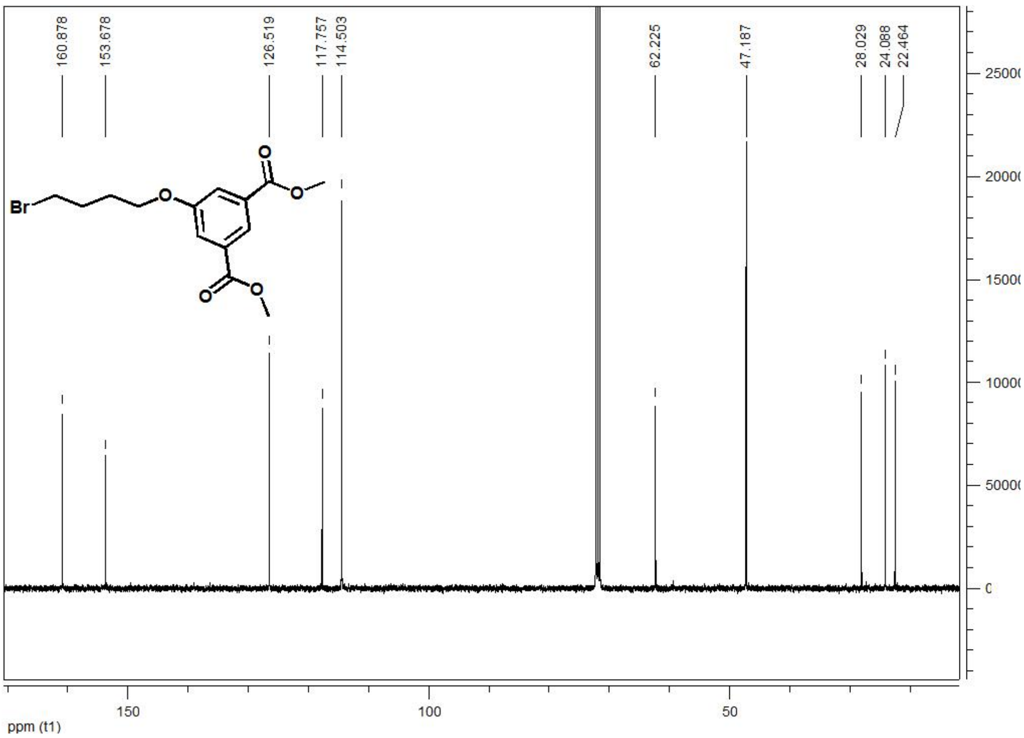
^{1}H NMR spectrum of **A4** in DMSO-d_6 (400MHz)



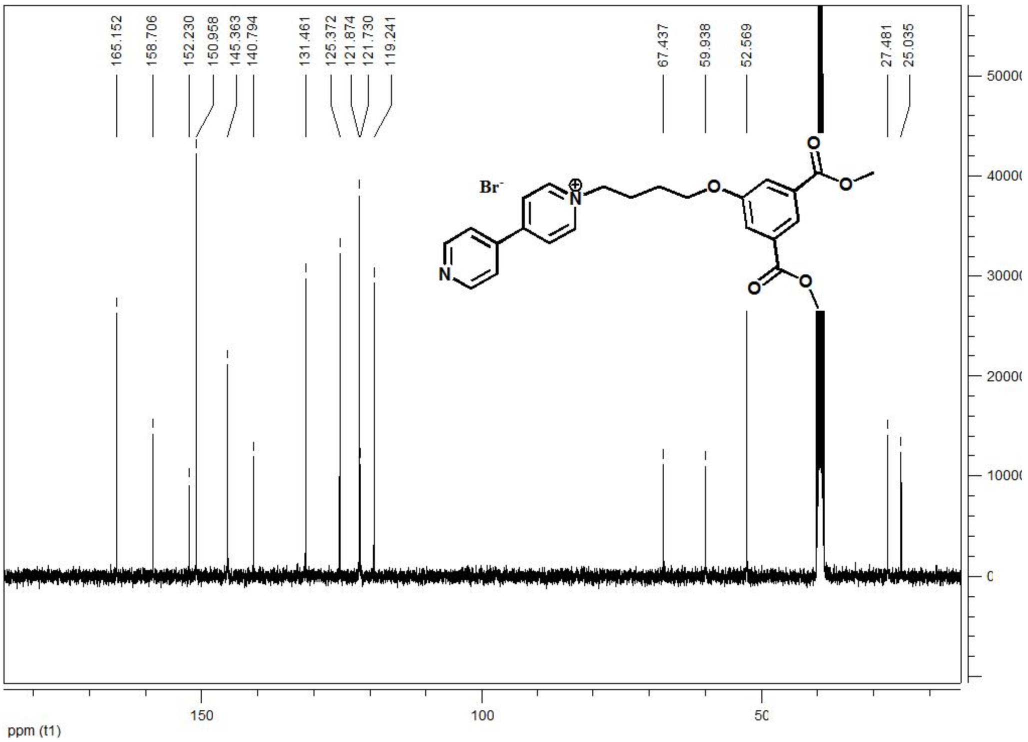
^{1}H NMR spectrum of **L** in DMSO-d_6 (400MHz)



