

Network Formation in Conjugated Microporous Polymers

Andrea Laybourn,^a Robert Dawson,^{a,b} Rob Clowes,^a Tom Hasell,^a Andrew I. Cooper,^a
Yaroslav Z. Khimyak^c and Dave J. Adams^a

^a *Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, U.K.*

^b *Institute of Chemistry, Functional Materials, Technische Universität Berlin, Hardenbergstraße 40, Berlin, 10623, Germany.*

^c *School of Pharmacy, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, U.K.*

SUPPORTING INFORMATION

1. ^1H solution NMR studies of reaction intermediates

Reactions halted before 40 minutes were analysed by solution ^1H -NMR as no solid product was collected, *i.e.* the intermediates were soluble in the methanol/DMF mixture. ^1H NMR spectra of the soluble intermediates are given in Figure S1.

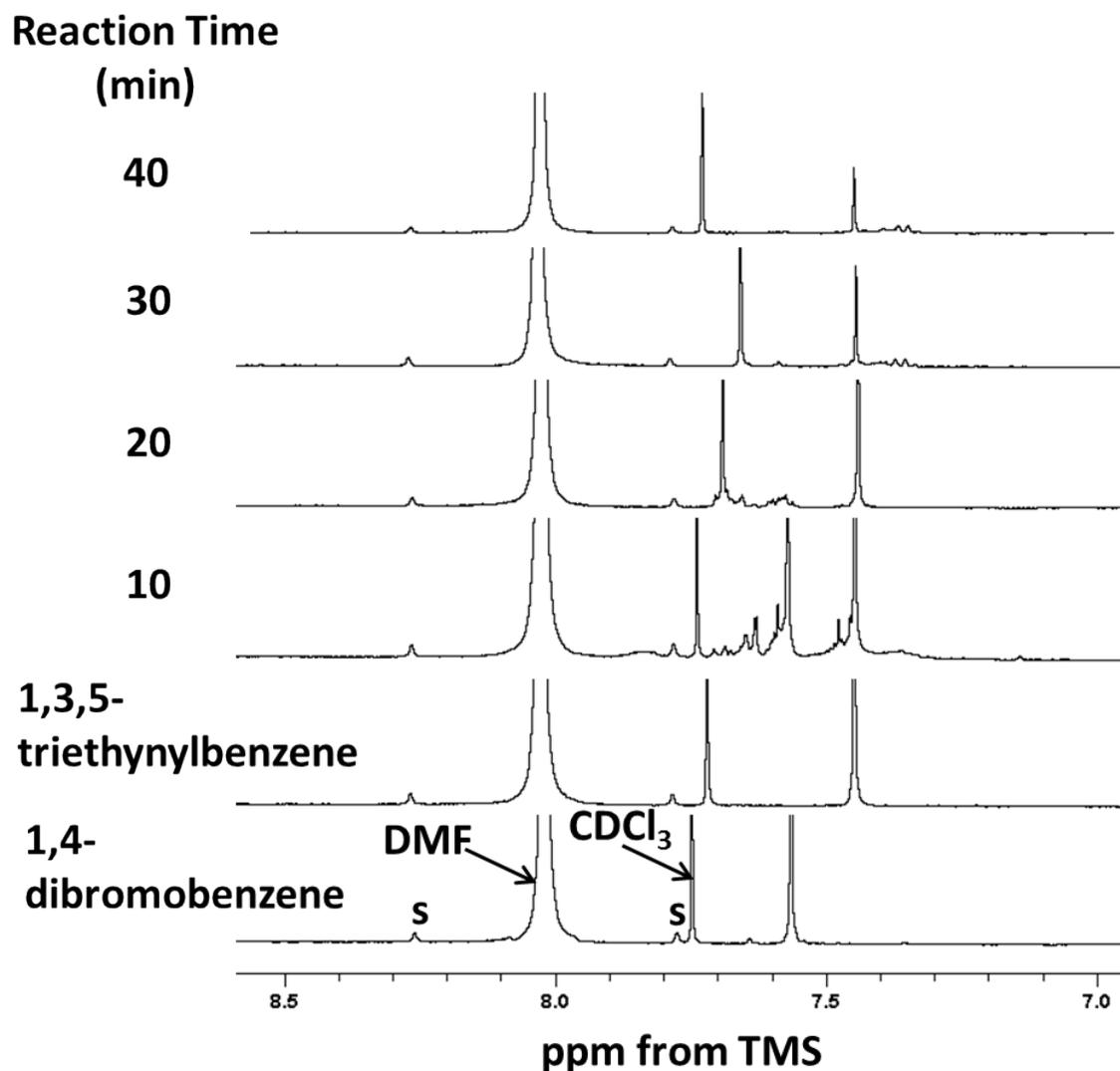


Figure S1. ^1H NMR of monomers and soluble reaction intermediates (all spectra have $8 \times$ magnification). Spectra calibrated to DMF at 8.20 ppm. 's' denotes satellite solvent peaks.

As the reaction mixtures contain varying amounts of solvent and intermediates, their chemical shifts vary between each ^1H NMR spectrum, preventing the accurate assignment all of the individual peaks. Also, the alkyne peak, which would appear at *ca.* 3.1 ppm, is obscured by a solvent peak. However, the spectra can be used to show the growth and precipitation of oligomers with time.

After 10 minutes, the ^1H NMR spectrum consisted of peaks corresponding to soluble materials with many un-symmetrical aromatic groups, suggesting that polymerisation is taking place. After 20 minutes, the overall intensity and number of different peaks decrease, suggesting that the intermediates have become more extended and precipitated out of solution. At 30 and 40 minutes even fewer aromatic peaks were detected, again this is an indication that the materials are now insoluble in the reaction mixture

2. Hypothetical Network Structures

Hypothetical network structures were generated, with a view to matching the EDX data (Table 2, main text). Figure S2 shows a structure with a Br content matching that for the network formed after 60 minutes. Figure S3 shows a structure with a Br content matching that for the network formed after 1080 minutes. For both these, the Pd and Cu contents were ignored.

