# A triazine-based three-directional rigid-rod tecton forms a novel 1D channel structure

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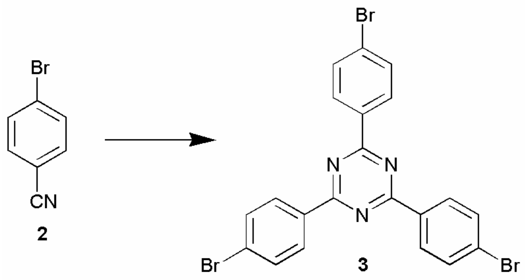
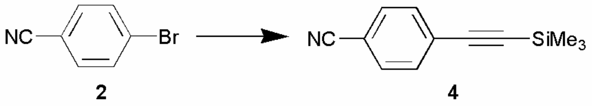
## Synthesis of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (3)



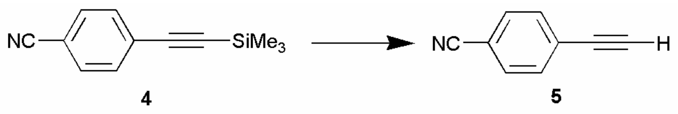
To a vigorously stirred solution of trifluoromethanesulfonic acid (2 mL, 0.022 mole) in dry chloroform (5 mL), cooled to 0°C and under a stream of nitrogen, 4-bromobenzonitrile, **2** (2 g, 0.011 mole) in dry chloroform (30 mL) was added dropwise. The reaction was slightly exothermic upon addition of the latter solution. Stirring was continued for 2 hours at 0°C. The mixture was further stirred for 24 hours at ambient temperature. It was then poured into water containing a small amount of ammonium hydroxide. The organic layer (chloroform) was washed four times with water and then dried over sodium sulphate. The solvent was evaporated *in vacuo*. The residue was recrystallized from chloroform. Yield: 1.5 g, 75%; mp > 300°C. EI MS m/z (%) 545 $[M]^+$, 181 (66) $[BrC_6H_4CN]^+$, 102 (52) $[CNC_6H_4]^+$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ ppm, 8.56 (d, 6H, *J* = 8.5 Hz), 7.68 (d, 6H, *J* = 8.5 Hz).

## Synthesis of 4-[2-(trimethylsilyl)ethynyl]benzonitrile (4)



A mixture of 4-bromobenzonitrile (3.00 g, 0.0165 mole), tetrakis(triphenylphosphine)palladium (0.29 g, 0.0003 mole) and copper iodide (0.11 g, 0.0006 mole) were taken in a round-bottomed flask. The flask was slowly flushed with nitrogen, followed by the addition of freshly distilled triethylamine (45 mL). To this stirred mixture, ethynyltrimethylsilane (3.8 mL, 0.027 mole) was added. The solution turned dark brown in colour well before heating was commenced. The mixture was heated to 80°C under a nitrogen atmosphere for 7.5 hours. Completion of the reaction was monitored by thin-layer chromatography (TLC). The mixture was concentrated *in vacuo* and diethylether (90 mL) was added to the residue. The mixture was filtered and concentrated *in vacuo* to give 3.2 g of crude **4** as a brown solid. The crude product was purified by column chromatography on silica gel using hexanes-ethyl acetate (35:1) as eluent. Recrystallization from hexane gave **4** as a white, crystalline solid. Yield 2.45 g (74 %); mp 97-98°C. EI MS m/z (%) 199 $[M]^+$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ ppm, 0.24 (s, 9H, Si(C$H_3$)$_3$, 7.24-7.56 (m, 4H, aromatic *H*).

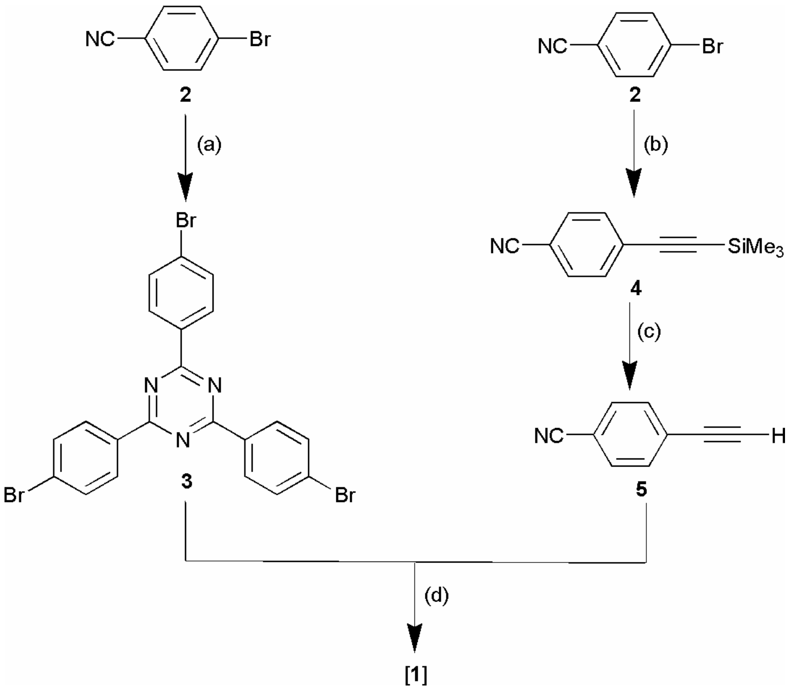
### Synthesis of 4-ethynylbenzonitrile (5)