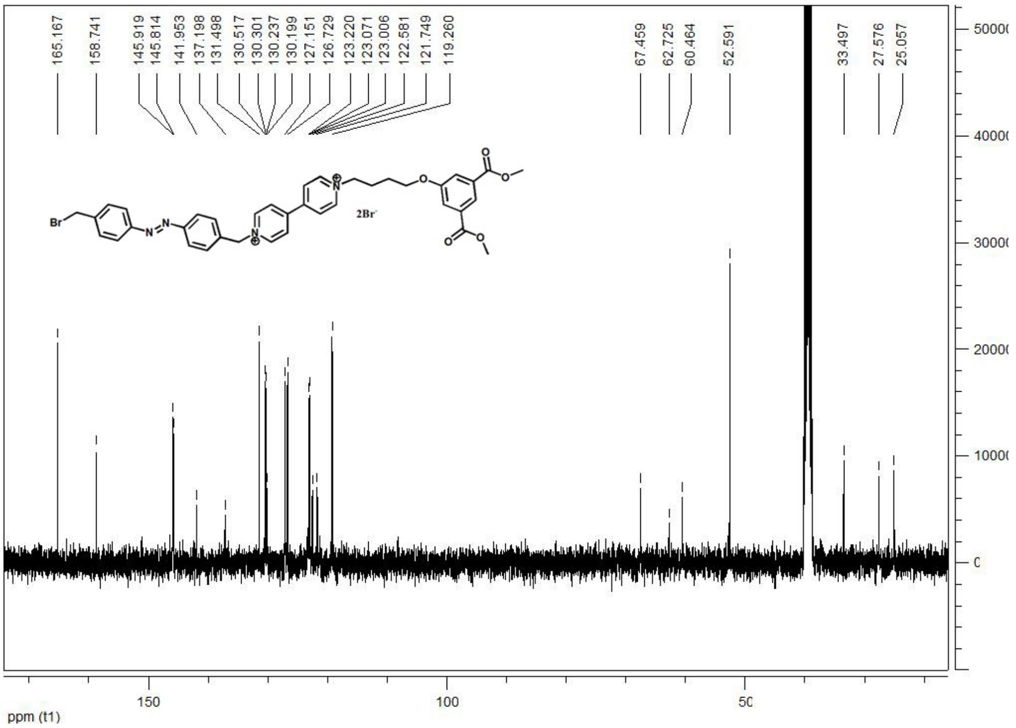
^{13}C NMR spectrum of **A2** in $CDCl_3$ (400MHz)



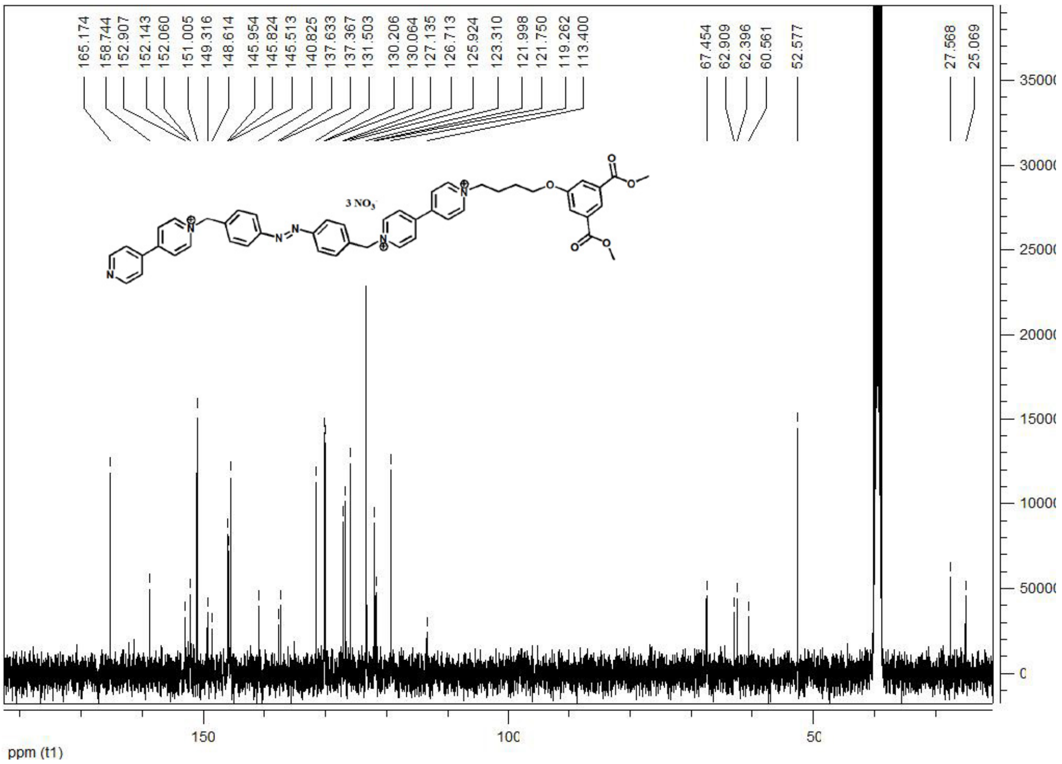
^{13}C NMR spectrum of **A3** in DMSO-d_6 (400MHz)