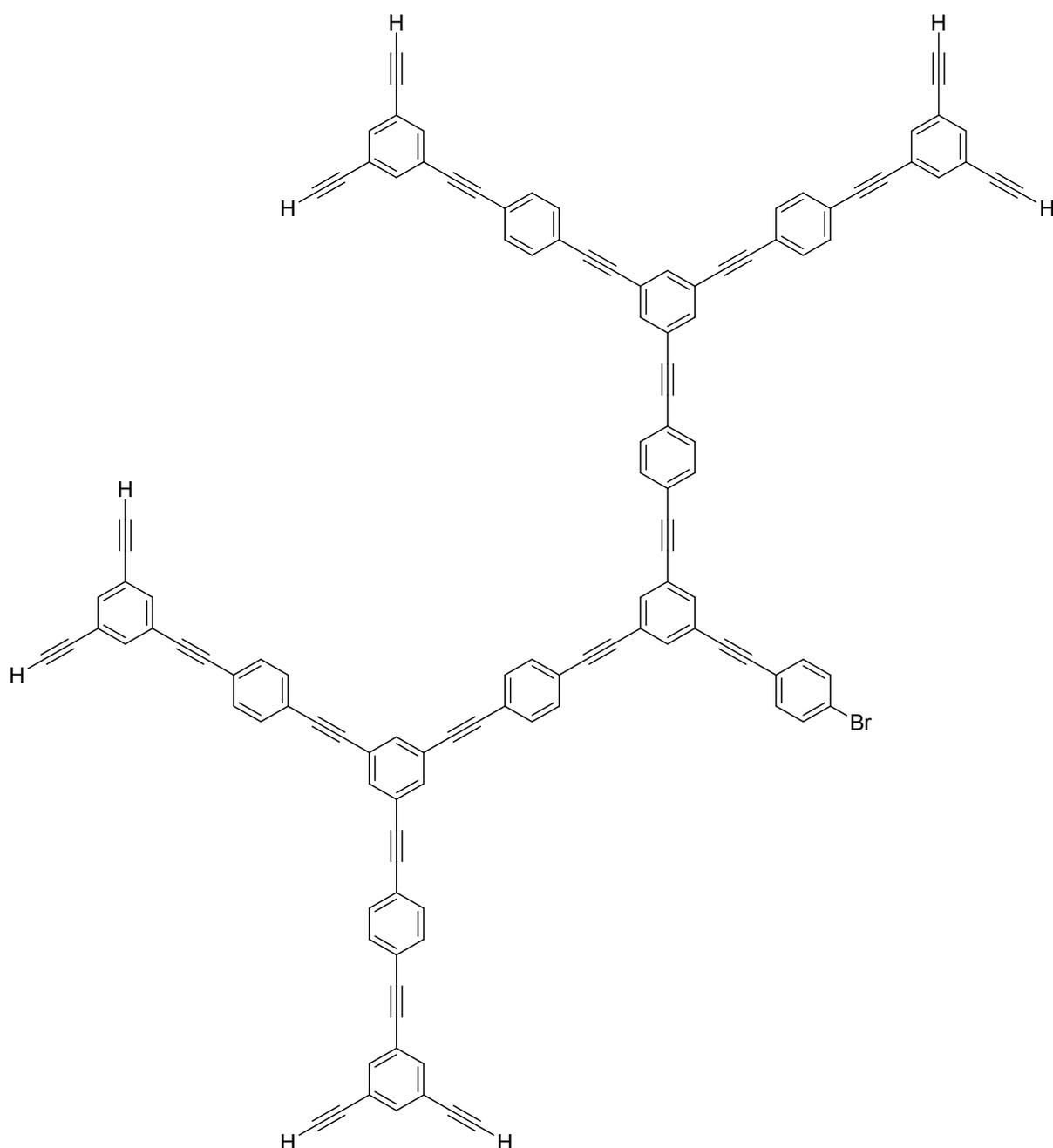


Figure S2. Hypothetic network chosen to match Br content of network formed after 60 minutes. Network is $C_{126}H_{57}Br$: C, 91.68 %; H, 3.48 %; Br, 4.84 %.