A mixture of 4-[2-(trimethylsilyl)ethynyl]benzonitrile, **4** (0.5 g, 0.0025 mole) and potassium carbonate (0.054 g, 0.0004 mole) in dry methanol (4 mL) was stirred at ambient temperature under a nitrogen atmosphere for ~18 hours. The mixture was concentrated *in vacuo* and partitioned between 5% aqueous sodium bicarbonate and 60 mL of dichloromethane. The dichloromethane solution was dried over sodium sulfate and concentrated *in vacuo* to give 0.23 g of crude, white product **5**. Recrystallization with 8:1 hexanes:dichloromethane gave pure **5** as a white solid. Yield 0.15 g (47 %); mp 158-159°C. EI MS m/z (%) 127 $[M]^+$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ ppm, 3.28 (s, 1H, ≡C-*H*), 7.54-7.62 (m, 4H, aromatic *H*).

## Synthesis of 2,4,6-tris(4-(4-ethynylbenzonitrile)phenyl)-1,3,5-triazine (1)

In a glove box, 2,4,6-tris(4-bromophenyl)1,3,5-triazine, **3** (0.2 g, 0.37 mmol, 1 equiv) and allylpalladium chloride dimer (0.01 g, 0.03 mmol, 7.5 mol%) were placed in a Schlenk flask, and degassed acetonitrile (1.5 mL) and toluene (50 mL) were added. Then, tris(*ter*-butyl)phosphine (0.023 g, 0.11 mmol, 30 mol%) and 4-ethynylbenzonitrile, **5** (0.17 g, 1.30 mmol, 3.5 equiv.), and 1,4-diazabicyclo(2.2.2)octane (DABCO) (0.25 g, 2.22 mmol, 6 equiv.) were added. The mixture was let to stir overnight at room temperature after which its color changed to dark brown. Stirring was terminated after 26 h and the mixture concentrated.



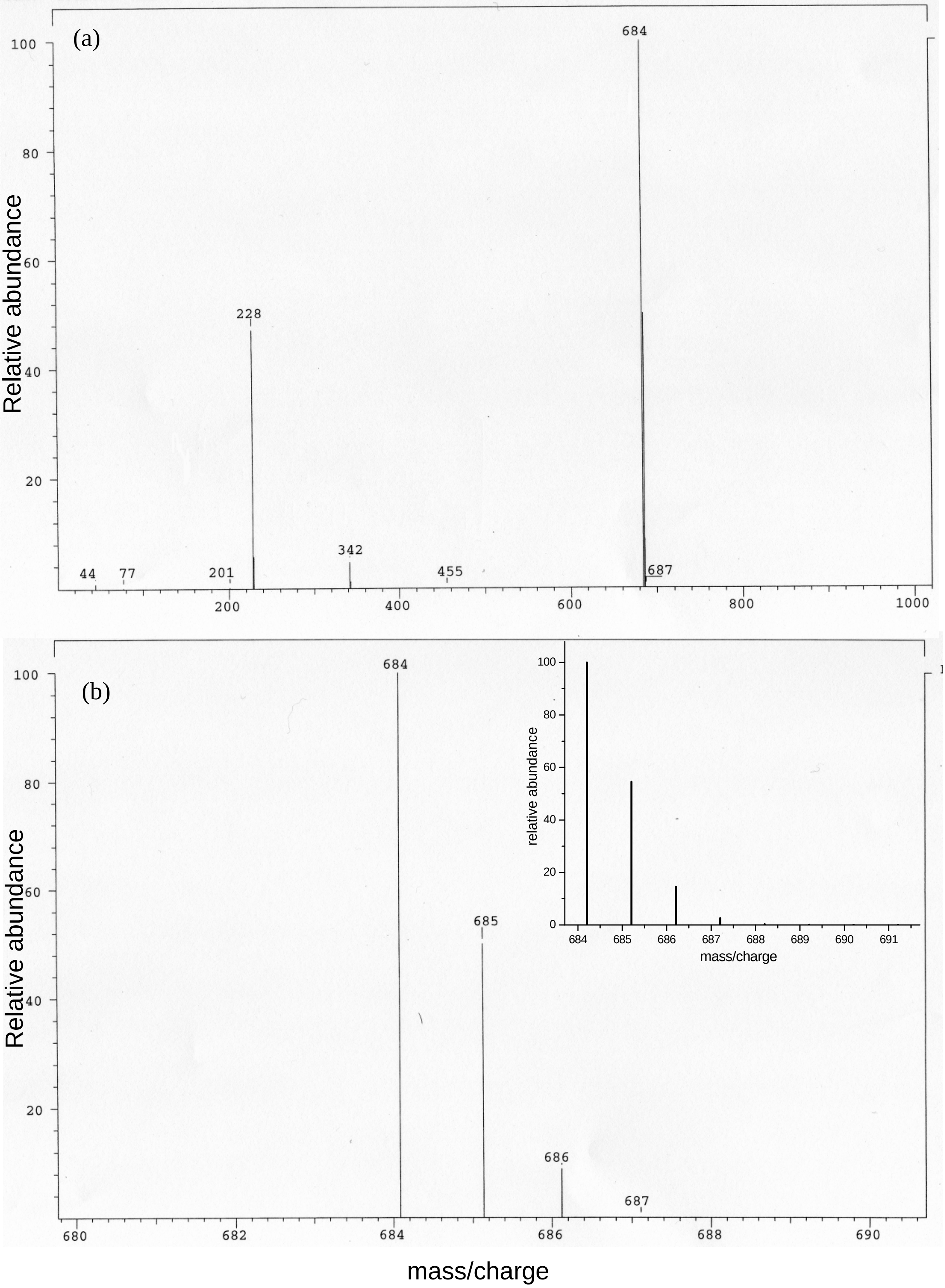
**ESI Scheme 1** (a) $CF_3SO_3H$, $CHCl_3$, room temperature. (b) Ethynyltrimethylsilane, $Et_3N$, CuI, $(PPh_3)_4Pd$, 80°C. (c) $K_2CO_3$, MeOH, RT. (d) Copper-free Sonogashira reaction conditions: **3**, $(AllylPdCl)_2$, P(*t*-Bu)$_3$, **5**, DABCO, acetonitrile/toluene (1.5/50 mL), RT.

