Electronic Supplementary Material (ESI) for Polymer Chemistry.

# Highly Red-Shifted NIR Emission from a Novel Anthracene Conjugated Polymer Backbone Containing Pt(II) Porphyrins

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## *Electronic supplementary information*

### Contents

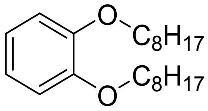
## 1. Experimental details

All reagents and solvents were used as received. MeOH, $CH_2Cl_2$ and *n*-hexane were HiPerSolv grade. $Et_2O$ and EtOAc were GPR grade. All other chemicals were used as supplied unless otherwise indicated. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise indicated. Air and moisture sensitive reagents were transferred by syringe. Reactions performed at temperatures other than rt were recorded as silicon oil bath temperatures. The phrase "concentrated *in vacuo*" refers to rotary evaporation. Brine refers to an aqueous solution of NaCl. Column chromatography was carried out using BDH (40-60 µm) silica gel and analytical thin layer chromatography was carried out using Merck Keiselgel aluminium-backed plates coated with silica gel. If necessary, components were visualised using combinations of ultra-violet light and potassium permanganate.

$^1H$ NMR spectra were recorded at 300 MHz on a Bruker AMX300 spectrometer, at 500 MHz on a Bruker Avance 500 spectrometer, or at 600 MHz on a Bruker Avance 600 spectrometer in the stated solvent using residual protic solvent $CHCl_3$ ($\delta$ = 7.26 ppm, s) or DMSO ($\delta$ = 2.56 ppm, qn) as the internal standard. Chemical shifts are quoted in ppm using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet; br, broad or a combination of these. The coupling constants (*J*) are measured in Hertz. $^{13}C$ NMR spectra were recorded at 75 MHz on a Bruker AMX300 spectrometer, at 125 MHz on a Bruker Avance 500 spectrometer or at 150 MHz on a Bruker Avance 600 spectrometer in the stated solvent using the central reference of $CHCl_3$ ($\delta$ = 77.0 ppm, t) or DMSO ($\delta$ = 39.52 ppm, septet) as the internal standard. Chemical shifts are reported to the nearest 0.1 ppm. UV-visible spectra were recorded at room temperature on a Thermo Unicam UV500 spectrometer in $CH_2Cl_2$ solutions at concentrations of ~$10^{-5}$ M. Thin films of polymers were spin coated from $CH_2Cl_2$ solutions of 10 mg/mL on a Laurell spin coater at 2000 rpm for 30 s. Mass spectra was obtained from the mass spectrometry service at the Department of Chemistry, University College London. Number-average (Mn) and weight-average (Mw) molecular weights were determined against a polystyrene standard using an Agilent Technologies 1200 series GPC in chlorobenzene at 80 °C. Thermal gravimetric analysis (TGA) measurements: ~0.2 mg material was used for the TGA experiments, which was performed under nitrogen at heating rate of 10˚C/min with a Mettler Toledo TGA system.

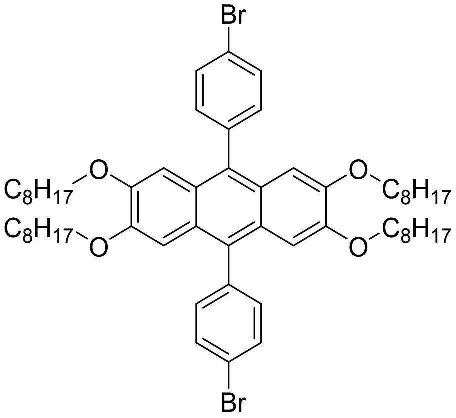
## 2. Polymer synthesis

### 1,2-bis(octyloxy)benzene



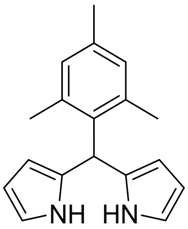
1-bromooctane (25.0 mL, 145.30 mmol) was added slowly to a solution of catechol (2.0 g, 18.18 mmol) and $K_2CO_3$ (10.0 g, 72.65 mmol) in acetone (100 mL) at 50 °C. The reaction mixture was stirred at reflux for 18 h. The reaction mixture was concentrated *in vacuo* and extracted with $CH_2Cl_2$ (2 x 50 mL) from brine (50 mL). The crude product was purified via column chromatography ($SiO_2$, Eluent Hexane) to give white crystals (4.39 g, 13.12 mmol, 72 %). $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.89 (s, *J* = 2.6 Hz, 4H, Ph*H*), 3.99 (t, *J* = 6.7 Hz, 4H, $PhOCH_2CH_2C_5H_{10}CH_3$), 1.88 – 1.73 (m, 4H, $PhOCH_2CH_2C_5H_{10}CH_3$), 1.54 – 1.20 (m, 20H, $PhOCH_2CH_2C_5H_{10}CH_3$), 0.95 – 0.82 (t, *J* = 8.8 Hz, 6H, $PhOCH_2CH_2C_5H_{10}CH_3$); MS ($EI^+$) *m/z* 334 $(M)^+$. All spectroscopic data is in accordance with literature values.[1]

### 9,10-bis(4-bromophenyl)-2,3,6,7-tetra(octyloxy)anthracene



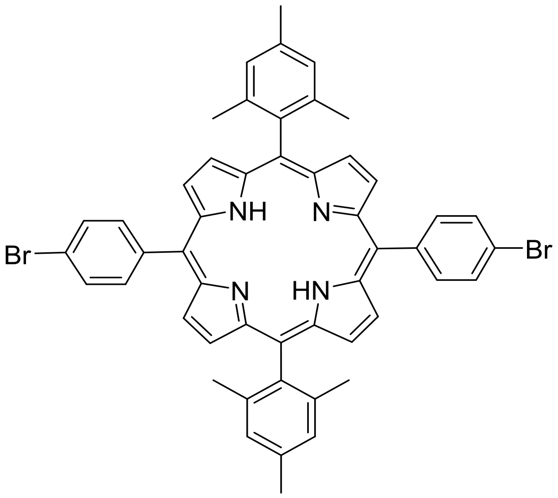
Following a modified procedure by Xia,[2] 1,2-bis(octyloxy)benzene (3.0 g, 8.97 mmol), 4-bromobenzaldehyde (2.5 g, 13.44 mmol) and $CHCl_3$ (30 mL) were added slowly to a 1:10 w/w solution of $P_2O_5$ (0.42 g) in $MeSO_3H$ (3.0 mL) at 0 °C under an atmosphere of argon. The reaction mixture was heated to reflux and stirred for 2 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2.0 g, 8.97 mmol) was added and the reaction was cooled to 40 °C and stirred for 2 h. The reaction mixture was washed with brine (2 x 30 mL) and the aqueous fractions were further extracted with $CHCl_3$ (2 x 50 mL). The organic fractions were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via column chromatography ($SiO_2$, Eluent $Et_2O$:Hexane (1:19)) and recrystallization from $CHCl_3$ and MeOH (716 mg, 0.72 mmol, 8 %). $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 4H, Ph*H*), 7.33 (d, *J* = 8.3 Hz, 4H, Ph*H*), 6.72 (s, 4H, $C_8H_{17}OCC\mathit{H}$), 3.85 (t, *J* = 6.5 Hz, 8H, $OC\mathit{H_2}CH_2C_5H_{10}CH_3$), 1.83 – 1.69 (m, 8H, $OCH_2C\mathit{H_2}C_5H_{10}CH_3$), 1.48 – 1.19 (m, 40H, $OCH_2CH_2C_5\mathit{H_{10}}CH_3$), 0.88 (t, *J* = 6.7 Hz, 12H, $OCH_2CH_2C_5H_{10}C\mathit{H_3}$); $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 149.0, 139.0, 133.0, 132.0, 131.5, 125.7, 121.6, 105.1, 68.7, 32.0, 29.5, 29.4, 29.0, 26.2, 22.8, 14.3; MS (ES$^+$) *m/z* 998, 1000, 1002 (M)$^+$; HRMS 998.4424 calculated for $C_{58}H_{80}{}^{79}Br_2O_4$ found 998.5254.

