NDI–Donor Polymers: Exploration of Donor Size and Electrostatic Complementarity

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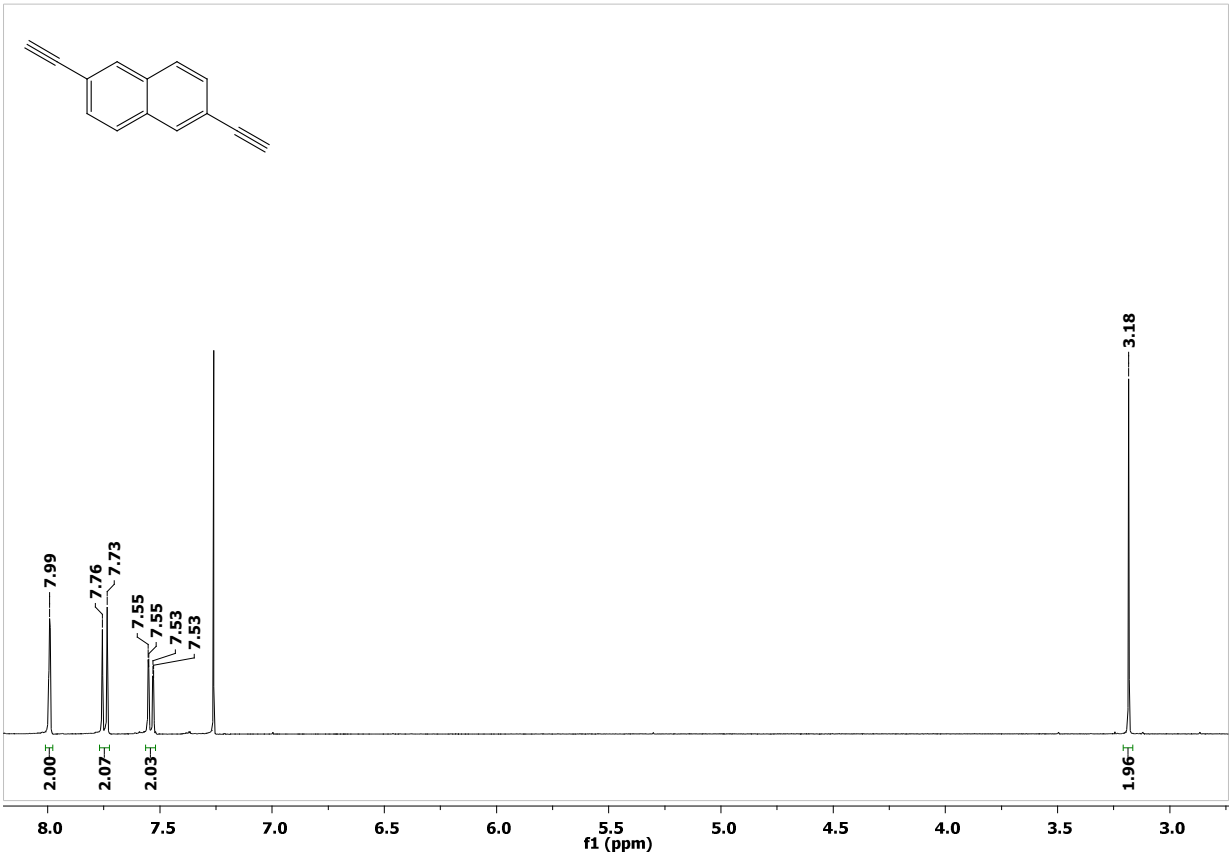
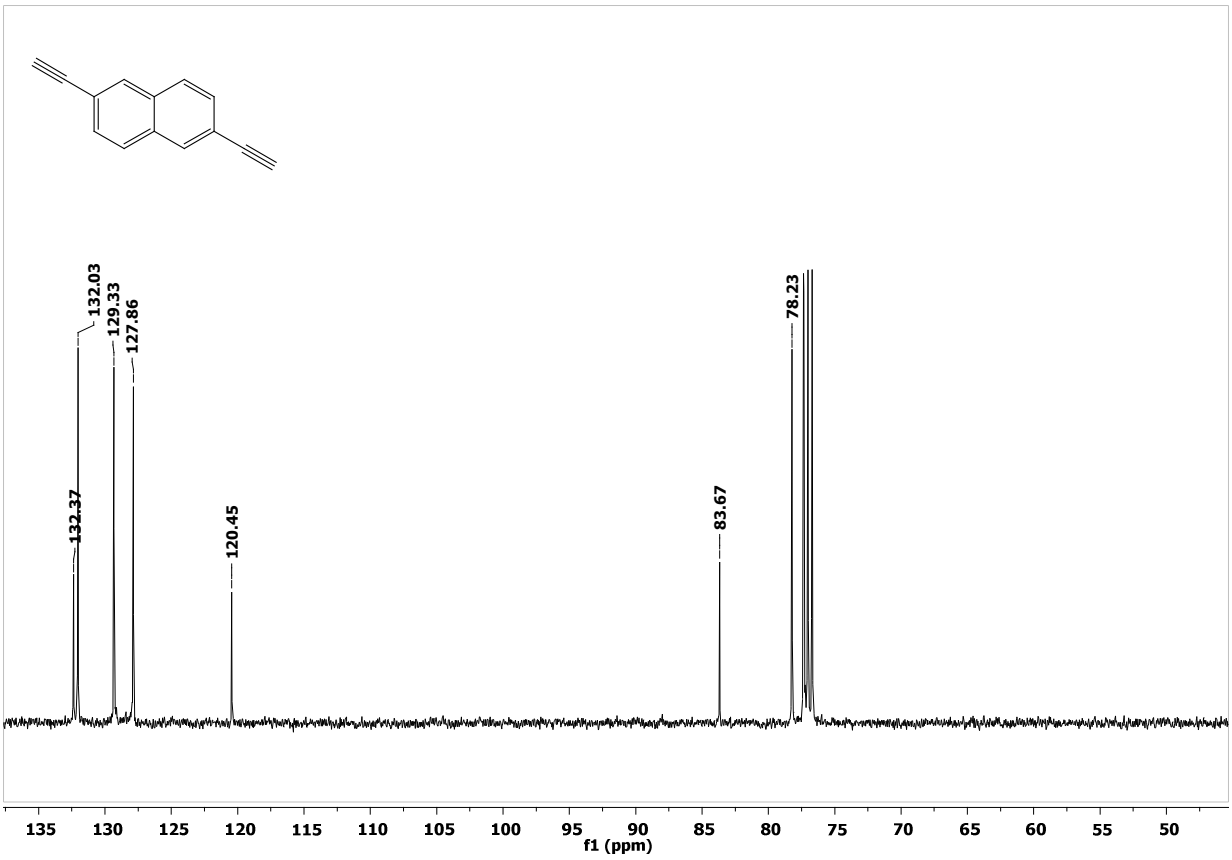
This Section Contains:

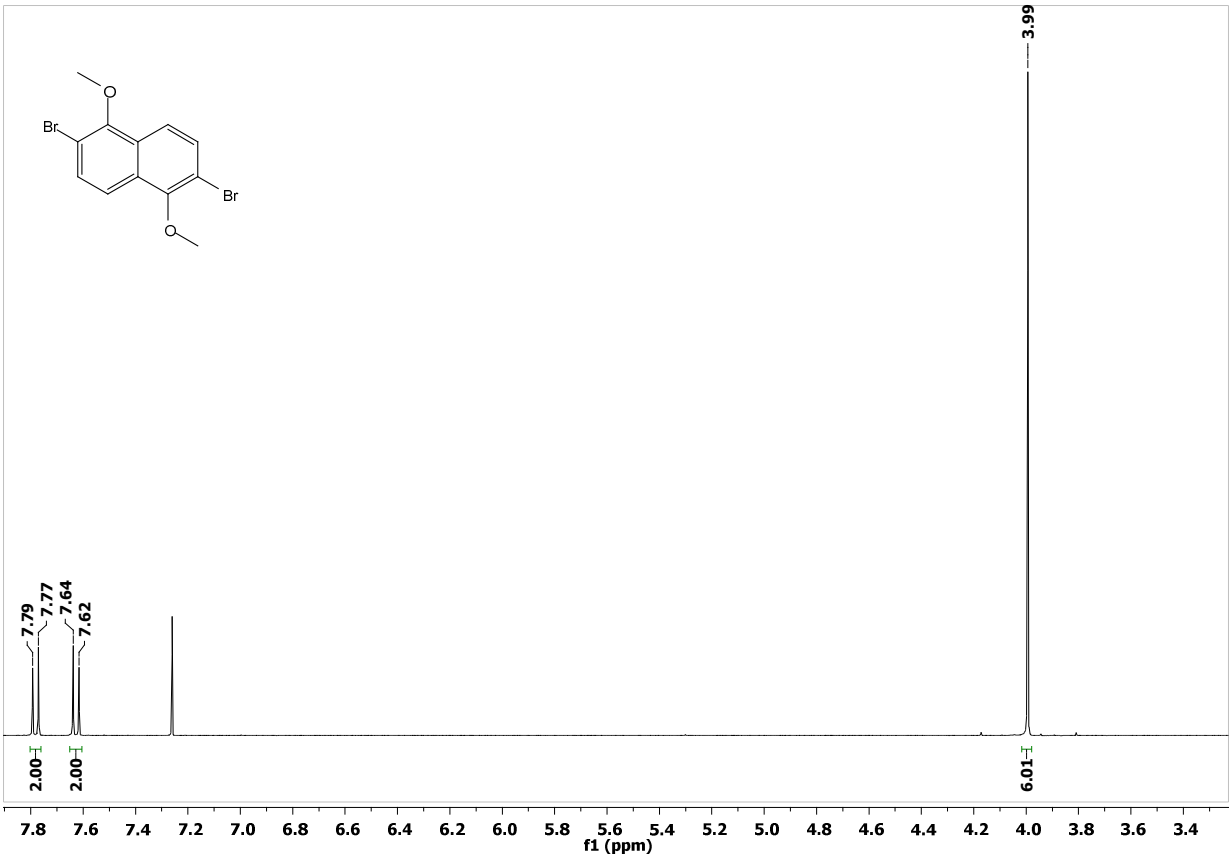
1) NMR Spectra



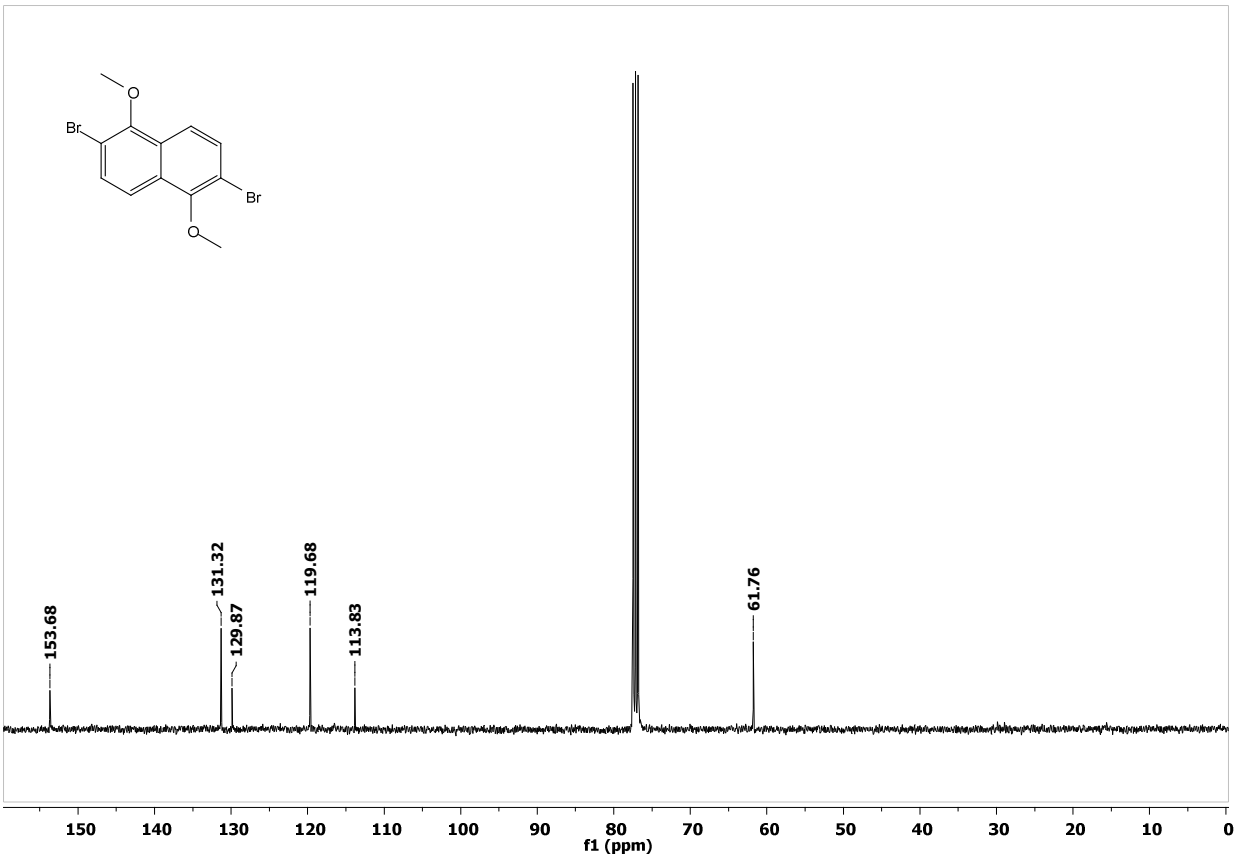
Intermediate **4** – ^{1}H



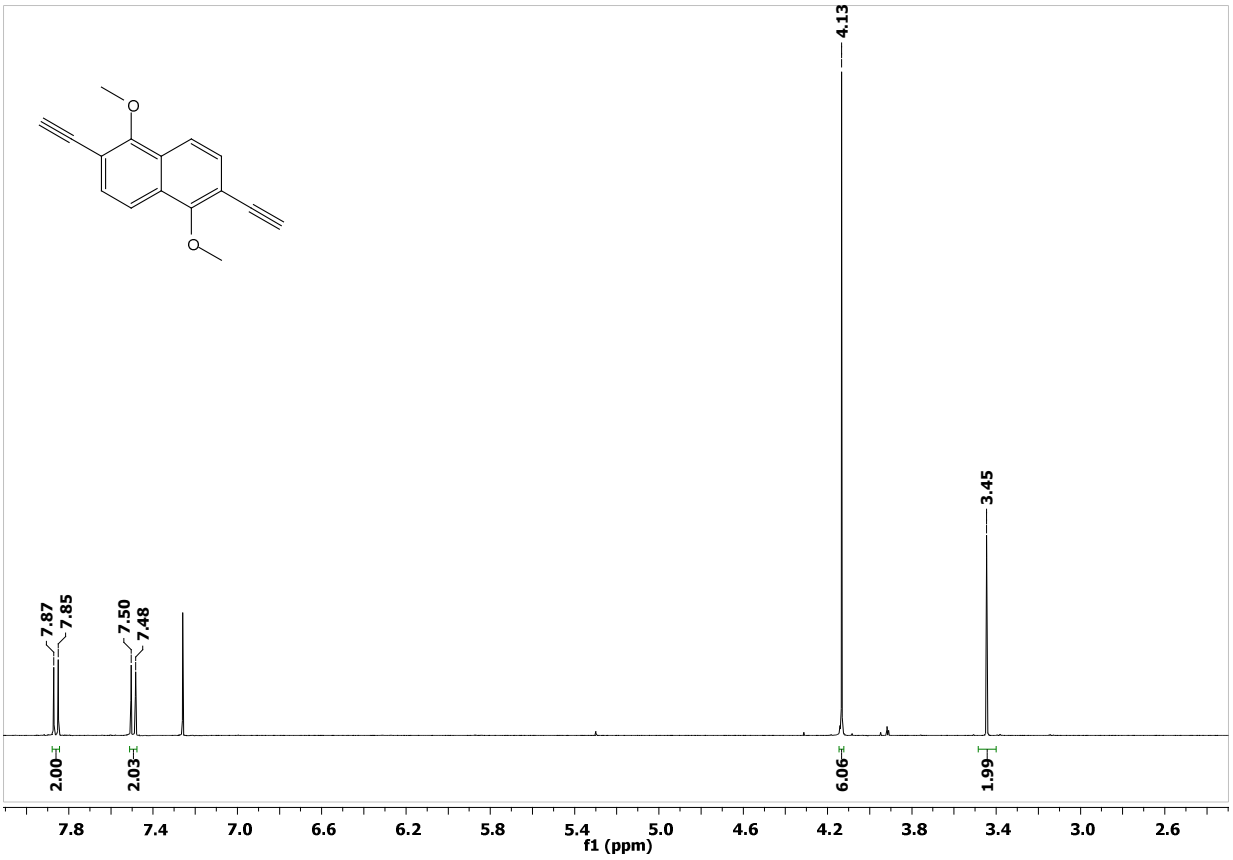