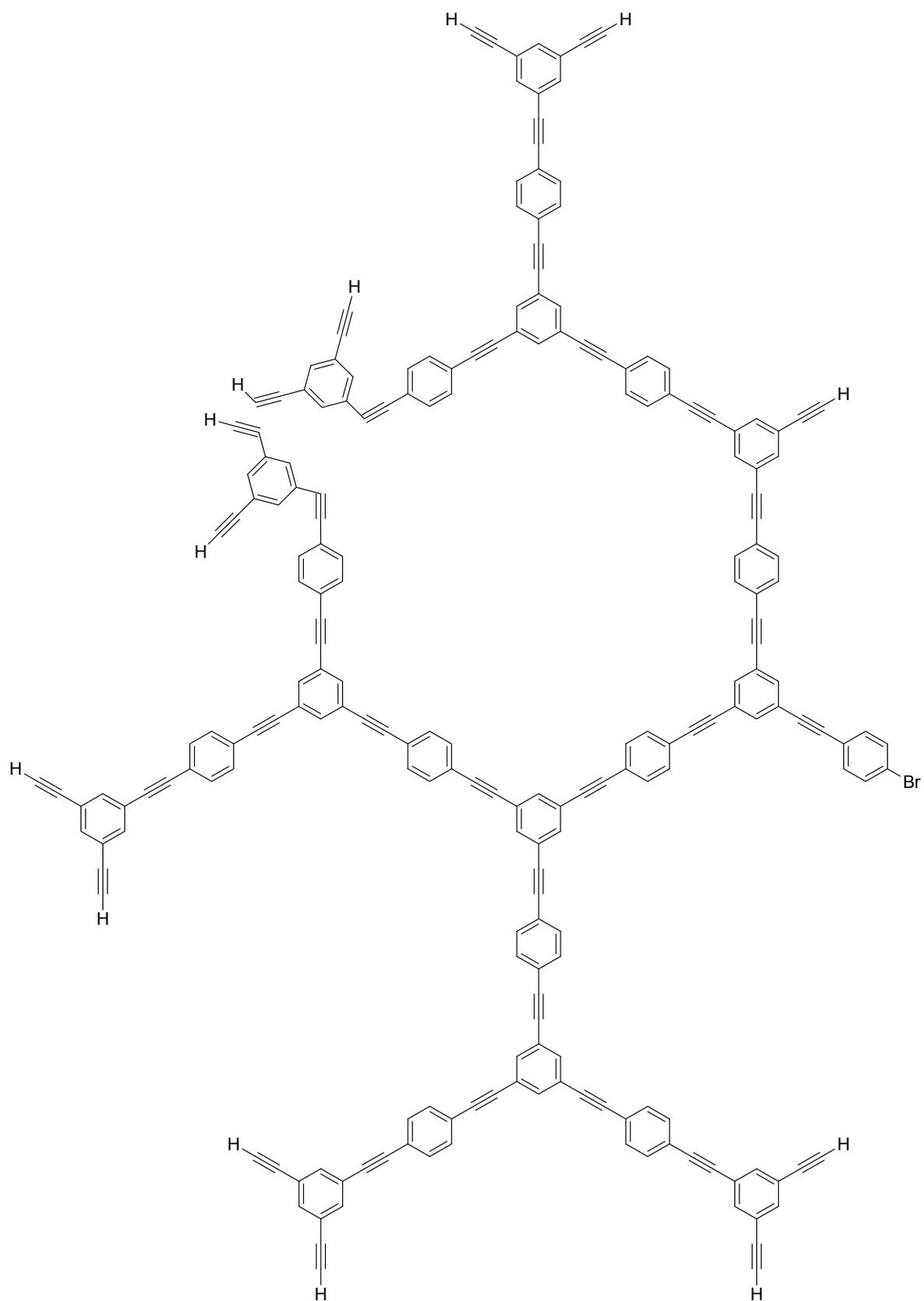


Figure S3. Hypothetic network chosen to match Br content of network formed after 1080 minutes. Network is $C_{126}H_{57}Br$: C, 93.59 %; H, 3.53%; Br, 2.88 %.

3. ^1H - ^{13}C CP/MAS NMR spectra of monomers

^1H - ^{13}C CP/MAS NMR spectra of the monomers are shown in Figure S2.

