

Supporting Information for

**Steric control of conformation in self-assembly metallacalix[4]arenes
derived from AlMe₃ or GaMe₃ with benzimidazolyl ligands**

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1. Experimental details for 1-4

All experiments were carried out under argon using standard Schlenk techniques in dual argon/vacuum lines in conjunction with an inert atmosphere glovebox. Carefully dried solvents (Aldrich) and oven-dried glassware were used throughout. Trimethylaluminium, trimethylgallium, benzimidazole, *ortho*-phenyldiamine, acetic acid and hydrochloric acid were commercially available (Aldrich) and used as received. 2-methylbenzimidazole was synthesized according to a literature procedure.[1] ^1H , ^{13}C and ^{27}Al NMR spectra were recorded on a Varian Gemini-200 MHz spectrometer at ambient probe temperature (293 K) in CDCl_3 . Chemical shifts are given relative to SiMe_4 (CDCl_3 : $\delta^1\text{H} = 7.27$; $\delta^{13}\text{C} = 77.23$; $\delta^{29}\text{Si} = 0$). Infrared spectra were recorded in KBr using a Bruker Vector 22 instrument. EI Mass spectra were recorded using a JEOL magnetic sector spectrometer MStation 700. Elemental Analyses (C, H, and N) were performed with a Vario EL III Elementar analyzer.

[1] M. A. Philips, *J. Chem. Soc.*, 1928, 2393-2399.

Preparation and characterization of 1:

Synthesis of $[(\mu^1, \mu^1\text{-Bzm})(\mu\text{-Al})\text{Me}_2]_4$ **1**. A solution of AlMe_3 (0.26 g, 3.61 mmol) in 15 mL of toluene was slowly added to a stirred solution of benzimidazole (0.41 g, 3.50 mmol) in 15 mL of toluene. The reaction mixture was stirred for 6 h at ambient temperature, concentrated and stored at $-20\text{ }^\circ\text{C}$. After 4 days, colorless crystals were obtained, filtered and dried under reduced pressure. Yield (0.55 g, 90 %). M.p.: 189–194 $^\circ\text{C}$. ^1H NMR (CDCl_3): δ 7.60 (m, 2H, Ar–H), 7.50 (m, 2H, Ar–H), 7.30 (s, 1H, Ar–H), -0.37 (s, 3H, Al– CH_3). ^{13}C NMR (CDCl_3): δ 147.8, 138.9, 124.3, 116.0, -9.7 . $\nu_{\text{max}}/\text{cm}^{-1}$ 3058.7(w), 2929.1(m), 2891.5(w), 1764.9 (w), 1611.9(m), 1491.4(s), 1463.1(s), 1430.5 (w), 1346.1(w), 1299.8(s), 1271.9(s), 1247.1(s), 1197.6(s), 1120 (w), 1042.5 (w), 1011 (w), 917.2 (m), 776.2 (m), 748.3 (s), 689.3 (s), 577.8 (w), 476.3(w), 425.2 (w). Calcd for $\text{C}_{36}\text{H}_{44}\text{N}_8\text{Al}_4$: C, 62.05; H, 6.36; N, 16.08. Found: C, 62.05, H, 6.36, N, 16.08.

Preparation and characterization of 2:

Synthesis of $[(\mu^1, \mu^1\text{-Bzm})(\mu\text{-Ga})\text{Me}_2]_4$ **2**. A solution of Me_3Ga (0.21 g, 1.82 mmol) in 15 mL of toluene was slowly added to a stirred of benzimidazole (0.20 g, 1.69 mmol) in 15 mL de toluene. The reaction mixture was stirred for 6 h at ambient temperature. The solution was concentrated to 10 mL and stored under argon at -20 C. Once the compound crystallized, it was isolated by cannula filtration and dried under dynamic vacuum. (0.35 g, 97%) Mp: 189–191 °C. ^1H NMR (CDCl_3): δ 7.49 (m, 2H, Ar–H), 7.21 (s, 1H, Ar–H), 7.00 (m, 2H, Ar–H), 0.16 (s, 6H, Ga– CH_3). ^{13}C NMR (CDCl_3): δ 146.8, 140.1, 123.9, 115.9, -6.8. $\nu_{\text{max}}/\text{cm}^{-1}$ 3056.2 (w), 2956.0 (m), 2539.8 (w), 1782.6 (w), 1760.0 (w), 1611.7 (m), 1485.8 (s), 1362.8 (w), 1300.3 (m), 1275.4 (m), 1245.3(s), 1206.5 (m), 1182.0 (m), 1117.3(w), 1008.2 (w), 911.4 (m), 776.6 (m), 745.0 (s), 776.1 (w), 649.4 (m), 585.2 (m), 544.4 (m), 474.6 (w), 426.1(w). Calcd for $\text{C}_{36}\text{H}_{44}\text{N}_8\text{Ga}_4$: C, 49.83; H, 5.11; N, 12.91. Found: C, 49.66; H, 5.17; N, 12.92.

Preparation and characterization of 3:

Synthesis of $[(\mu^1, \mu^1\text{-mBzm})(\mu\text{-Al})\text{Me}_2]_4$ **3**. A solution of Me_3Al (0.20 g, 2.77 mmol) in 15 mL of toluene was slowly added to a stirred of 2-methylbenzimidazole (0.30 g, 2.27 mmol) in 15 mL de toluene. The reaction mixture was stirred for 12 h at ambient temperature. The solution was concentrated to 10 mL and stored under argon at -20 °C. Once the compound crystallized, it was isolated by cannula filtration and dried under dynamic vacuum. Yield (0.53 g, 92 %). Decomposes at 216 °C. ^1H NMR (CDCl_3): δ 7.70 (m, 2H, Ar–H), 7.20 (s, 1H, Ar–H), 1.91 (, 3H, $-\text{CH}_3$), -0.22 (s, 6H, Ga– CH_3). ^{13}C NMR (CDCl_3): δ 158.8, 139.7, 123.6, 115.7, 16.0, -5.9 . $\nu_{\text{max}}/\text{cm}^{-1}$ 3059.61(w), 2934.01(m), 1606.96(w), 1449.32 (m), 1400.31(m), 1268.45(m), 1199.98(m), 1019.63(w), 923.34(w), 863.66(s), 802.39(s), 748.31(w), 682.30(s), 582.39(w). A satisfactory carbon analysis was not obtained due to the formation of aluminum carbides. Calcd for $\text{C}_{40}\text{H}_{52}\text{N}_8\text{Al}_4$: C, 63.82; H, 6.96; N, 14.88. Found: C, 61.82; H, 6.81; N, 14.42.