**2,2'-(mesitylmethylene)bis(1H-pyrrole)**



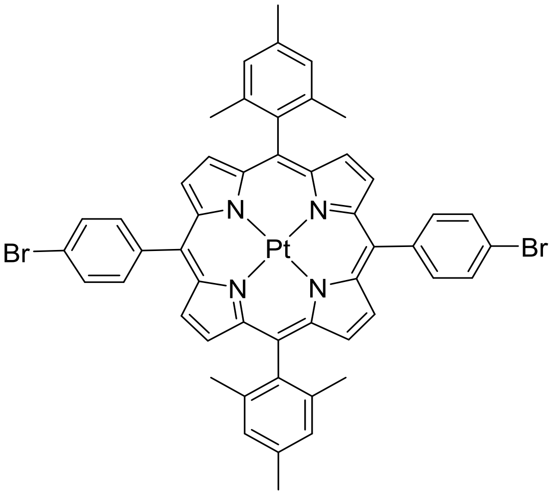
Pyrrole (188 mL) and mesitaldehyde (4.0 mL, 27.2 mmol) were degassed for 10 min. Magnesium bromide (0.5 g, 2.7 mmol) was added and the reaction mixture was stirred at rt for 2 h. NaOH solution was added and the reaction mixture was passed through a plug of silica using $CH_2Cl_2$ as eluent. Concentration *in vacuo* afforded a solid that was washed with pentane (50 mL) to yield the product as a white solid (5.5 g, 20.8 mmol, 77 %). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.94 (br s, 2H, N*H*), 6.87 (s, 2H), 6.66 (s, 2H), 6.18 (dd, J = 5.6, 2.8 Hz, 2H), 6.01 (s, 2H), 5.93 (s, 1H), 2.28 (s, 3H), 2.07 (s, 6H); MS (EI$^+$) *m/z* 264 (M)$^+$. All spectroscopic data is in accordance with literature values.[3]

### 5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrin (MPP)



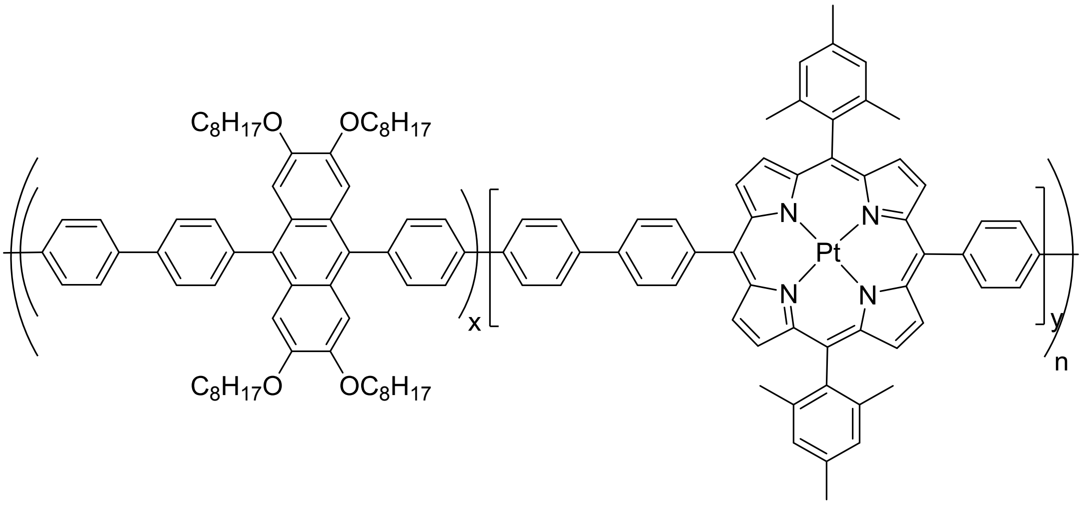
A solution of 2,2'-(mesitylmethylene)bis(1H-pyrrole) (0.54 g, 2.04 mmol) and 4-bromobenzaldehyde (0.38 g, 2.04 mmol) in $CH_2Cl_2$ (250 mL) was degassed and TFA (0.28 mL, 3.68 mmol) was added slowly in the dark under an argon atmosphere. The reaction mixture was stirred for 30 min. DDQ (0.56 g, 2.45 mmol) was added and the reaction mixture was stirred for a further 4 h. The reaction mixture was passed through a plug of silica using $CH_2Cl_2$ as eluent. Concentration *in vacuo* and washing with MeOH (100 mL) yielded the product as purple crystals (156 mg, 0.19 mmol, 18 %). $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.7 Hz, 4H, NHCC*H*CH), 8.70 (d, *J* = 4.7 Hz, 4H, NHCCHC*H*), 8.09 (d, *J* = 8.2 Hz, 4H, CBrC*H*CH), 7.88 (d, *J* = 8.2 Hz, 4H, CBrCHC*H*), 7.29 (s, 4H, Ph-*H*), 2.63 (s, 6H, Ph-C*H₃*), 1.83 (s, 12H, Ph-C*H₃*), -2.66 (s, 2H, N*H*); $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 141.0, 139.5, 138.3, 138.0, 135.9, 132.6, 131.1, 130.0, 127.9, 122.5, 118.8, 118.0, 114.4, 21.8, 21.6. MS (EI$^+$) *m/z* 855, 857 and 859 (M[+H])$^+$; HRMS 855.1698 calculated for $C_{50}H_{41}{}^{79}Br_2N_4$ found 855.1660.

### 5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrinato platinum(II) (MPP-Pt)



A solution of $PtCl_2$ (30 mg, 0.117 mmol) in benzonitrile (10 mL) was heated to 100 $^{o}$C. 5,15-dimesityl-10,20-diparabromophenyl porphyrin (50 mg, 0.058 mmol) was added in one portion and the reaction mixture was heated to reflux and stirred for 18 h. The reaction mixture was then cooled and concentrated *in vacuo*. The crude product was passed through a plug of silica using $CHCl_3$ as eluent, concentrated *in vacuo* and washed with MeOH (70 mL) to give the product as a red powder (35 mg, 0.033 mmol, 56 %). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.0 Hz, 4H, NHCC*H*CH), 8.61 (d, *J* = 5.0 Hz, 4H, NHCCHC*H*), 8.04 (d, *J* = 8.3 Hz, 4H, CBrC*H*CH), 7.86 (d, *J* = 8.3 Hz, 4H, CBrCHC*H*), 7.26 (s, 4H, Ph-*H*), 2.61 (s, 6H, Ph-C*H$_3$*), 1.83 (s, 12H, Ph-C*H$_3$*); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 140.8, 140.5, 140.4, 139.2, 138.1, 137.4, 135.3, 131.0, 130.1, 129.9, 128.0, 122.6, 120.9, 120.3, 21.6, 21.5.; MS (TOF ES$^-$) *m/z* 1049 (M)$^-$.