The residue was dissolved in ethylacetate (15 mL) and water (5 ml). The layers were separated and the aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over sodium sulfate, filtered and partially concentrated.

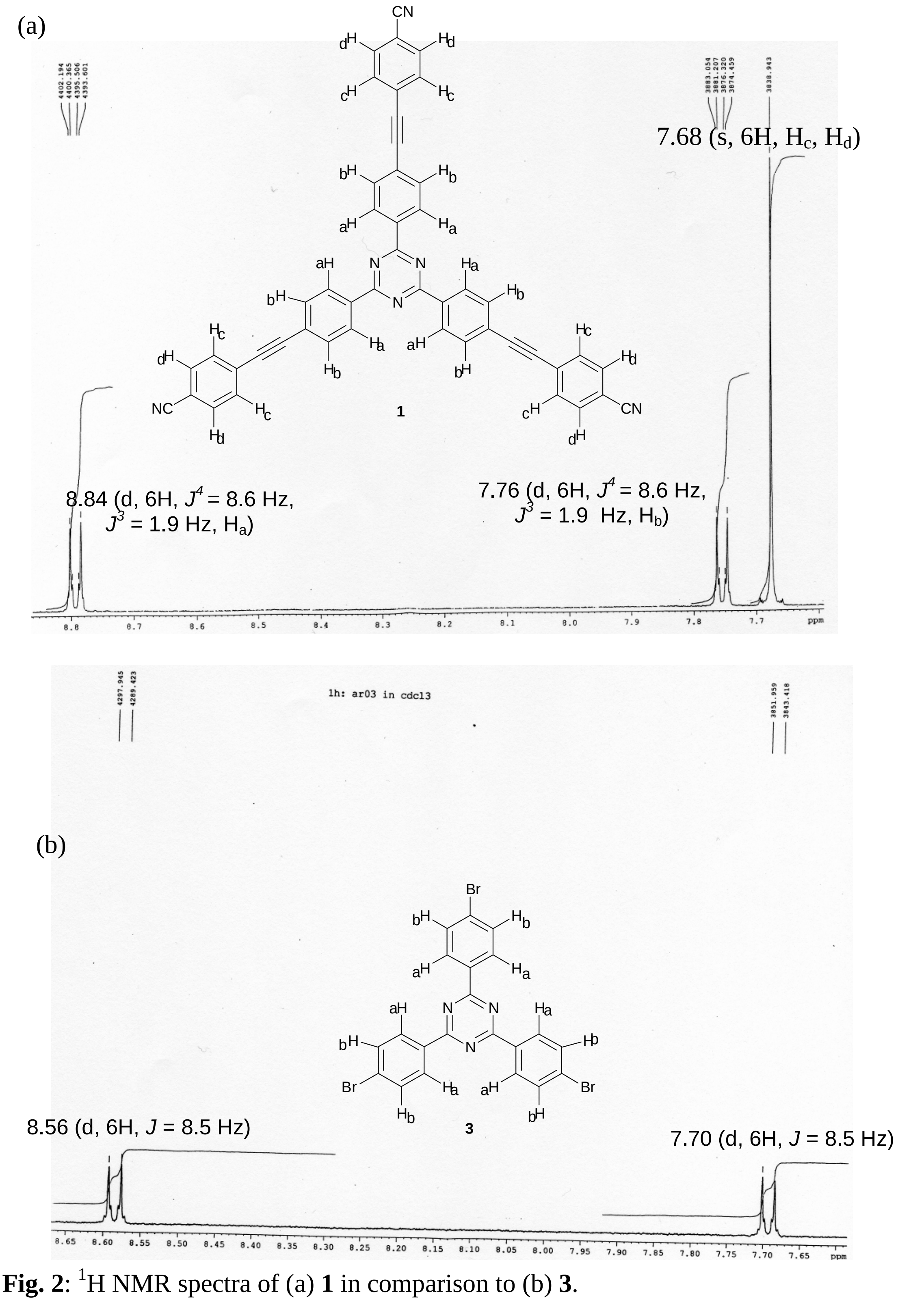
On addition of ~20 mL hexane to this solution, a brown-yellow precipitate appeared. The solution was filtered and further purification was done using the dried residue. Column chromatography was performed on the brownish-yellow residue using chloroform as the eluent. Yield: 0.010 g, 4 %. $R_f$ = 0.8.