Preparation and characterization of 4:

Synthesis of $[(\mu^1, \mu^1\text{-mBzm})(\mu\text{-Ga})\text{Me}_2]_4 \cdot 6\text{C}_6\text{H}_6$ **4**. A solution of Me_3Ga (0.17 g, 0.15 mmol) in 15 mL of toluene was slowly added to a stirred of Hmbzim (0.20 g, 0.15 mmol) in 15 mL de toluene. The reaction mixture was stirred for 12 h at ambient temperature. The solution was concentrated to 10 mL and stored under argon at $-20\text{ }^\circ\text{C}$. Once the compound crystallized, it was isolated by cannula filtration and dried under dynamic vacuum. Yield (0.31 g, 90 %). M.p.: $206\text{--}207\text{ }^\circ\text{C}$. ^1H NMR (CDCl_3): δ 7.63 (m, 2H, Ar-H), 7.17 (m, 2H, Ar-H), 1.84 (s, 3H, Ar- CH_3) 0.17 (s, 6H, Ga- CH_3). ^{13}C NMR (CDCl_3): δ 158.1, 140.2, 122.7, 115.2, 15.5, -3.2 . $\nu_{\text{max}}/\text{cm}^{-1}$ 2958.88 (m), 1610.53 (m), 1450.51 (s), 1398.44 (s), 1272.47 (s), 1208.01 (m) 1015.90 (m), 918.68 (w), 857.50 (w), 801.99 (w) 744.00 (s), 689.24 (w), 645.60 (m), 575.40 (m), 542.49 (m), 498.97 (w). Calcd for $\text{C}_{40}\text{H}_{52}\text{N}_8\text{Ga}_4$: C, 52.01; H, 5.67; N, 12.12. Found: C, 51.96; H, 5.88; N, 11.59.

2. NMR spectra and mass spectrograms

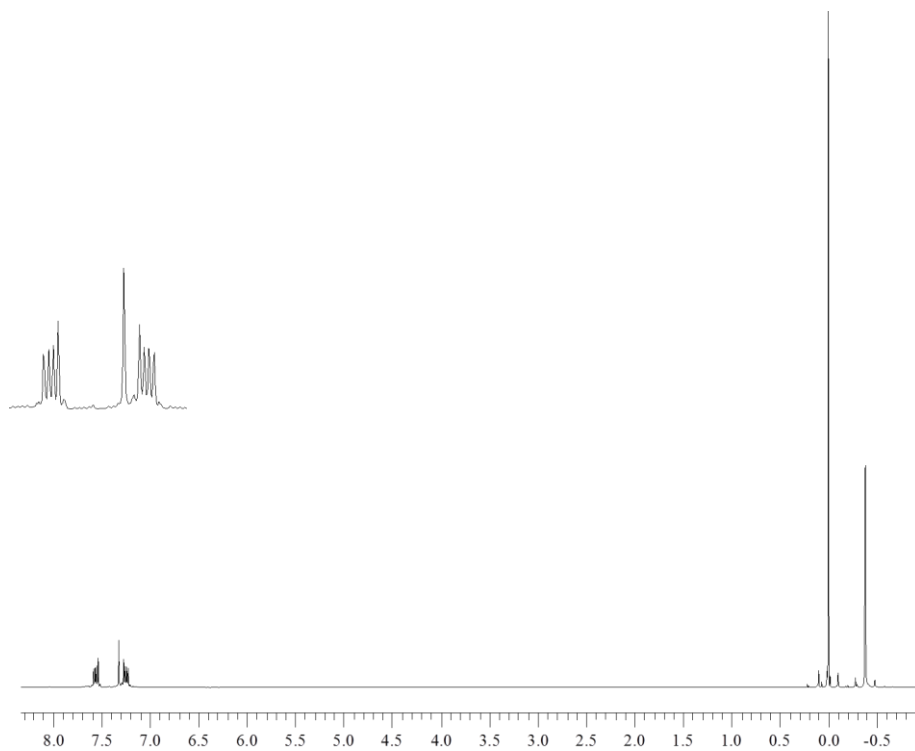


Fig 1 ^1H NMR spectrum of **1** (200 MHz, CDCl_3 , 298 K)

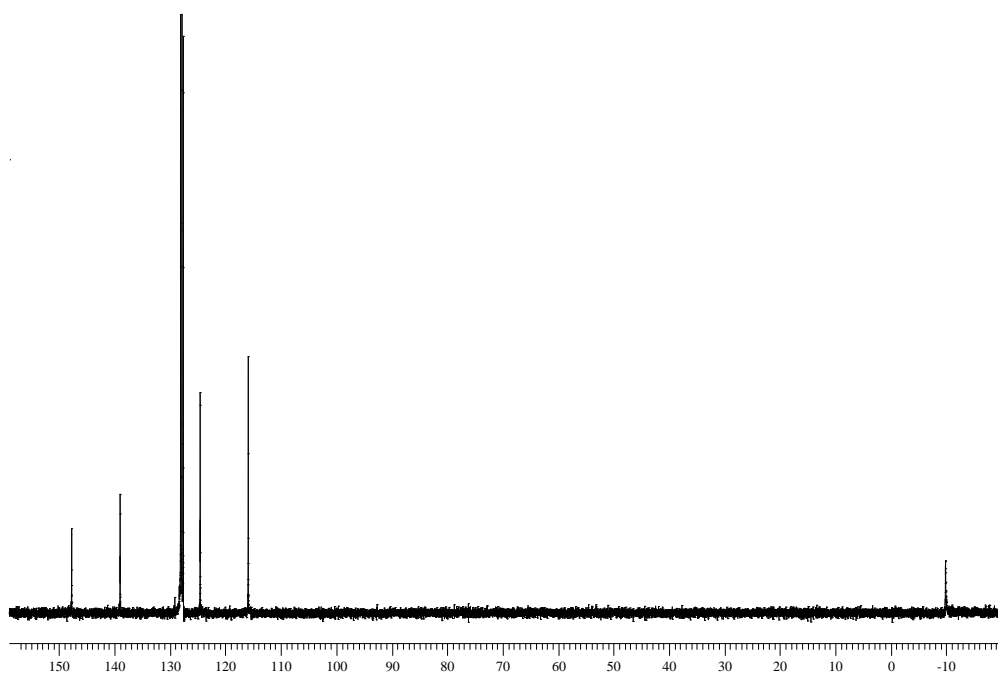


Fig 2 ^{13}C NMR spectrum of **1** (400 MHz, CDCl_3 , 298 K)

