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Supplementary Information

A π-conjugated inorganic polymer constructed from boron difluoride formazanates and platinum(II) diynes

Jasveer S. Dhindsa, Ryan R. Maar, Stephanie M. Barbon, María Olivia Avilés,
Zachary K. Powell, François Lagugné-Labarthet, and Joe B. Gilroy*

Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research
(CAMBR), The University of Western Ontario, 1151 Richmond St. N., London, Ontario,
Canada, N6A 5B7. Tel: +1-519-661-2111 ext. 81561; E-mail: joe.gilroy@uwo.ca

Experimental Section

General considerations

Reactions and manipulations were carried out under an N_2 atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum and stored under a nitrogen atmosphere over 4 Å molecular sieves. Reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received. K_2PtCl_4 was purchased from Precious Metals Online and used as received. Alkyne-functionalized BF_2 formazanates,[1] *cis*-$[Pt(PBu_3)_2Cl_2]$,[2] *trans*-$[Pt(PBu_3)_2Cl_2]$,[2] and chlorobis(tri-*n*-butylphosphine)phenylacetylene platinum(II)[3] were prepared according to literature procedures.

NMR spectra were recorded on 400 MHz (^{1}H: 399.8 MHz, ^{13}C: 100.6 MHz, ^{11}B: 128.3 MHz, ^{19}F: 376.1 MHz, ^{31}P: 161.8 MHz) Bruker or 600 MHz (^{1}H: 599.5 MHz, ^{13}C: 150.7 MHz) Varian INOVA instruments. ^{1}H NMR spectra were referenced to residual $CHCl_3$ (7.26 ppm) and $CHDCl_2$ (5.32 ppm) and $^{13}C\{^1H\}$ NMR spectra were referenced to $CDCl_3$ (77.2 ppm) and CD_2Cl_2 (53.8 ppm). ^{11}B NMR spectra were referenced to $BF_3\cdot OEt_2$ (0 ppm), ^{19}F NMR spectra were referenced to $CFCl_3$ (0 ppm), and $^{31}P\{^1H\}$ NMR spectra were referenced to H_3PO_4 (0 ppm). Mass spectrometry data were recorded in positive-ion mode using a high-resolution Finnigan MAT 8200 spectrometer using electron impact ionization or a Micromass LCT electrospray ionization time-of-flight mass spectrometer. UV-vis absorption spectra were recorded using a Cary 5000 instrument between 200 and 2000 nm. Four separate concentrations were run for each sample and molar extinction coefficients were determined from the slope of a plot of absorbance against concentration. FT-IR spectra were recorded using an attenuated total reflectance (ATR) attachment using a Bruker Vector 33 FT-IR spectrometer.

Elemental Analysis Statement

Elemental analysis (C, H, N) for compound **3** was carried out by the Laboratoire d'Analyse Élémentaire de l'Université de Montréal, Montréal, QC. In the case of polymer **2** and compounds **4** and **5**, discrete solid samples were not isolated upon purification and our ability to remove residual solvent was limited. Thus, elemental analyses data were not obtained for these compounds. Rather, clean ^{1}H NMR spectra are combined with high-resolution mass spectrometry data as proof of purity/identity.

X-ray Crystallography Methods

Single crystals suitable for X-ray diffraction studies were grown by vapor diffusion of hexanes into a saturated solution of compound **3** in toluene. The sample crystal was mounted on a MiTeGen polyimide micromount with a small amount of Paratone *N* oil. X-ray diffraction measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The data collection strategy involved a number of ω and φ scans which allowed for data acquisition over a range of angles, 2θ. The frame integration was performed using SAINT.[4] The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[5] The structure was solved by using a dual space methodology using the SHELXT program.[6] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELX suite of crystallographic software.[7] See Table S1 and CCDC 1828452 for additional crystallographic data.

Table S1 X-ray crystallographic data collection and refinement details for compound **3**.

Formula	$C_{66}H_{82}B_2F_4N_8P_2Pt$
Formula Weight (g mol^{-1})	1342.04
Crystal Dimensions (mm)	0.232 × 0.197 × 0.057
Crystal Color and Habit	Blue Block
Crystal System	Triclinic
Space Group	$P\bar{1}$
Temperature (K)	110
a (Å)	10.503(3)
b (Å)	11.094(4)
c (Å)	14.692(5)
α (deg)	106.564(16)
β (deg)	90.122(12)
γ (deg)	95.097(16)
V (Å^3)	1633.7(10)
Number of reflections to determine final unit cell	9978
Min and Max 2θ for cell determination (deg)	5.22, 70.3
Z	1
F(000)	688
ρ (g cm^{-3})	1.364
λ (Å)	0.71073 (MoK$_\alpha$)
μ (cm^{-1})	2.253
Number of reflections measured	64788
Unique reflections measured	19782
R_{merge}	0.0363
Number of reflections included in refinement	19782
Number of parameters in least-squares	376
R_1 [$I > 2\sigma(I)$]	0.0414
ωR_2 [$I > 2\sigma(I)$]	0.0642
R_1 (all data)	0.0550
ωR_2 (all data)	0.0676
GOF	1.003
Min & Max peak heights on final ΔF Map (e^- Å^{-3})	–3.038, 2.844

