Supporting information

Discrete 0D and polymeric 2D and 3D derivatives assembled from hetero-metallic $[(CuL)_2Zn]^{2+}$ and dicyanamide blocks (H_2L = salen type di-Schiff bases): Genuine supramolecular isomers with distinct topologies

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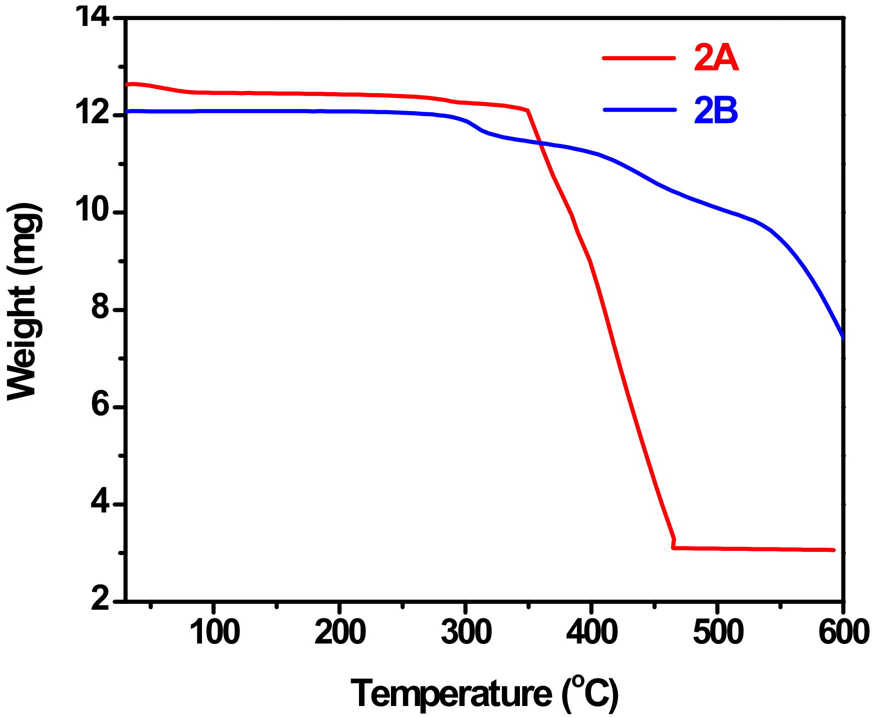

Fig. S1. Thermograms of complexes **2A** and **2B**.

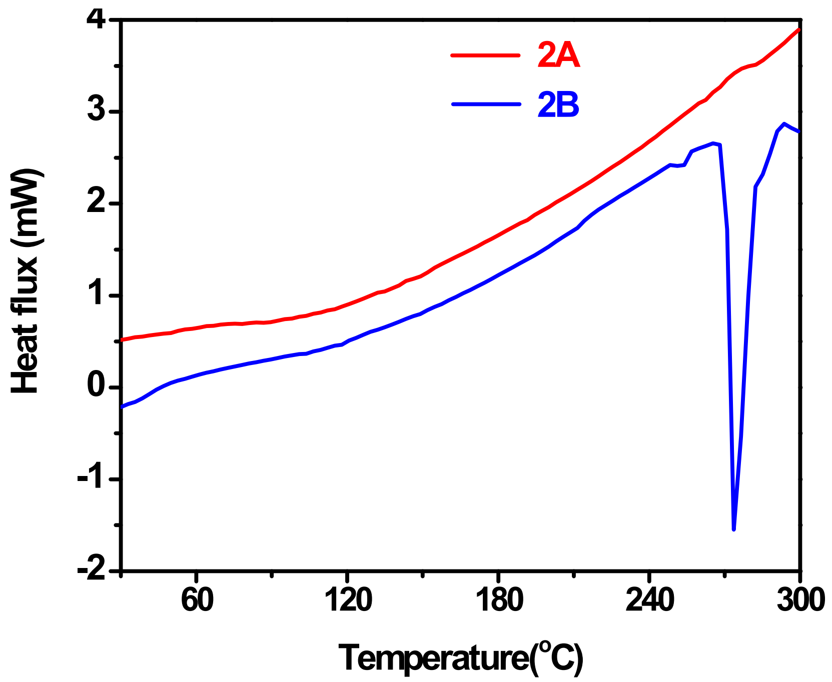

Fig. S2. Differential scanning calorimetry (DSC) of complexes **2A** and **2B**.