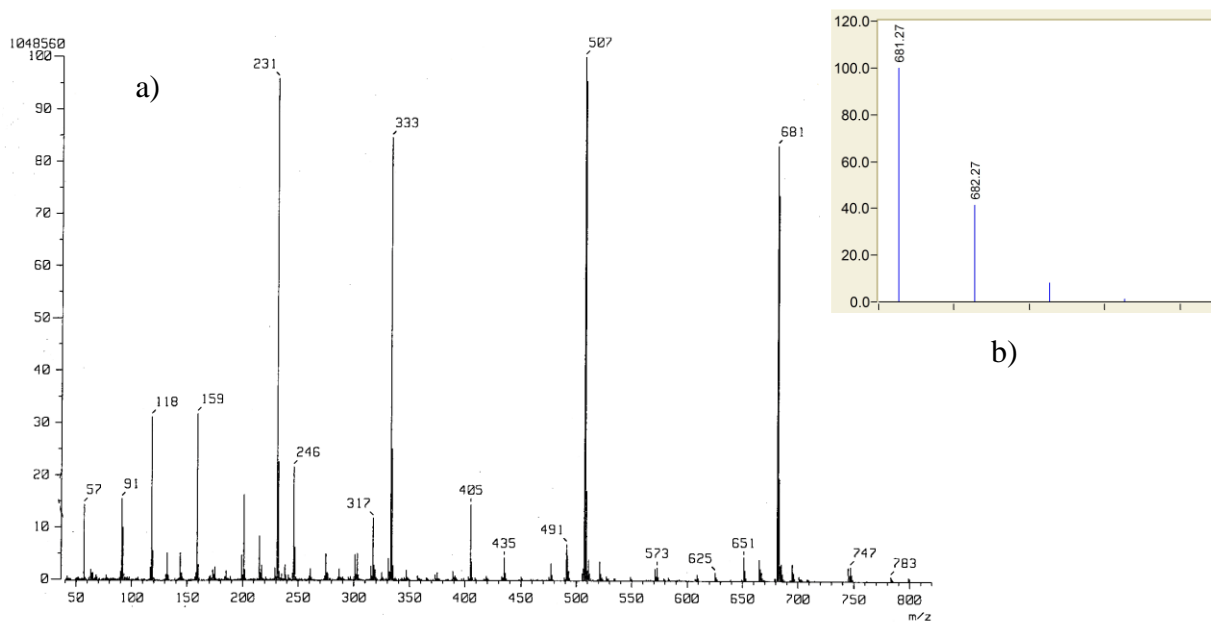


Fig 3 a) EI⁺ mass spectrogram of **1**. b) Modeled M⁺

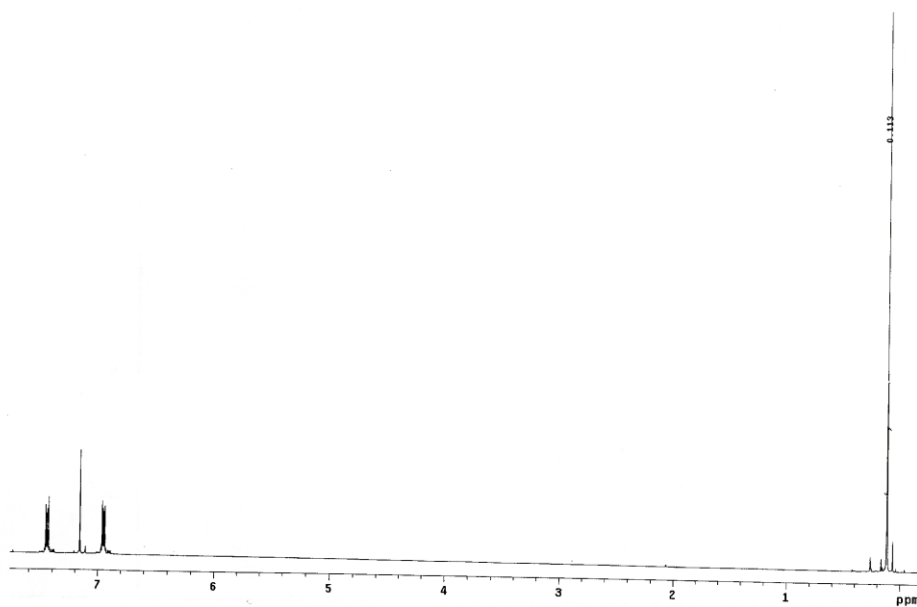


Fig 4 ¹H NMR spectrum of **2** (200 MHz, CDCl₃, 298 K)

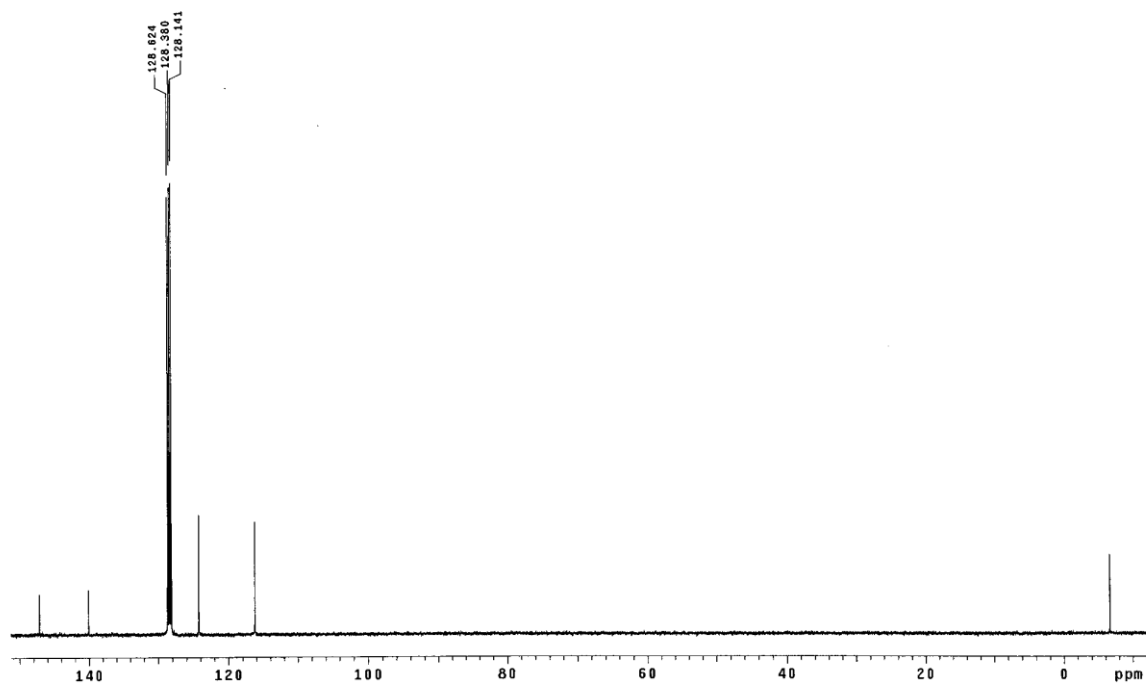


Fig 5 ^{13}C NMR spectrum of **2** (200, MHz, CDCl_3 , 298K)