**PDPA MPP(Pt) – Poly 2,3,6,7-(octyloxy)diphenylanthracene 5,15-dimesityl-10,20-diphenylporphyrin(Pt)**



4 polymers were synthesised with varying weight percentages of porphyrin to diphenylanthracene; 0.0 %, 1.0 %, 5.0 % and 10.0 %; **PDPA**, **PDPA MPP(Pt) 1**, **PDPA MPP(Pt) 5** and **PDPA MPP(Pt) 10** respectively.

**General Synthesis**

A mixture of 9,10-bis(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene, 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene, 5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrinato platinum(II), $Pd_2(dba)_3$, $(o\text{-tol})_3P$, aliquat 336, and toluene was degassed in a microwave vial for 30 min. A degassed 1.0 M solution of $Na_2CO_3$ was added and the reaction mixture was stirred for 3 d at 120 $^{o}$C. The reaction was allowed to cool and the product was precipitated from MeOH and filtered. The polymer product was then washed with acetone and hexane and extracted with $CHCl_3$.

**PDPA:** Reagents and solvents used were 9,10-bis(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene (108.9 mg, 0.109 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (35.9 mg, 0.109 mmol), $Pd_2(dba)_3$ (2.0 mg, 0.002 mmol), $(o\text{-tol})_3P$ (2.6 mg, 0.009 mmol), aliquat 336 (1 drop), 1.0 M $Na_2CO_3$ (1.0 mL), and toluene (4.0 mL). Polymer was obtained as per the above synthesis (79 mg, 79 %). UV (chlorobenzene) $\lambda$max 381; GPC (PS): $M_n$ = 7800, $M_w$ = 10000, PDI = 1.3.

**PDPA MPP(Pt) 1:** Reagents and solvents used were 9,10-bis(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene (216.1 mg, 0.216 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (71.8 mg, 0.218 mmol), 5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrinato platinum(II) (2.2 mg, 0.002 mmol), $Pd_2(dba)_3$ (4.0 mg, 0.004 mmol), $(o\text{-tol})_3P$

(5.2 mg, 0.017 mmol), aliquat 336 (1 drop), 1.0 M $Na_2CO_3$ (2.0 mL), and toluene (8.0 mL). Polymer was obtained as per the above synthesis (120 mg, 60 %). UV (chlorobenzene) λmax 382; GPC (PS): $M_n$ = 8800, $M_w$ = 12000, PDI = 1.4.

**PDPA MPP(Pt) 5:** Reagents and solvents used were 9,10-bis(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene (103.7 mg, 0.104 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (35.9 mg, 0.109 mmol), 5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrinato platinum(II) (5.4 mg, 0.005 mmol), $Pd_2(dba)_3$ (2.0 mg, 0.002 mmol), $(o\text{-tol})_3P$ (2.6 mg, 0.009 mmol), aliquat 336 (1 drop), 1.0 M $Na_2CO_3$ (1.0 mL), and toluene (4.0 mL). Polymer was obtained as per the above synthesis (80 mg, 80 %). UV (chlorobenzene) λmax 408; GPC (PS): $M_n$ = 12000, $M_w$ = 20000, PDI = 1.7.

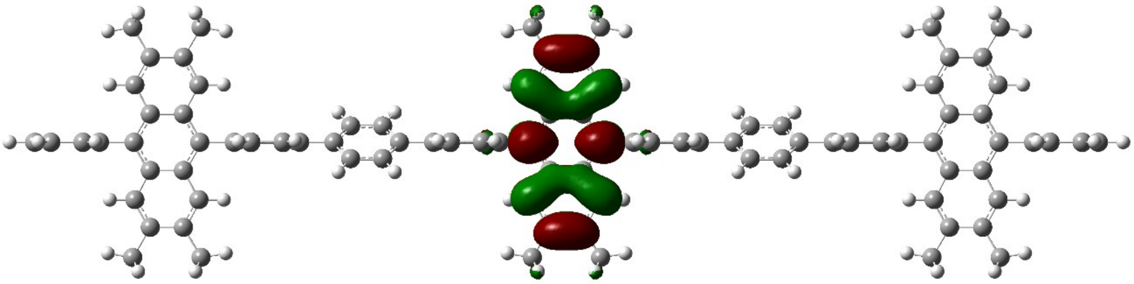
**PDPA MPP(Pt) 10:** Reagents and solvents used were 9,10-bis(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene (98.2 mg, 0.098 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (35.9 mg, 0.109 mmol), 5,15-bis(4-bromophenyl)-10,20-dimesitylporphyrinato platinum(II) (10.9 mg, 0.010 mmol), $Pd_2(dba)_3$ (2.0 mg, 0.002 mmol), $(o\text{-tol})_3P$ (2.6 mg, 0.009 mmol), aliquat 336 (1 drop), 1.0 M $Na_2CO_3$ (1.0 mL), and toluene (4.0 mL). Polymer was obtained as per the above synthesis (42 mg, 42 %). UV (chlorobenzene) λmax 411; GPC (PS): $M_n$ = 11000, $M_w$ = 21000, PDI = 1.8.

## 3. DFT and NMR of polymers

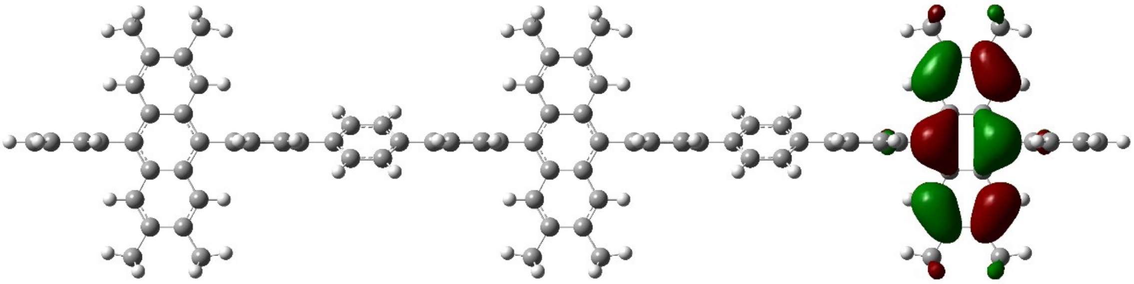
### *DFT of polymers*

DFT B3LYP was run with a 6-31G* basis set on an approximation of the relevant polymers. **PDPA** is reported in the main text, ***figure 2***. **AlkPDPA** is reported below.