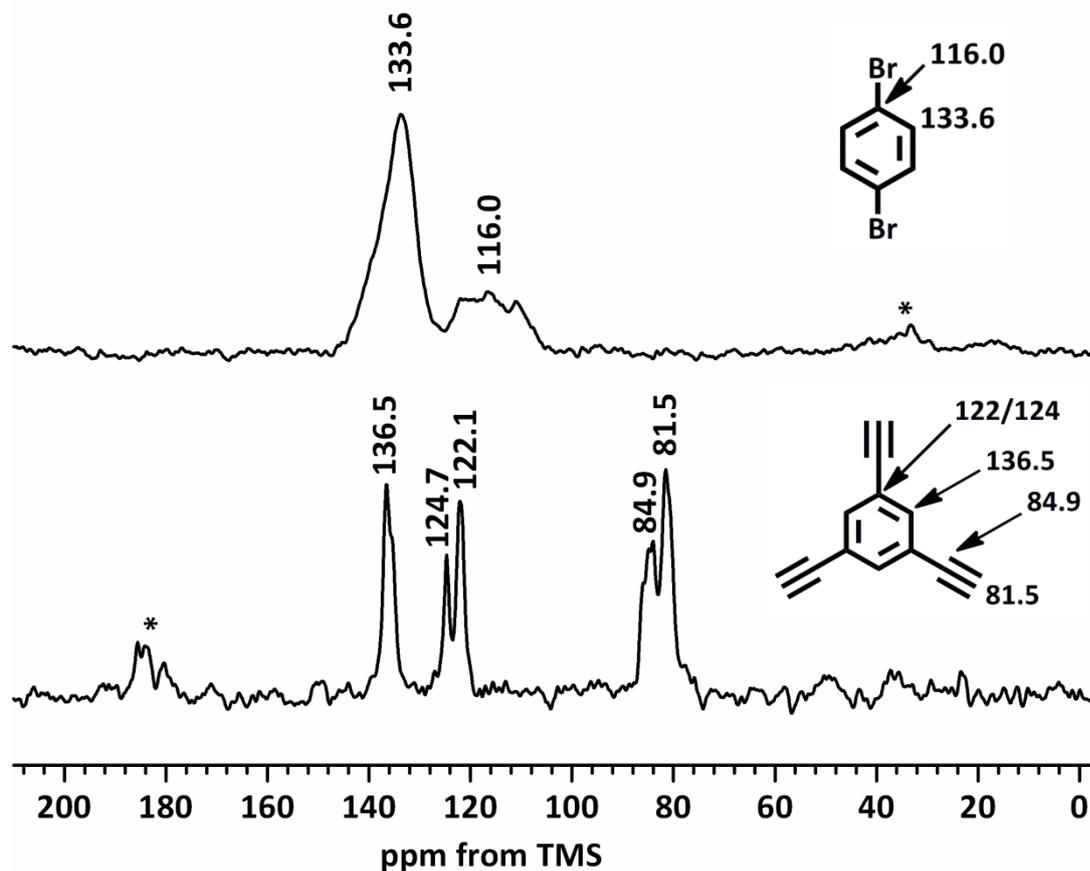


Figure S4. ^1H - ^{13}C CP MAS NMR spectra of monomers recorded at an MAS rate of 10 kHz. Structure of monomers labelled with peak assignments (inset). Asterisks denote spinning sidebands. Multiple peaks at 116 and 122-124 ppm are a consequence of ^{13}C - $^{79/81}\text{Br}$ residual dipolar coupling and different environments in the crystal structure, respectively.

Both monomers exhibit aromatic peaks in the range of 122.1-133.6 ppm. These peaks overlap with those displayed in the NMR spectra of the polymerised networks (Figure 2). Each monomer also displays a peak at *ca.* 136 ppm. This peak is well-pronounced for the alkyne monomer and appears as only a shoulder peak for the brominated-monomer (Figure S2). Conveniently, each monomer also displays its own characteristic peak at 116.0 ppm ($-\text{C}_{\text{Ar}}-\text{Br}$) for 1,4-dibromobenzene and *ca.* 83 ppm ($-\text{C}\equiv\text{C}-\text{H}$) for 1,3,5-triethynylbenzene. Comparison between the spectra of the monomers and the spectra of the reaction intermediates enables unambiguous assignment of the peaks.

The CMP-1 materials in this work exhibit small peaks at 116.0 ppm in their spectra (Figure 2), therefore they contain only low amounts of halogen end groups, this is consistent with EDX analysis. The CMP-1 materials display peaks at *ca.* 83 ppm, corresponding to an alkyne end group (Figure S2). With the absence of a peak at 116.0 ppm and the presence of a peak at *ca.* 83 ppm, one can conclude that the shoulder resonance observed at 137 ppm in the spectra of the reaction intermediates (Figure 2) is a consequence of alkyne end groups and not brominated end groups.

