Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Studies on Homologous Random and Alternating Segmented Conjugated Polymers With and Without Silicon Synthesized by ADMET

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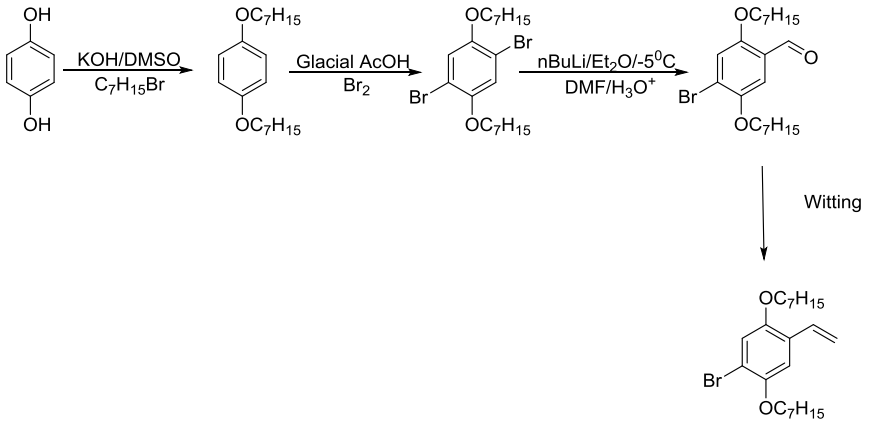
Precursor Synthesis

Synthetic route to 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene[67]



Synthesis of 1,4-bis(heptyloxy)benzene

40 g of potassium hydroxide pellets were suspended in 200 ml of dimethylsulfoxide and stirred at room temperature for 0.5h. Hydroquinone (9.35 g, 85 mmol) was added to the solution and stirred for another 0.5 h. 1-Bromoheptane (50 mL, 318 mmol) was transferred via syringe and the resulting mixture was stirred at room temperature for 2h. The reaction mixture was then poured into ice cold water (500 mL). The solid product was filtered, washed twice with ethanol and further purified by recrystallization from ethanol to obtain 1,4-bis(heptyloxy)benzene as white crystals (22 g, 85 %). ^{1}H NMR (600 MHz, $CDCl_3$): 0.86 (t, 6H, ^3J = 7.02 Hz), 1.20-1.48 (m, 16H), 1.64-1.80 (m, 4H), 3.87 (t, 4H, ^3J = 6.64 Hz), 6.79 (s, 4H).

Synthesis of 1,4-dibromo-2,5-bis(heptyloxy)benzene

1,4-bis(heptyloxy)benzene (1.90 g, 6.21 mmol) was dissolved in 40 mL of glacial acetic acid and the solution is immersed in an ice bath. Bromine (0.83 mL, 16.14 mmol) was added drop wise and the ice bath was removed after bromine addition. The resulting mixture was stirred overnight at room temperature. The reaction mixture was then poured into 100 mL of ice cold water, stirred for 10 minutes followed by solvent extraction with chloroform. After evaporating the solvent, the compound was further purified by recrystallization from cyclohexane. 1,4-dibromo-2,5-bis(heptyloxy)benzene was obtained as white crystals (3.5 g, 75 % yield). ^{1}H NMR (600 MHz, $CDCl_3$): 0.87 (t, 6H, ^3J = 7.09 Hz), 1.25-1.37 (m, 12H), 1.42-1.48 (m, 4H), 1.75-1.81 (m, 4H), 3.92 (t, 4H, ^3J = 6.57 Hz), 7.06 (s, 2H).

Synthesis of 4-bromo-2,5-bis(heptyloxy)benzaldehyde

1,4-dibromo-2,5-bis(heptyloxy)benzene (2.72 g, 5.87 mmol) was dissolved in 30 mL of anhydrous diethyl ether. The solution was cooled to -5^{0}C and n-BuLi (2.35 mL, 2.5 M in hexanes, 5.87 mmol) was added through a syringe. The mixture was stirred at -5^{0}C for 0.5h and *N*,*N*-Dimethylformamide (0.55 mL, 7.05 mmol) was added. The resulting mixture was stirred at -5^{0}C for additional 1.5h. 10% HCl (20 mL) was then poured into reaction mixture and stirred for 0.5h. The product was extracted by solvent extraction with diethyl ether. After evaporating the solvent, the crude product was purified using a 70-230 mesh size silica gel column in hexane:toluene (2:1) mixture. 4-bromo-2,5-bis(heptyloxy)benzaldehyde was yielded as a yellowish white solid (1.95 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): 0.87 (t, ^3J = 6.54 Hz, 6H), 1.21-1.51 (m, 16H), 1.72-1.87 (m, 4H), 3.95-4.04 (m, 4H), 7.20 (s, 1H), 7.29 (s, 1H), 10.39 (s, 1H).

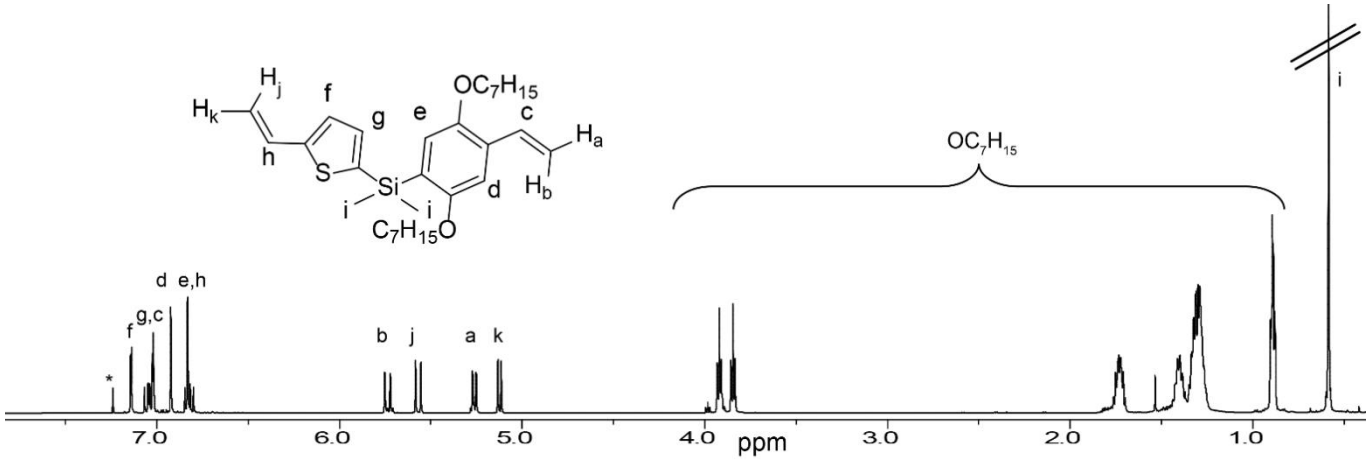
Synthesis of 1-bromo-2,5-bis(heptyloxy)-4-vinylbenzene

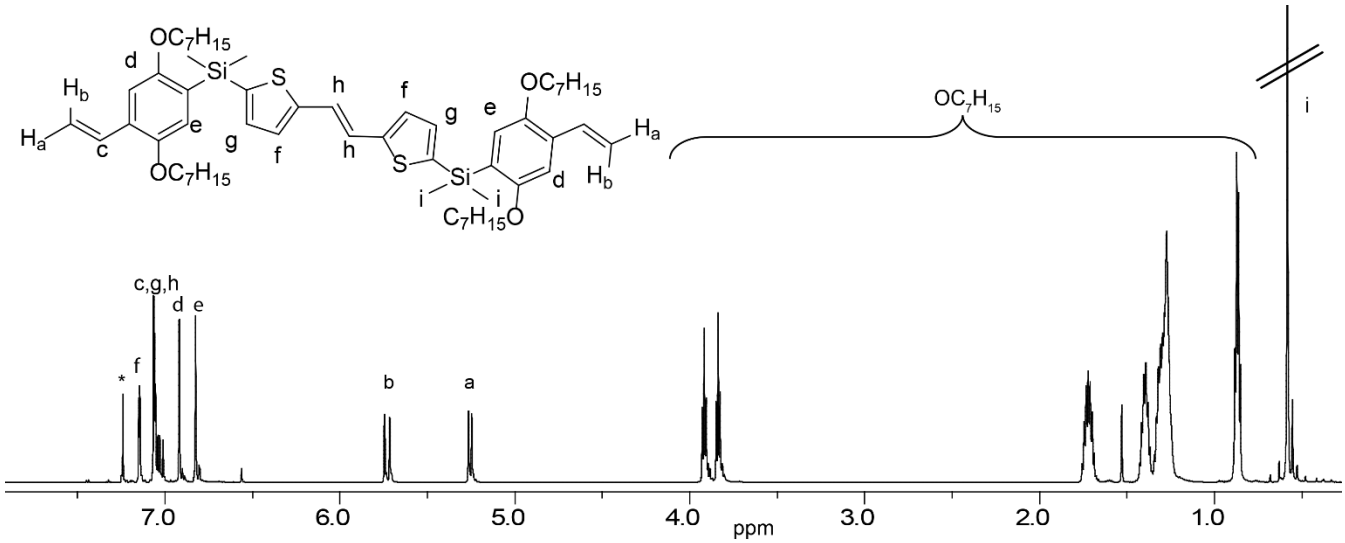
Methyltriphenylphosphonium bromide (2.39 g, 6.68 mmol) was suspended in 50 ml dry THF. To this suspension n-BuLi (2.54 mL, 2.5 M in hexanes, 6.35 mmol) was added dropwise at 0^0C. The reaction mixture was stirred at 0^0C for 3h. To this resulting solution 4-bromo-2,5-bis(heptyloxy)benzaldehyde (2.76 g, 6.68 mmol) dissolved in 10ml of dry THF, was added slowly at 0^0C. The resulting solution was allowed to reach room temperature and stirred overnight. The reaction mixture was then concentrated under reduced pressure followed by washing with hexane. The hexane layer was treated with sodium sulfate and then filtered. The organic phase was then concentrated under reduced pressure to give the crude product. Further purification was carried by column chromatography with hexane-toluene (1:1) solvent mixture as the eluent to obtain a greenish white solid (2.1 g, 76% yield). ^{1}H NMR (600 MHz, $CDCl_3$): 0.88 (t, ^{3}J = 6.85 Hz, 6H), 1.22-1.51 (m, 16H), 1.73-1.85 (m, 4H), 3.88 (t, ^{3}J = 6.54 Hz, 2H) 3.96 (t, ^{3}J = 6.50 Hz, 2H) 5.25 (d, ^{3}J = 11.36 Hz, 1H), 5.70 (d, ^{3}J = 17.88 Hz, 1H), 6.92-6.97 (dd, ^{4}J = 11.35 Hz, ^{3}J = 17.88 Hz, 1H), 6.99 (s, 1H), 7.02 (s, 1H).