**AlkPDPA LUMO**



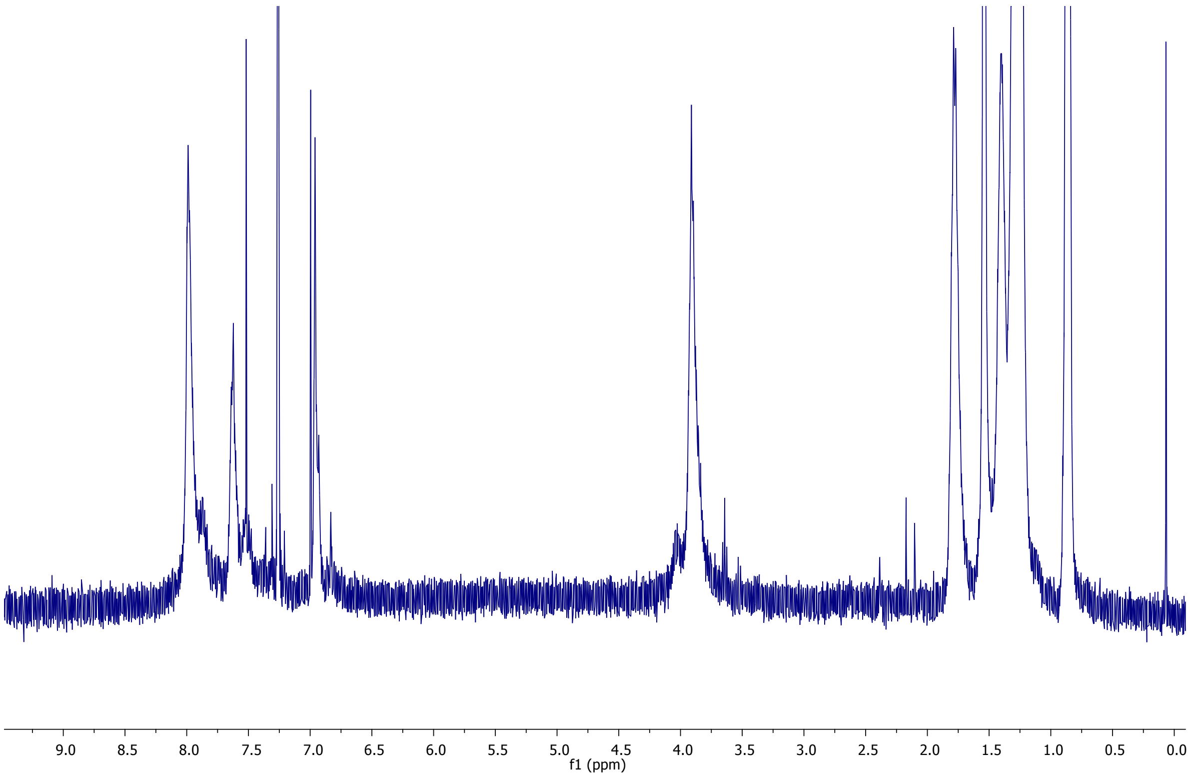
**AlkPDPA HOMO**



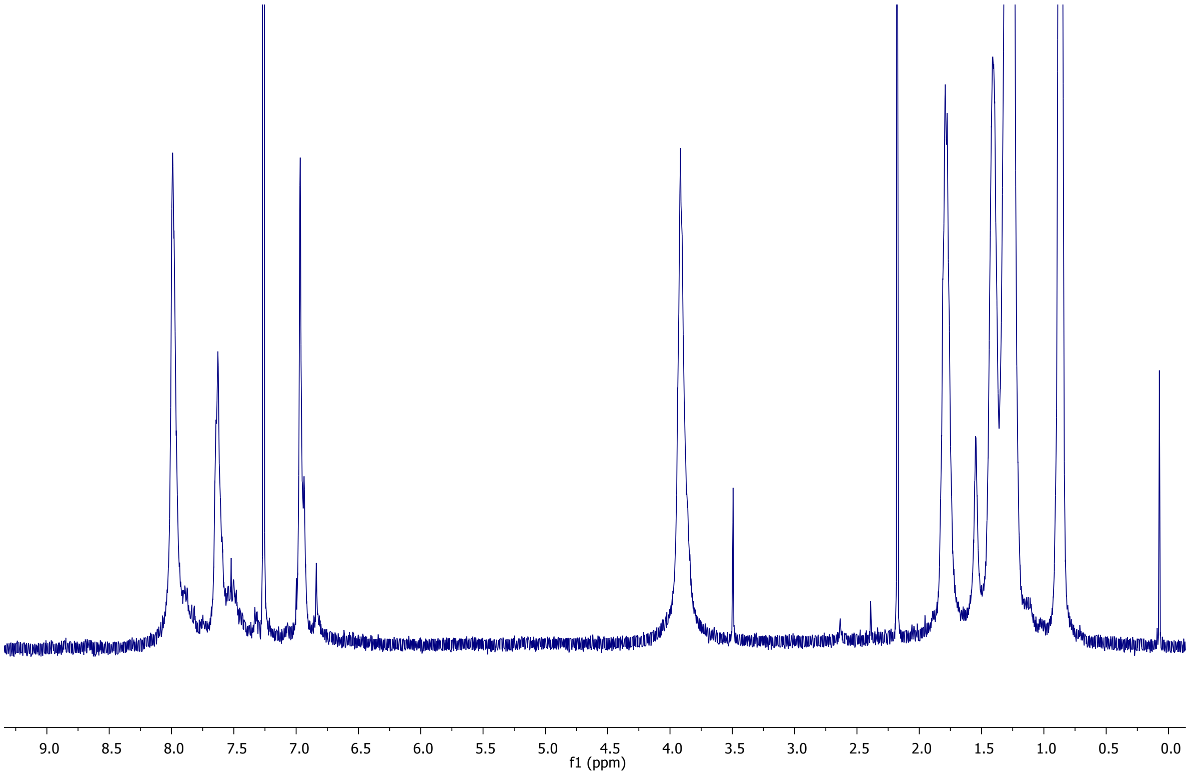
### *NMR of polymers*

$^1$H NMR spectroscopy was utilised to estimate the incorporation ratio of the polymers. This was obtained by measuring the ratio of the peak at 3.90 ppm to the peak at 8.85 ppm (*i.e.* the ratio of the methylene protons α to oxygen on the alkoxy chains to the pyrollic protons of the porphyrin dopant).