3. Example Deconvolutions of $^{13}\text{C}\{^1\text{H}\}$ HPDEC MAS NMR

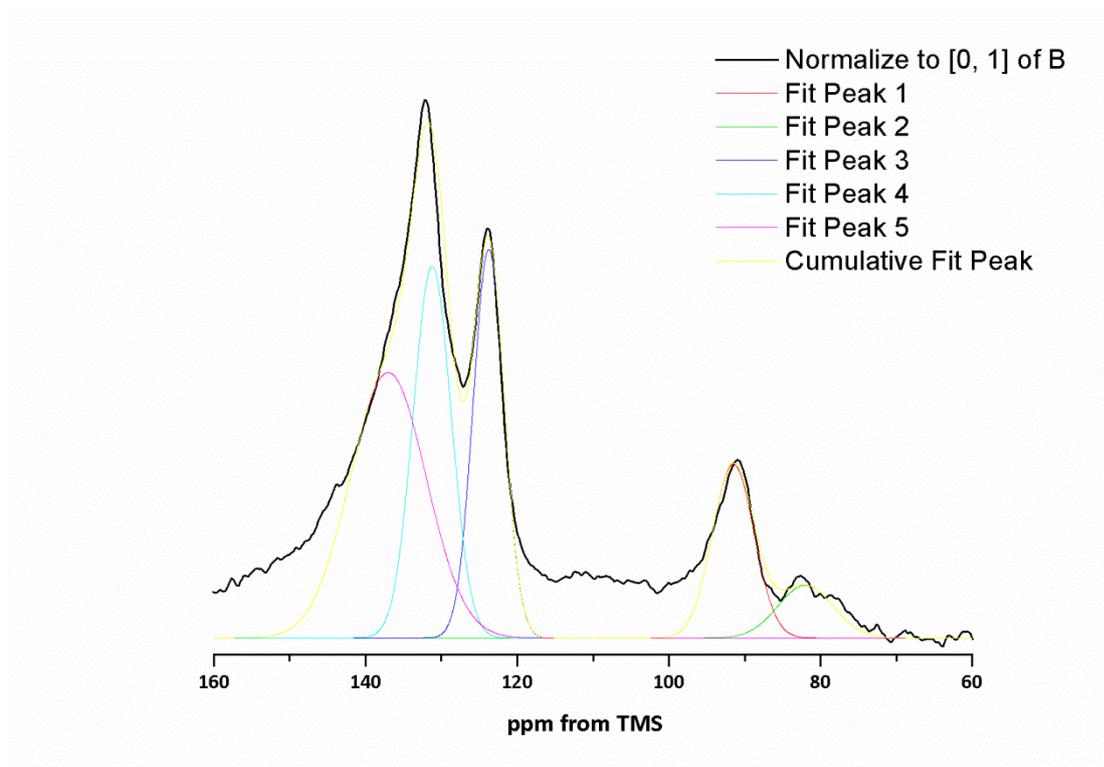


Figure S5. Deconvolution of spectrum obtained for the isolated material at 60 minutes (CHI squared = 0.90)