It was inferred that the Sonogashira coupling reactions in the presence of copper-iodide and/or at higher temperatures under various conditions almost always resulted in complicated mixtures without any discrete, separable spots on the TLC plates. Also, enhancing the reaction temperature or prolonging the reaction time did not favour the formation of the desired product and instead gave only the homocoupled dialkynyl compound. It was quite obvious that the co-catalyst, copper-iodide was the stumbling block and hence a copper-free reaction protocol was followed.

EI MS m/z (%) = 684 (100) $[M]^+$, 228 (45) $[NCC_6H_4CCC_6H_4CN]^+$. $^1$H NMR (300 MHz, $CDCl_3$) δ ppm, 8.84 (d, 6H, $J^4$ = 8.6 Hz, $J^3$ = 1.9 Hz; $H_a$), 7.76 (d, 6H, $J^4$ = 8.6 Hz, $J^3$ = 1.9 Hz; $H_b$), 7.68 (s, 6H, $H_c$, $H_d$ – accidentally degenerate). $^{13}$C NMR ($CDCl_3$) δ ppm, 171.0 (triazine-C), 126.6, 127.8, 128.9, 132.0, 132.1, 132.2, 136.3 (aromatic C), 118.4 (C≡N), 111.9 ($\underline{C}$-C≡N), 90.4, 93.3 (C≡C). IR 2224 $cm^{-1}$ (C≡N).



**ESI Fig. 1** (a) EI mass spectrum of **1**. (b) Experimental isotope pattern of **1**. Inset shows the simulated isotope pattern.



7.68 (s, 6H, $H_c$, $H_d$)

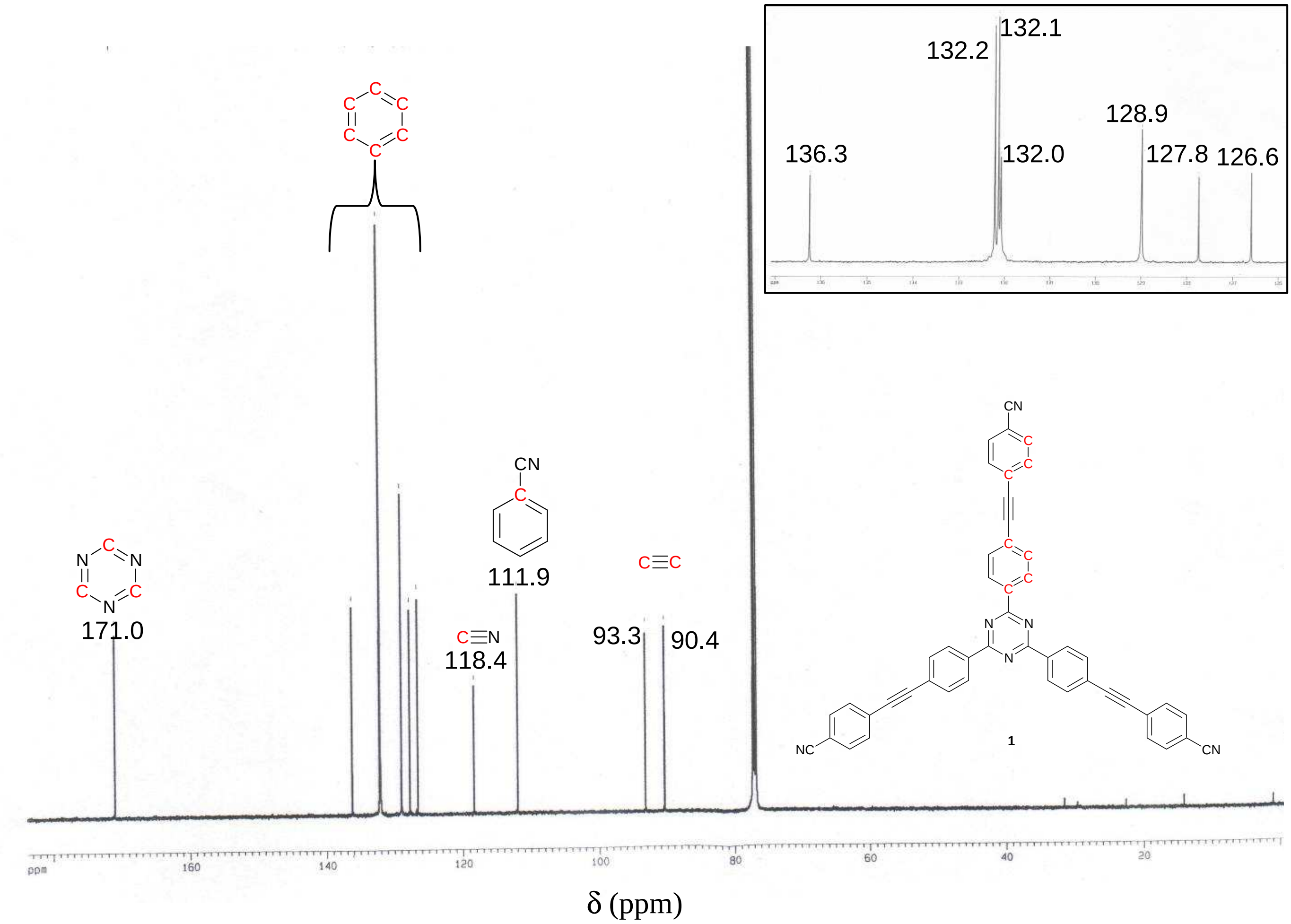
8.84 (d, 6H, $J^4$ = 8.6 Hz, $J^3$ = 1.9 Hz, $H_a$)