Where:

$R_1 = \Sigma(|F_o|-|F_c|)/\Sigma F_o$

$\omega R_2 = [\Sigma(\omega(F_o^2-F_c^2)^2)/\Sigma(\omega F_o^4)]^{½}$

GOF = $[\Sigma(\omega(F_o^2-F_c^2)^2)/(\text{No. of reflns.}-\text{No. of params.})]^{½}$

Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR spectra were recorded for a 290 μM solution of the reduced form of polymer **2** in 20:1 CH_2Cl_2:CH_3CN in a 0.4 mm quartz tube using a JEOL JES-FA200 EPR spectrometer. All measurements were made at 25 °C and *g*-values were referenced relative to a built-in MnO_2 marker within the resonant cavity of the instrument.

Thin-film preparation

Thin films of polymer **2** were prepared by filtering (PTFE membrane, 0.22 µm) approximately 200 µL of a 10 mg mL^{-1} solution in chlorobenzene directly onto a microscope glass coverslip. The sample was then accelerated at a rate of 100 rpm s^{-1} to 500 rpm for 15 s followed by acceleration at a rate of 500 rpm s^{-1} to 3000 rpm for 30 s. The films obtained appear homogeneous by eye, but AFM studies revealed the presence of nanostructured aggregates on the film surface (Fig. S13). Thin films of the reduced form of polymer **2** (1.5 equiv. of cobaltocene) were prepared by drop casting a 6 mg mL^{-1} CH_3CN solution directly onto a glass slide and allowing it to dry inside an nitrogen-filled glove box. Prior to analysis by UV-vis absorption spectroscopy, a second slide was placed on top of the thin film with the edges sealed by a thin layer of silicon grease to prevent oxidation.

Atomic Force Microscopy (AFM)

Non-contact AFM images were acquired with a JPK Instruments Nanowizard II (Berlin, Germany). AFM silicon tips with a typical resonance frequency of 190 kHz were used (NCL, Nanoworld Innovative technologies, k = 48 $N.m^{-1}$). The thickness of the film was measured with the AFM after scratching the polymer thin film surface with a small needle and measuring the step height.

Electrochemical methods

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum wire counter electrode and silver wire *pseudo* reference electrode. Experiments were run at scan rates of 250 mV s^{-1} in degassed CH_2Cl_2 solutions of the analyte (~1 mM) and supporting electrolyte (0.1 M $[n\mathrm{Bu}_4][\mathrm{PF}_6]$). Cyclic voltammograms were referenced against an internal standard (~1 mM ferrocene) and corrected for internal cell resistance using the BASi Epsilon software.

Gel permeation chromatography (GPC)

GPC experiments were conducted in chromatography-grade THF at concentrations of 5 mg mL^{-1} using a Viscotek GPCmax VE 2001 GPC instrument equipped with an Agilent PolyPore guard column (PL1113-1500) and two sequential Agilent PolyPore GPC columns packed with porous poly(styrene-co-divinylbenzene) particles (MW range: 200–2,000,000 g mol^{-1}; PL1113-6500) regulated at a temperature of 30 °C. Signal responses were measured using a Viscotek VE 3580 refractive index detector, and molecular weights were determined by comparison of the maximum refractive index response with a calibration curve (10 points, 1500–786,000 g mol^{-1}) established using monodisperse polystyrene standards purchased from Viscotek.

Thermal Analysis

Thermal degradation studies were performed using a TA Instruments Q50 TGA instrument under an atmosphere of nitrogen. Samples of polymer **2** were placed in a platinum pan and heated at a rate of 10 °C min^{-1} from 20 °C to 1000 °C under a flow of nitrogen (60 mL min^{-1}). Glass transition temperatures were determined under an atmosphere of nitrogen using differential scanning calorimetry (DSC) on a TA Instruments DSC Q20. Samples of polymer **2** were placed in an aluminum Tzero pan and heated from –70 °C to 225 °C at 10 °C min^{-1} under a flow of nitrogen (50 mL min^{-1}) and cooled to –70 °C at 10 °C min^{-1}, before they underwent two more heating/cooling cycles.