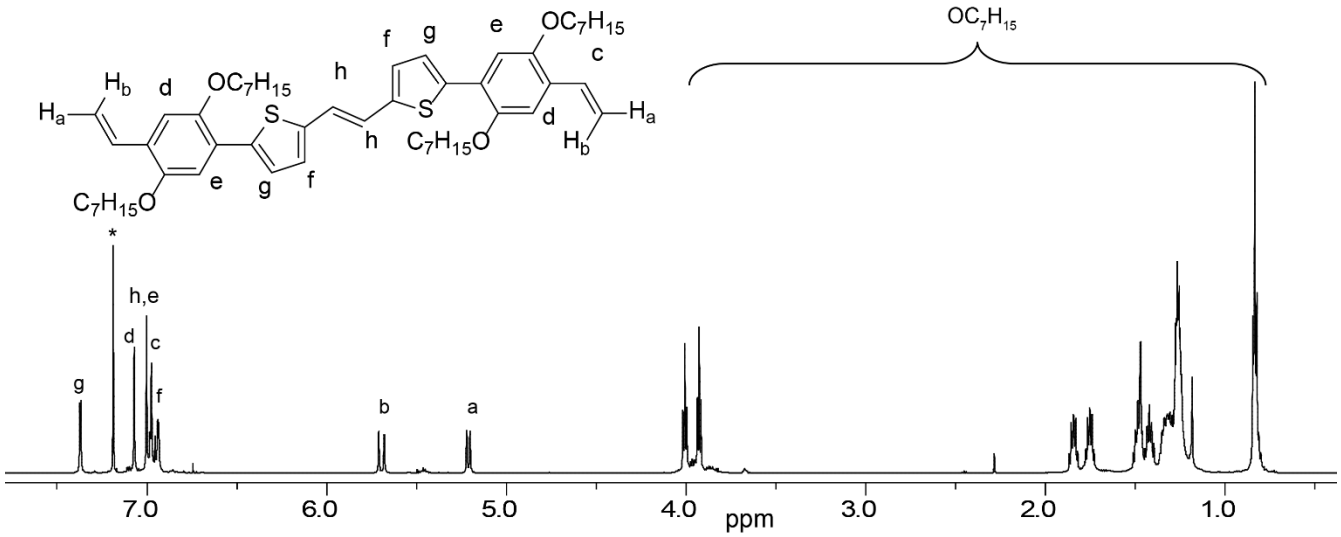
Synthesis of 2-bromo 5-vinylthiophene[67]

Methyltriphenylphosphonium bromide (3.01 g, 8.41 mmol) was suspended in 40 ml dry THF. To this suspension n-BuLi (3.20 mL, 2.5 M in hexanes, 7.99 mmol) was added dropwise at 0^0C. The reaction mixture was stirred for 3h. To this resulting solution 2-bromo 5-thiophene carbaldehyde (1.00 mL, 8.41 mmol) dissolved in 10 mL of dry THF was added slowly at 0^0C. The resulting solution was allowed to reach room temperature, stirred overnight at and then concentrated under reduced pressure followed by washing with hexane. The hexane layer was treated with sodium sulfate and then filtered. The organic phase was then concentrated under reduced pressure to give the crude product. Further purification was carried by column chromatography with hexane-dichloromethane (7:3) solvent mixture as the eluent to obtain a reddish yellow liquid (0.95 g, 60 % yield). ^{1}H NMR (600MHz, $CDCl_3$): 6.89 (d, ^{3}J = 3.70 Hz, 1H), 6.69 (d, ^{3}J = 3.70 Hz, 1H), 6.67 (dd, ^{4}J = 10.64 Hz, ^{3}J = 17.74 Hz, 1H,), 5.45 (d, ^{3}J = 17.43 Hz, 1H), 5.13 (d, ^{3}J = 11.10 Hz, 1H).

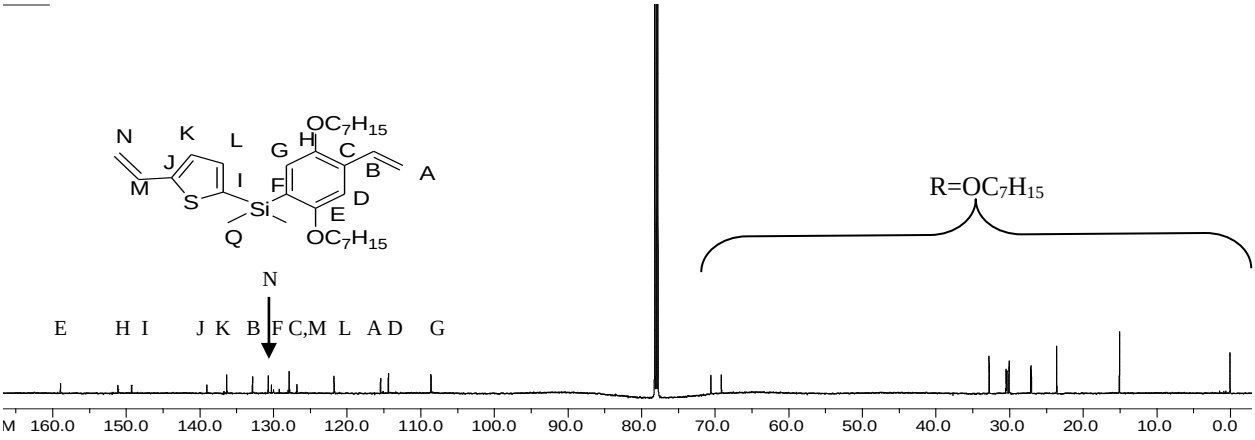
Monomers: H-NMR Spectra (600MHz) in $CDCl_3$