Intermediate **4** – ^{13}C



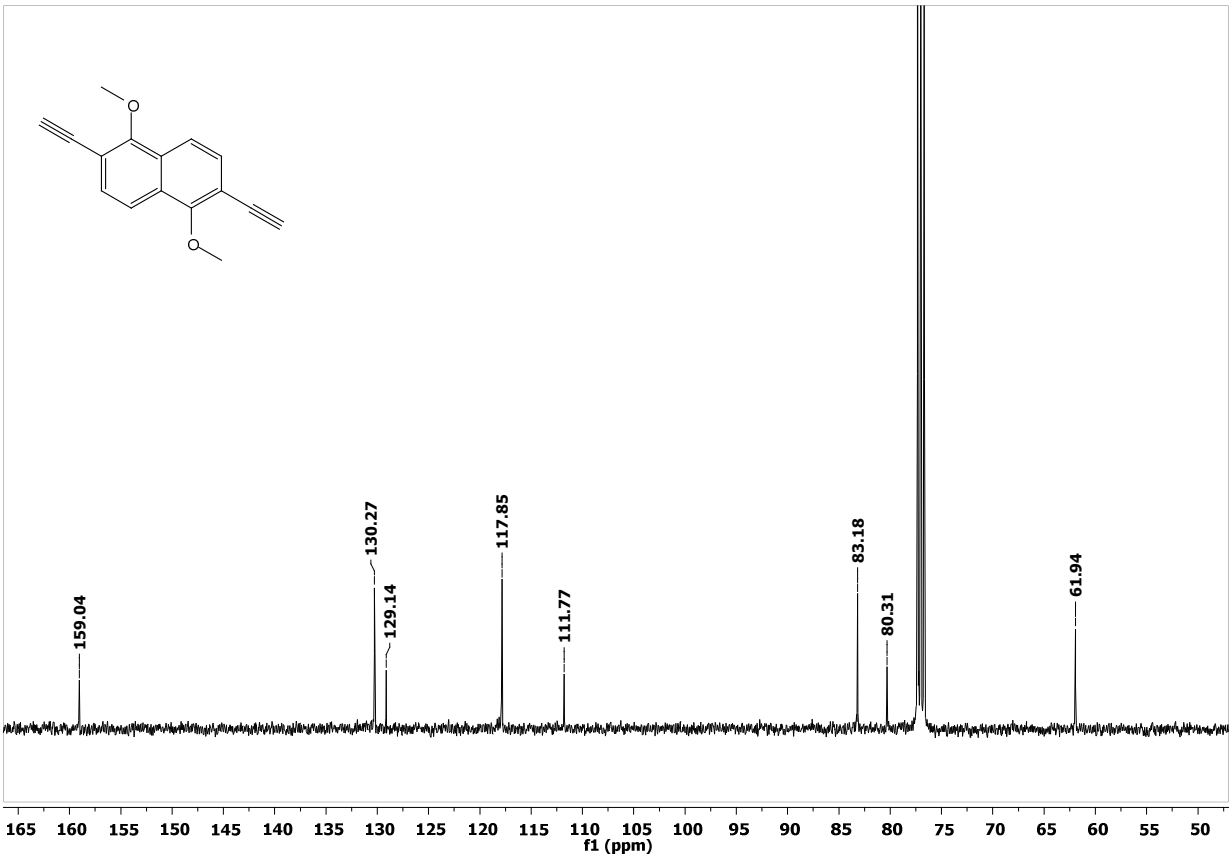
Intermediate **6** – ^{1}H



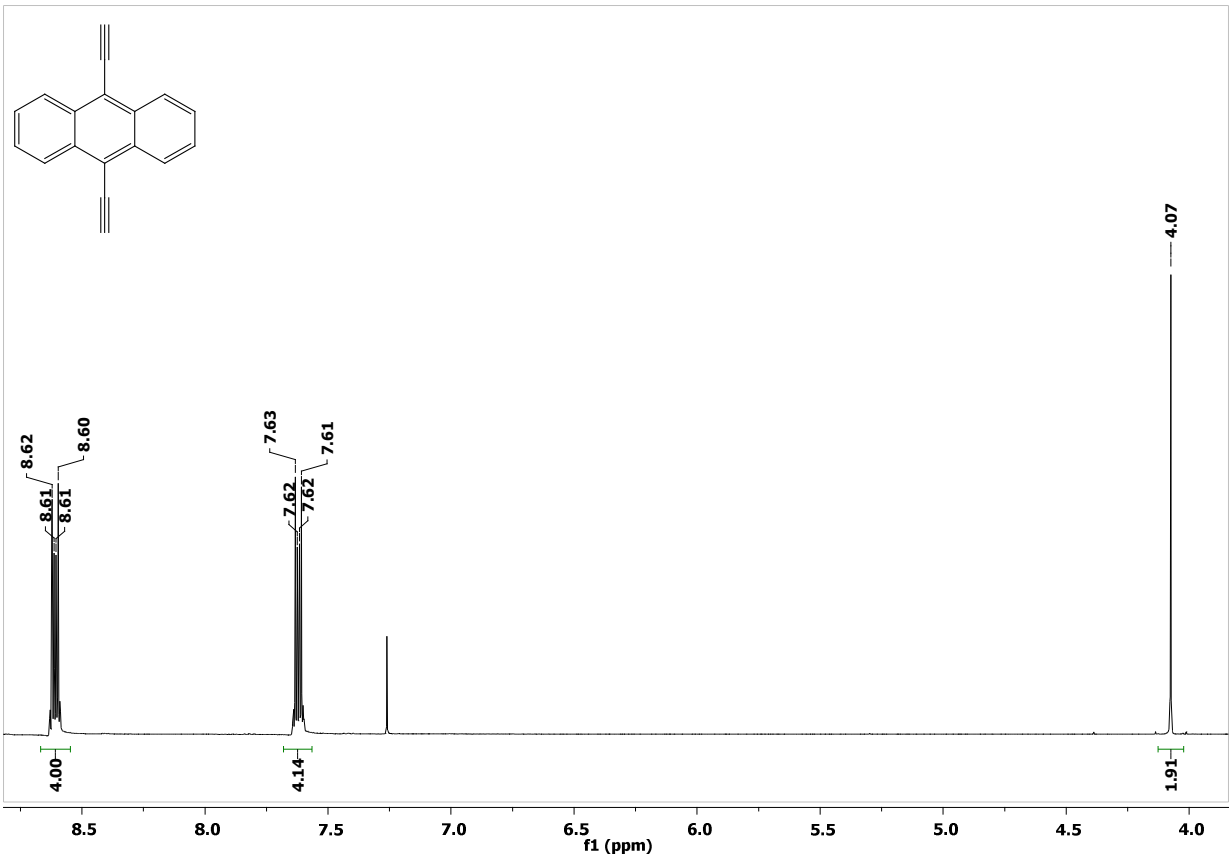