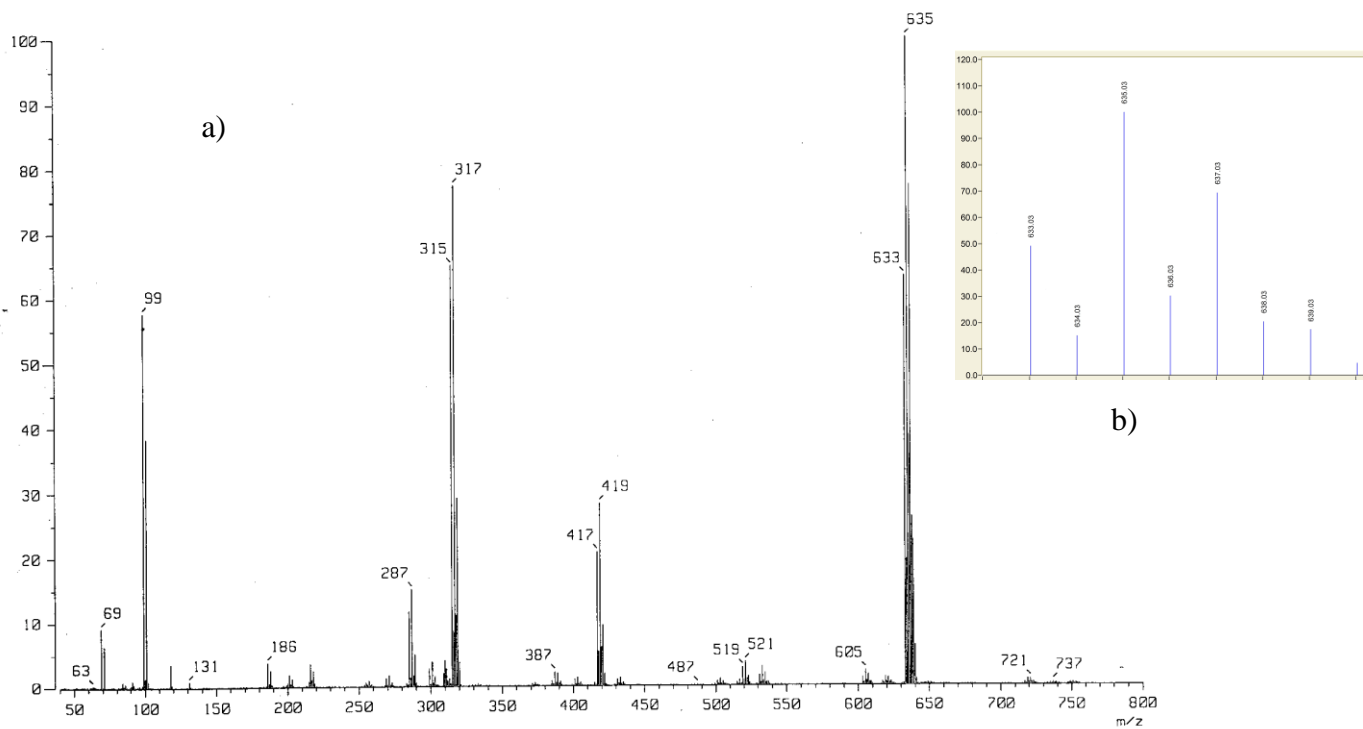


Fig 6 a) EI^+ mass of spectrum of **2**. b) Modeled M^+

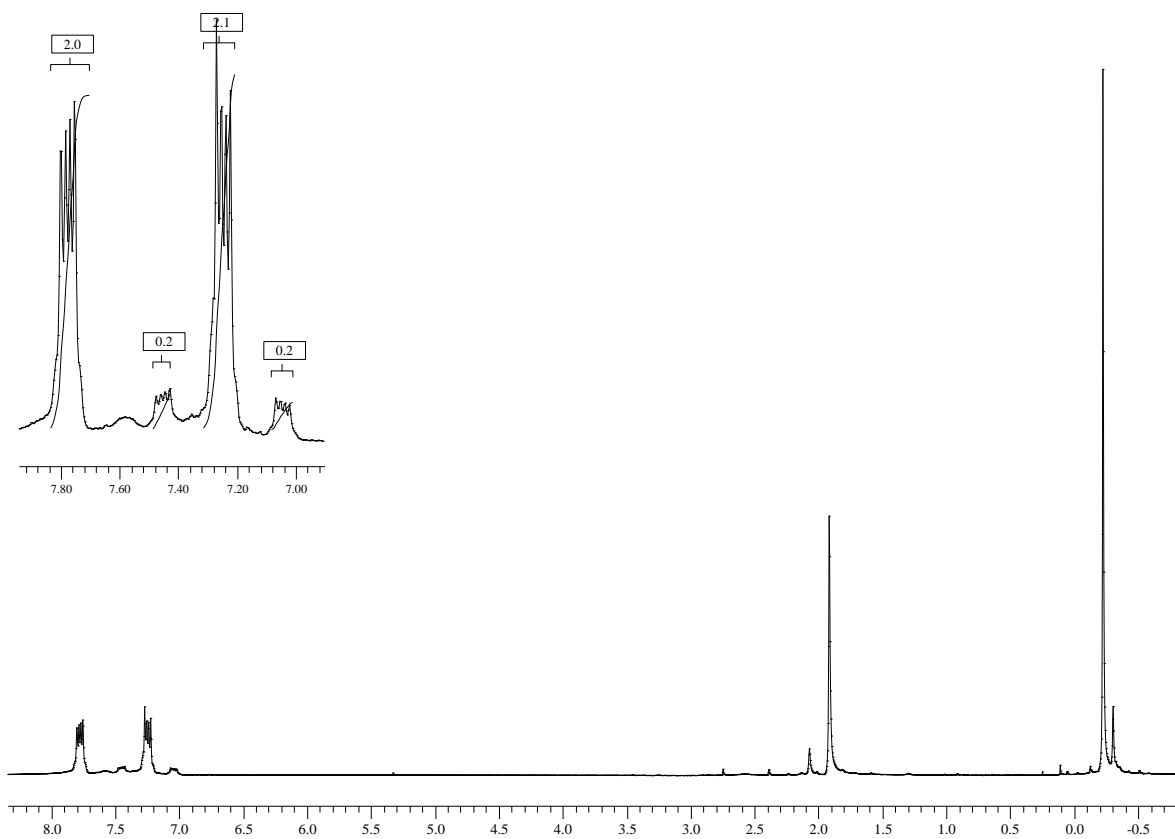


Fig 7 ^1H NMR spectrum of **3** (200 MHz, CDCl_3 , 298 K)

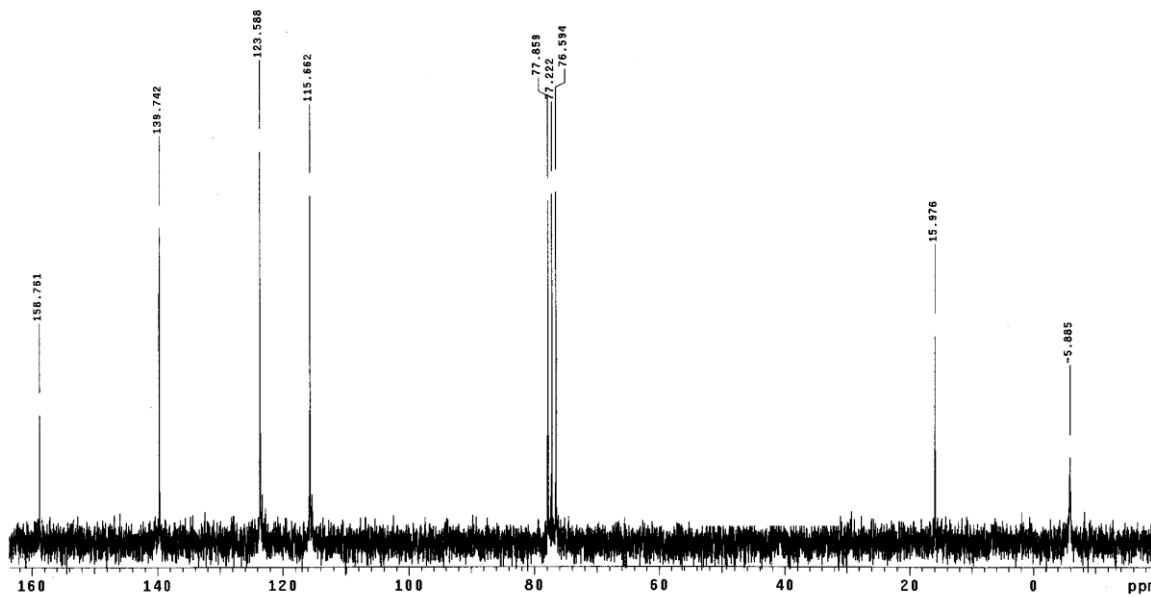


Fig 8 ^{13}C NMR spectrum of **3** (200 MHz, CDCl_3 , 298 K)