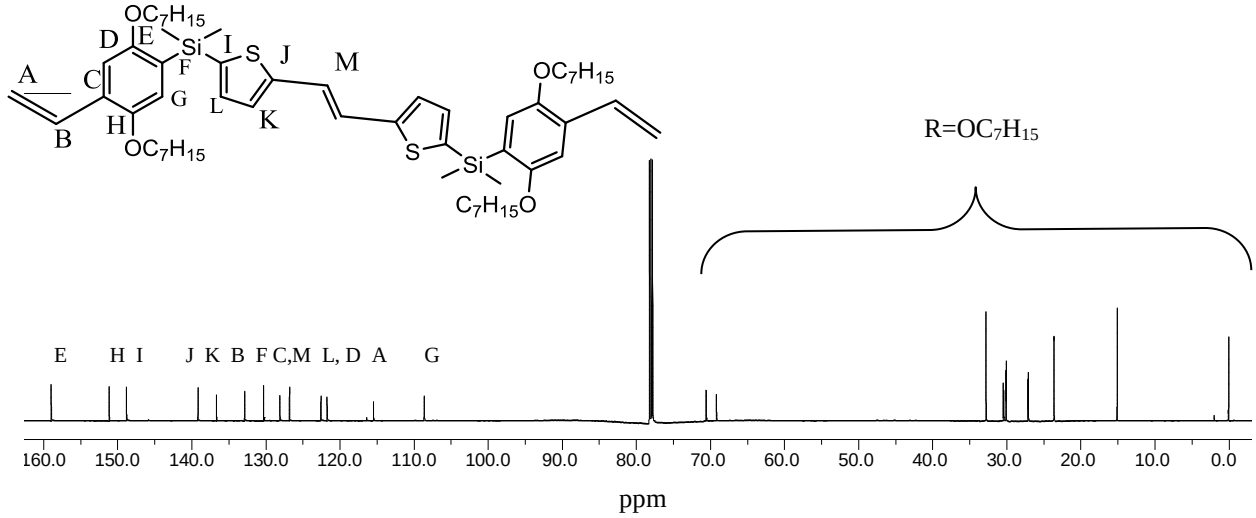


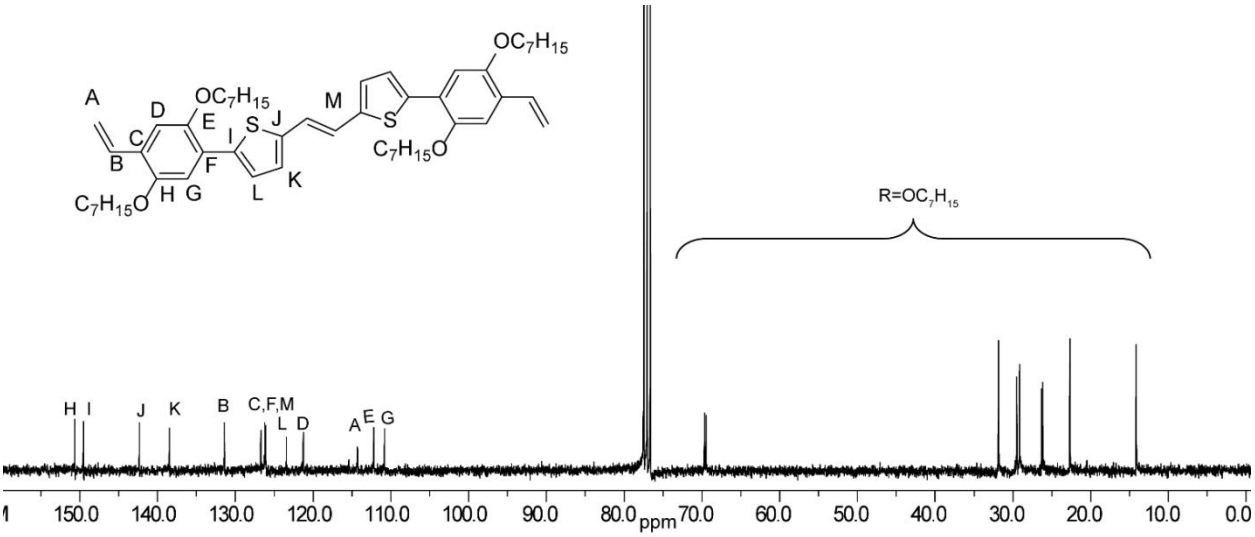




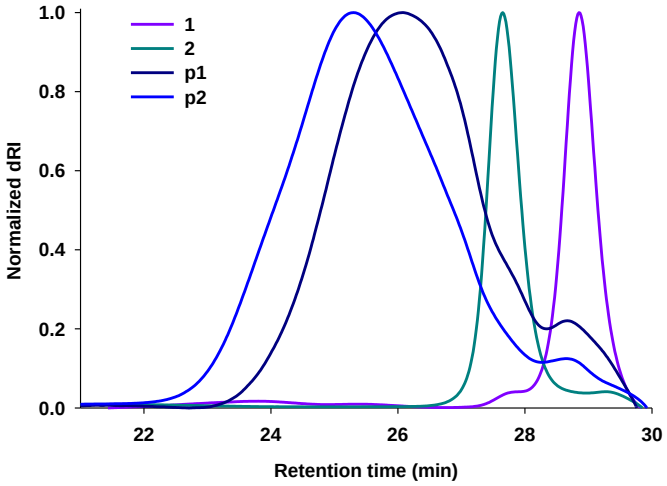
Monomers: ^{13}C-NMR Spectra (125 MHz) in $CDCl_3$







GPC chromatograms of **1-3** and **P1-P3**



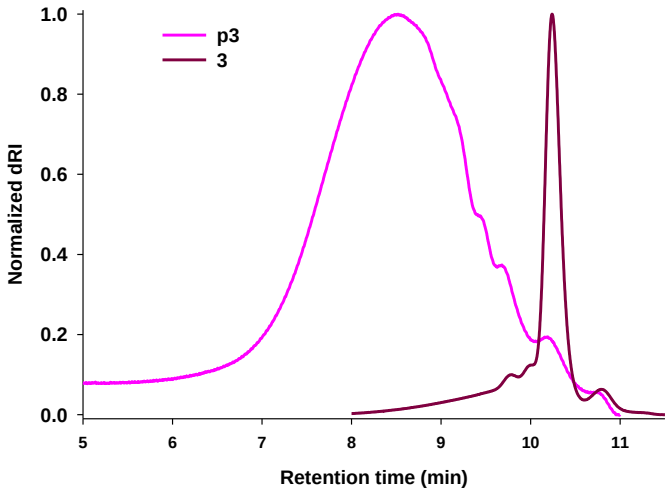
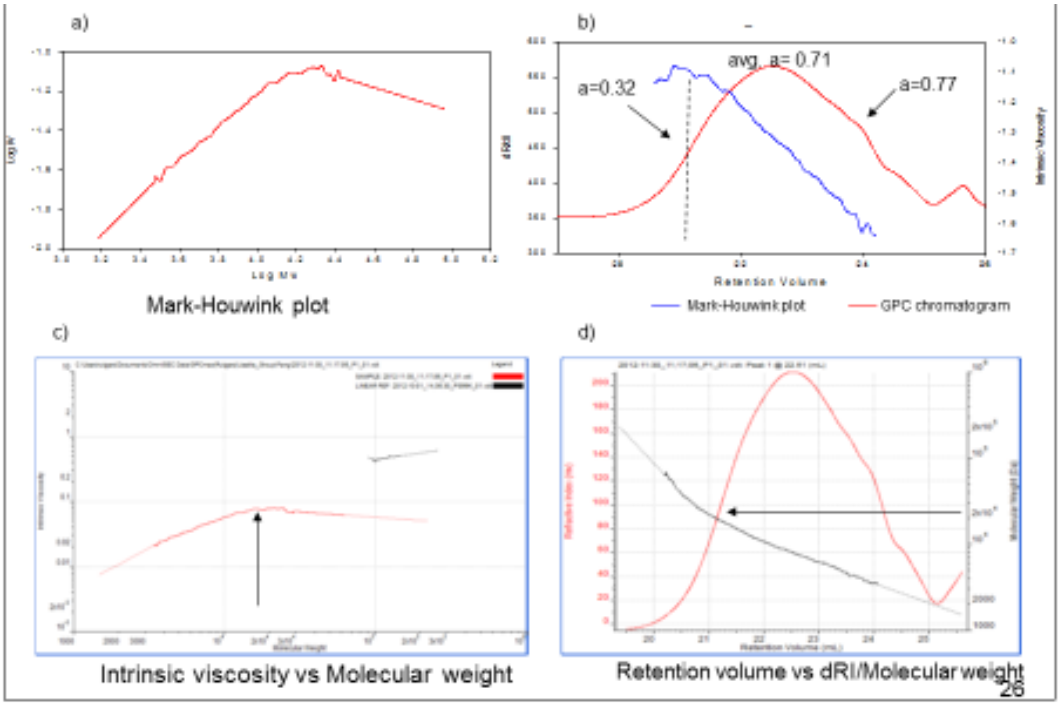


Table. Summary of GPC results in above Figures

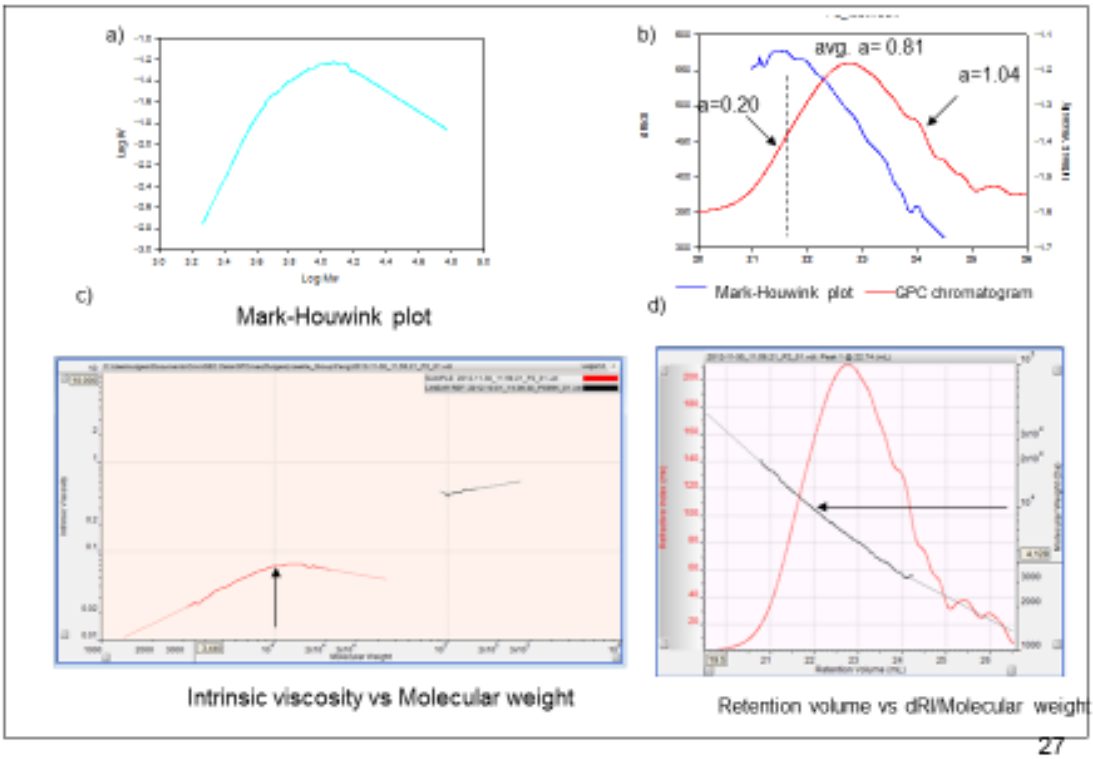
	Mn (g/mol)		Mw/Mn
	NMR	GPC	
1	n.a	459	1.02
P1	8829	3705	1.59
2	n.a	892	1.02
P2	14589	4330	1.42
3	n.a	1039	1.01
P3	4982	3139	2.01

Mark-Howink Analyses

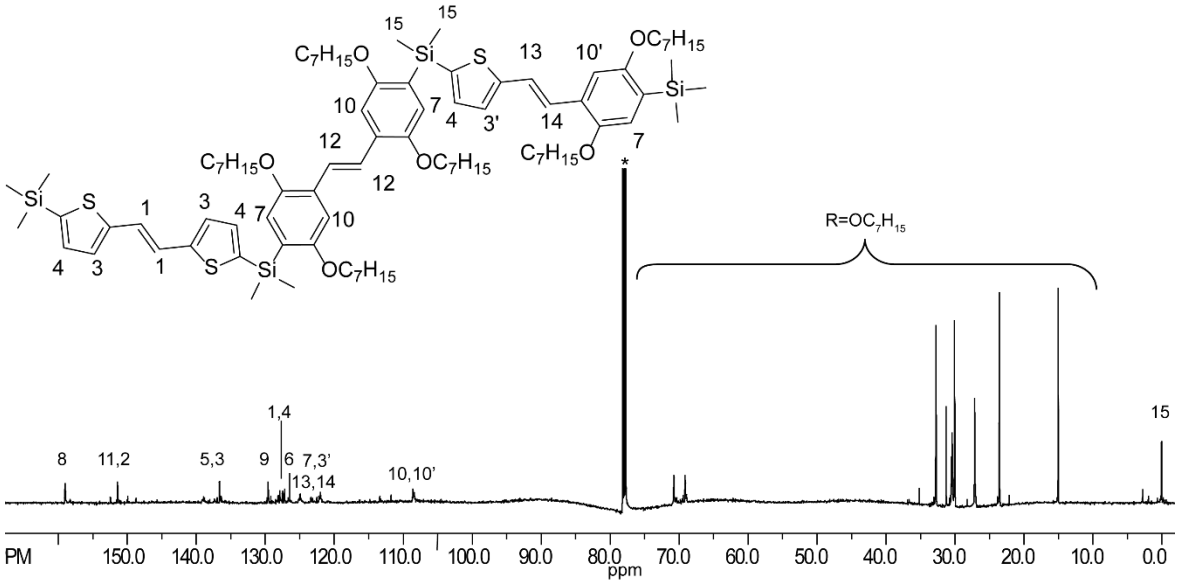
P1:

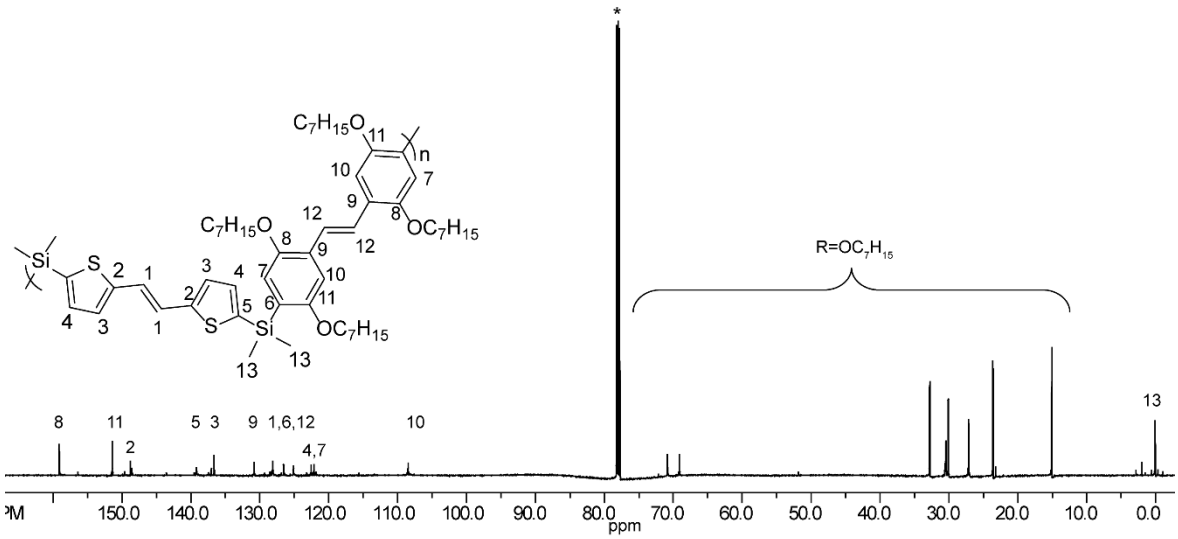


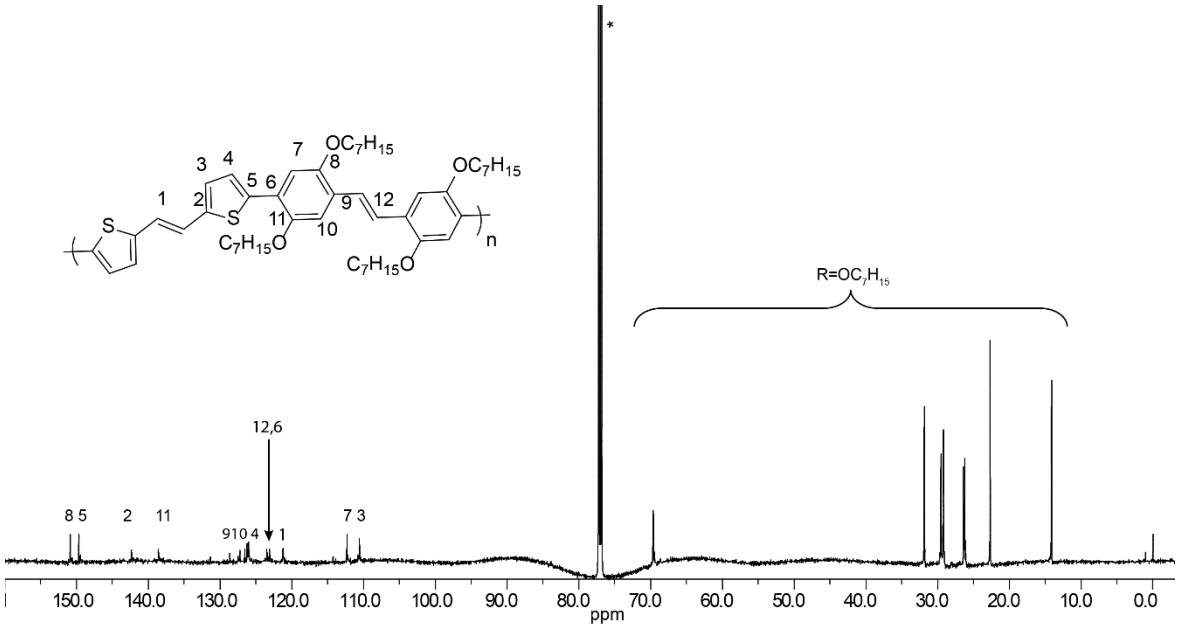
P2:



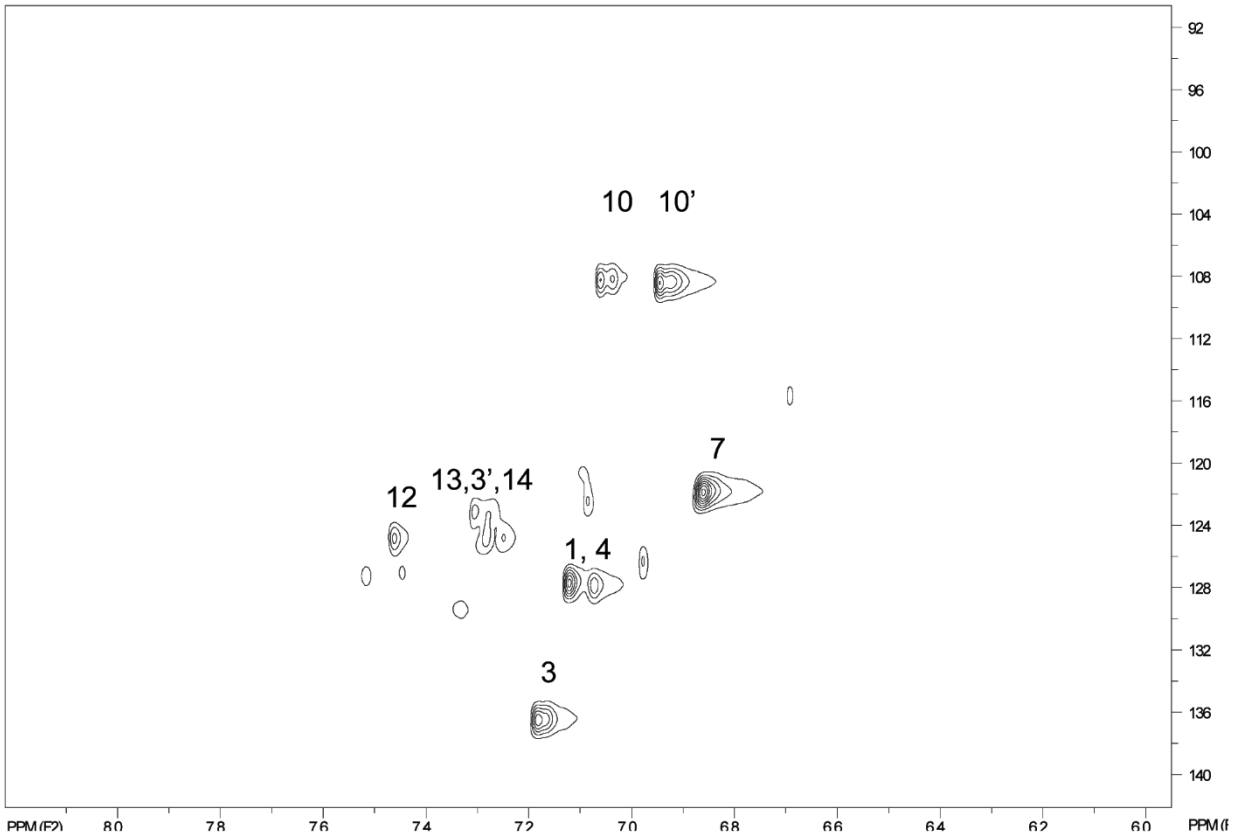
Polymers: ^{13}C-NMR Spectra (125 MHz) of p1-p3 in $CDCl_3$