Intermediate **6** – ^{13}C



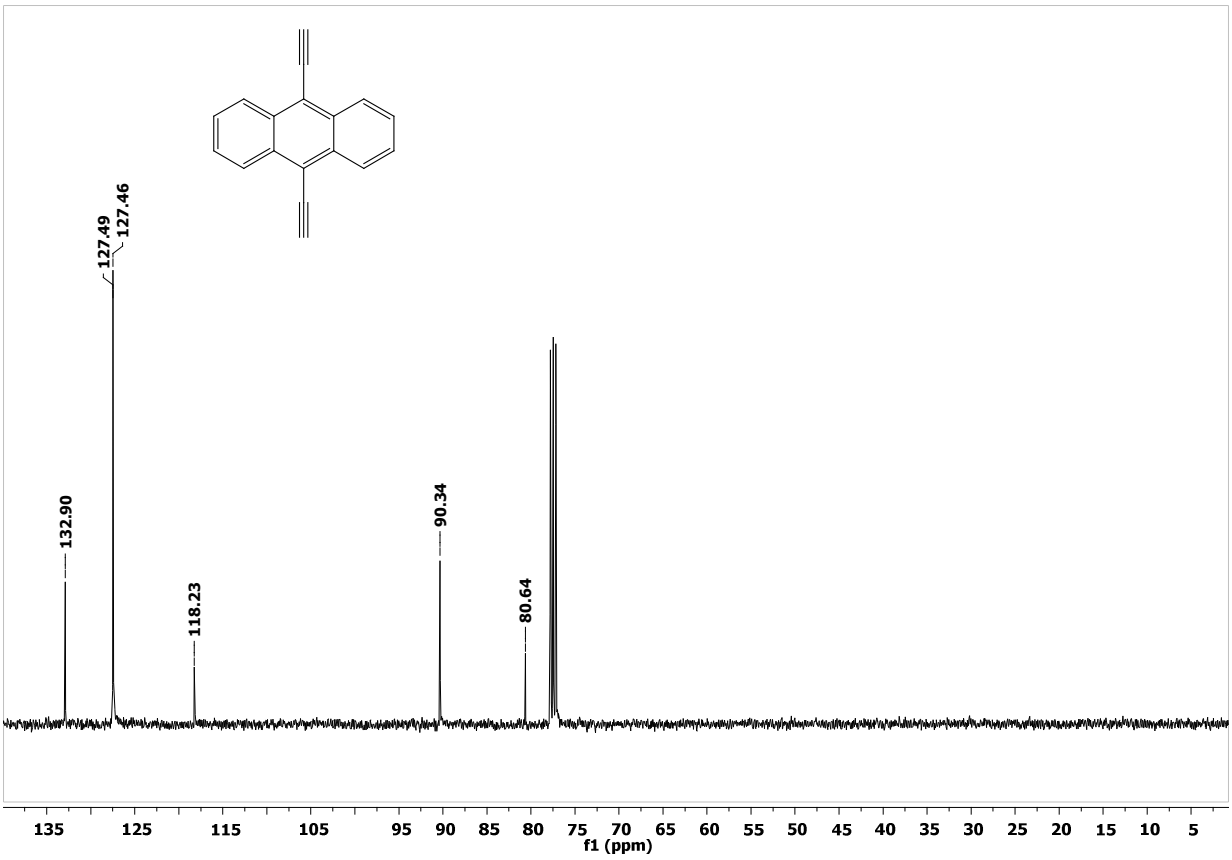
Intermediate **7** – ^{1}H



Intermediate **7** – ^{13}C

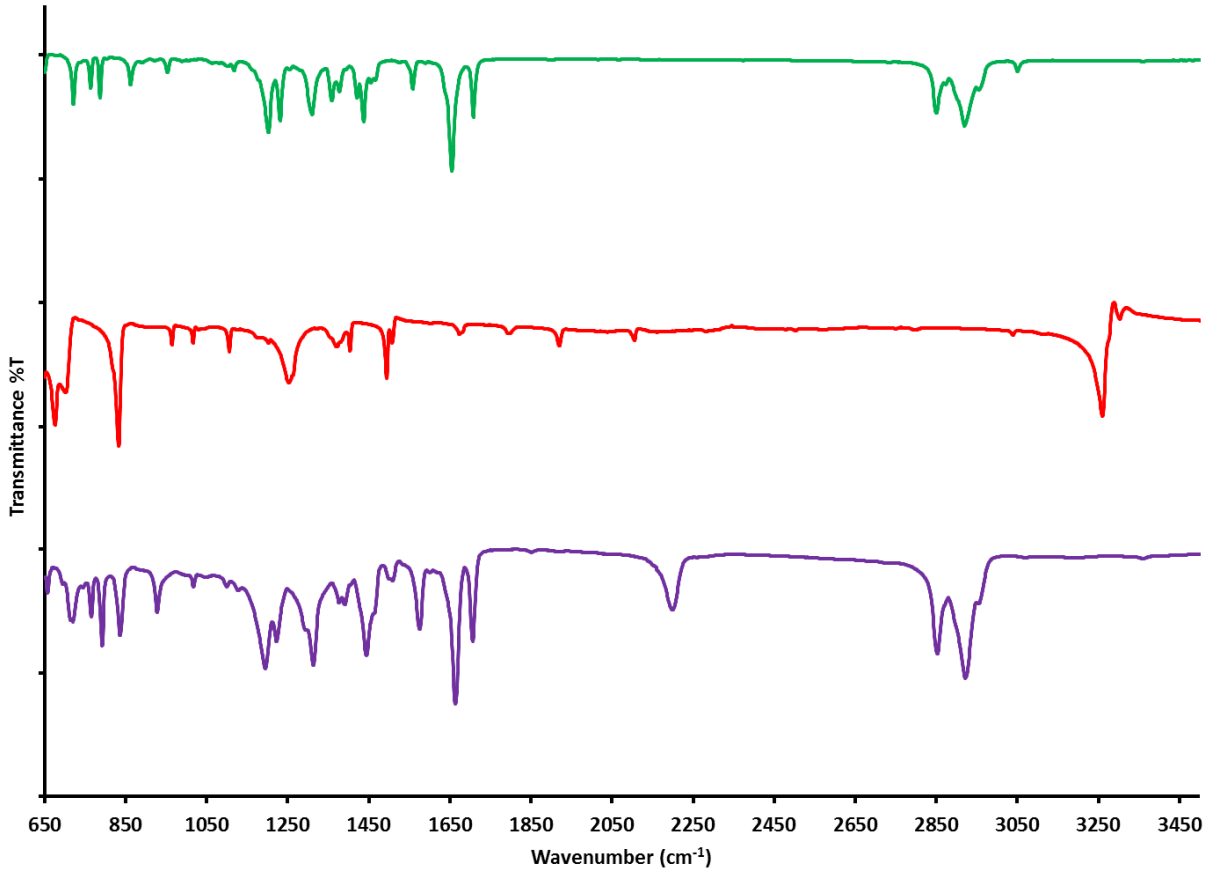