7.76 (d, 6H, $J^4$ = 8.6 Hz, $J^3$ = 1.9 Hz, $H_b$)

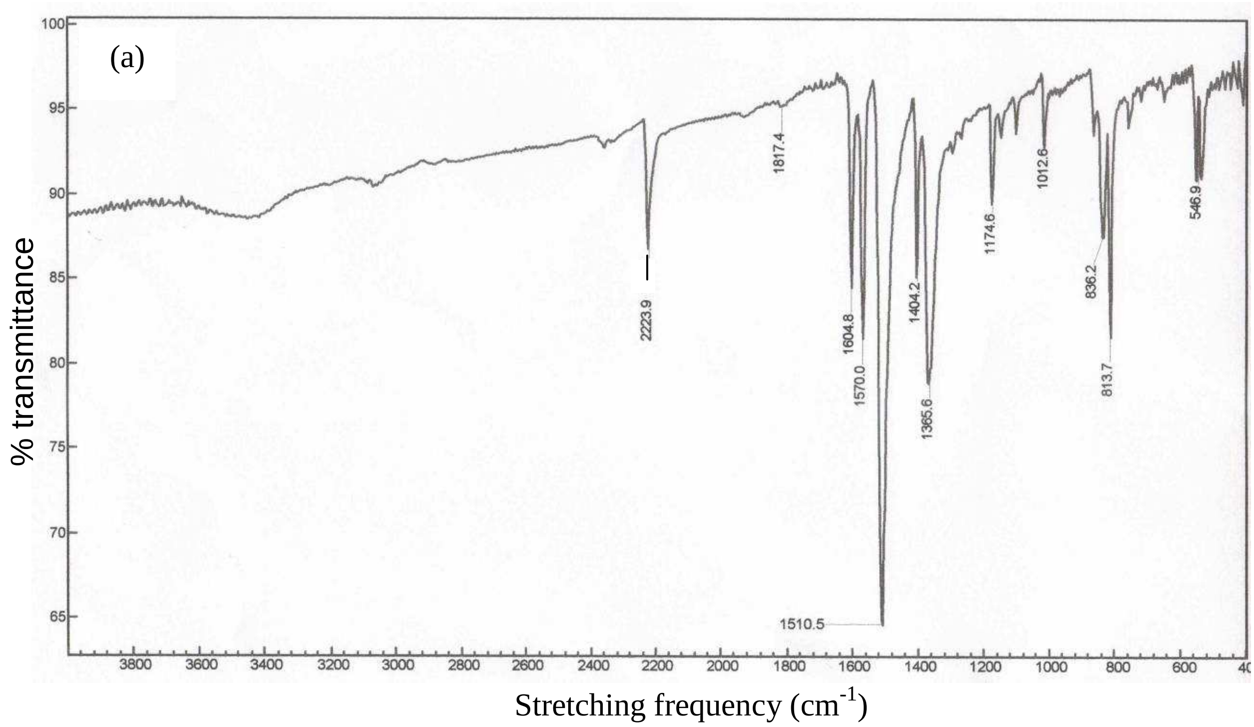
8.56 (d, 6H, $J$ = 8.5 Hz)

7.70 (d, 6H, $J$ = 8.5 Hz)