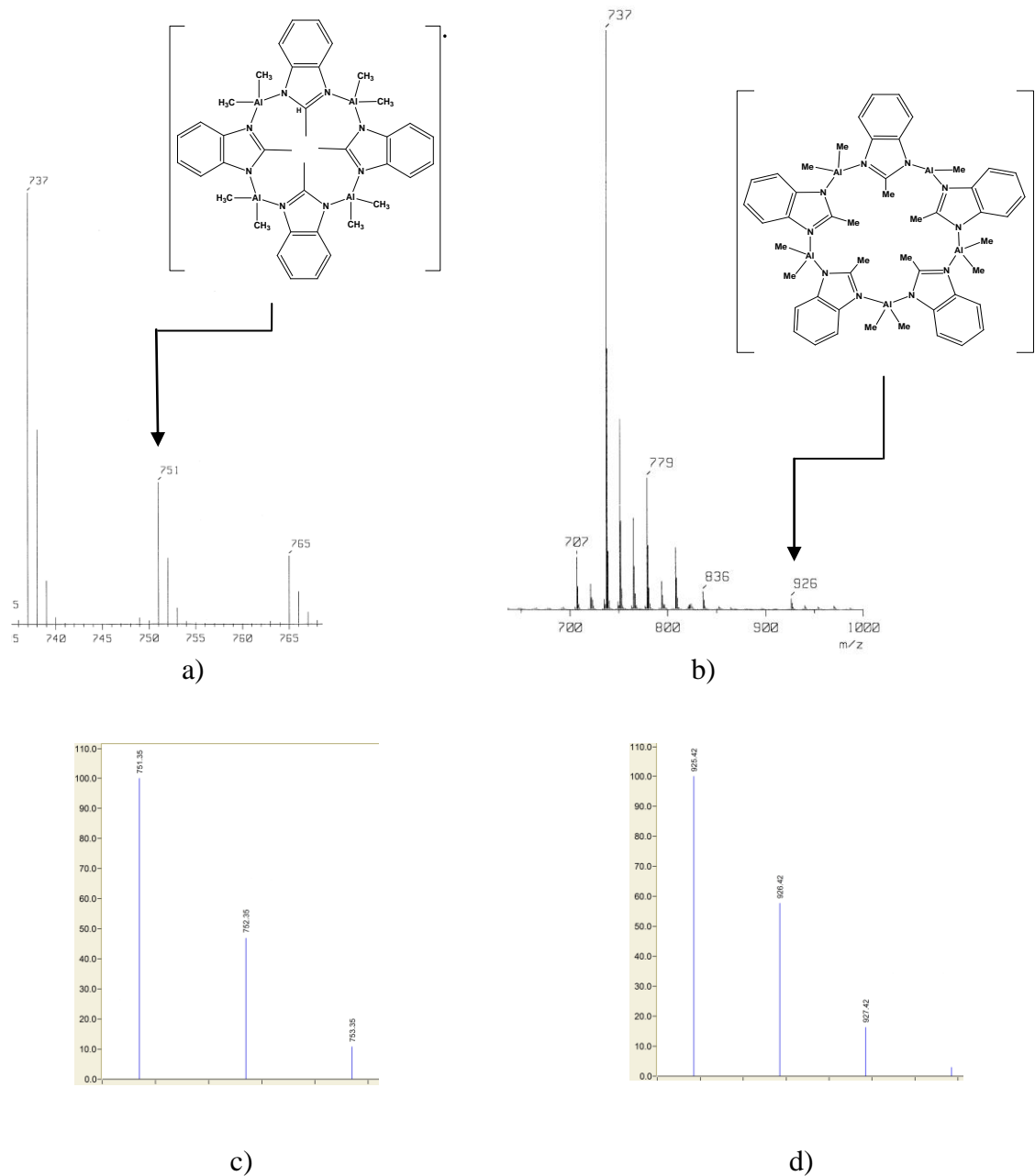


Fig 9 EI^+ mass of spectrum of compound **3**: a) tetramer, b) pentamer, c) modeled M^+ of the tetramer, and d) modeled M^+ of the pentamer

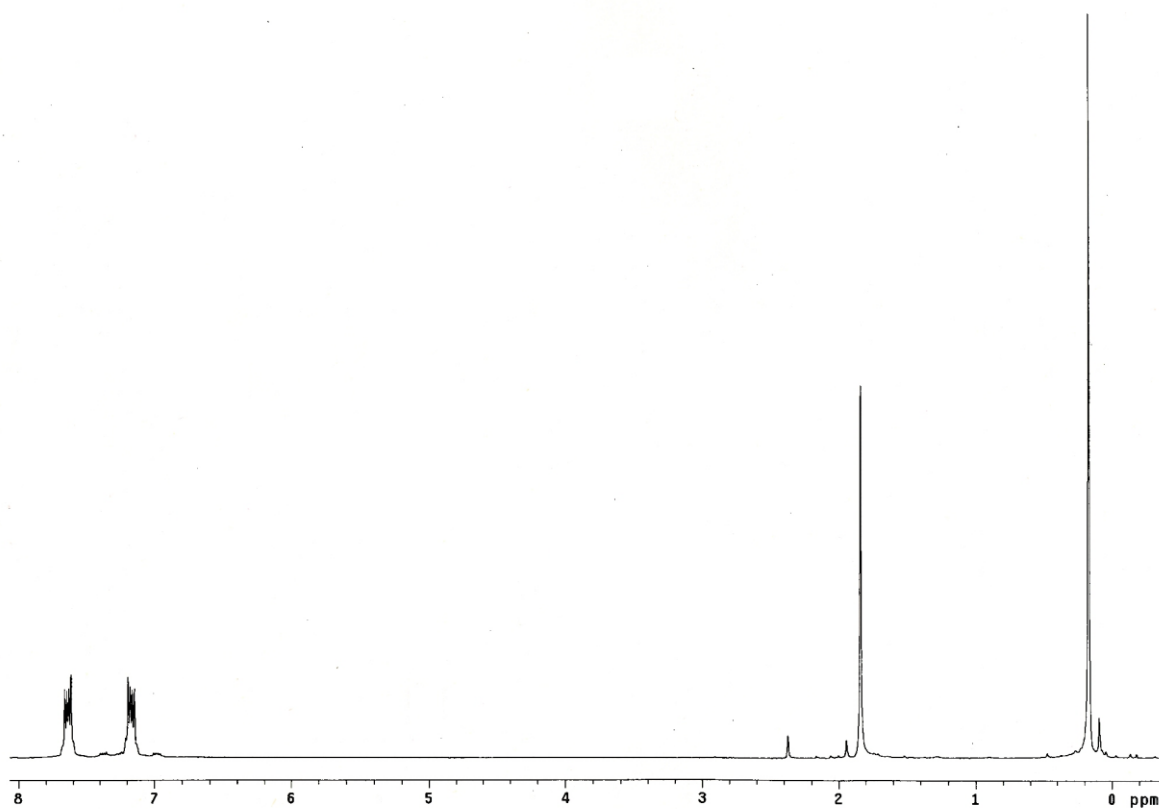


Fig 10 ^1H NMR spectrum of **4** (200 MHz, CDCl_3 , 298 K)