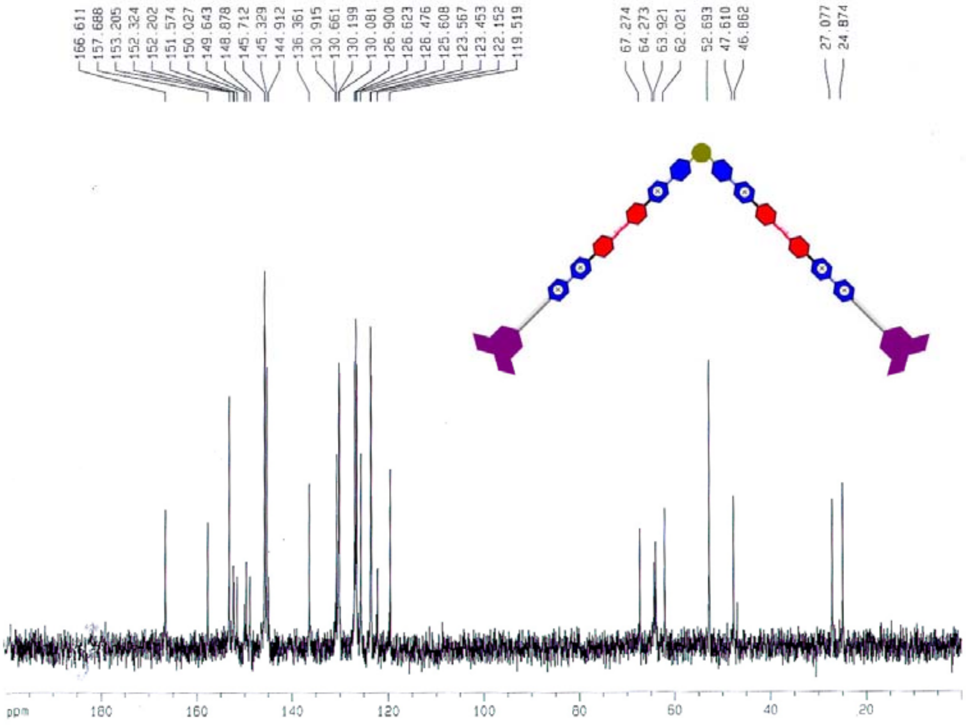
^{13}C NMR spectrum of **A4** in DMSO-d_6 (400MHz)