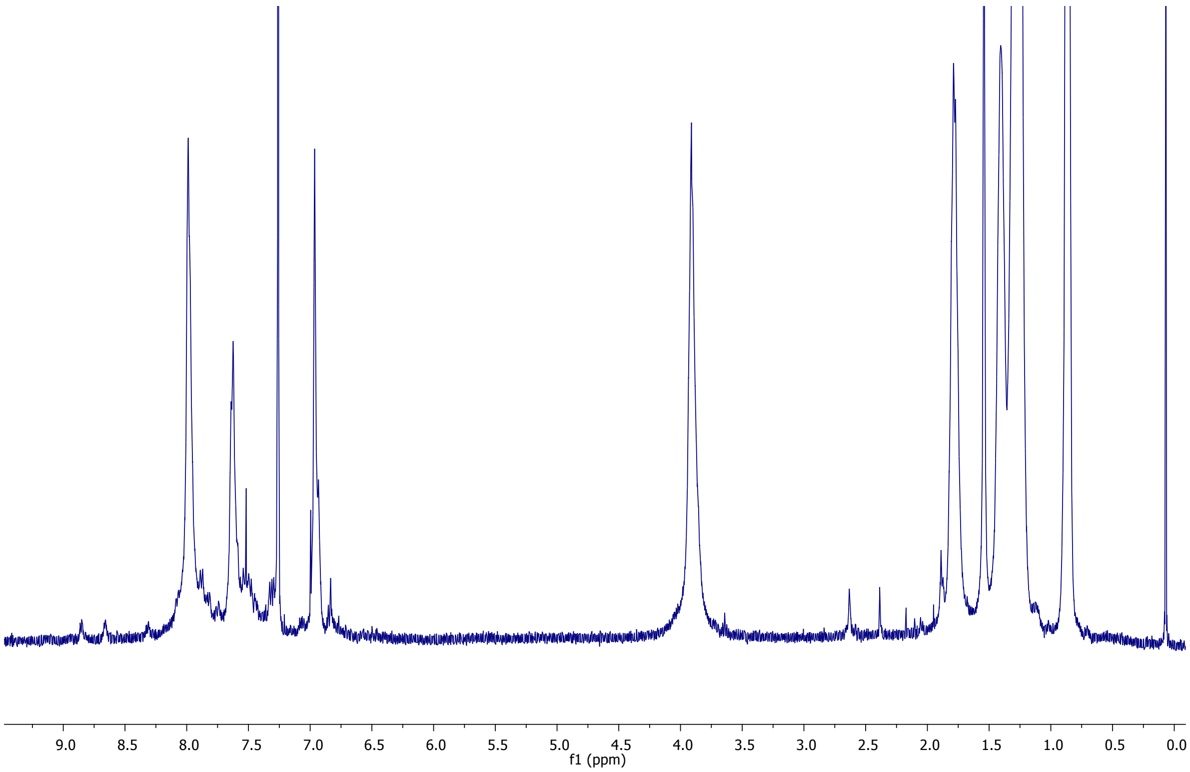
**PDPA**



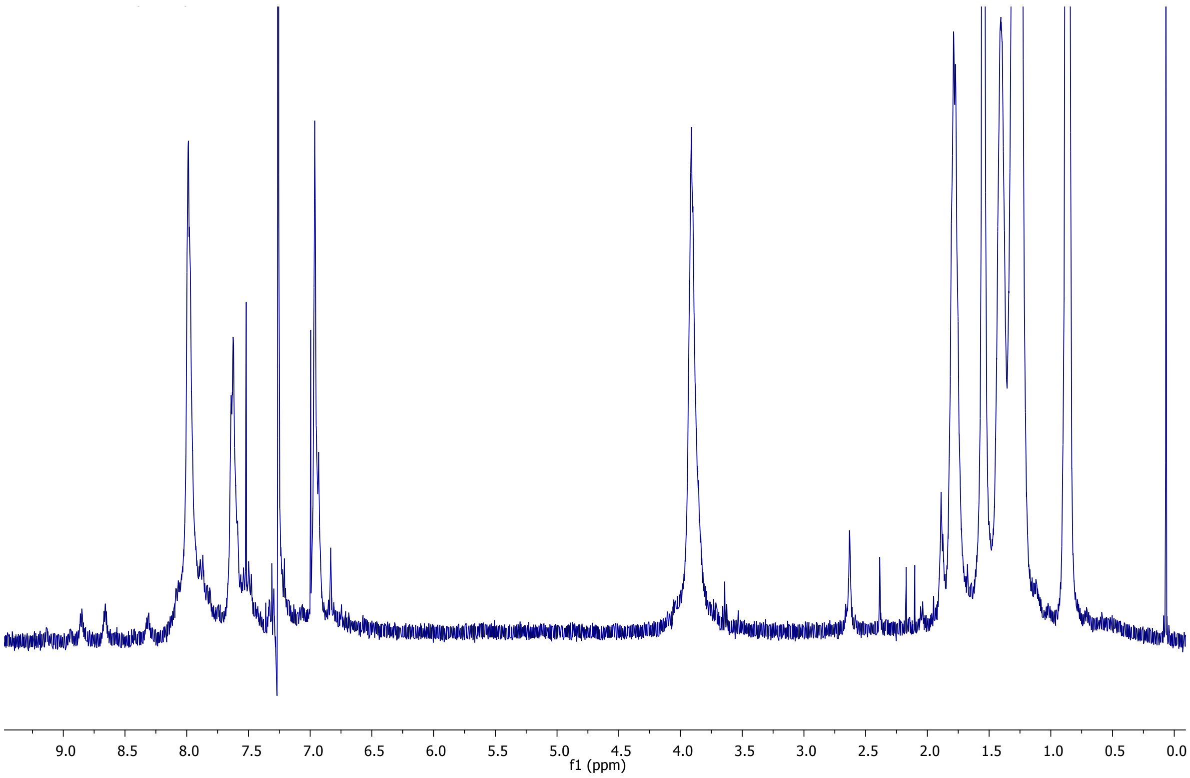
**PDPA MPP(Pt) 1**

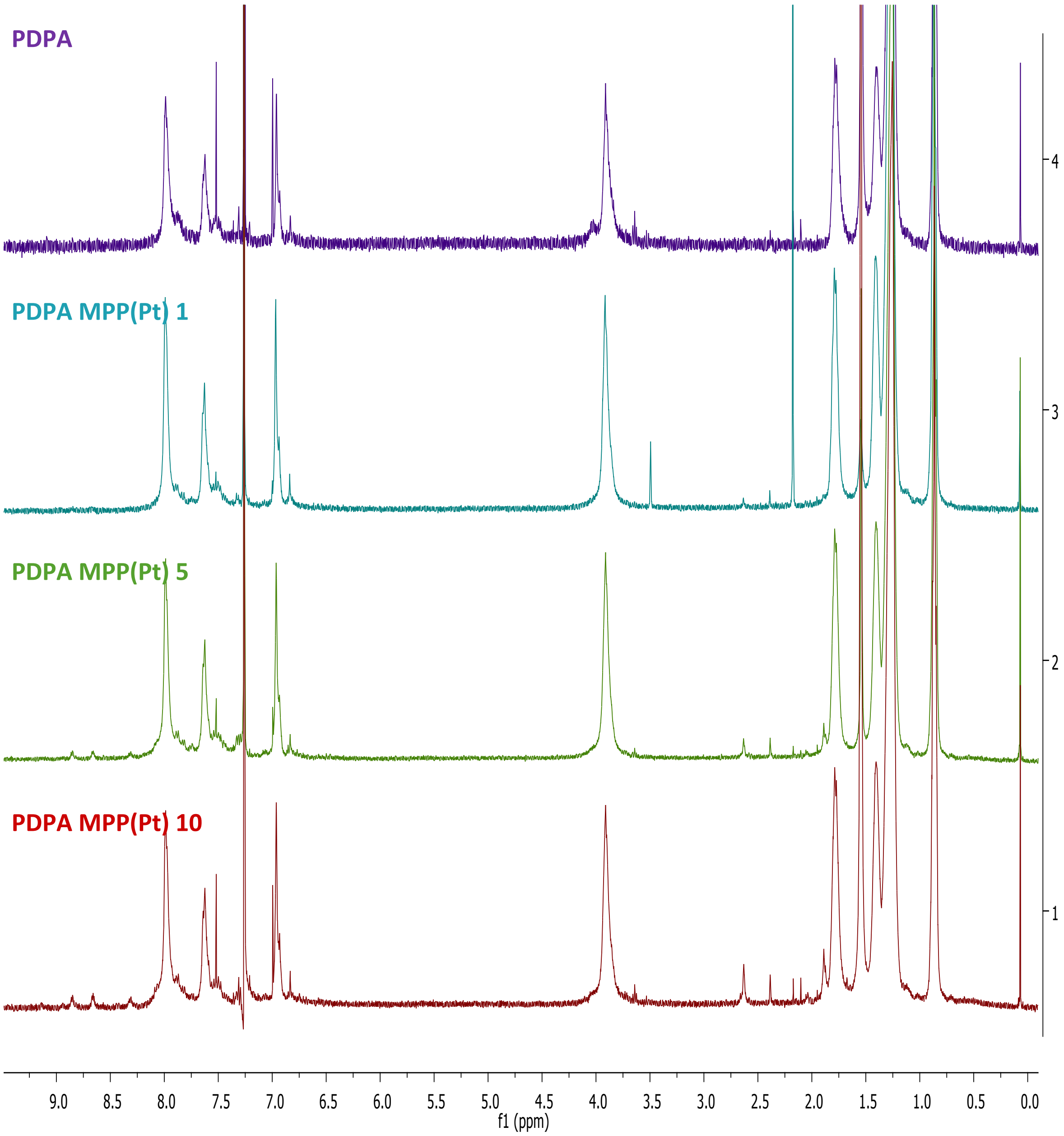


**PDPA MPP(Pt) 5**



**PDPA MPP(Pt) 10**

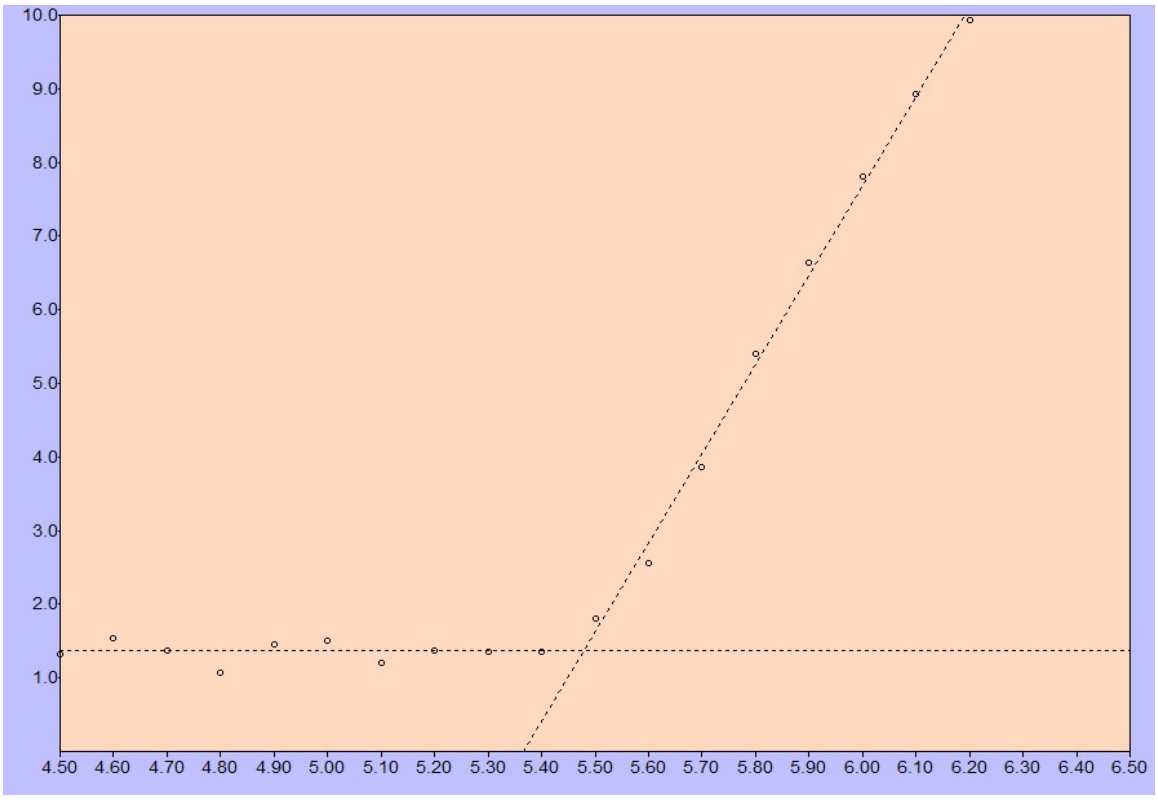



PDPA
PDPA MPP(Pt) 1
PDPA MPP(Pt) 5