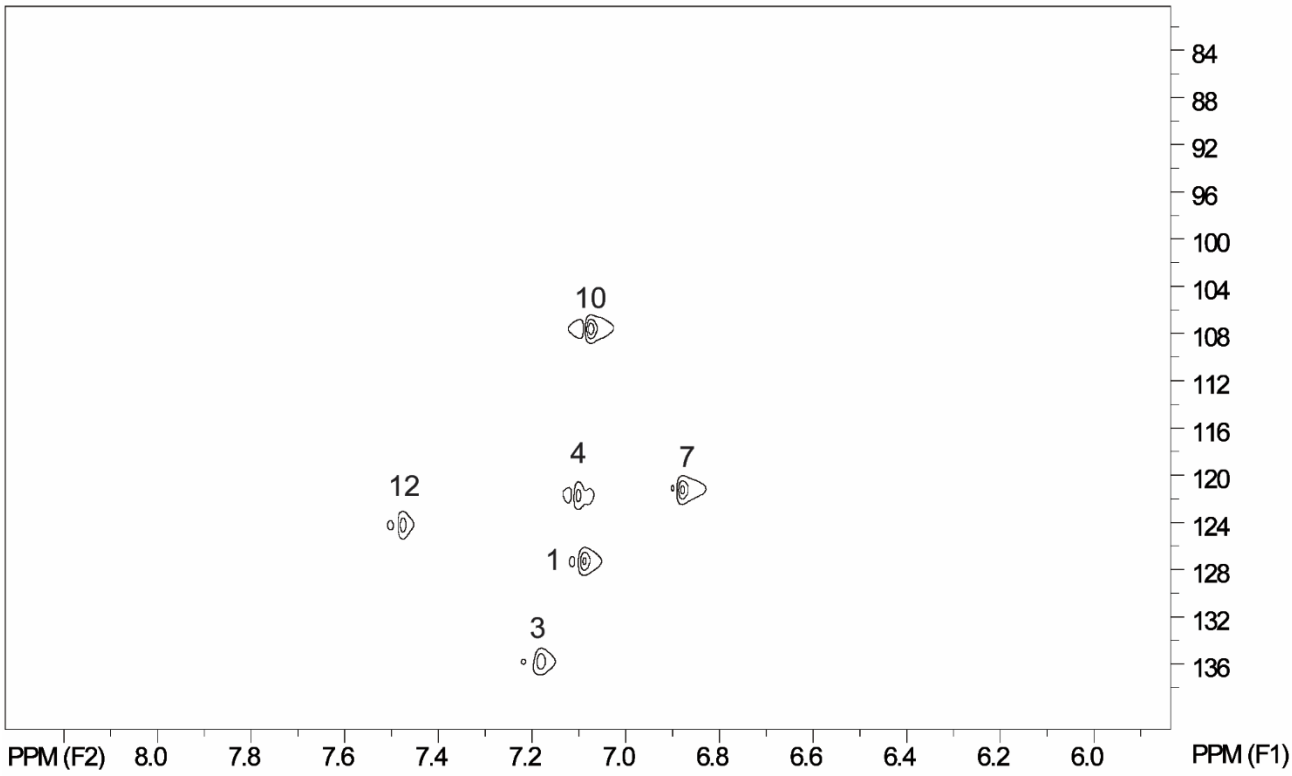




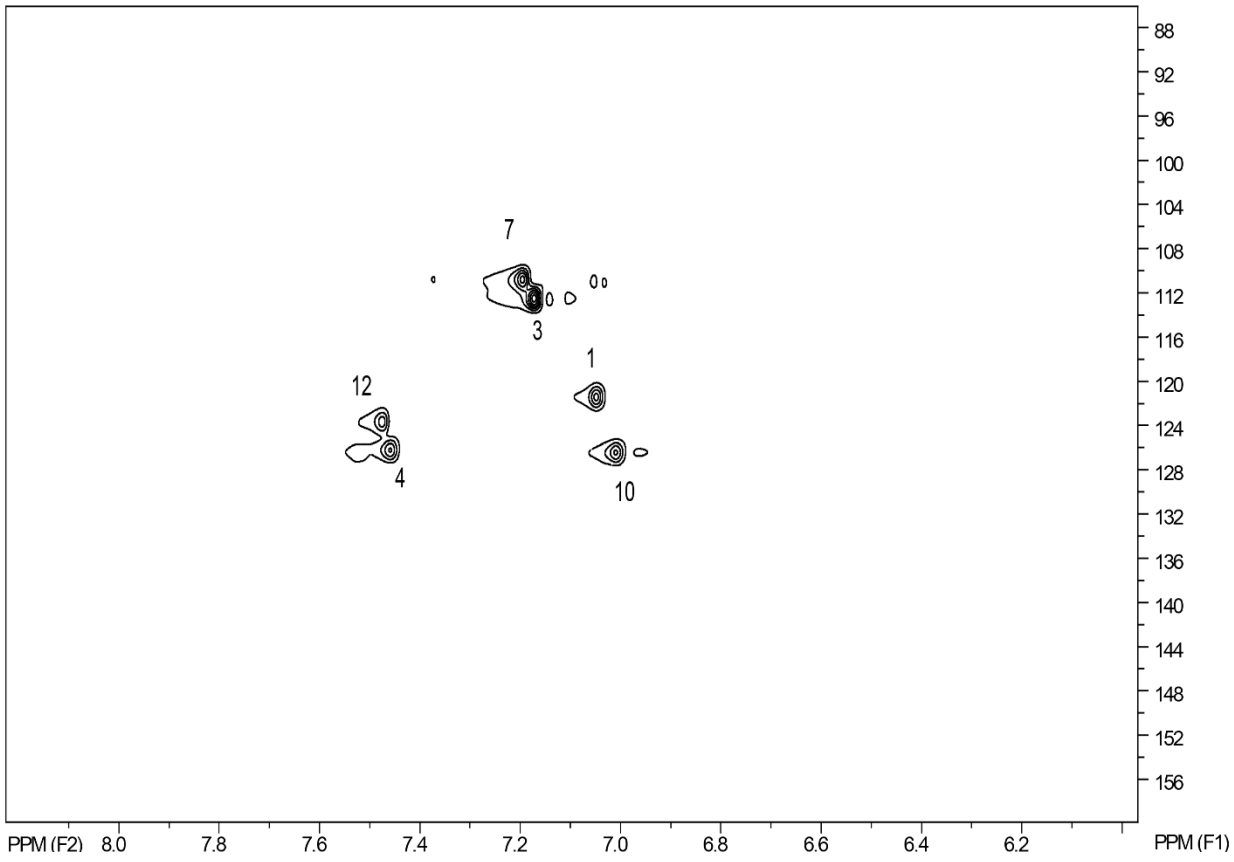
HSQC spectrum of **p1:**



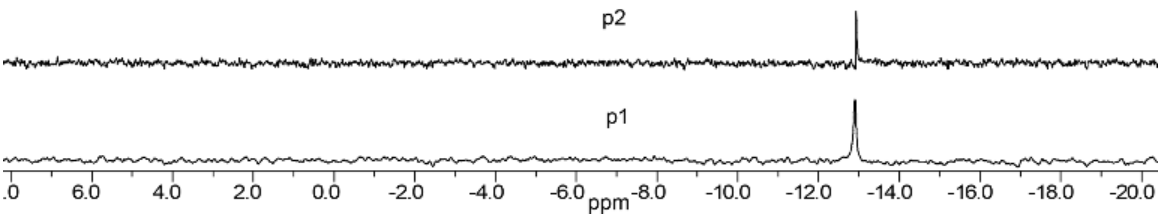
HSQC spectrum of **p2:**



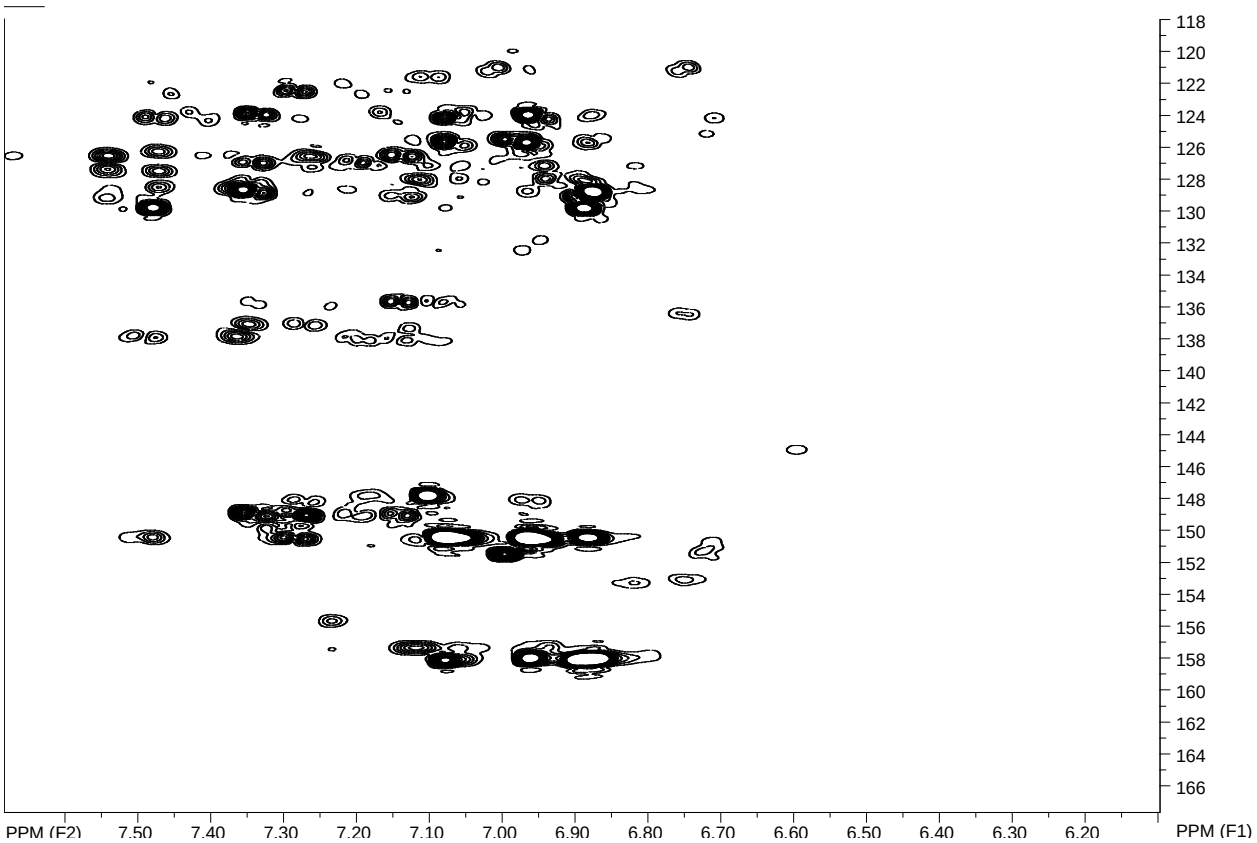
HSQC spectrum of **p3:**



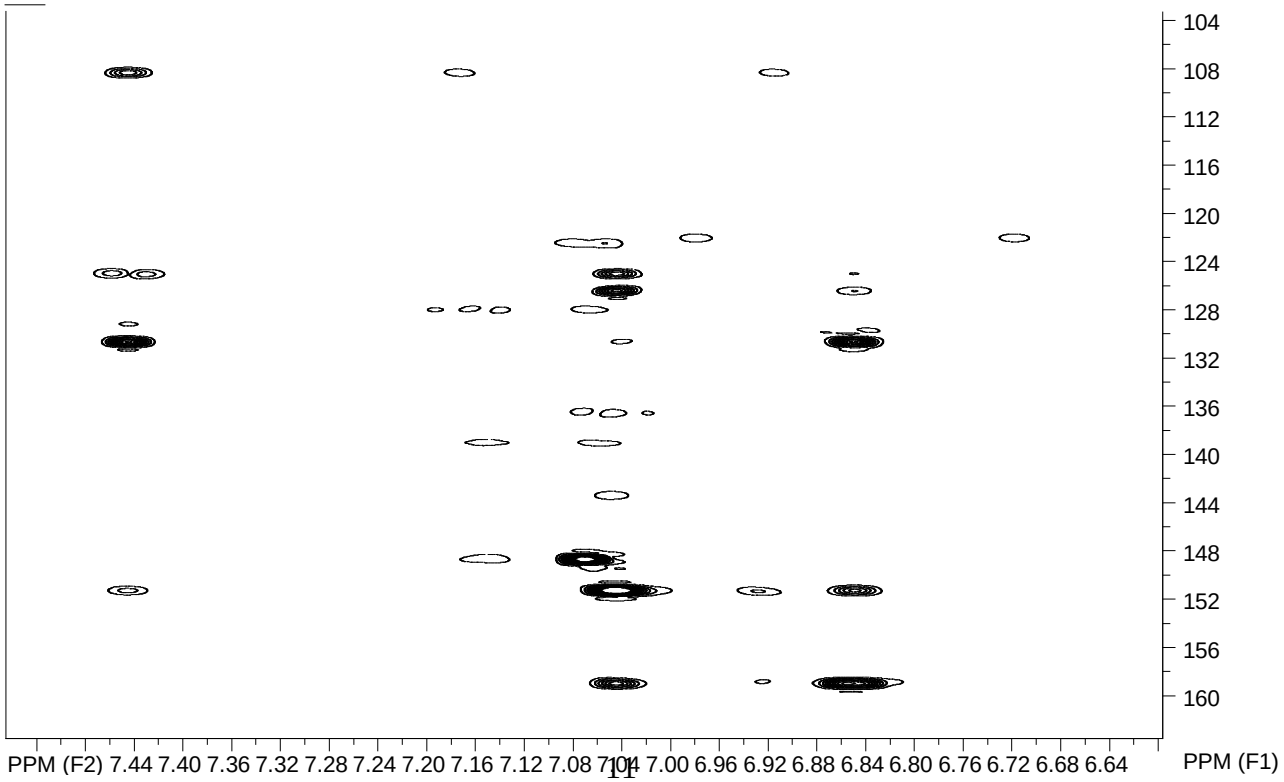
^{29}Si-NMR Spectra of **p1** and **p2** in $CDCl_3$