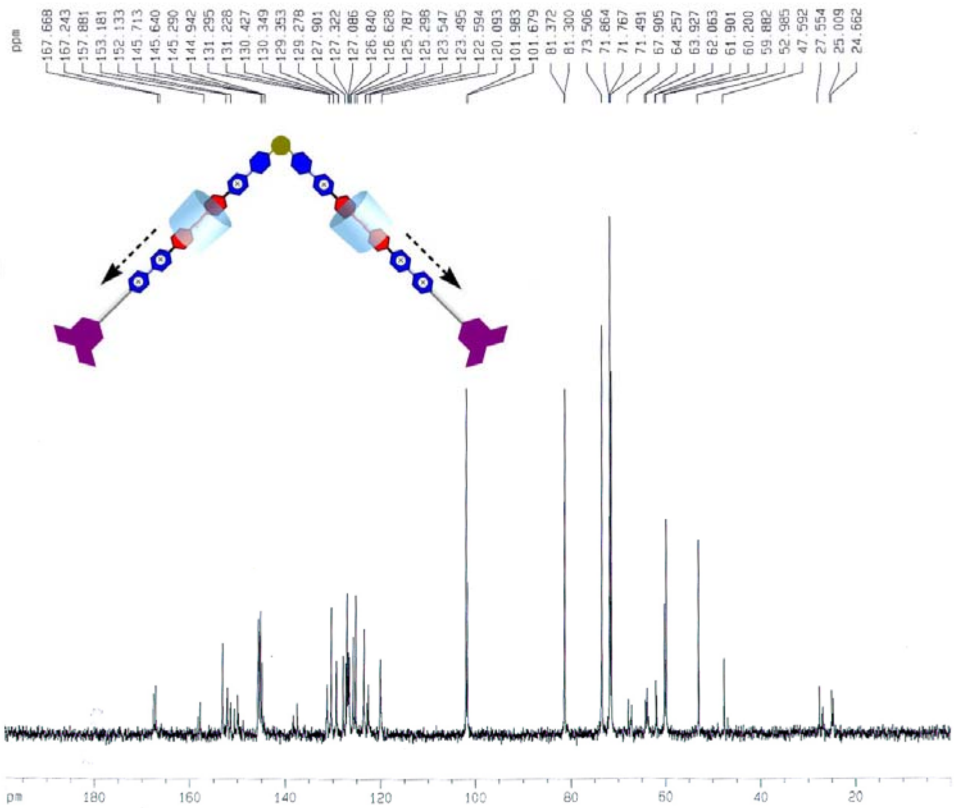
^{13}C NMR spectrum of **[L]**[NO$_3$]$_3$ in DMSO-d$_6$ (400MHz)



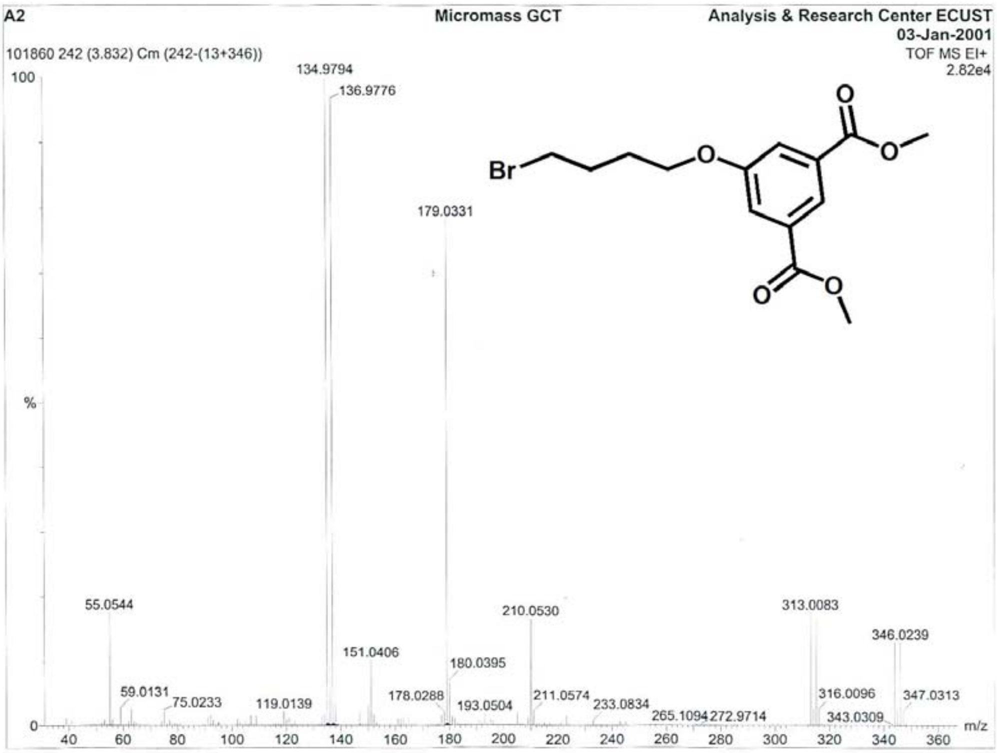
^{13}C NMR spectrum of **[Pt-2L]**[NO$_3$]$_8$ in D$_2$O (500MHz)