Preparation of Polymer 2. In a grease-free Schlenk flask, BF_2 formazanate **1** (0.100 g, 0.252 mmol), *trans*-[$Pt(PBu_3)_2Cl_2$] (0.170 g, 0.252 mmol), CuI (0.006 g, 0.03 mmol) were dissolved in a mixture of dry and degassed CH_2Cl_2 (20 mL) and NEt_3 (10 mL) in a glove box. After stirring at 20 °C for 48 h, the reaction mixture was evaporated to dryness *in vacuo*. The residue was washed with deionized H_2O (3 × 50 mL) and extracted with CH_2Cl_2 (25 mL) before the organics were collected, dried over $MgSO_4$, gravity filtered and concentrated *in vacuo*. The resultant polymer residue was dissolved in CH_2Cl_2 and precipitated thrice into a large excess of cold *n*-pentane to afford a blue solid after centrifugation. The solid was then transferred to a round bottom flask via dissolution in CH_2Cl_2 and taken to dryness *in vacuo* to yield polymer **2** as a dark blue film. Yield = 0.180 g, 72%. ^1H NMR (399.8 MHz, $CDCl_3$): δ 8.12−8.10 (m, 2H, Ph *o-H*), 7.82−7.80 (m, 4H, aryl C*H meta* to alkyne), 7.47−7.41 (m, 3H, Ph *m-H* and *p-H*), 7.32–7.30 (m, 4H, aryl C*H ortho* to alkyne), 2.11 (br s, 12H, $PCH_2CH_2CH_2CH_3$), 1.61 (br s, 12H, $PCH_2CH_2CH_2CH_3$), 1.48−1.42 (m, 12H, $PCH_2CH_2CH_2CH_3$), 0.95–0.91 (m, 18H, $PCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (150.7 MHz, $CDCl_3$): δ 148.4, 141.1, 134.2, 131.3, 130.7, 128.9, 128.6, 125.5, 122.9, 115.5, 110.6, 26.4, 24.4 (t, J_{CP} = 7 Hz), 24.0 (t, J_{CP} = 17 Hz), 13.8. *Note – despite analyzing a saturated $CDCl_3$ solution of polymer **2** for 10,000 scans, less $^{13}C\{^1H\}$ NMR resonances than expected were observed. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ –0.4 (t, $^1J_{BF}$ = 29 Hz). ^{19}F NMR (376.1 Hz, $CDCl_3$): δ –143.7 (q, $^1J_{FB}$ = 30 Hz). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): δ 3.4 (s, $^1J_{PPt}$ = 2333 Hz). FT-IR (ATR): 2957 (m), 2931 (m), 2861 (m), 2088 (s), 1588 (s), 1494 (m), 1376 (m), 1298 (s), 1168 (s), 965 (s), 836 (s) cm^{-1}. UV-vis (CH_2Cl_2):

λ_{max} 661 nm (ε = 45,500 M^{-1} cm^{-1}), 329 nm (ε = 31,900 M^{-1} cm^{-1}), 282 nm (ε = 26,400 M^{-1} cm^{-1}), 260 nm (ε = 27,100 M^{-1} cm^{-1}). GPC (THF, conventional calibration relative to polystyrene standards): M_n = 20,430 g mol^{-1}, M_w = 37,860 g mol^{-1}, $Đ$ = 1.85.

Stepwise Reduction of Polymer 2

In a nitrogen-filled glovebox, 0.5 mL of a 1.59 mM solution of polymer **2** in a 1:1 (v/v) mixture of CH_3CN and CH_2Cl_2 was added to multiple 10 mL volumetric flasks. To each flask was added various quantities (0, 0.25, 0.50, 0.75, 0.88, 0.95, 1.00, 1.25, 1.50 molar equiv.) of a 3.29 mM cobaltocene solution in the same solvent mixture. The resulting solutions were then diluted to 10 mL to achieve an overall polymer concentration of 80 µM, transferred to a screw-cap cuvette, and their UV-vis absorption spectra were recorded.

Stepwise Oxidation of the Reduced form of Polymer 2

Starting from a solution of the fully reduced form of polymer **2** (1.5 equiv. described above) in a 1:1 (v/v) mixture of CH_3CN and CH_2Cl_2, the reversibility of the chemical reduction process was explored. The solution was transferred to a vial in air, and swirled for 10 s, before it was transferred to a sealed UV-vis cuvette. Spectra were recorded after 1, 5, 9, 13, 17, 25, 37, and 45 min to monitor the stepwise oxidation of the reduced form of polymer **2**. After 45 min, polymer **2** had been quantitatively regenerated.