Intermediate **10** – ^{1}H

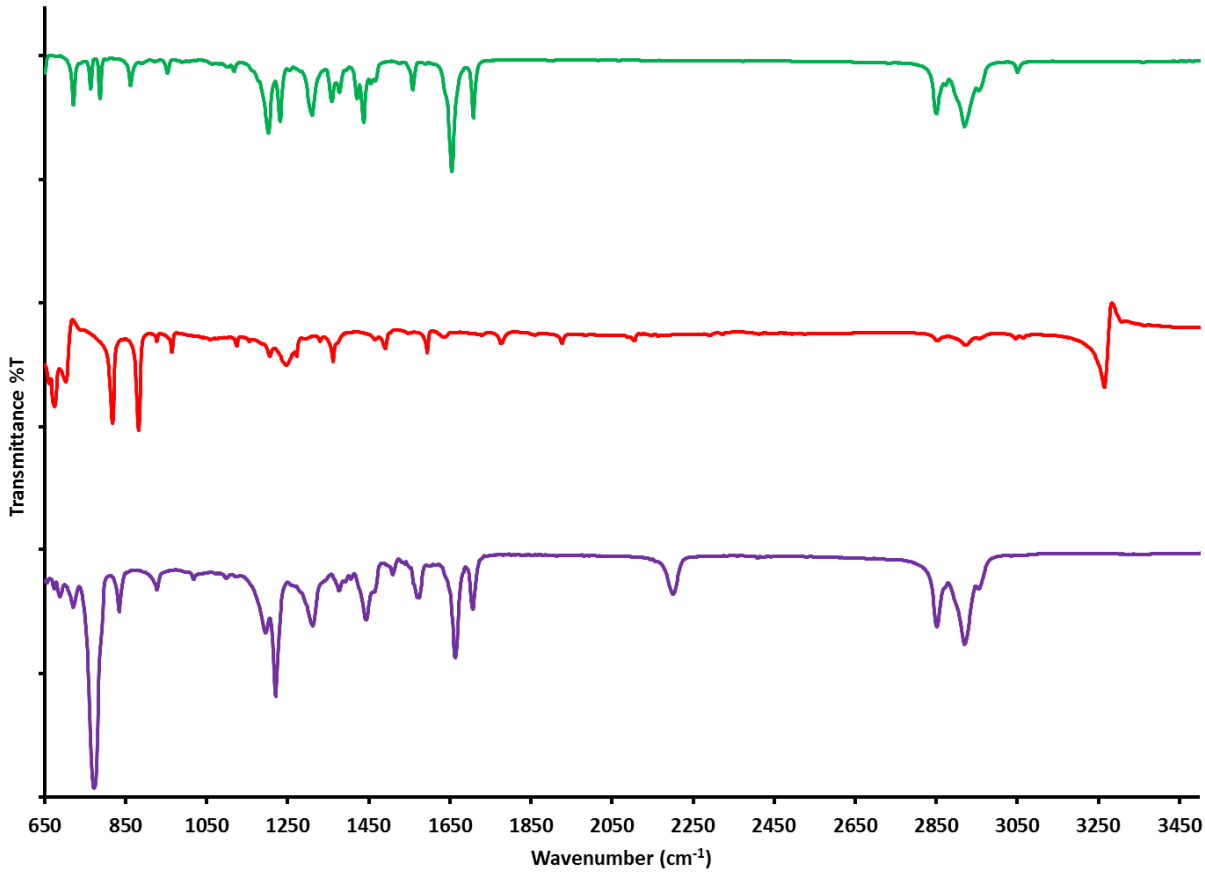


Intermediate **10** – ^{13}C

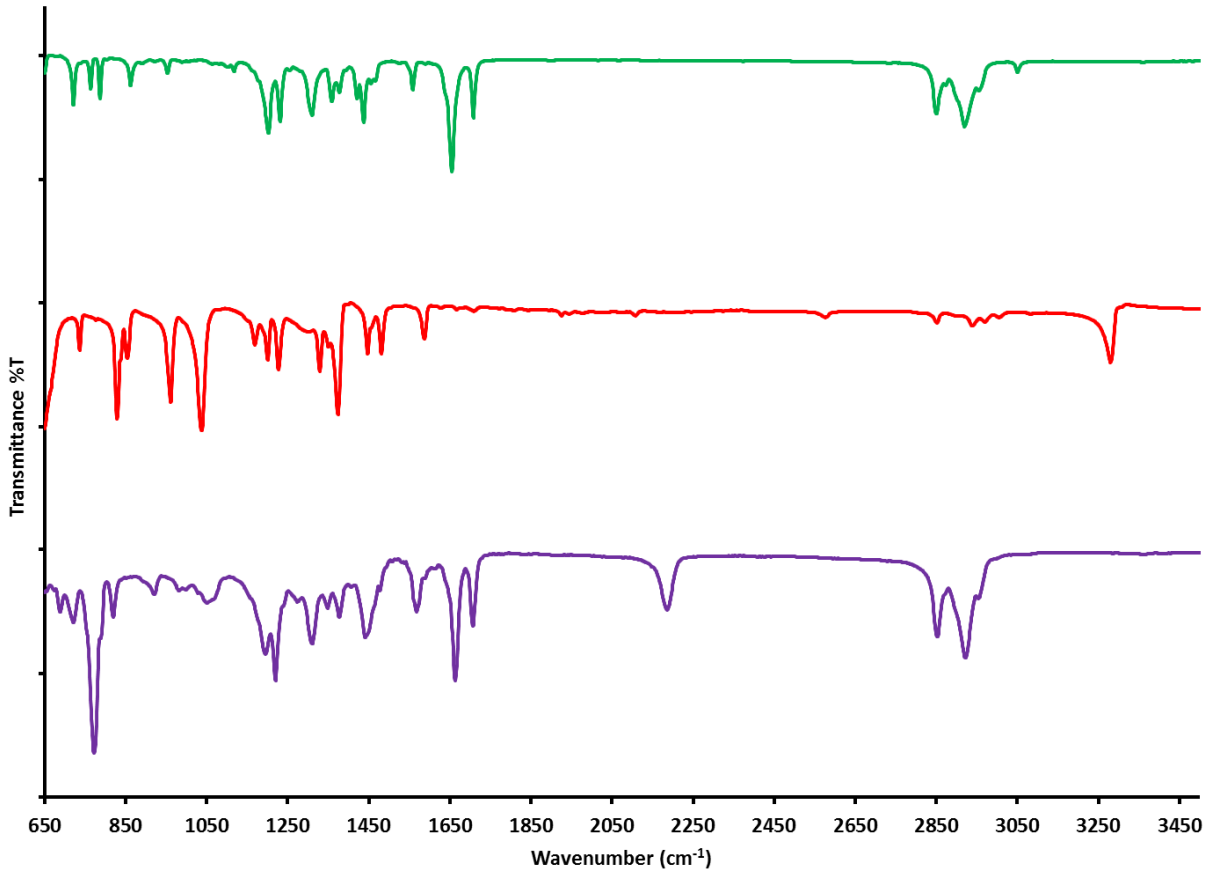
2) IR Spectra