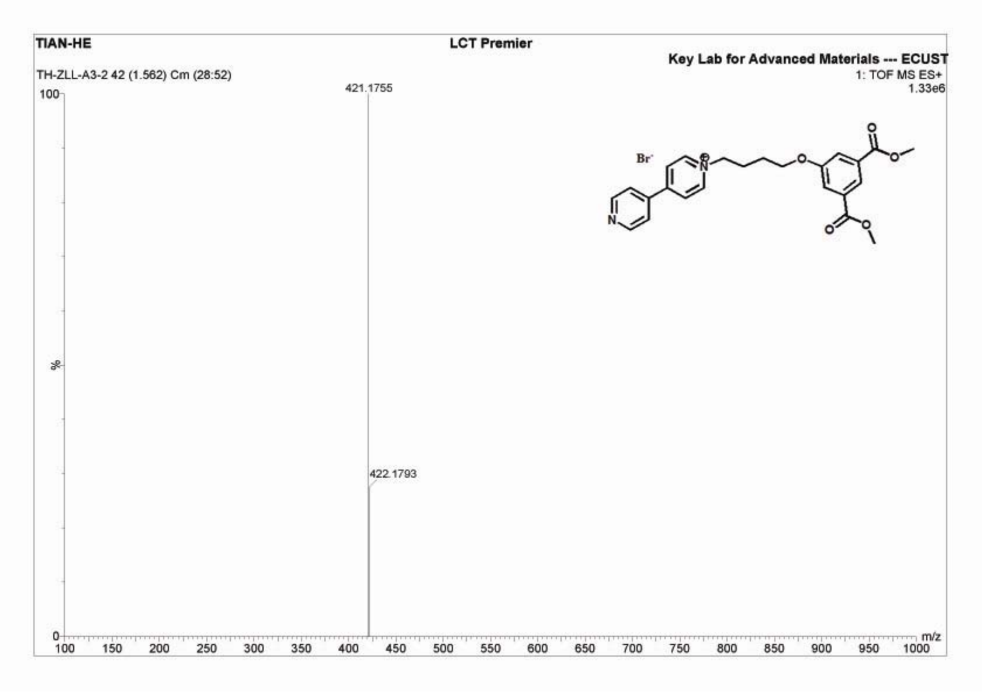
^{13}C NMR spectrum of **[Pt-2L**(α-CD)$_2$][NO$_3$]$_8$ in D$_2$O (500MHz)



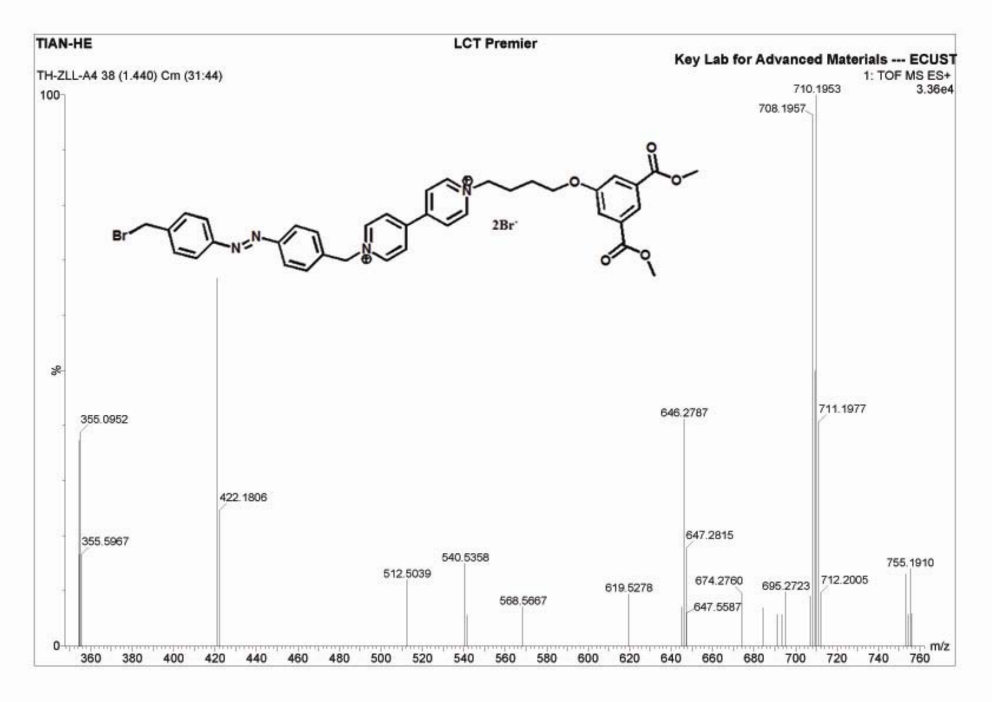
MS spectrum (EI) of **A2**



MS spectrum (ESI) of **A3**



MS spectrum (ESI) of **A4**



MS spectrum (ESI) of $[\mathbf{L}(\alpha\text{-CD})][NO_3]_3$