HMBC spectrum of **p1:**



HMBC spectrum of **p2**:



HMBC spectrum of **p3**:

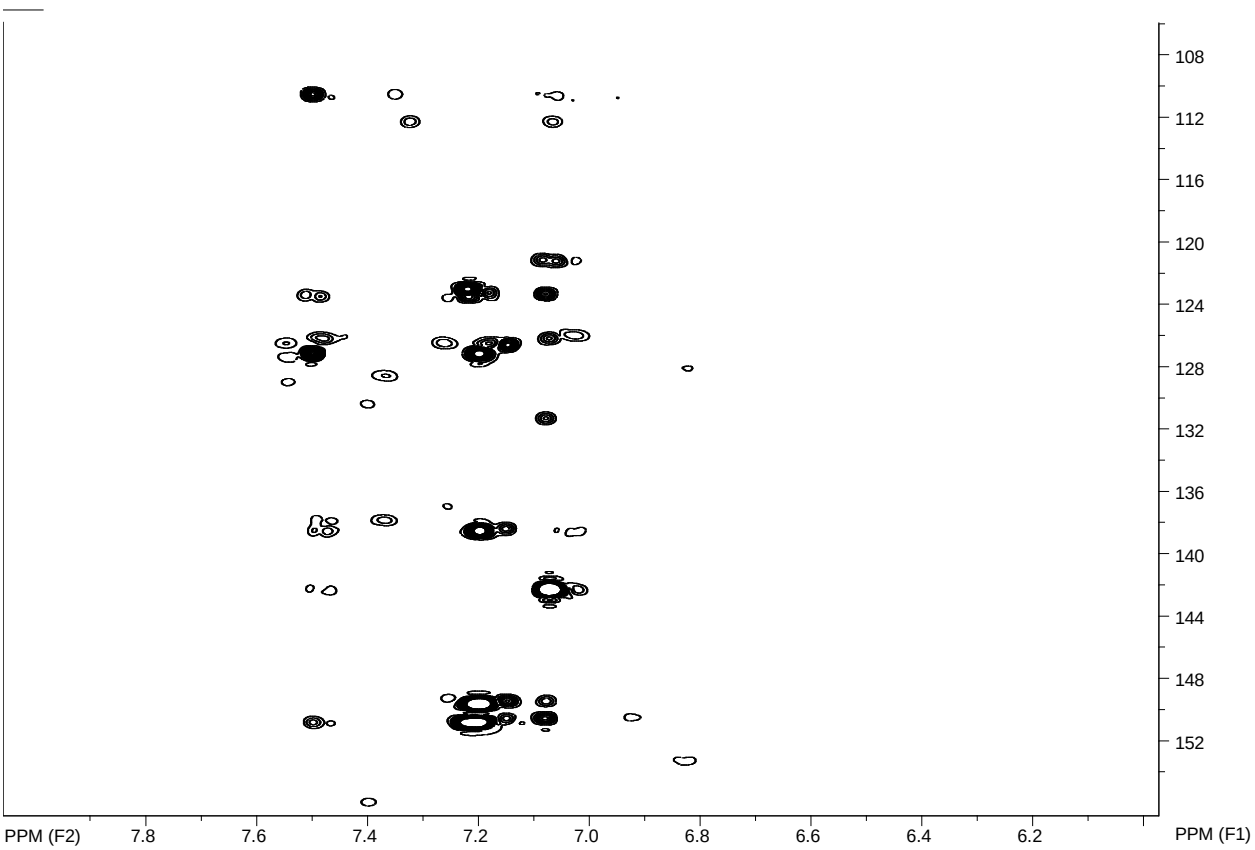
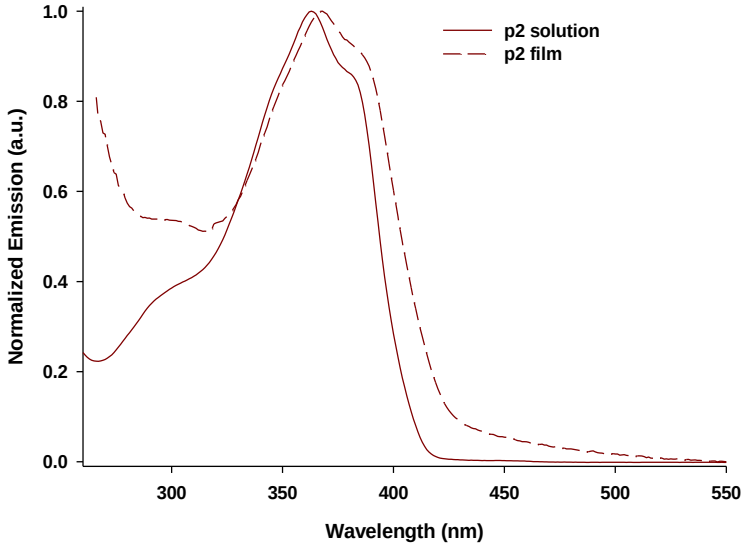
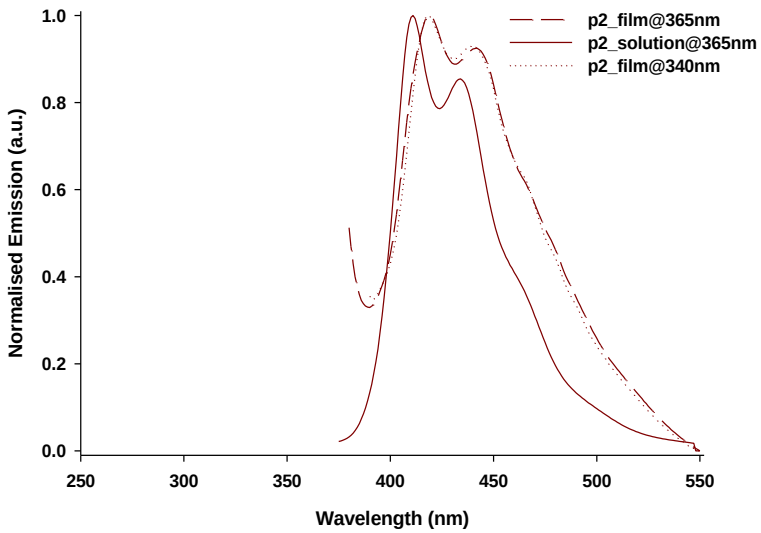


Table . ^{13}C and ^{1}H NMR assignments of **p2** combining 1-D and 2-D NMR spectroscopy