Preparation of Complex 3. A solution of *cis*-[Pt(PBu_3)$_2$$Cl_2$] (0.095 g, 0.14 mmol) and 1,3-diphenyl-5-(4-ethynylphenyl) BF_2 formazanate complex (0.100 g, 0.270 mmol) was dissolved in dry, degassed $HNEt_2$ (8 mL) before CuI (0.003 g, 0.02 mmol) was added. The mixture was then stirred for 2 h at 20 °C. The $HNEt_2$ was removed *in vacuo* from the dark blue solution, and the resulting solid was purified by column chromatography (2:1 toluene:hexanes, silica gel) to afford complex **3** as a dark blue microcrystalline solid. Yield = 0.166 g, 87%. Melting Point =

196−198 °C. ^{1}H NMR (399.8 MHz, $CDCl_3$): δ 8.13–8.11 (m, 4H, Ph *o-H*), 7.91−7.88 (m, 4H, Ph *o-H*), 7.83 (d, 4H, $^3J_{HH}$ = 8 Hz, aryl C*H meta* to alkyne), 7.49−7.41 (m, 12H, Ph *m-H* and *p-H*), 7.33−7.31 (m, 4H, aryl C*H ortho* to alkyne), 2.15−2.09 (m, 12H, $PCH_2CH_2CH_2CH_3$), 1.63−1.59 (m, 12H, $PCH_2CH_2CH_2CH_3$), 1.48−1.42 (m, 12H, $PCH_2CH_2CH_2CH_3$), 0.93 (t, 18H, $^3J_{HH}$ = 8 Hz, $PCH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (150.7 MHz, $CDCl_3$): δ 148.9, 144.2, 141.0, 134.0, 131.5, 131.4, 129.4, 129.35, 129.27, 128.8, 125.6, 123.4, 123.3, 116.4, 110.7, 26.5, 24.6 (t, J_{CP} = 7 Hz), 24.1 (t, J_{CP} = 17 Hz), 14.0. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ –0.5 (t, $^1J_{BF}$ = 29 Hz). ^{19}F NMR (376.1 Hz, $CDCl_3$): δ –144.1 (q, $^1J_{FB}$ = 29 Hz). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$): δ 3.5 (s, $^1J_{PPt}$ = 2328 Hz). FT-IR (ATR): 2950 (m), 2927 (m), 2858 (m), 2089 (s), 1585 (s), 1492 (m), 1290 (m), 1218 (m), 1167 (s), 1116 (m), 1004 (m), 966 (m), 836 (m) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 598 nm (ε = 77,400 M^{-1} cm^{-1}), 325 nm (ε = 54,400 M^{-1} cm^{-1}), 280 nm (ε = 52,600 M^{-1} cm^{-1}), 262 nm (ε = 54,200 M^{-1} cm^{-1})· Mass Spec. (ESI, +ve mode): exact mass calculated for $[C_{66}H_{82}N_8B_2F_4P_2{}^{195}Pt + H]^+$: 1342.5986; exact mass found: 1342.6006; difference: +1.5 ppm. Anal. Calcd. (%) for $C_{66}H_{82}B_2F_4N_8P_2Pt$: C, 59.07; H, 6.16; N, 8.35. Found: C, 59.08; H, 6.33; N, 8.26.