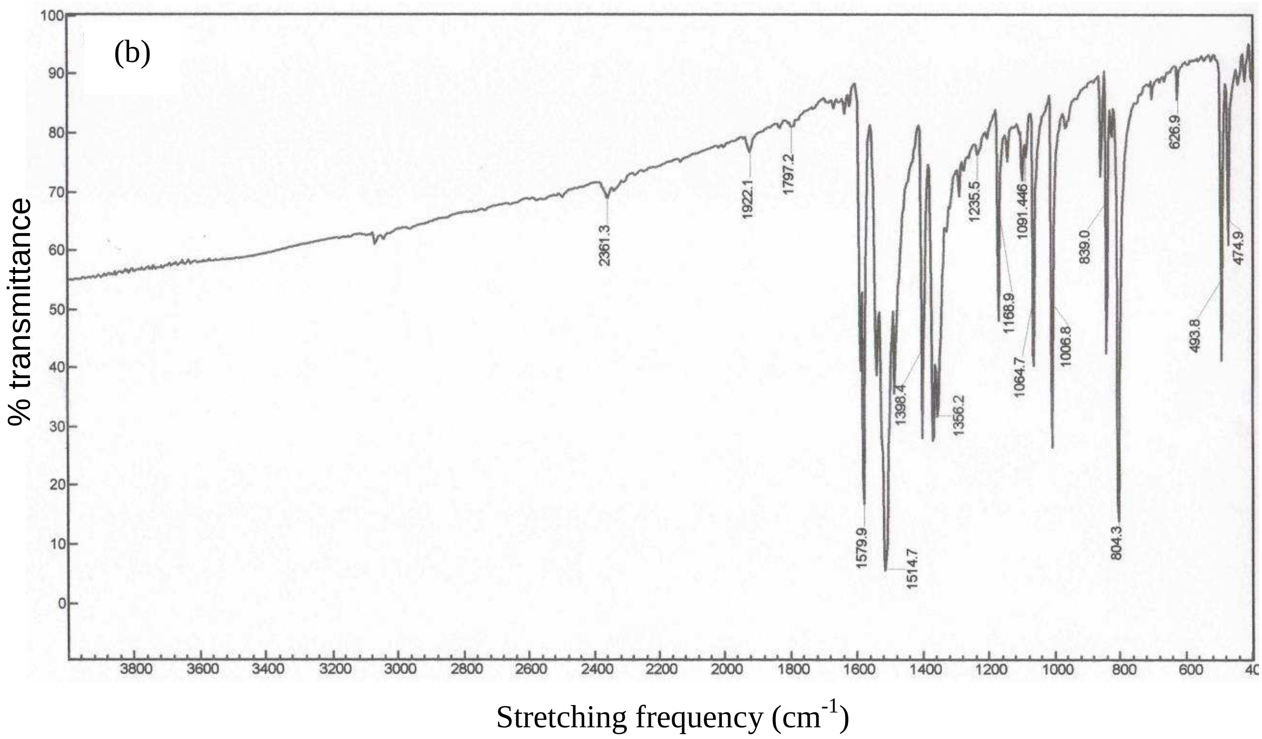
**ESI Fig. 2**: $^1$H NMR spectra of (a) **1** in comparison to (b) **3**.



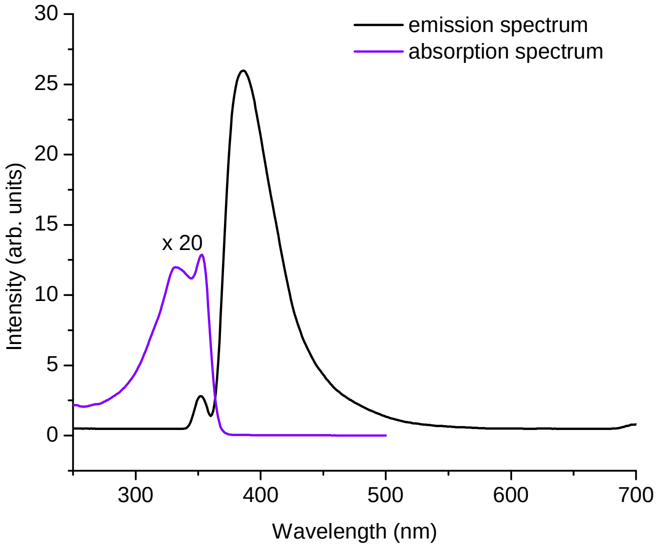
**ESI Fig. 3**: $^{13}$C NMR spectrum of **1**. The seven peaks in the inset represent the phenyl ring carbon atoms. The corresponding seven carbon atoms are marked in red in the chemical diagram.