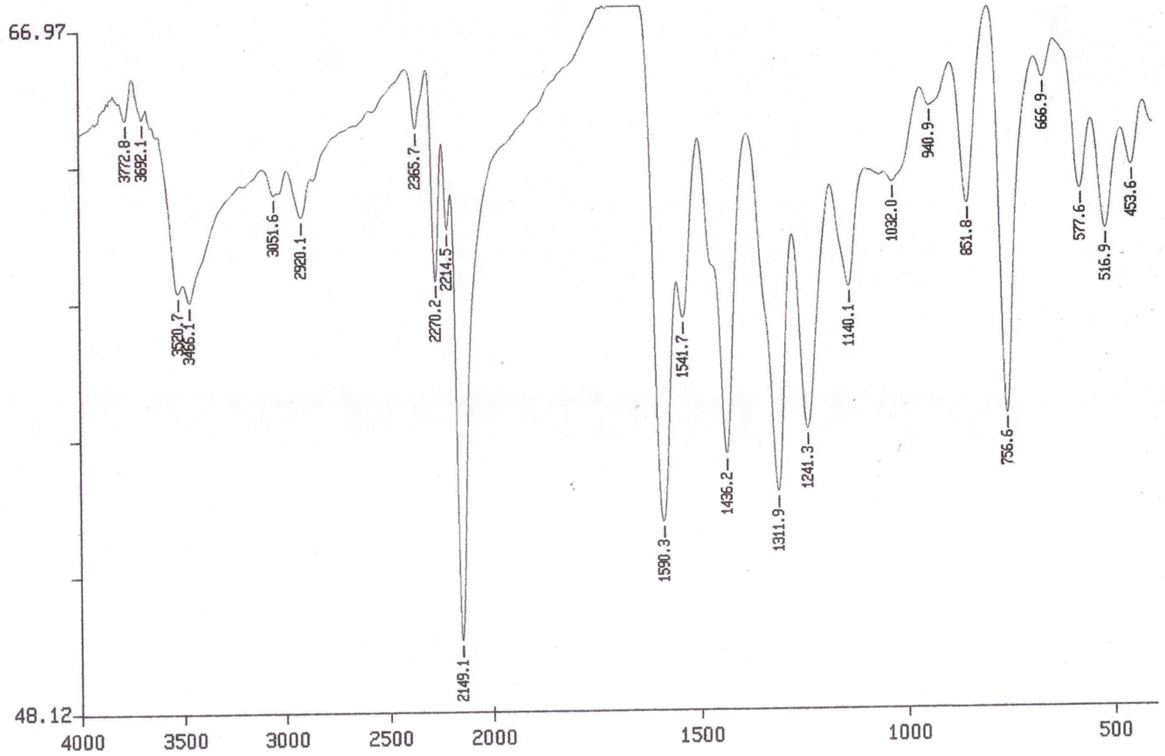

Fig. S3. IR spectrum of complex **1**.