Preparation of Complex 4. A solution of chlorobis(tri-*n*-butylphosphine)phenylacetylene platinum(II) (0.200 g, 0.271 mmol) and 1,3-diphenyl-5-(4-ethynylphenyl) BF_2 formazanate complex (0.101 g, 0.271 mmol) was dissolved in dry, degassed $HNEt_2$ (10 mL) before CuI (0.005 g, 0.03 mmol) was added. The mixture was then stirred for 1 h at 20 °C. The $HNEt_2$ was removed *in vacuo* from the dark blue-purple solution, and the resulting solid was purified by column chromatography (1:1 toluene:hexanes, silica gel) to afford complex **3** as a greasy dark blue-purple solid. Yield = 0.229 g, 79%. ^{1}H NMR (399.8 MHz, CD_2Cl_2): δ 8.13–8.10 (m, 2H, Ph *o-H*), 7.88 (d, 2H, $^3J_{HH}$ = 8 Hz, Ph *o-H*), 7.81 (d, 2H, $^3J_{HH}$ = 8 Hz, aryl C*H meta* to alkyne), 7.52–7.42 (m, 6H, Ph *m-H* and *p-H*), 7.35−7.31 (m, 2H, aryl C*H ortho* to alkyne), 7.26−7.18 (m, 4H, Ph *m-H* and *o-H*), 7.13−7.11 (m, 1H, Ph *p-H*), 2.16–2.10 (m, 12H, $PCH_2CH_2CH_2CH_3$), 1.66−1.58 (m, 12H, $PCH_2CH_2CH_2CH_3$), 1.50−1.41 (m, 12H, $PCH_2CH_2CH_2CH_3$), 0.93 (t, 18H, $^3J_{HH}$ = 8 Hz, $PCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (150.7 MHz, CD_2Cl_2): δ 149.3, 144.7, 141.3, 134.5, 132.3, 131.8, 131.3, 131.2, 129.8, 129.7, 129.33, 129.25, 128.4, 126.0, 125.4, 123.7, 123.4, 118.4, 110.5, 109.8, 108.3, 27.0, 25.0 (t, J_{CP} = 7 Hz), 24.5 (t, J_{CP} = 17 Hz), 14.2. ^{11}B NMR (128.3 MHz, CD_2Cl_2): δ –0.5 (t, $^1J_{BF}$ = 29 Hz). ^{19}F NMR (376.1 Hz, CD_2Cl_2): δ –143.8 (q, $^1J_{FB}$ = 29 Hz). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2): δ 3.5 (s, $^1J_{PPt}$ = 2338 Hz). FT-IR (ATR): 3066 (w), 2953 (m), 2927 (m), 2856 (m), 2091 (s), 1589 (s), 1485 (m), 1295 (s), 1221 (m), 1170 (s), 968 (m), 966 (m), 837 (m) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 588 nm (ε = 20,000 M^{-1} cm^{-1}), 325 nm (ε = 23,100 M^{-1} cm^{-1}), 282 nm (ε = 21,300 M^{-1} cm^{-1}), 263 nm (ε = 22,400 M^{-1} cm^{-1}). Mass Spec. (ESI, +ve mode): exact mass calculated for $[C_{53}H_{73}N_4BF_2P_2{}^{194}Pt + Na]^+$: 1093.4896; exact mass found: 1093.4904; difference: +0.7 ppm.

Preparation of Complex 5. 1,3-diphenyl-5-(4-ethynylphenyl) BF_2 formazanate complex (0.100 g, 0.269 mmol) was dissolved in CH_2Cl_2 (8 mL) and piperidine (0.114 g, 0.140 mL, 1.34 mmol) open to air before $Cu(OAc)_2{\cdot}H_2O$ (0.005 g, 0.03 mmol) was added. The mixture was then stirred for 14 h at 20 °C before it was brought to dryness *in vacuo*. The resulting solid was purified by chromatography (1:1 toluene:hexanes, silica gel) to afford complex **5** as a dark purple solid. Yield = 0.076 g, 76%. Melting point = 215−217 °C. ^1H NMR (399.8 MHz, $CDCl_3$): δ 8.11 (d, 4H, $^3J_{HH}$ = 8 Hz, Ph *o-H*), 7.94 (d, 8H, $^3J_{HH}$ = 8 Hz, aryl C*H meta* to alkyne and Ph *o-H*), 7.63 (d, 4H, $^3J_{HH}$ = 8 Hz, aryl C*H ortho* to alkyne), 7.53–7.45 (m, 12H, Ph *m-H* and *o-H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 149.3, 144.3, 143.9, 133.4, 133.3, 130.2, 129.5, 129.2, 128.8, 125.6, 123.6, 123.2, 122.7, 82.5. ^{11}B NMR (128.3 MHz, $CDCl_3$): δ –0.5 (t, $^1J_{BF}$ = 28 Hz). ^{19}F

NMR (376.1 Hz, $CDCl_3$): δ –143.4 (q, $^1J_{FB}$ = 28 Hz). FT-IR (ATR): 3063 (w), 3045 (w), 2203 (w), 1594 (m), 1495 (m), 1352 (m), 1297 (s), 1261 (s), 1221 (m), 1175 (m), 1119 (m), 1024 (m), 962 (m), 837 (m) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 564 nm (ε = 57,100 M^{-1} cm^{-1}), 323 nm (ε = 44,600 M^{-1} cm^{-1}), 264 nm (ε = 30,700 M^{-1} cm^{-1}). Mass Spec. (EI, +ve mode): exact mass calculated for $[C_{42}H_{28}N_8B_2F_4]^+$: 742.2559; exact mass found: 742.2572; difference: +1.8 ppm.