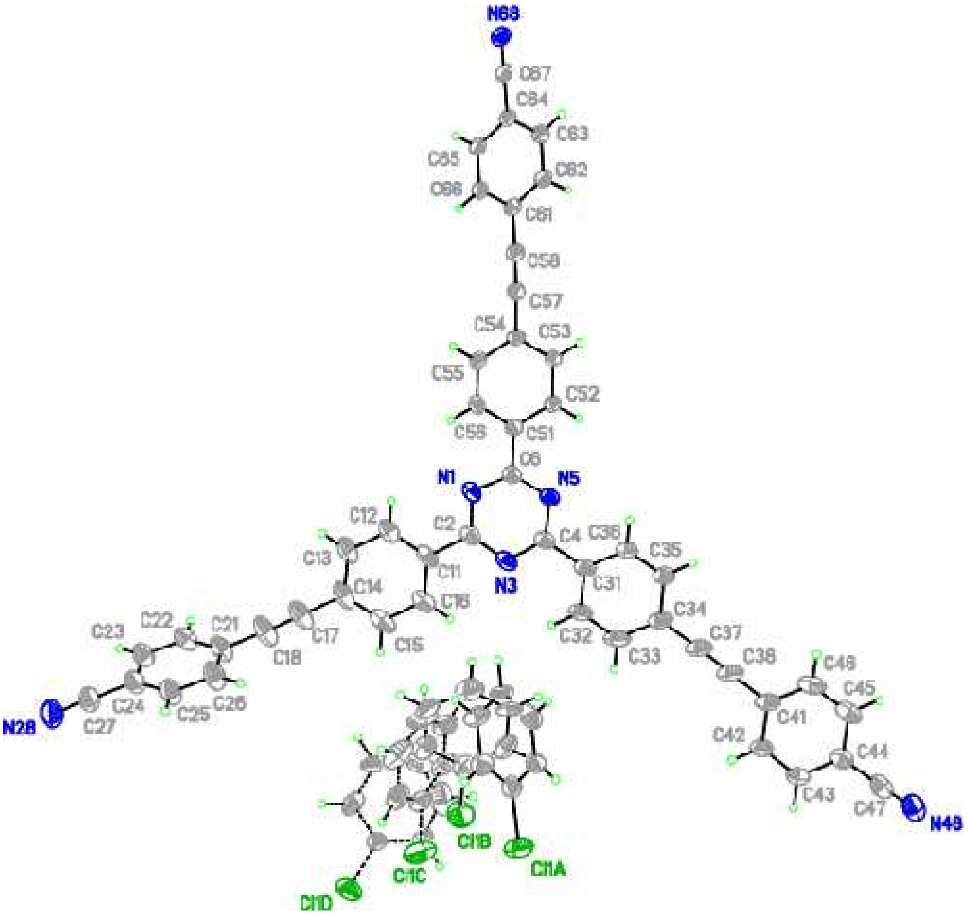
IR ($cm^{-1}$) 2224 (-C≡N, -C≡C-)



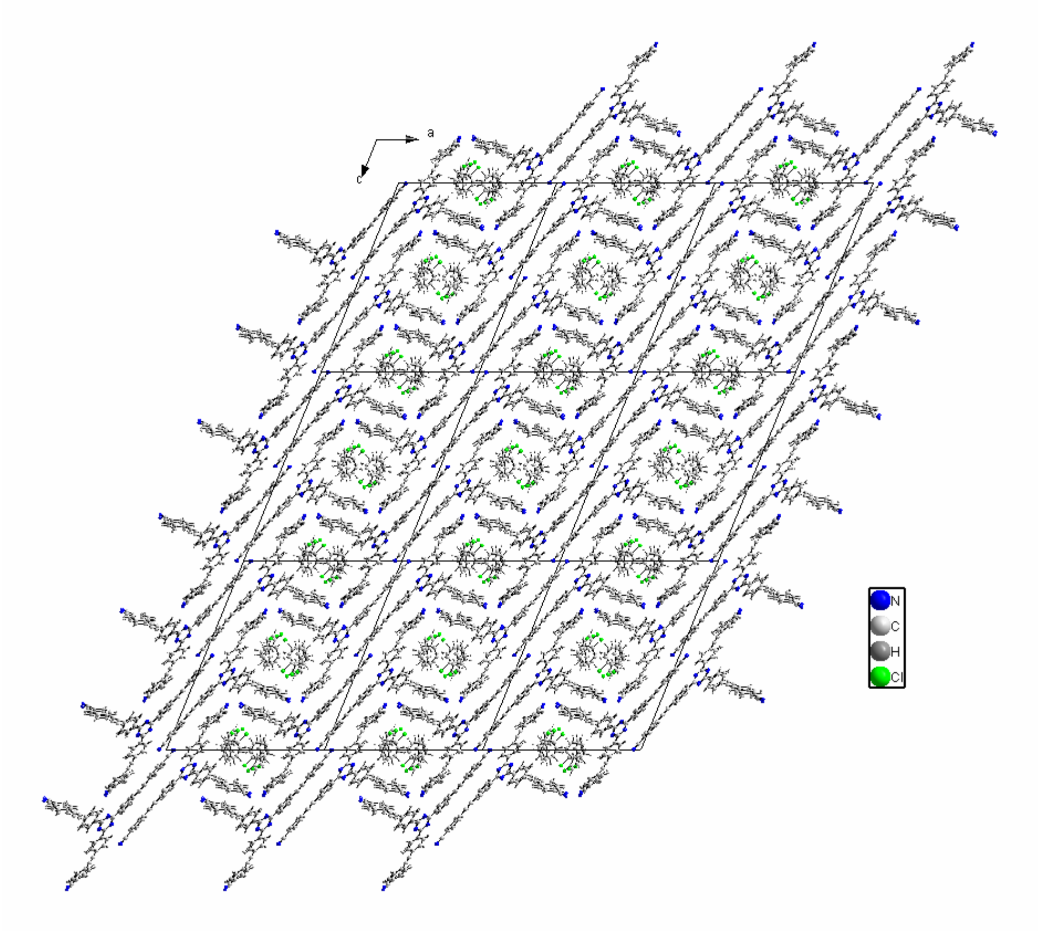
**ESI Fig. 4**: Infra-red spectra of (a) **1** shown in comparison to that of (b) **3**.