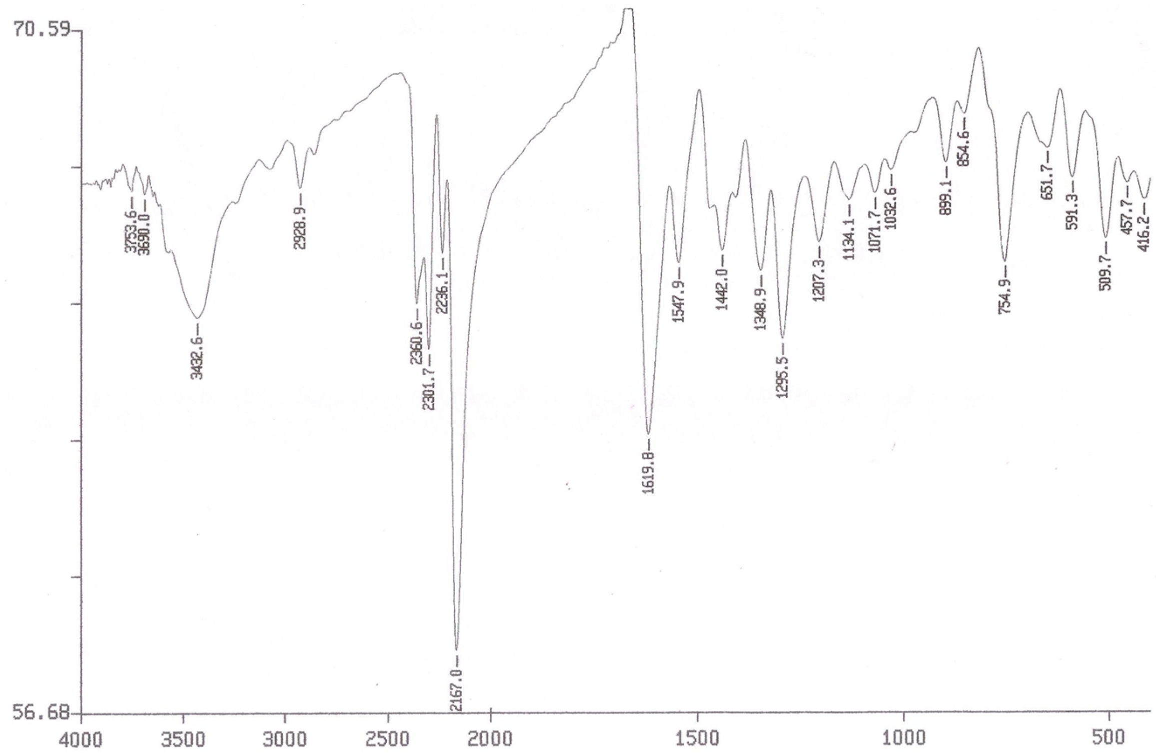

Fig. S4. IR spectrum of complex **2A**.

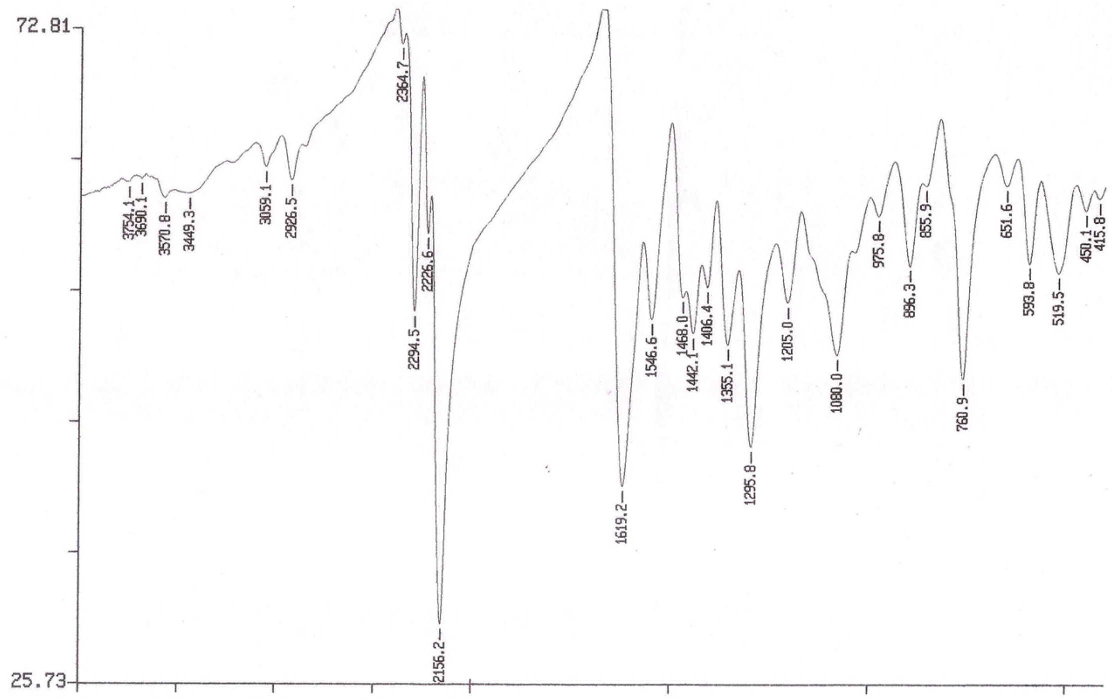

Fig. S5. IR spectrum of complex **2B**.