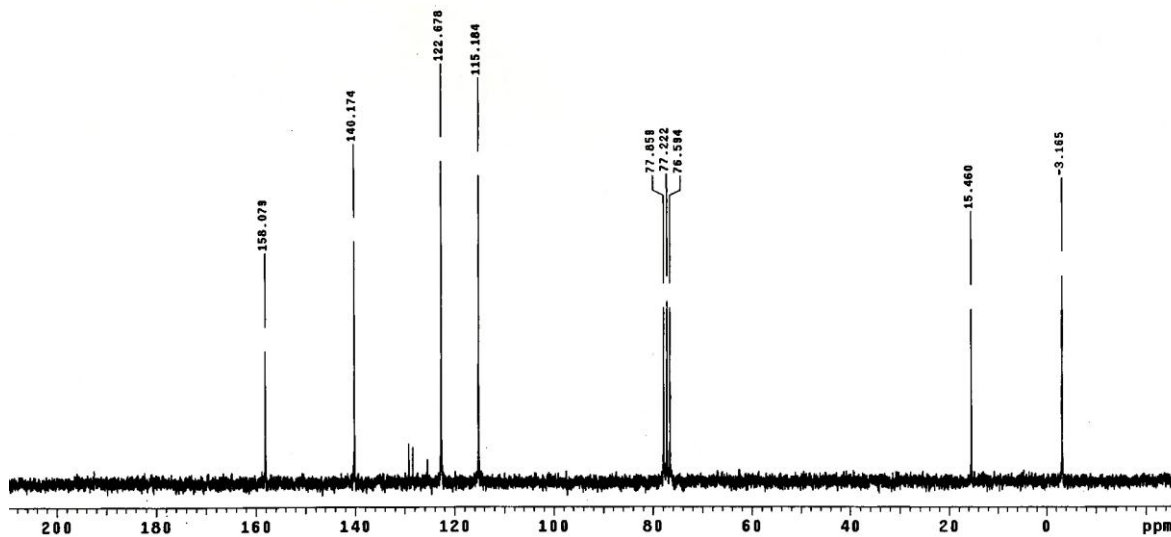
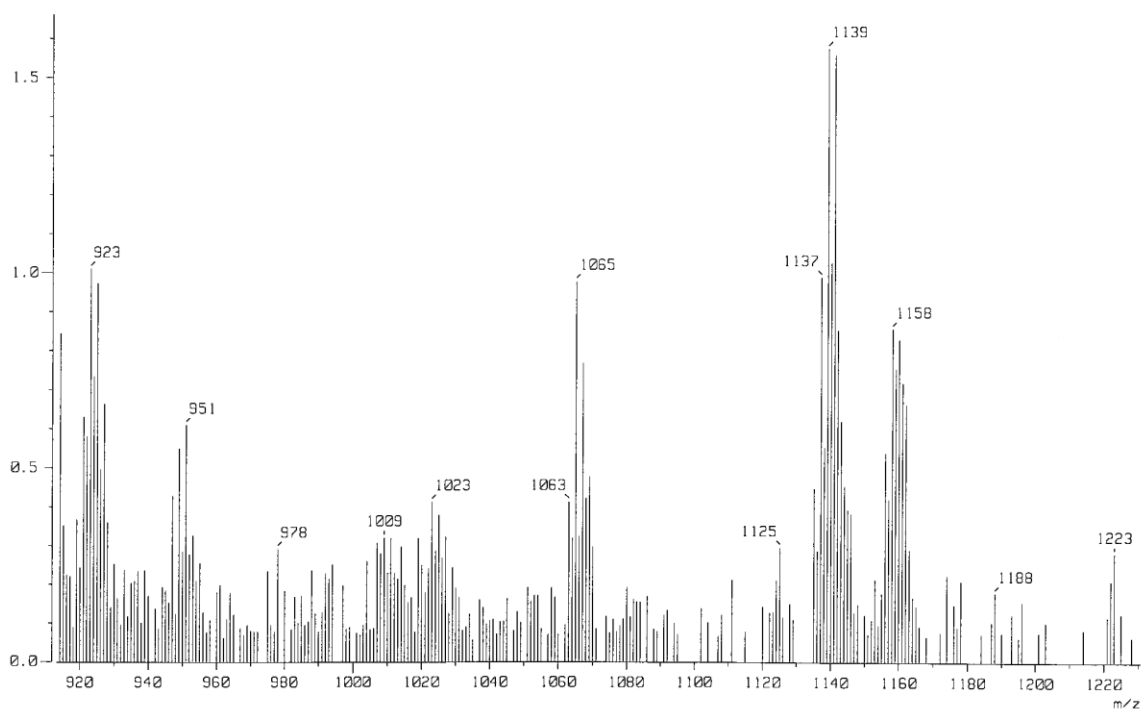
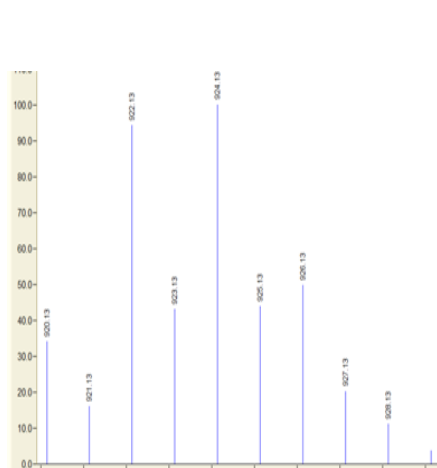


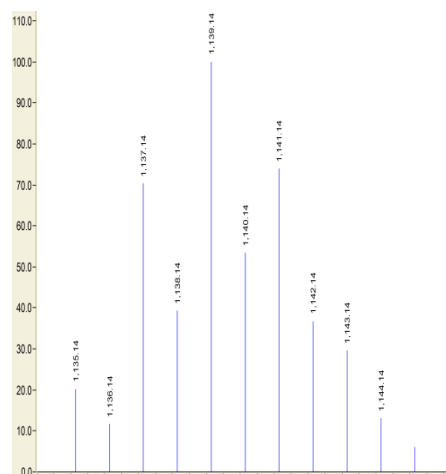
Fig 11. ^{13}C NMR spectrum of **4** (200 MHz, CDCl_3 , 298 K)



a)



b)



c)

Fig 12 a) FAB^+ mass spectrogram of **4**, b) modeled M^+ of the tetramer, and c) modeled M^+ of the pentamer

3. X-ray crystal structure determinations

Single crystal X-ray crystallography. X-ray data for **1-4** were collected using the program SMART[2] on a Bruker APEX CCD diffractometer with monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K for **1**, **2** and **4** and at 173 K for **3**. Cell refinement and data reduction were carried out with the use of the program SAINT, the program SADABS was employed to make incident beam, decay and absorption corrections in the SAINT-Plus v. 6.0 suite.[3] The structures were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL v. 6.1 suite.[4] Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. Further details of the structure analyses are given in CCDC 803985-803988.