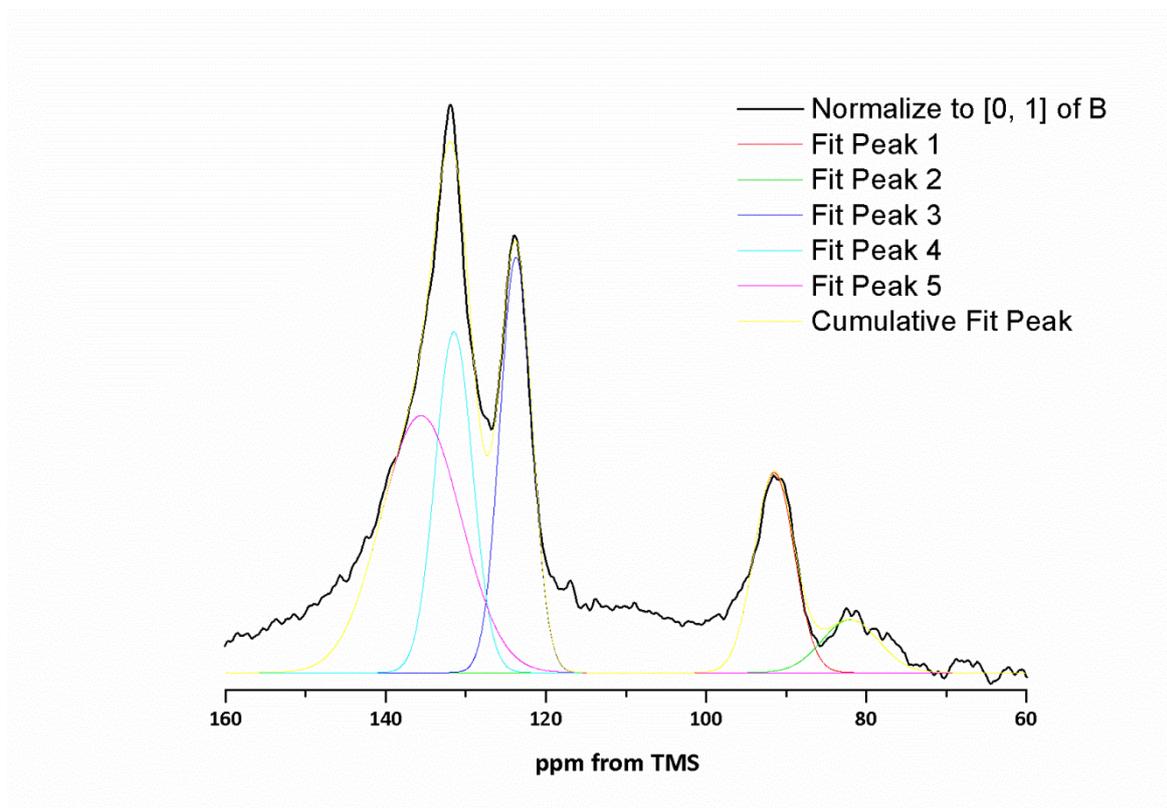


Figure S6. Deconvolution of spectrum obtained for the isolated material at 120 minutes (CHI squared = 0.92)