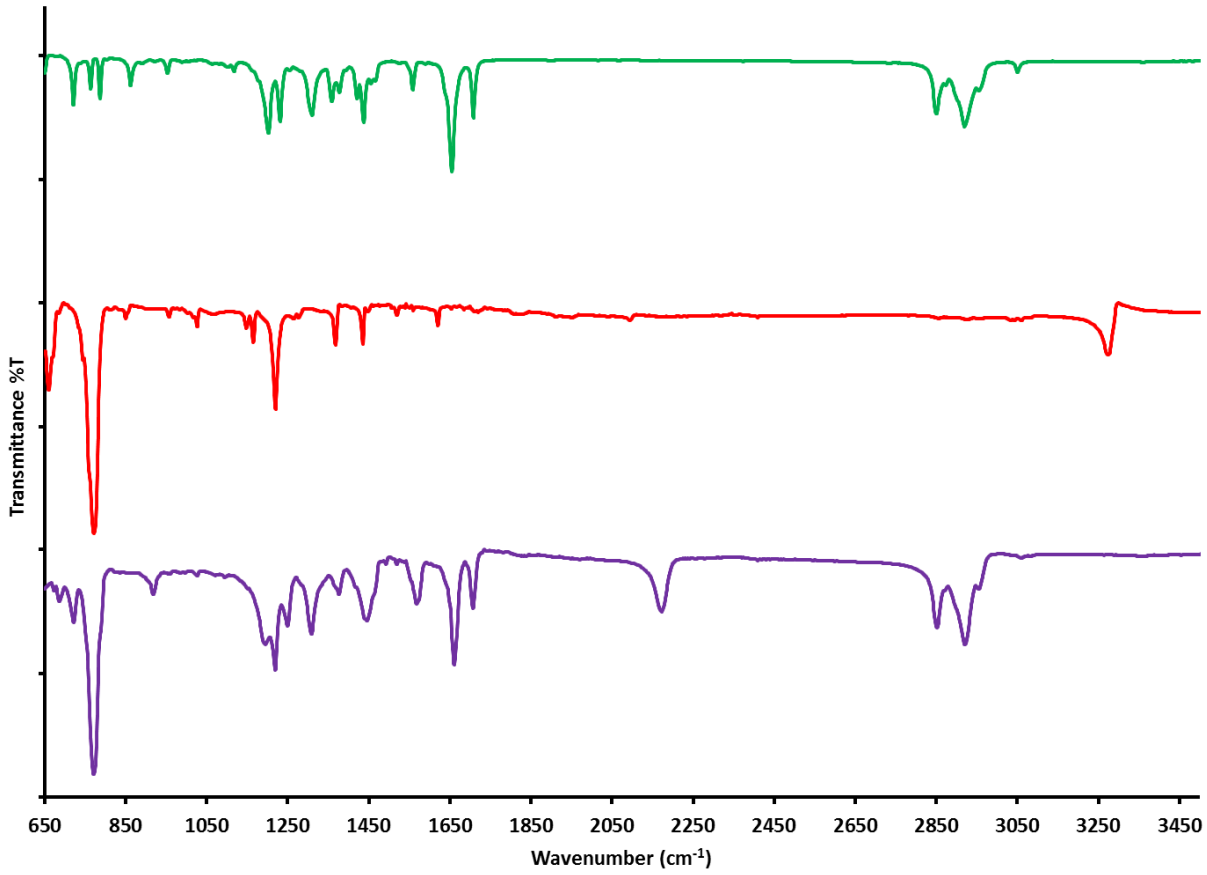
IR spectra of **12** (green), **1** (red) and **P2** (purple)



IR spectra of **5** (green), **4** (red) and **P5** (purple)