[2] G. M. Sheldrick, *SMART Bruker AXS*, Inc., Madison, WI, USA, 2000

[3] G. M. Sheldrick, *SAIN-Plus 6.0 Bruker AXS*, Inc., Madison, WI, USA, 2000.

[4] G. M. Sheldrick, *SHELXTL 6.10 Bruker AXS*, Inc., Madison, WI, USA, 2000.

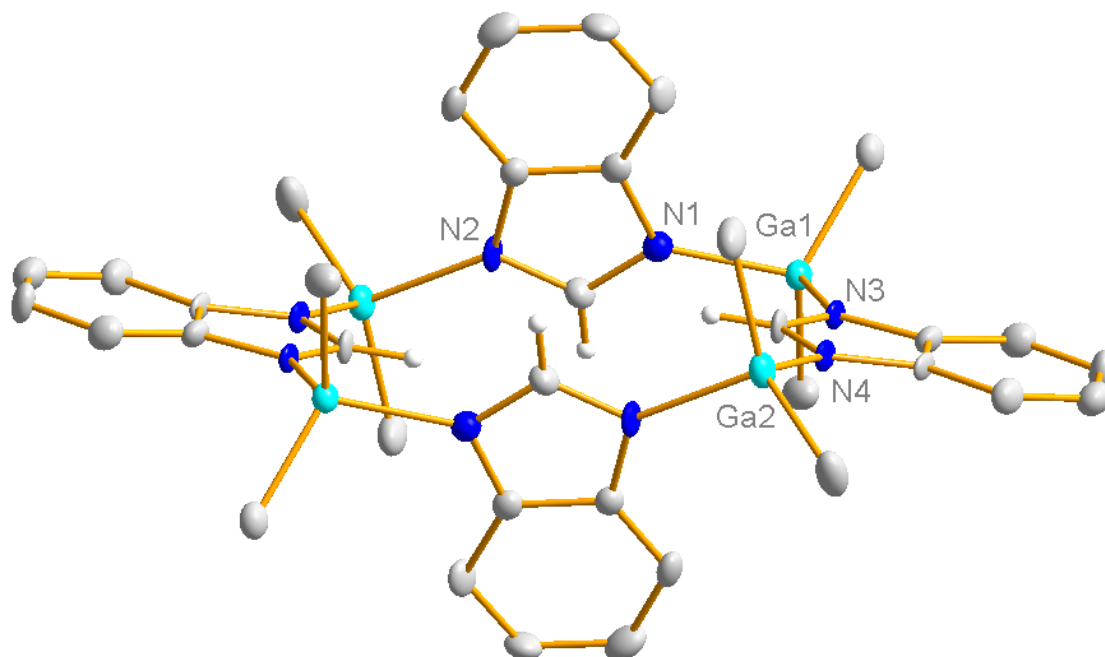


Fig 13 Molecular structure of **2** showing thermal ellipsoids at the 50% with most hydrogen atoms omitted for clarity

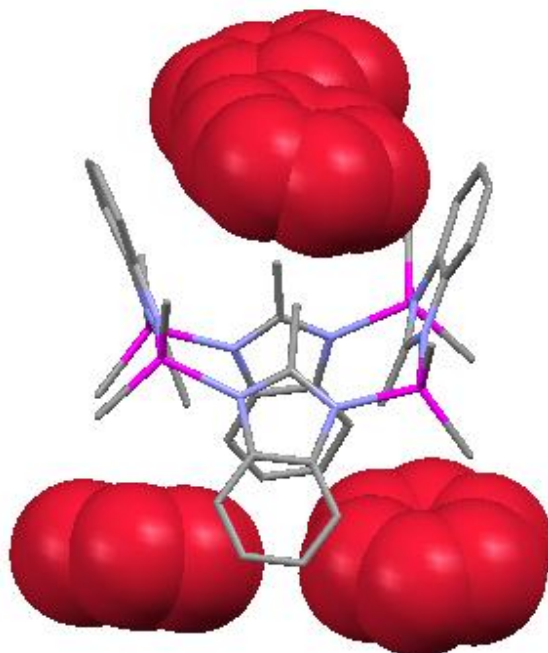


Fig 14 Molecular structure of **4** with thermal ellipsoids at the 50% probability level and included benzene molecules in space-filling representation. Hydrogen atoms have been removed for clarity