UV-Vis spectra of the compounds

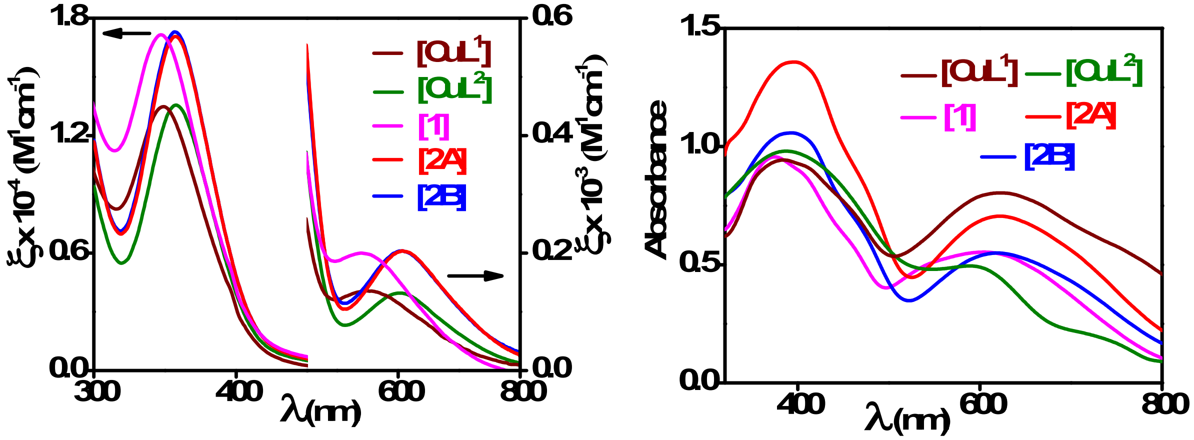

Fig.S6. Electronic spectra of the compounds in MeOH (left) and solid state (right).

The UV-Vis spectra of the compounds in methanol solution and their solid state diffused reflectance spectra are shown in Fig. S6. The compounds exhibit a broad absorption band in the visible region at 542, 607 and 608 nm in methanol solution and at 625, 623 and 620 nm in the solid state for **1**, **2A** and **2B**, respectively, while the [CuL^1] and [CuL^2] “metalloligands” show band maxima at 545 and 602 nm in MeOH and at 622 and 592 nm in the solid state, respectively. These bands are attributed to d–d transitions of Cu(II) ions. The spectra of these hetero-metallic derivatives and of their respective mononuclear precursors [CuL^1] and [CuL^2] in methanol are almost identical indicating the square planar coordination environment of Cu(II) ions in all of them. However, in the solid state, the band position of **1** is almost the same as in a mononuclear precursor [CuL^1], although the coordination environment around Cu(II) in [CuL^1] and **1** is square planar and square pyramidal, respectively. On the other hand, the band positions for **2A** and **2B** are 31 and 28 nm red shifted with respect to [CuL^2], presumably due to the short axial Cu–N distances (2.304(3) and 2.409(3) Å in **2A** and 2.473(5) Å in **2B**) in these two isomers. Besides these bands, all the products show a sharp single absorption maximum near 347, 356 and 356 nm in methanol and 377, 394 and 394 nm in the solid state for **1**, **2A** and **2B**, respectively, attributed to ligand-to-metal charge transfer transitions.

Electrospray ionization mass spectrometry of the complexes

In order to investigate the species present in solution, the electrospray ionization mass spectra (ESI-MS positive) of **1**, **2A** and **2B** were recorded in methanolic solution (Figs. S7-S9). Complex **1** shows the base peak at m/z = 743.2 (*calc*. 743.2) which can be assigned to the cationic species $[(CuL^1)_2H]^+$. Species like $[(CuL^1)H]^+$, $[(CuL^1)Na]^+$, $[(CuL^1)_2Na]^+$ and $[(CuL^1)_3Na]^+$ are also observed at m/z = 372.1, 394.09, 765.2 and 1138.3, respectively. On the other hand, the spectra of **2A** and **2B** show a similar pattern. Both the complexes show the base peak at m/z = 708.8 (*calc*. 709.0) which can be assigned to the cationic species $[(CuL^2)_2Na]^+$. The appearance of other peaks at m/z = 343.9, 365.9, 686.9 and 1053.8 for both the complexes may be attributed to the presence of $[(CuL^2)H]^+$, $[(CuL^2)Na]^+$, $[(CuL^2)_2H]^+$ and $[(CuL^2)_3Na]^+$, respectively. It is to be noted that no peak corresponding to the trinuclear unit is observed for any of the compounds. In all the cases, Na-containing species dominate presumably due to the fact that the Na^+ ion is released from the matrix form more stable complex than Zn^{2+} with “metalloligands”. Thus, the observed solid state structures of all the compounds are lost in the solutions and the freed “metalloligands” associate with either H^+ or Na^+ to form corresponding cationic species.