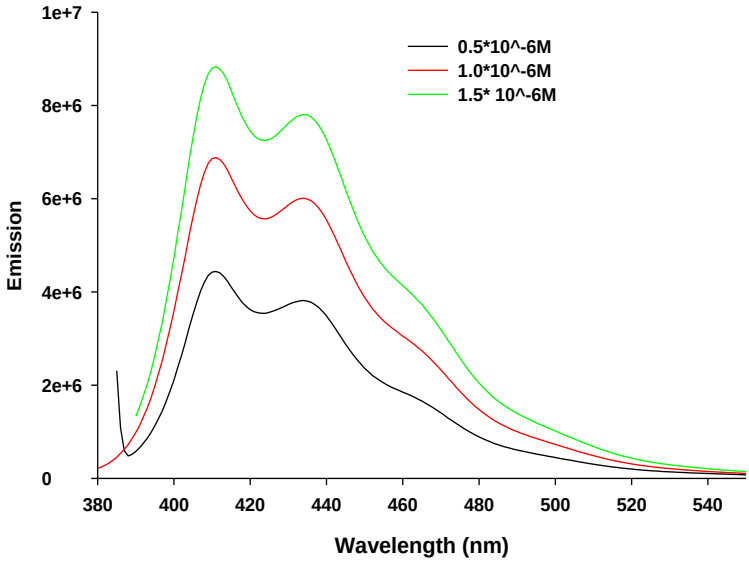
Assignment #	^{1}H NMR shift	^{13}C NMR shift	HSQC peak (^{1}H,^{13}C)	HMBC ($^{1}H \rightarrow ^{13}C$)
1	7.06	128.11	7.06,128.11	148.76, 136.66
2	n.a.	148.76	n.a.	n.a.
3	7.15	136.66	7.15, 136.66	148.76, 139.20
4	7.05	122.57	7.05, 122.57	136.66
5	n.a.	139.20	n.a.	n.a.
6	n.a.	126.50	n.a.	n.a.
7	6.85	122.14	6.85, 122.14	159.10, 151.40, 130.80
8	n.a.	159.10	n.a.	n.a.
9	n.a.	130.80	n.a.	n.a.
10	7.04	108.44	7.04, 108.44	151.40, 159.10, 126.50
11	n.a.	151.40	n.a.	n.a.
12	7.44	125.10	7.44, 125.10	130.80, 108.44
13	3.95	69.11	3.95, 69.11	159.10
14	3.86	70.85	3.86, 70.85	151.40
15	0.59	0.05	0.59, 0.05	139.20, 126.50
R	0.79-1.82	15-34	n.a.	n.a.

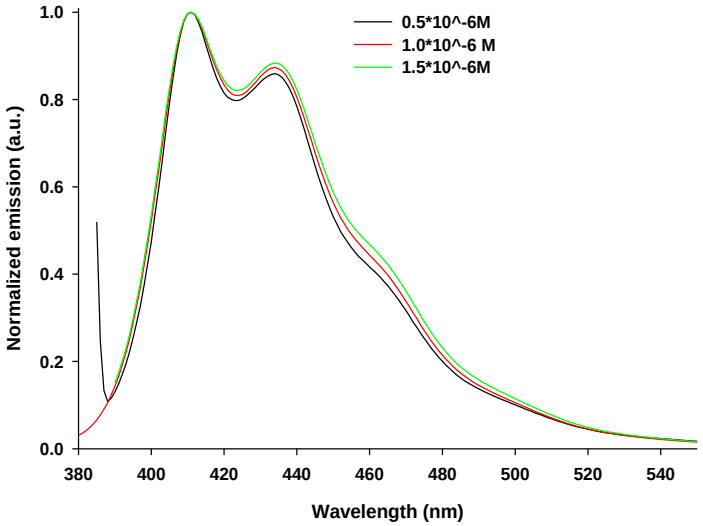
Absorption (left) and emission spectra (right) of **p2** in solution (hexanes) and film



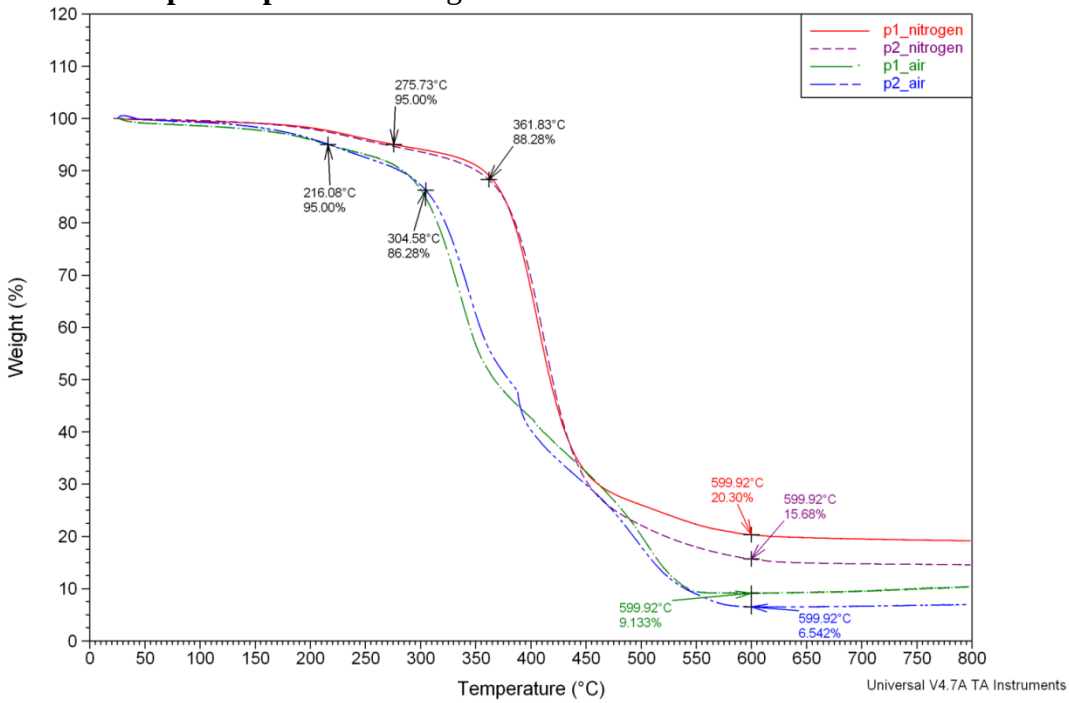


PL spectra of **p2** at different concentrations (normalized)

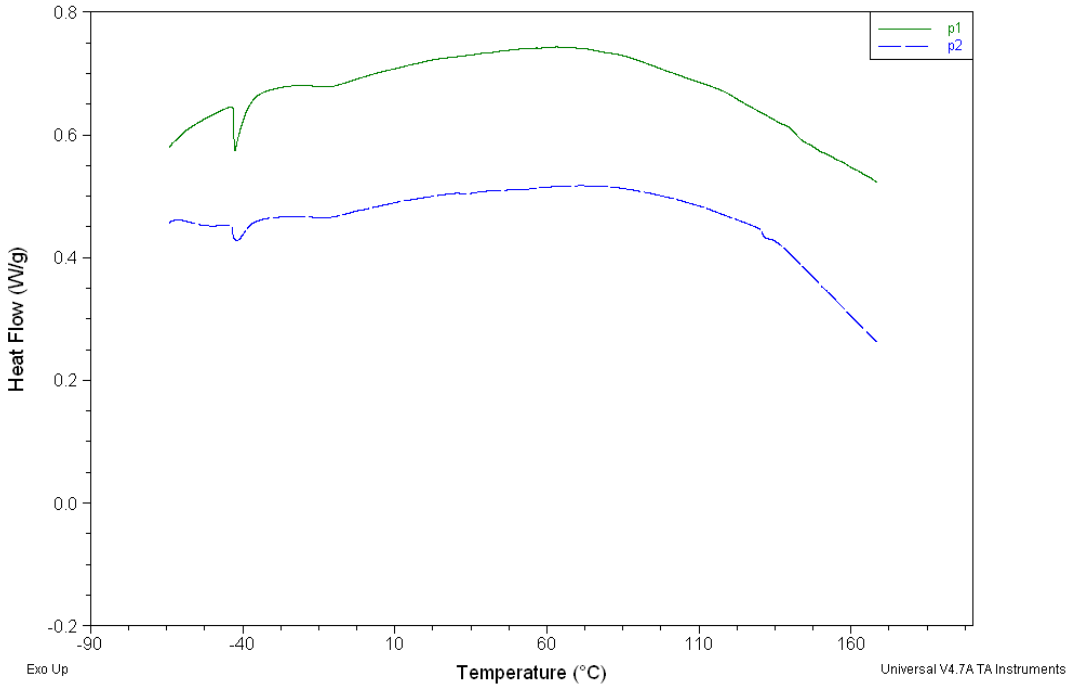




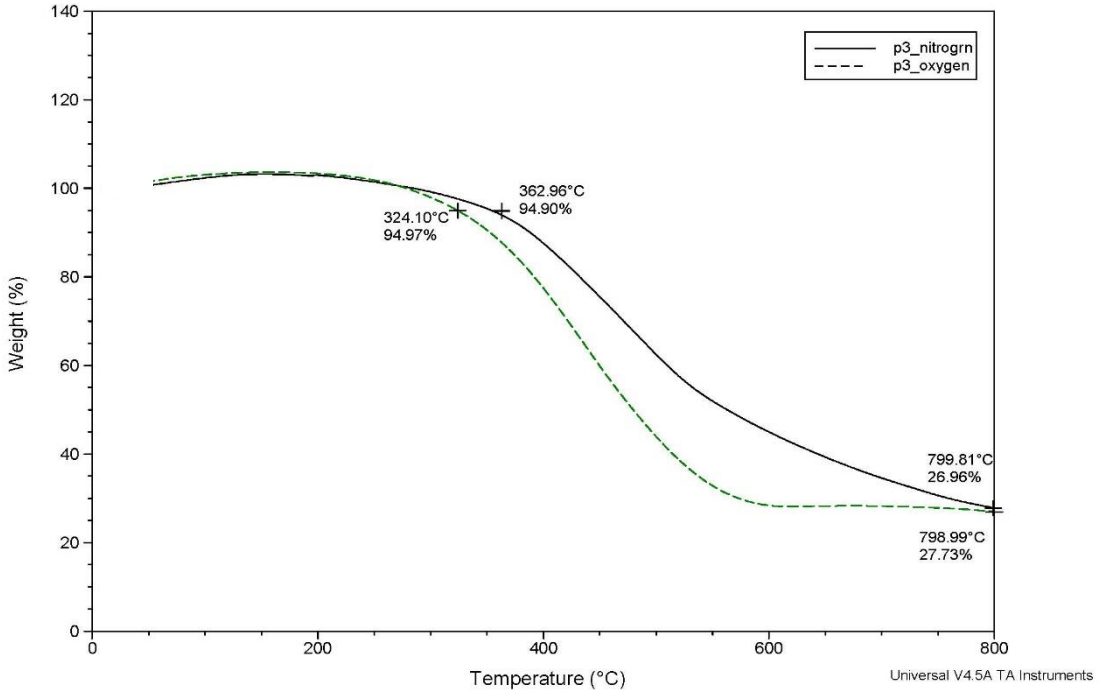
TGA curves of **p1** and **p2** under nitrogen and air