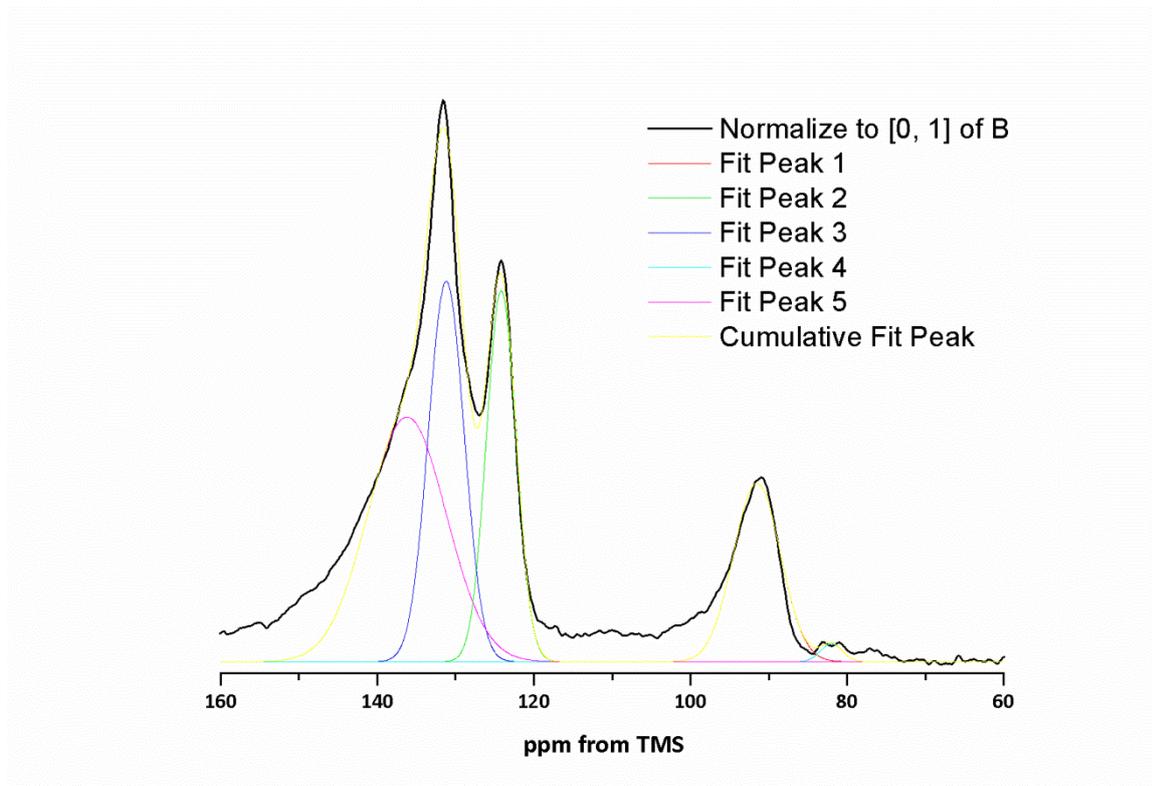


Figure S7. Deconvolution of spectrum obtained for the isolated material at 300 minutes (CHI squared = 0.94)

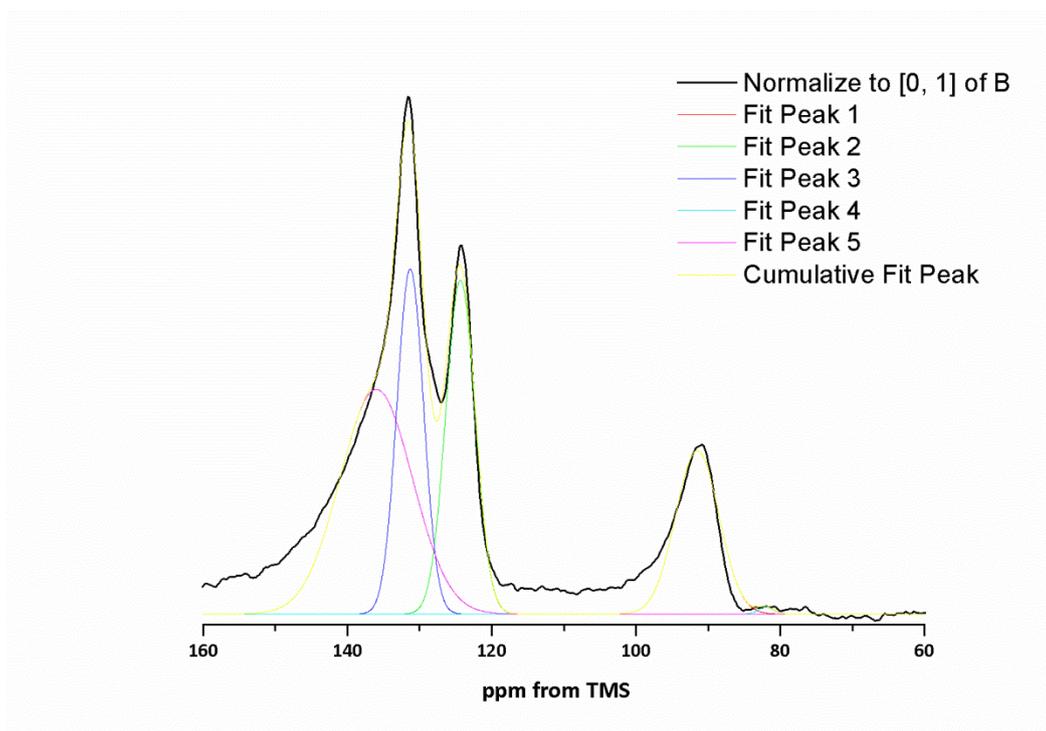


Figure S8. Deconvolution of spectrum obtained for the isolated material at 1080 minutes (CHI squared = 0.94)