PDPA MPP(Pt) 10
4
3
2
1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

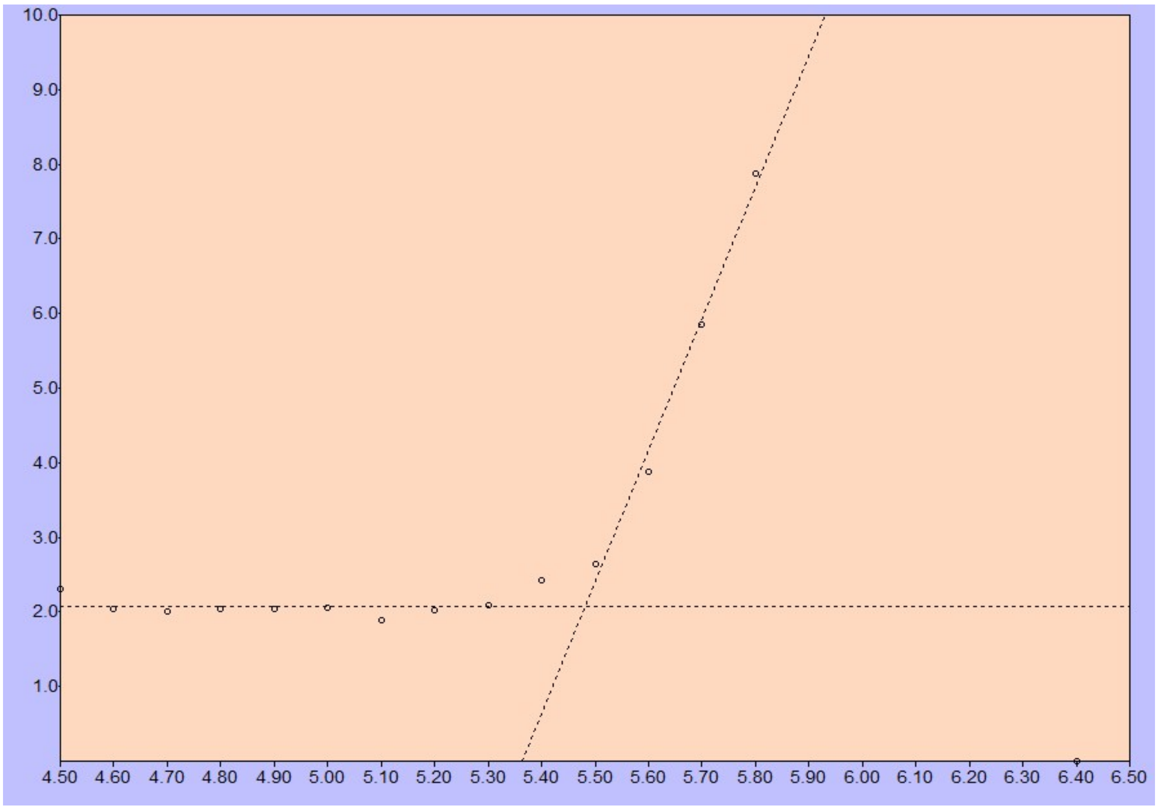
## 4. PESA spectra

PESA was used to obtain the HOMO energy levels for the polymers. Shown below are representative spectra of each of the 4 polymers discussed.