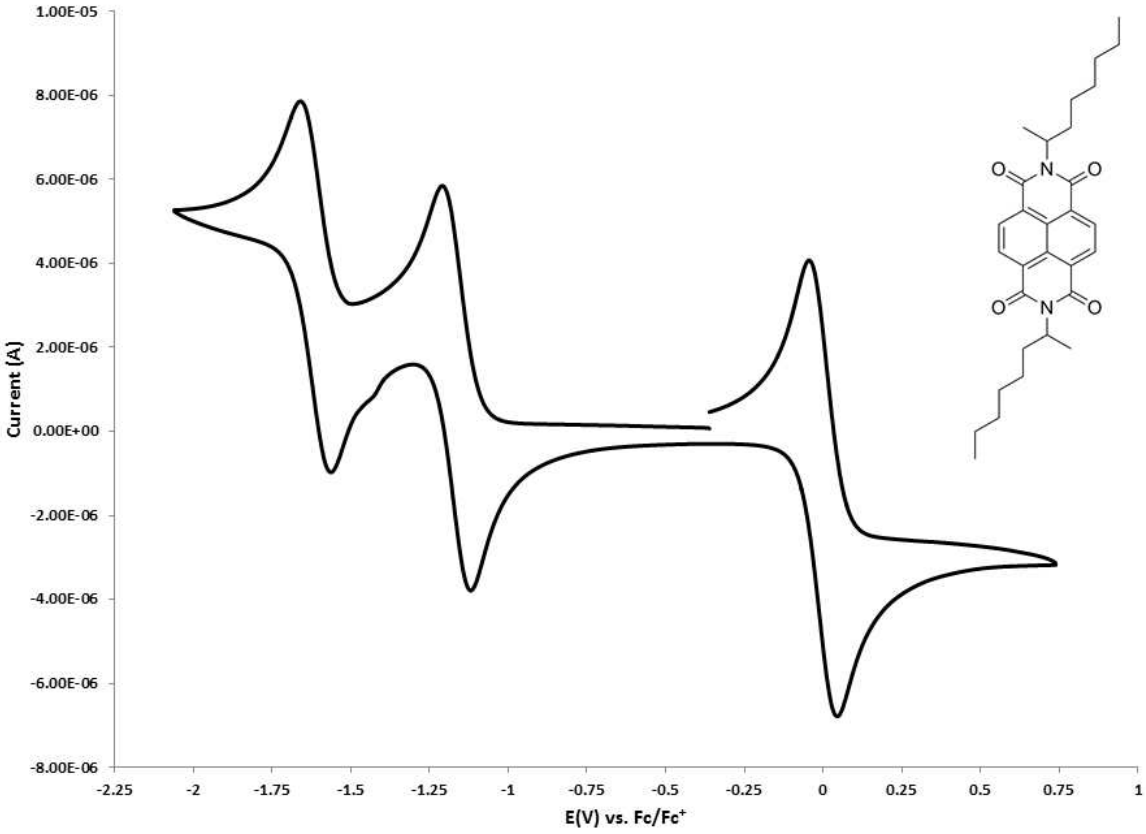


IR spectra of **12** (green), **7**(red) and **P8** (purple)



IR spectra of **12** (green), **10** (red) and **P11** (purple)

3) Cyclic Voltammogram of an NDI unit



A CV of the NDI unit pictured above (1 mM) taken in a 0.1 M TBAP/CH_2Cl_2 solution. The scan rate was 50 mV s^{-1}. Ferrocene was used as the internal standard (included in this CV) and its $E_{1/2}$ was set to 0.0 V for LUMO energy level estimation. The $E_{1/2}$ of the first reduction peak and corresponding LUMO value obtained from this CV closely matches those values (after converting from SCE to Fc/Fc^+) previously reported[1].

4) Cyclic Voltammograms of the Polymers

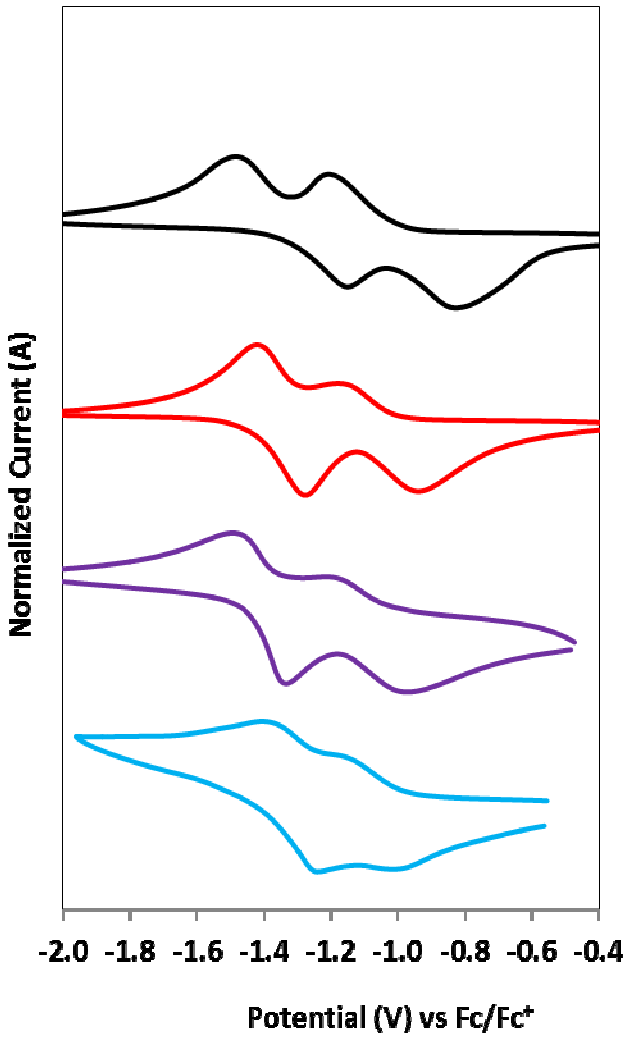
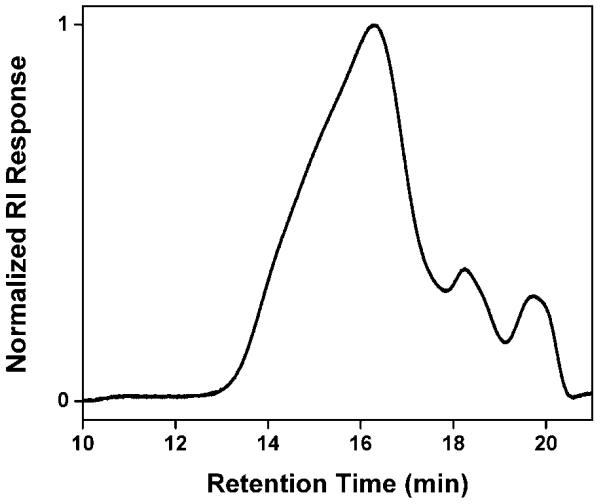
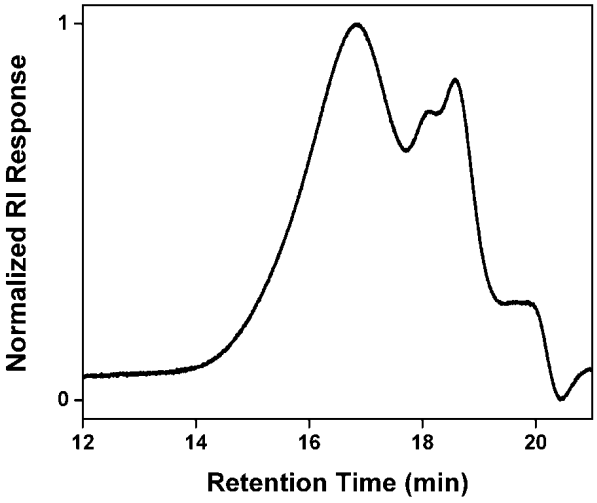


Figure shows the normalized cyclic voltammogram of **P2** (black), **P5** (red), **P8** (purple), and **P11** (teal) as a thin film on a platinum electrode in 0.1 M TBAP/MeCN at a scan rate of 50 mV s^{-1}.