**ESI Fig. 5**: Blue curve is the absorbance ($\lambda_{max}$ = 353 nm) spectrum of **1,** which is multiplied by a factor of 20 to bring it to scale. The corresponding fluorescence (emission) spectrum is shown by black curve ($\lambda_{em}$ = 386 nm).



**ESI Fig. 6** ORTEP diagram of molecule **1** with the corresponding atom labels. Hydrogen atom labels are removed for clarity. Anisotropic displacement ellipsoids are at 50% probability level.



**ESI Fig. 7** Representation of channels formed by **1** in three-dimensional arrangement. The channels (viewed down the b-axis) are filled by chlorobenzene molecules.

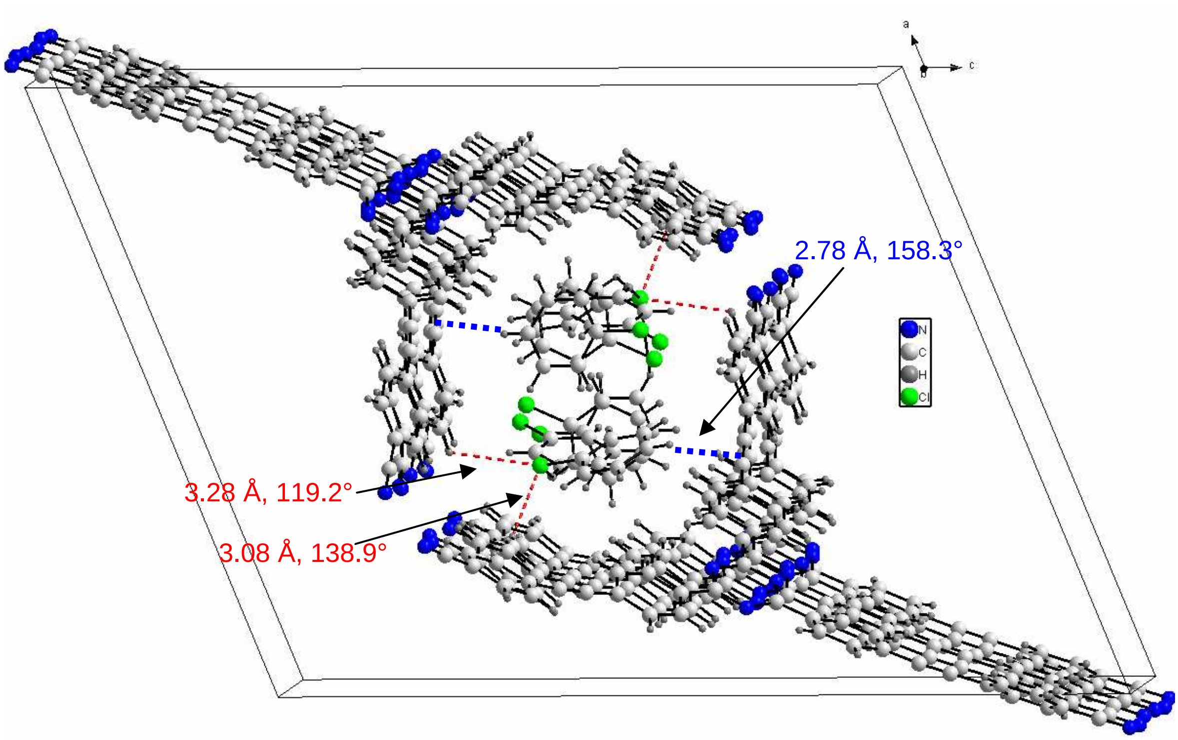
**Table 1.** Unique C-H···N hydrogen bonds found in the crystal structure of **1** with chlorobenzene solvent molecules.

| **No.** | **Type of hydrogen bond** | **C-H (Å)** | **H···N (Å)** | **C···N (Å)** | **C-H···N (°)** |
|---|---|---|---|---|---|
| 1 | C(43)-H(43A)...N(28)#1 | 0.95 | 2.57 | 3.433(3) | 151.6 |
| 2 | C(25)-H(25A)...N(48)#2 | 0.95 | 2.71 | 3.626(3) | 163.1 |
| 3 | C(13)-H(13A)...N(48)#3 | 0.95 | 2.77 | 3.418(3) | 126.0 |
| 4 | C(35)-H(35A)...N(68)#4 | 0.95 | 2.59 | 3.458(3) | 152.4 |
| 5 | C(65)-H(65A)...N(68)#5 | 0.95 | 2.65 | 3.263(2) | 122.5 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x+1,-y+1,-z #3 x,-y+3/2,z+1/2

#4 -x,y+1/2,-z+1/2 #5 -x,-y+1,-z+1



**ESI Fig. 8**: Very weak C-H···Cl (red dashed lines) and C-H···$\pi_m$ (blue dashed lines, $\pi_m$ is the midpoint of the C≡C bond) contacts observed between the host network and the chlorobenzene molecules. The H···A distances and C-H···A angles (A: H-bond acceptor) are given.