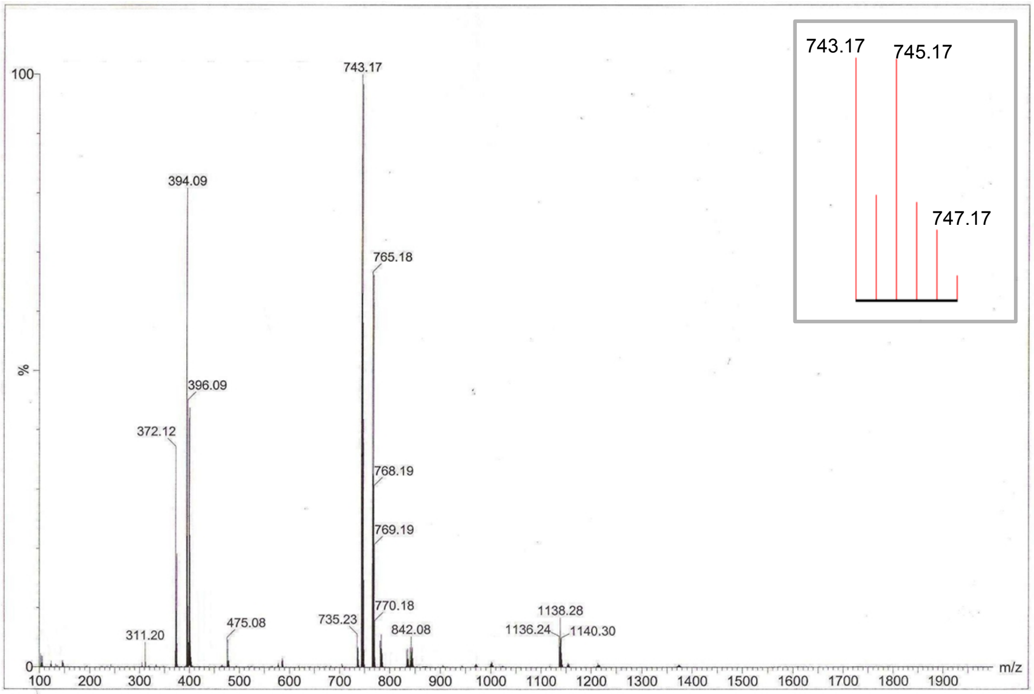

Fig. S7. Exprimental ESI mass spectrum of complex **1** in methanol. The theoretical pattern of the base peak is shown in inset. The line to line separation is 1.0.