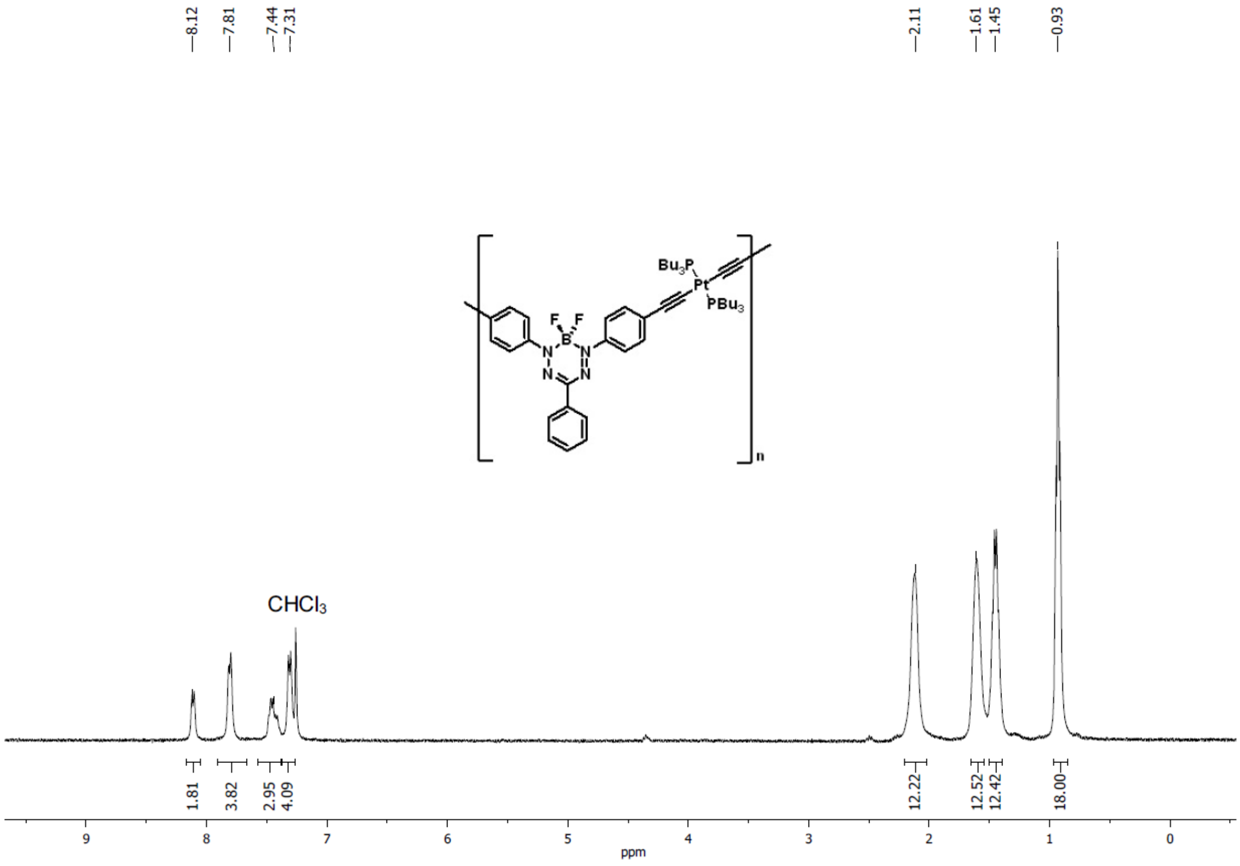

Fig. S1 ^{1}H NMR spectrum of polymer **2** in $CDCl_3$.