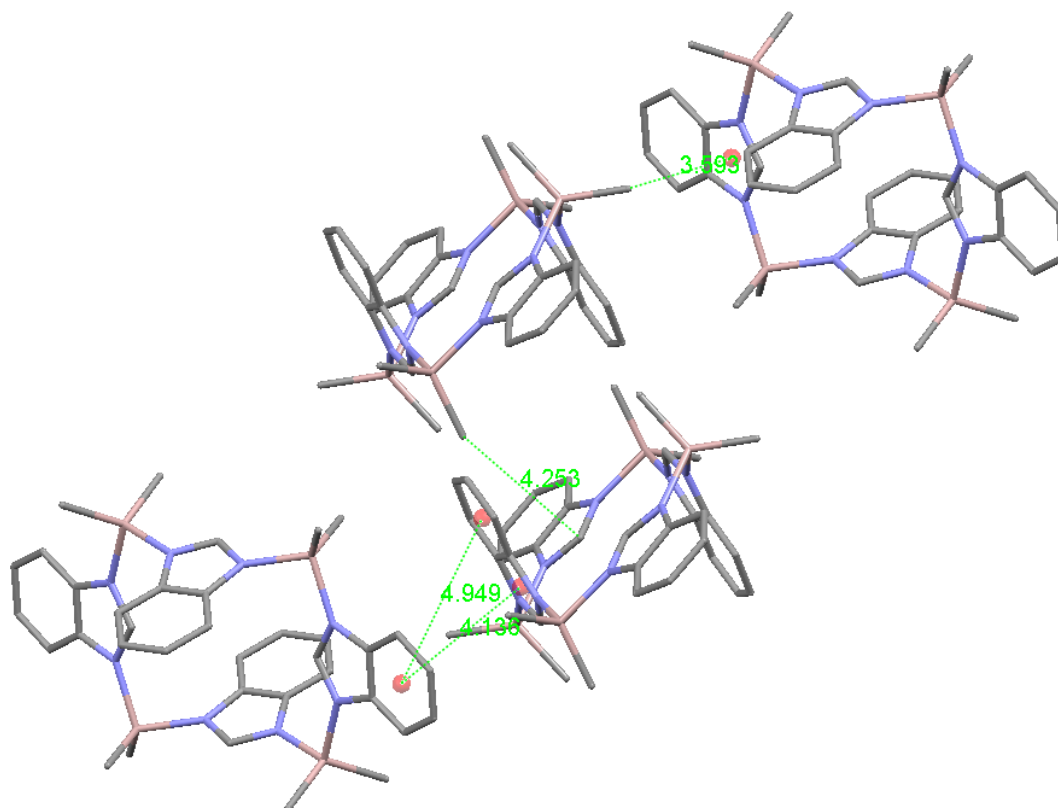


Fig 15 CH $\cdots\pi$ and $\pi \cdots\pi$ intermolecular interactions for **1**

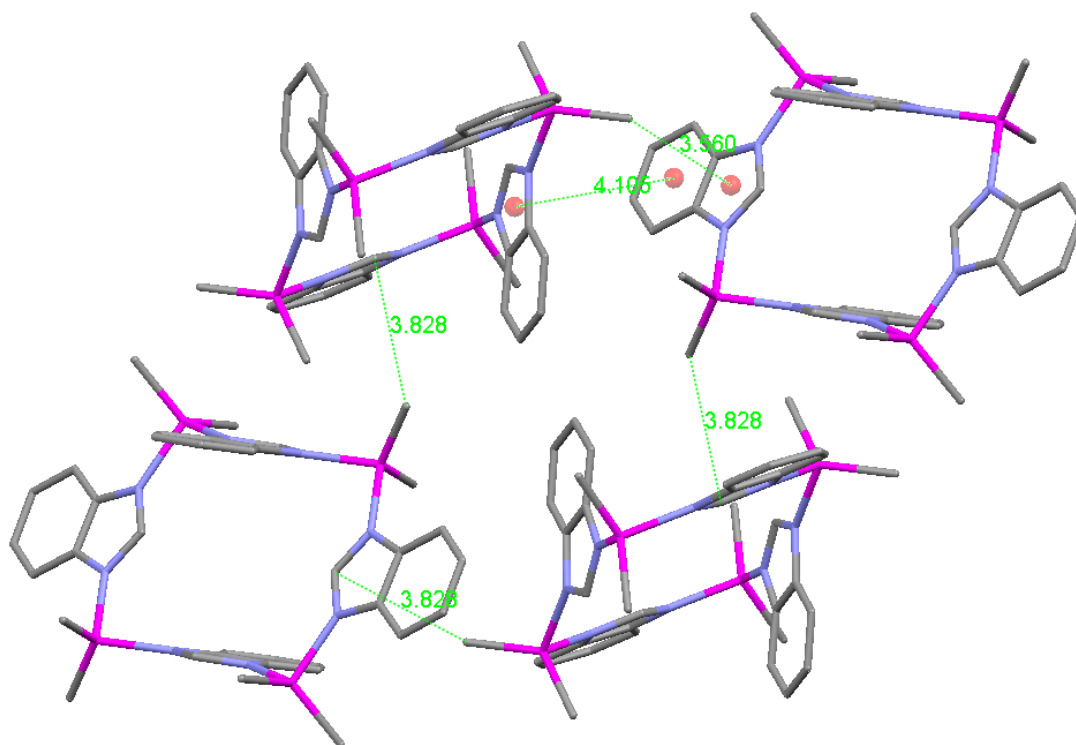


Fig 16 CH $\cdots\pi$ and $\pi \cdots\pi$ intermolecular interactions for **2**

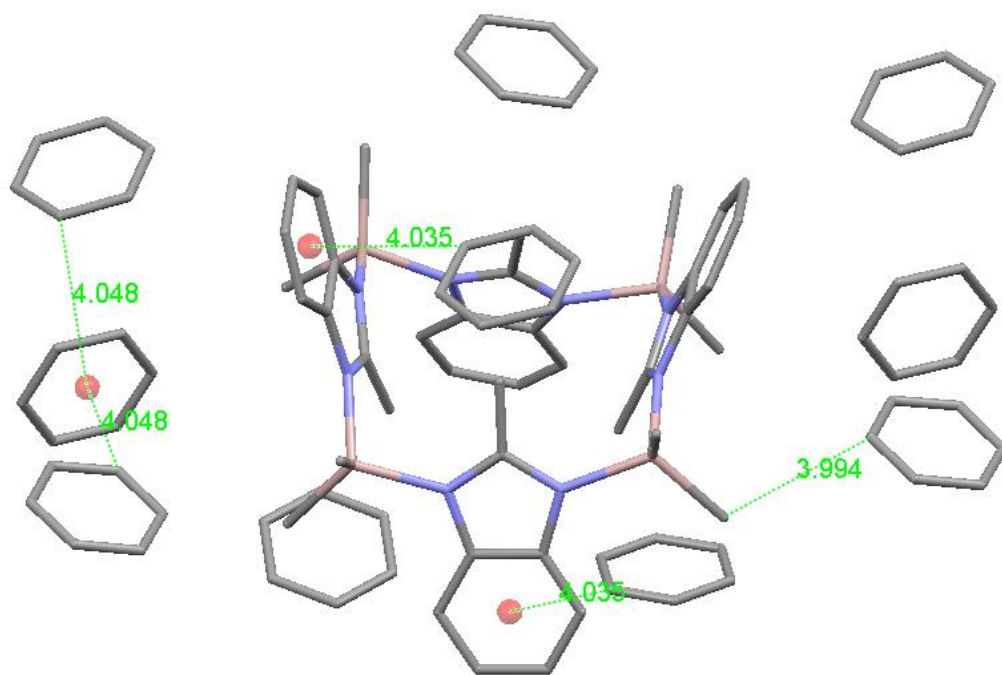


Fig 17 CH $\cdots\pi$ and AlCH $_3\cdots$ HC intermolecular interactions for **3**

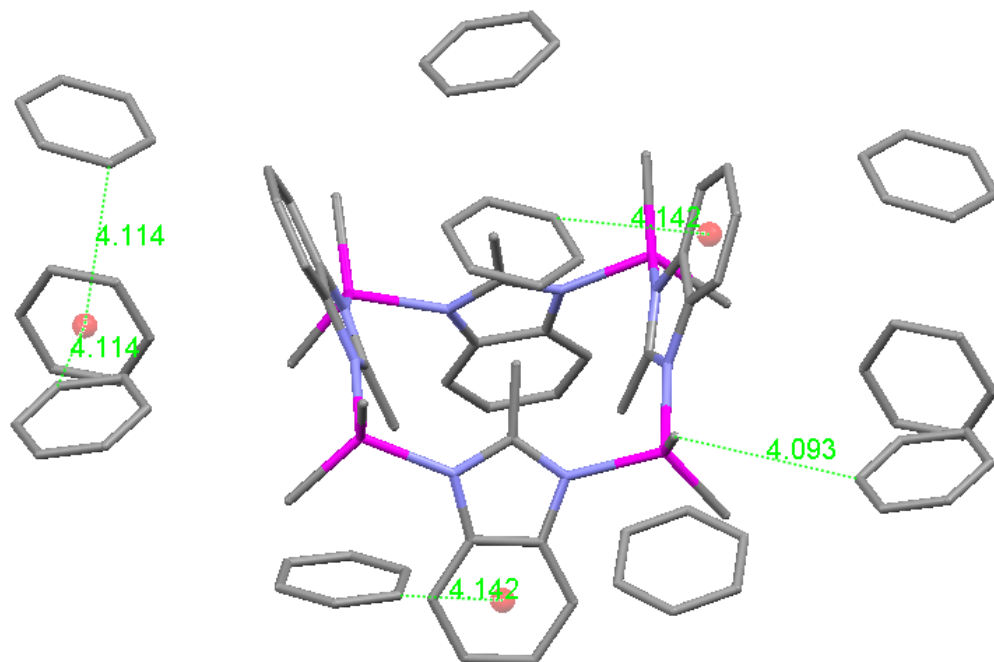


Fig 18 CH $\cdots\pi$ and GaCH $_3\cdots$ HC intermolecular interactions for **4**