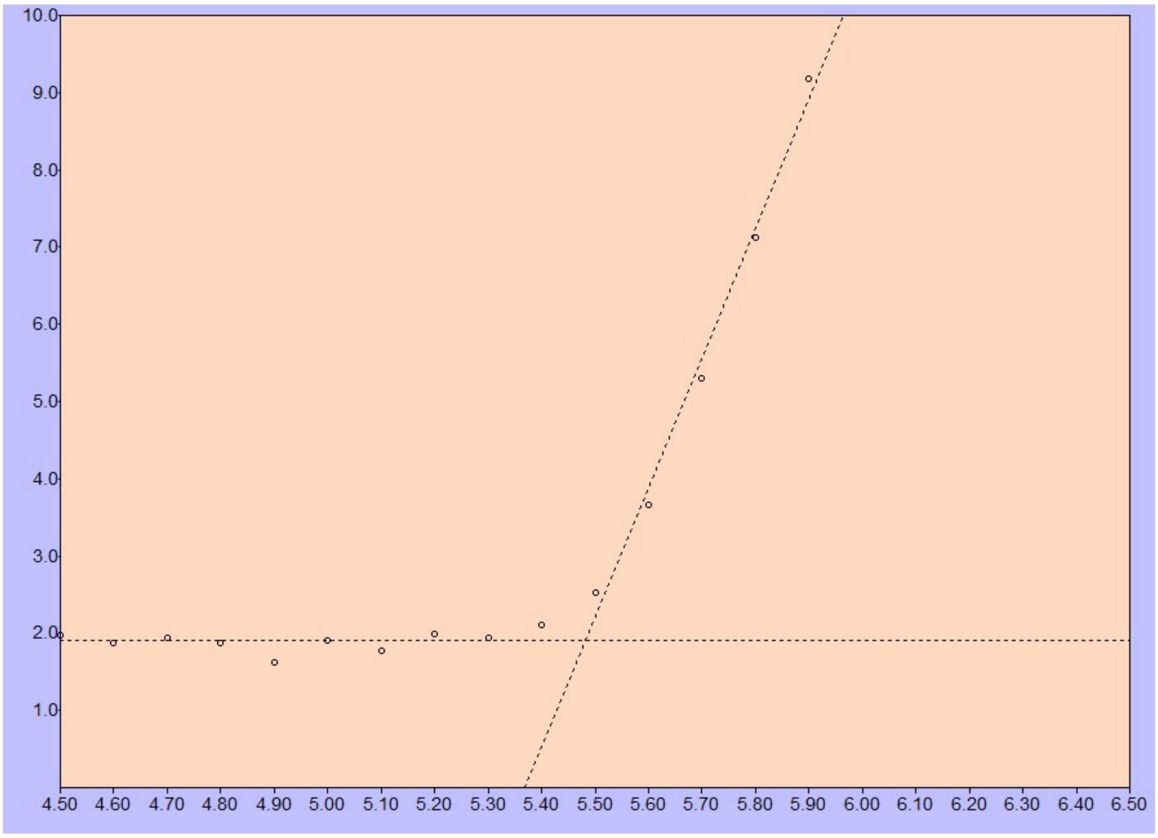
***PDPA***



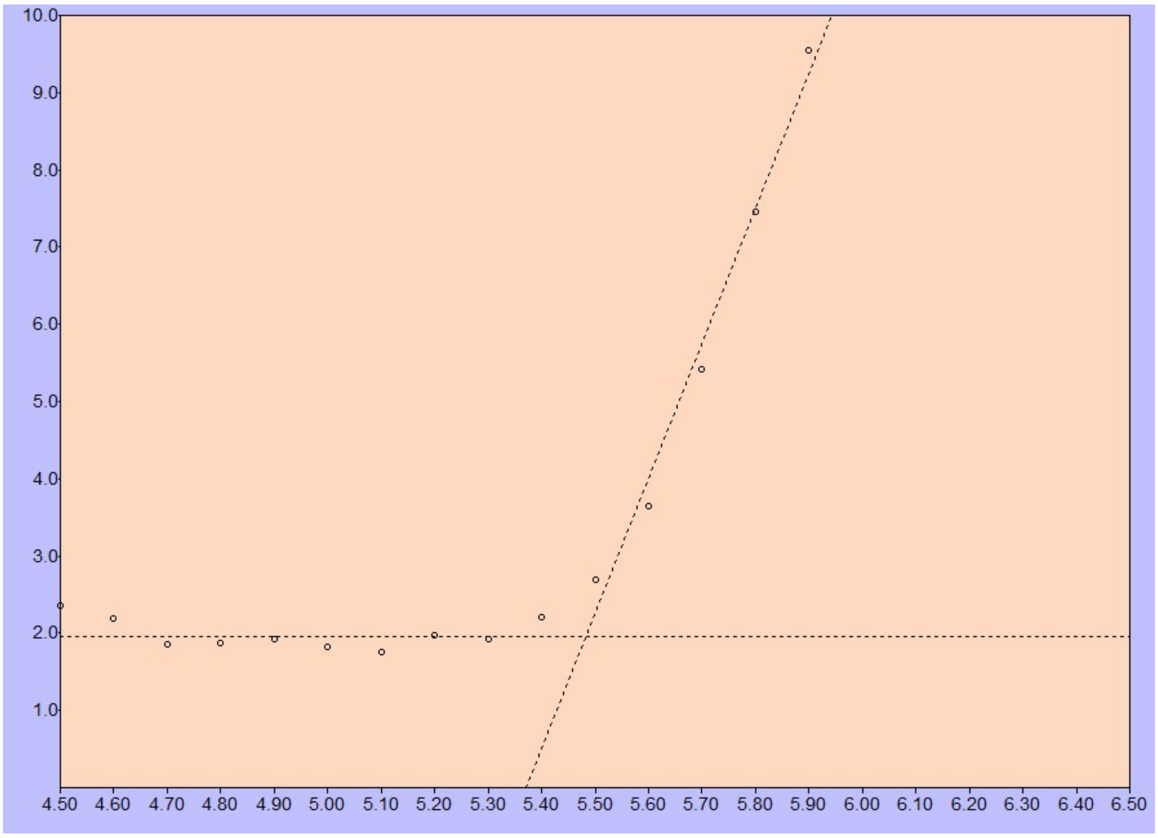
***PDPA MPP(Pt) 1***



***PDPA MPP(Pt) 5***

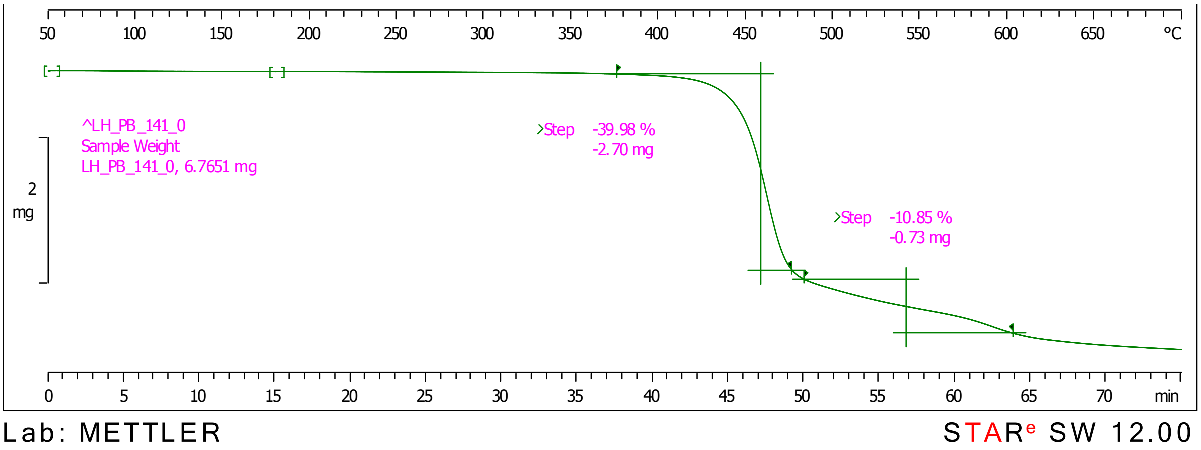


***PDPA MPP(Pt) 10***



## 5. TGA spectra

### PDPA



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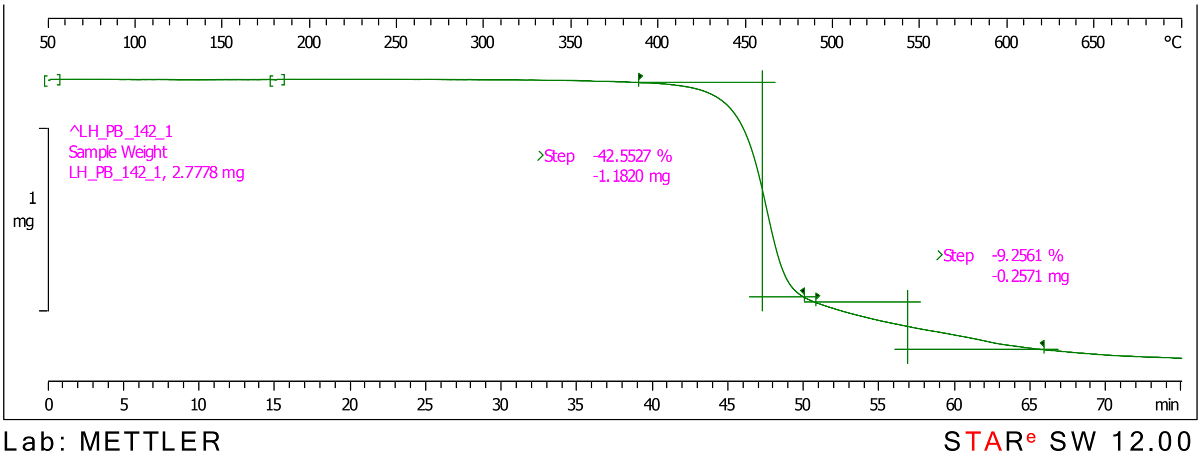

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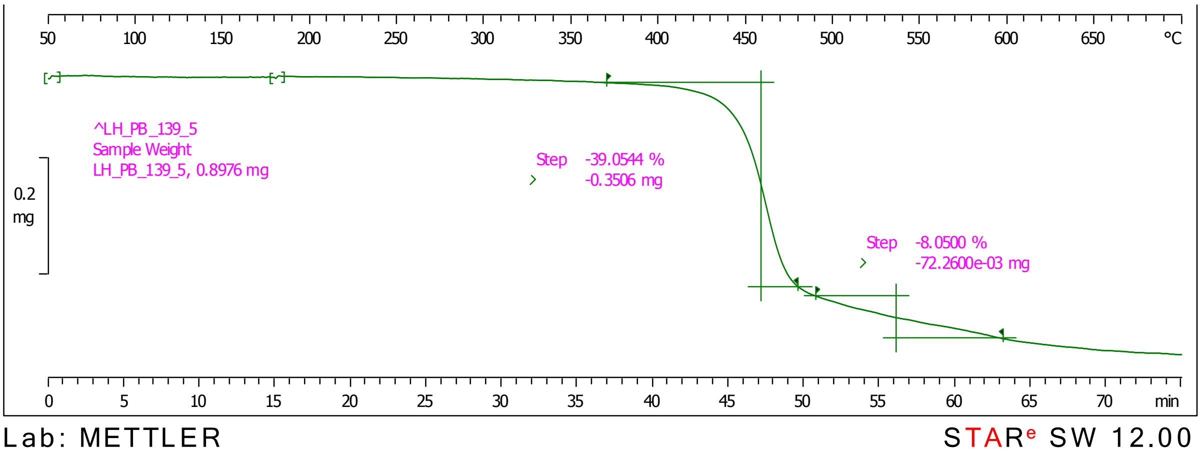