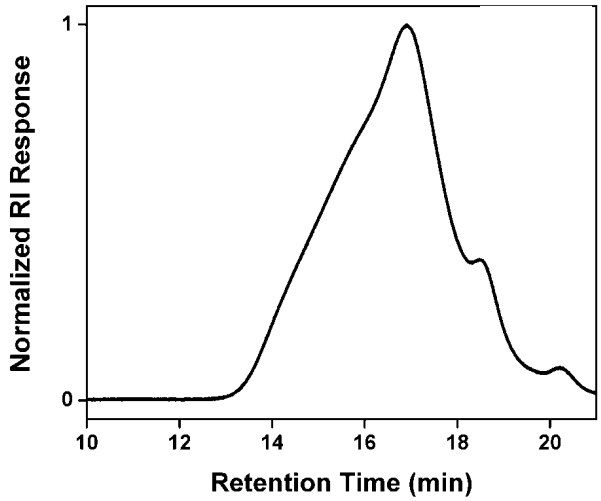
5) GPC traces for all polymers



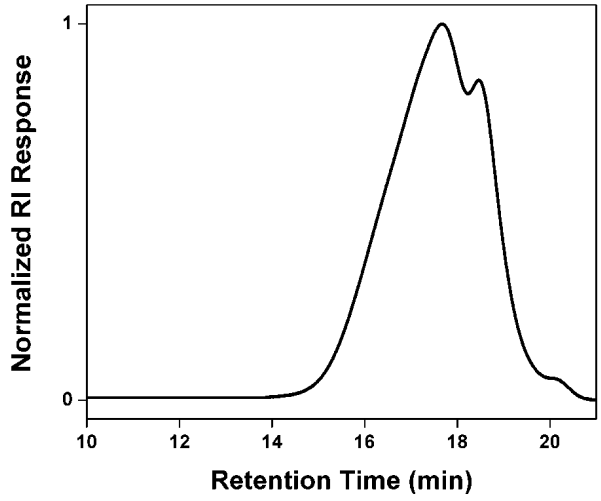
GPC trace of **P2**



GPC trace of **P5**

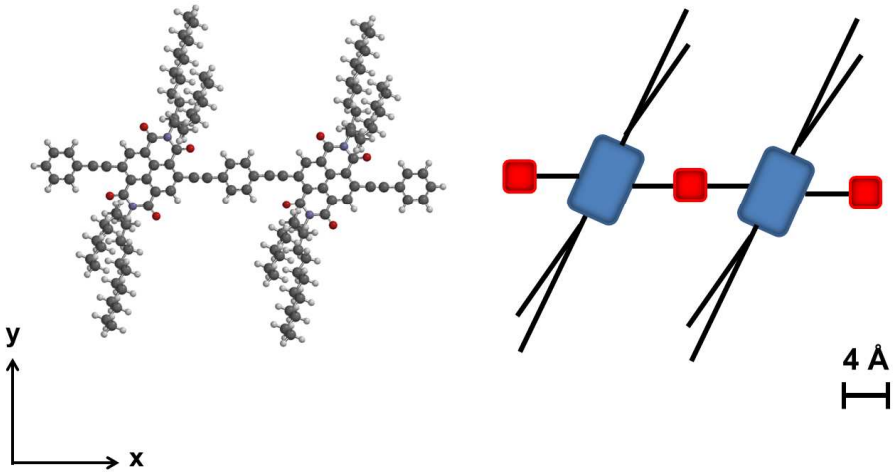


GPC trace of **P8**

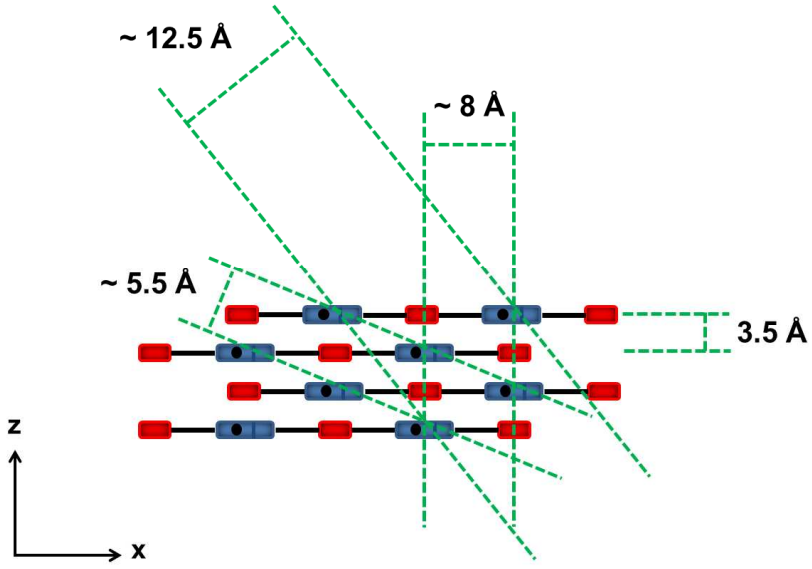


GPC trace of **P11**

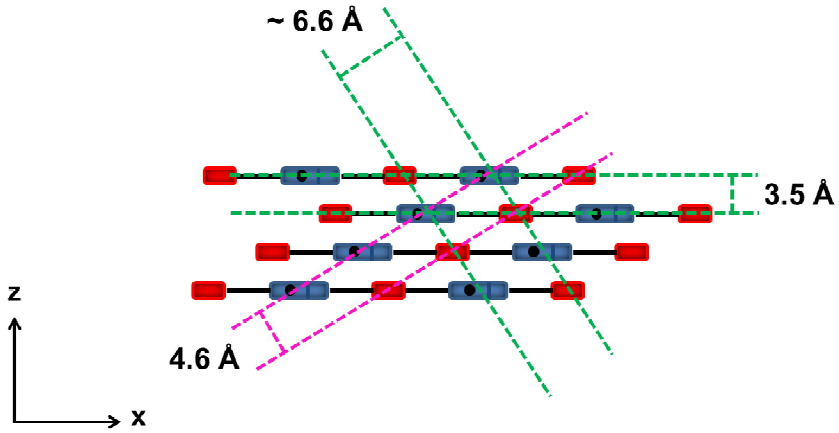
6) Additional Interchain Packing Models



Two additional models (Blue = NDI, Red = Benzene) were concieved using the scale representation of **P2** shown above. Neither model accounted for all of the major *d*-spacing values in the XRD patterns.



The first model (shown above) orients the polymer chains with benzene stacked in an alternating face-to-face fashion with NDI. Polymer chains are separated by a distance of 3.5 Å as supported by XRD. Side-chains were removed for clarity and marked by a black dot on the blue NDI. The resultant parallel planes of this orientation are indicated by green brackets and their approximate *d*-spacing values are listed. With the exception of ~ 12.5 Å and 3.5 Å , there were no XRD peaks with *d*-spacing values that resembled ~ 5.5 Å or ~ 8 Å.



The second model (shown above) orients the polymer chains such that the benzene and NDI are stacked in an offset face-to-face fashion with a centroid-to-centroid distance of 4.6 Å (XRD). Polymer chains are separated by a distance of 3.5 Å as supported by XRD. Side-chains were removed for clarity and marked by a black dot on the blue NDI. A set of two parallel planes separated by a distance of 4.6 Å is not supported in this model as the two planes that would be drawn as a result of the centroid-to-centroid distance are not identical (highlighted by pink dashed lines). A set of parallel planes does exist at ~ 9.2 Å (distance between planes composed of NDI, extend the pink lines to double 4.6 Å) but this is not supported by XRD. Other resultant parallel planes of this orientation are indicated by green brackets and their approximate *d*-spacing values are listed. The angle of the parallel planes with *d*-spacing ~ 6.6 Å can be adjusted to form another set of parallel planes with a *d*-spacing of ~ 6.6 Å. Again, there was no XRD peak with a *d*-spacing value that resembled ~ 6.6 Å.

7) References

[1] (a) Chopin, S.; Chaignon, F.; Blart, E.; Odobel, F. *J. Mater. Chem*. **2007**, *17*, 4139. (b) Guo, X.; Watson, M. D. *Org. Lett*. **2008**, *10*, 5333.