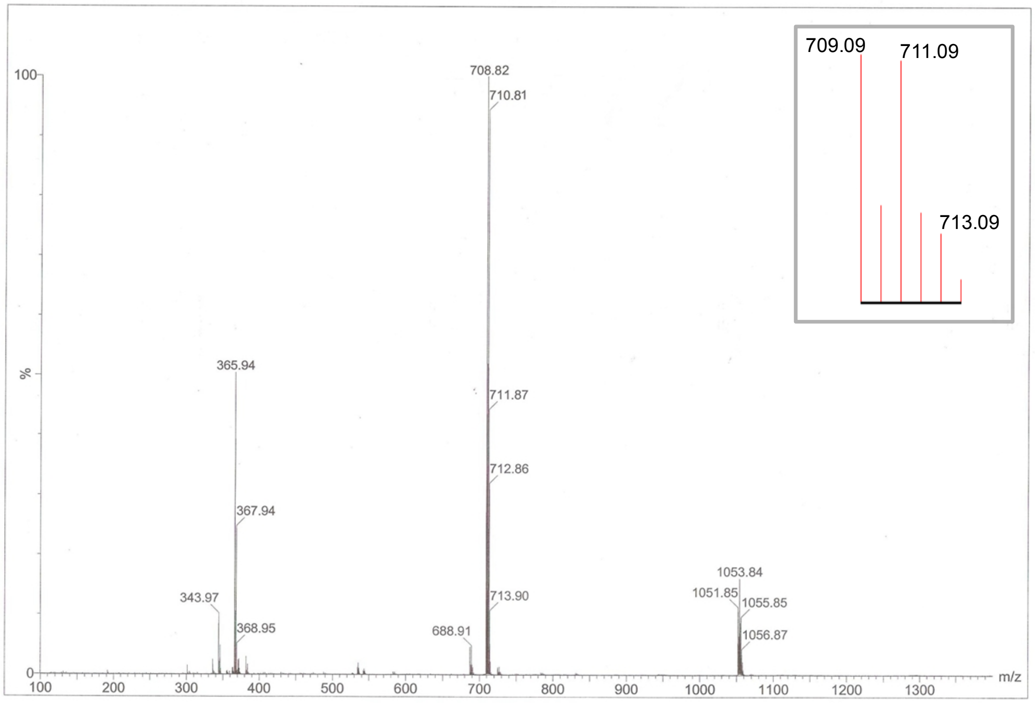

Fig. S8. Exprimental ESI mass spectrum of complex **2A** in methanol. The theoretical pattern of the base peak is shown in inset. The line to line separation is 1.0.

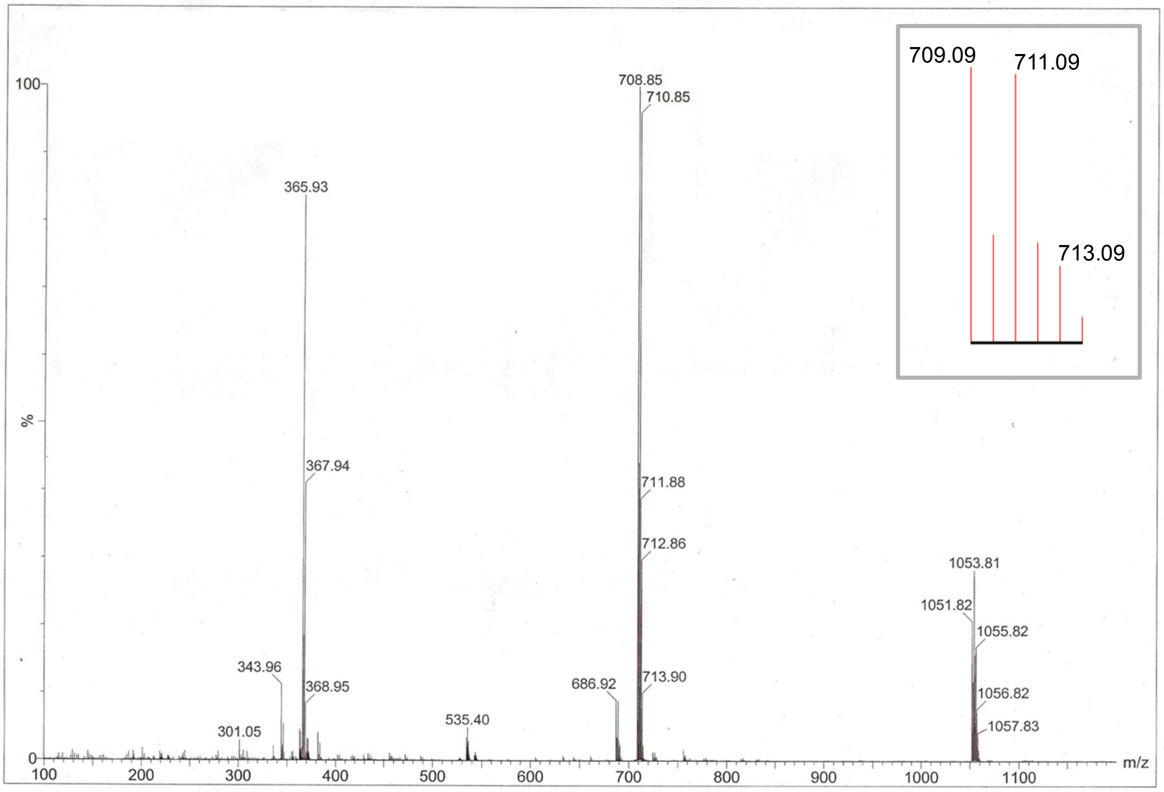

Fig. S9. Exprimental ESI mass spectrum of complex **2B** in methanol. The theoretical pattern of the base peak is shown in inset. The line to line separation is 1.0.