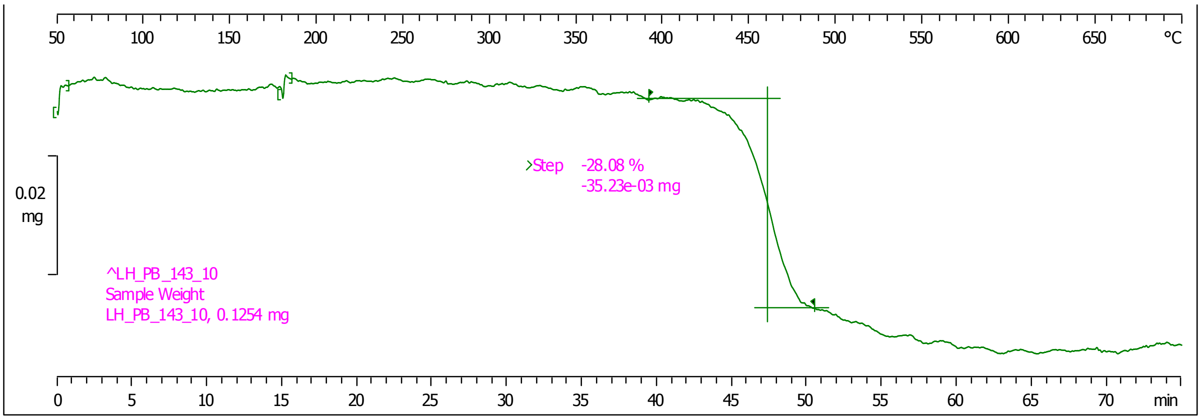


## PDPA MPP(Pt) 10



Lab: METTLER

STAR$^e$ SW 12.00

## References

(1) Q. Zhang; H. Peng; G. Zhang; Q. Lu; J. Chang; Y. Dong; X. Shi and J. Wei, *J Am Chem Soc,* 2014, **136**, 5057.

(2) Z.-Y. Xia; J.-H. Su; W.-Y. Wong; L. Wang; K.-W. Cheah; H. Tian and C. H. Chen, *J Mater Chem,* 2010, **20**, 8382.

(3) K. D. Seo; M. J. Lee; H. M. Song; H. S. Kang and H. K. Kim, *Dyes Pigments,* 2012, **94**, 143.