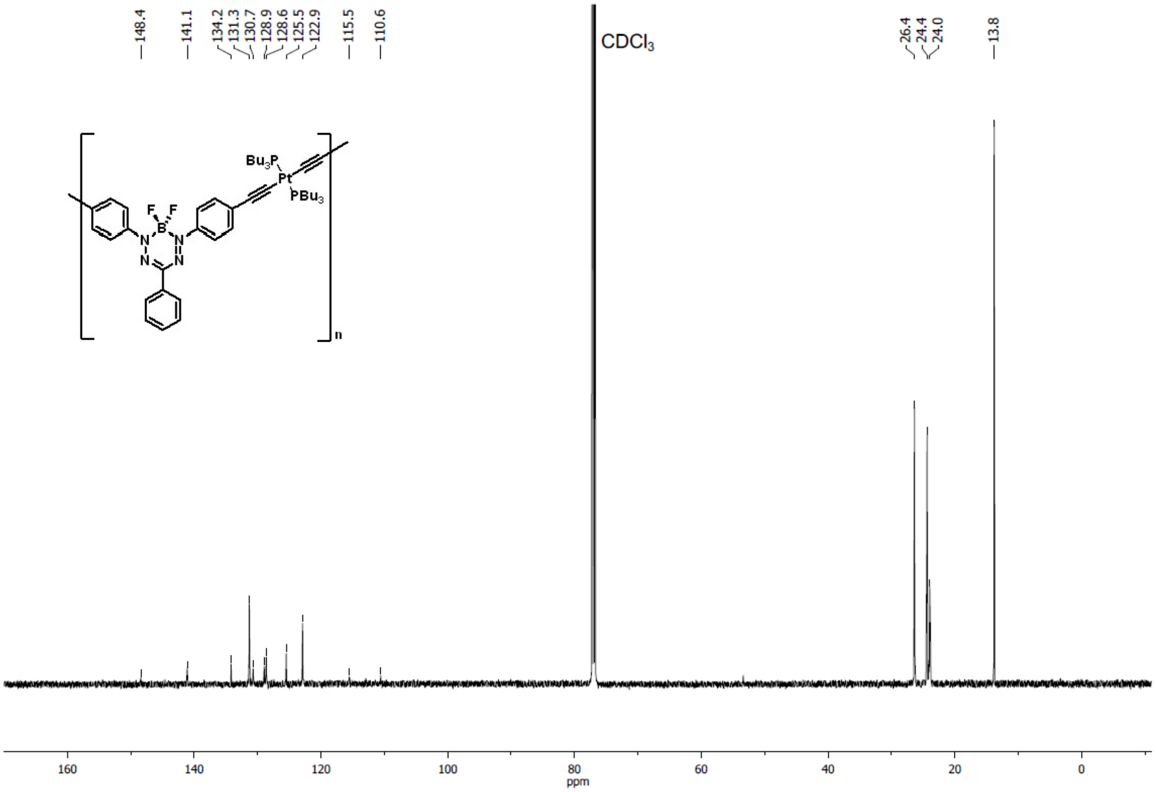

Fig. S2 ^{13}C{^{1}H} NMR spectrum of polymer **2** in CDCl$_3$.

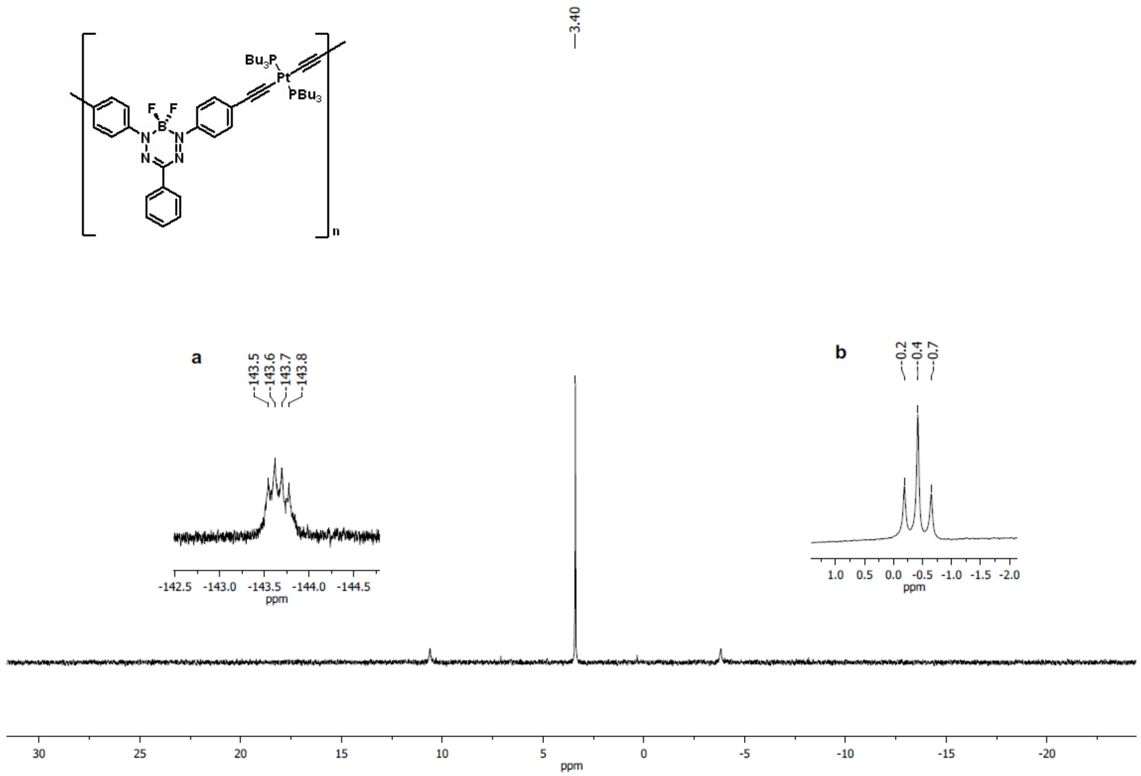

Fig. S3 ^{31}P{^{1}H}, ^{19}F (inset a) and ^{11}B (inset b) NMR spectra of polymer **2** in CDCl$_3$.