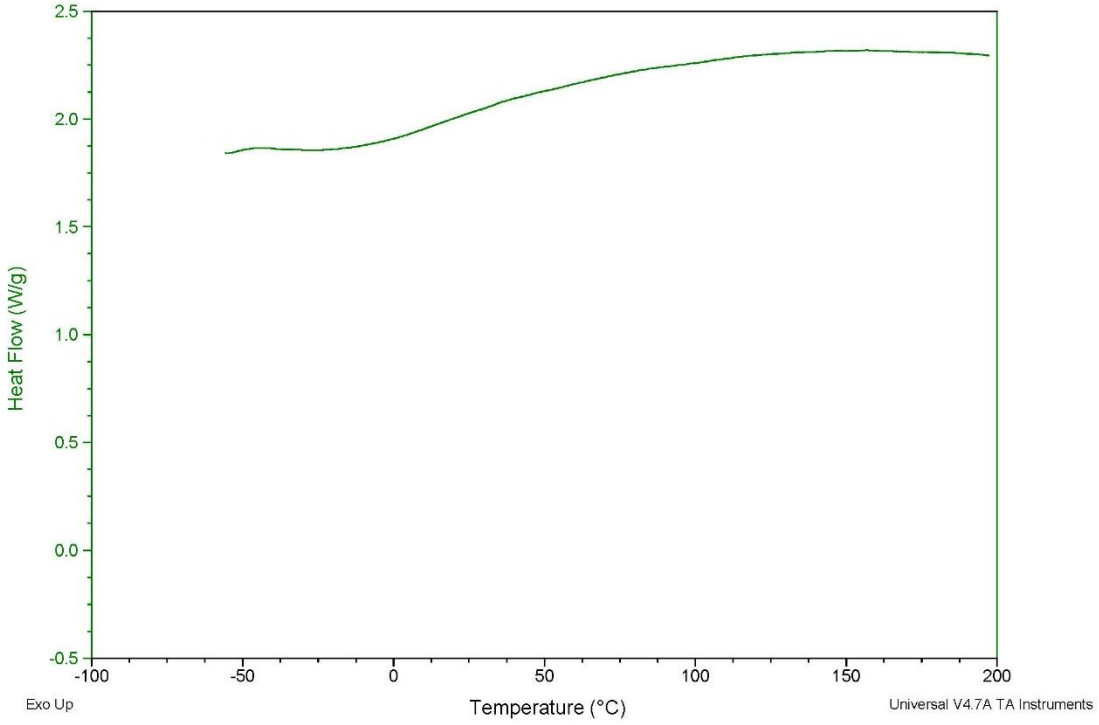
DSC curves of **p1** and **p2** under nitrogen



TGA curves of **p3** under nitrogen and air

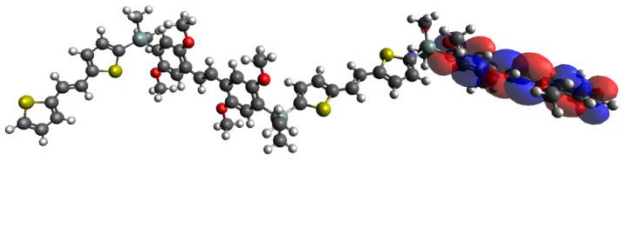


DSC curve of **p3** under nitrogen

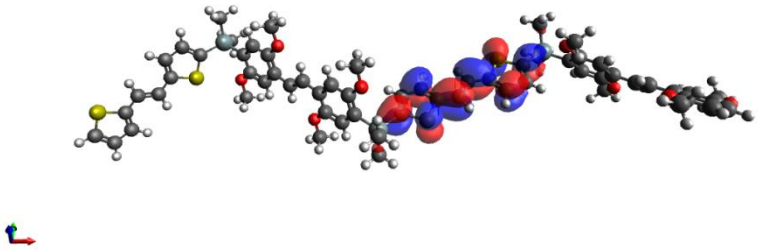


Additional Details from DFT calculations

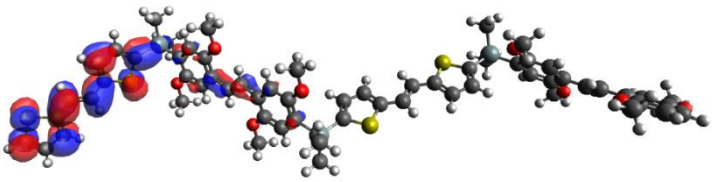
Selected orbital plots and results summary of P2 models calculated at the DFT/B3LYP/6-31g(d,p) level.



LUMO+2



LUMO+1



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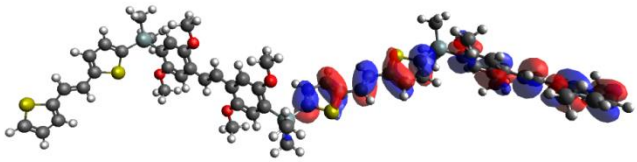
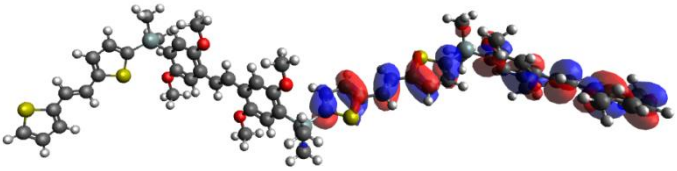
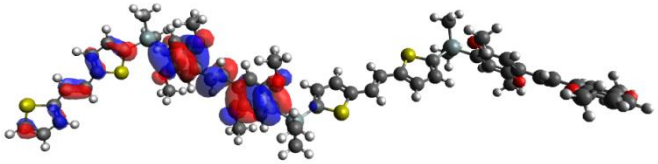


HOMO



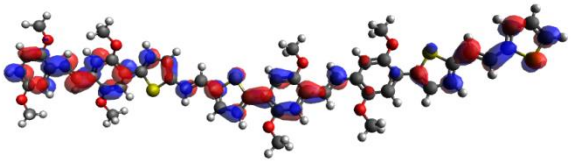
HOMO-1



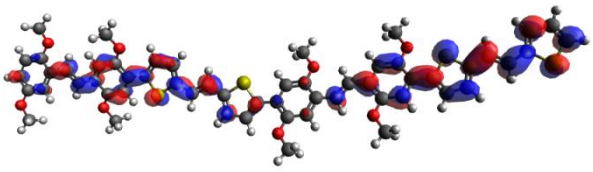
HOMO-2

HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	Band Gap
-4.94eV	-4.93eV	-4.92eV	-1.55eV	-1.46eV	-1.33eV	3.37 eV

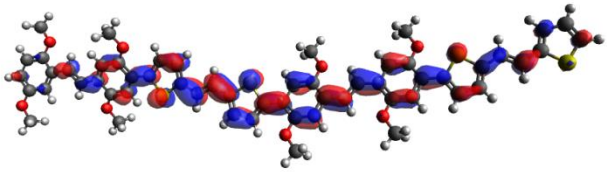
Selected orbital plots and results summary of P3 models calculated at the DFT/B3LYP/6-31g(d,p) level.



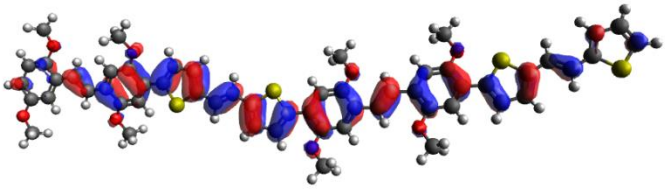
LUMO+2



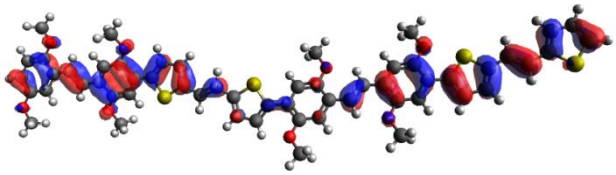
LUMO+1



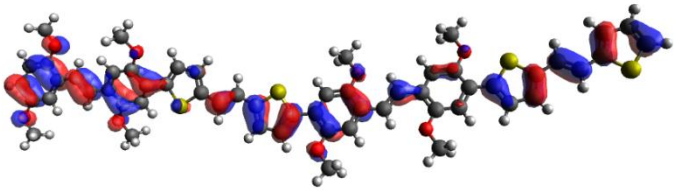
LUMO



HOMO



HOMO-1



HOMO-2

HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	Band Gap
-5.03eV	-4.68eV	-4.39eV	-1.98eV	-1.68eV	-1.26eV	2.41 eV