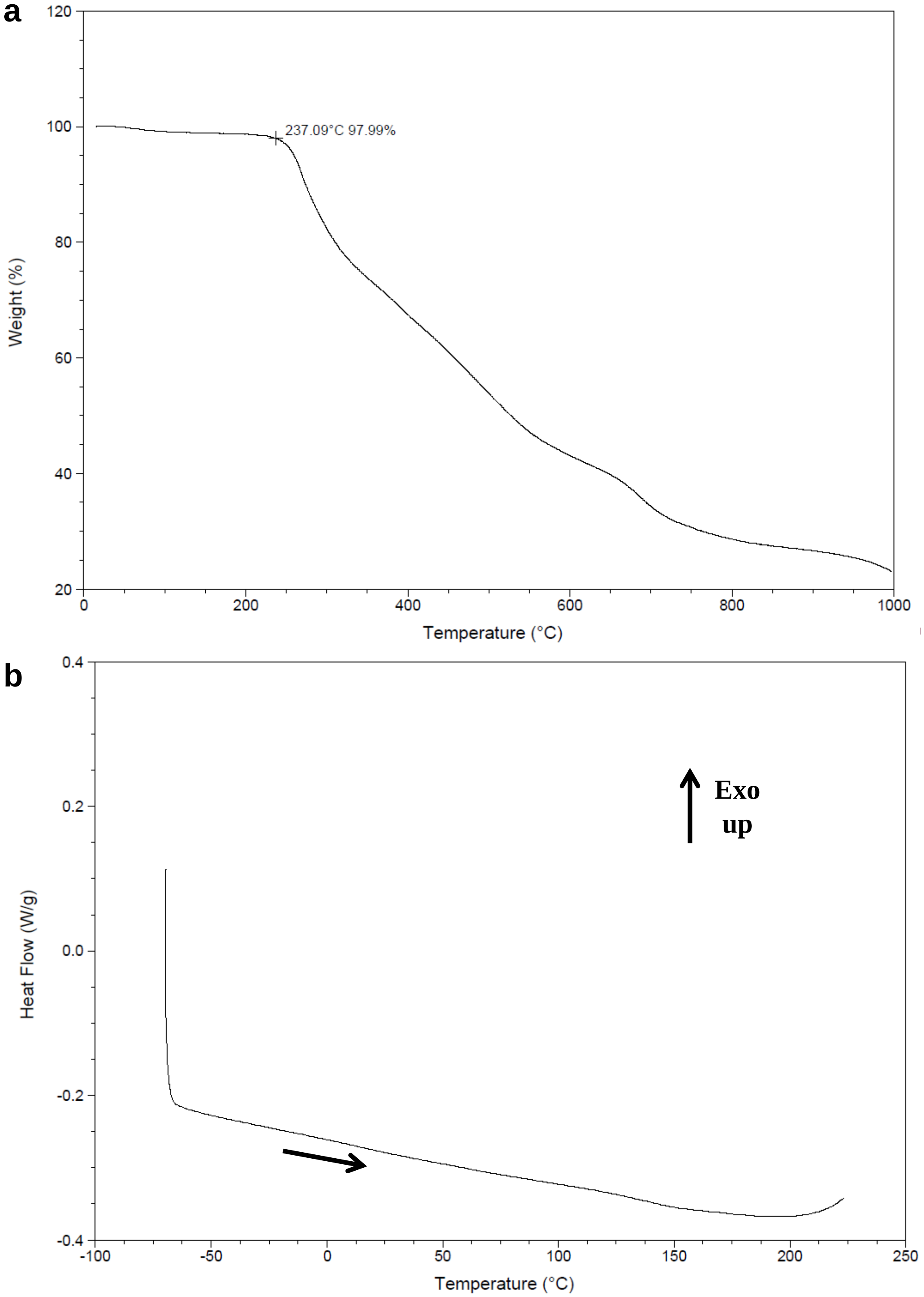

Fig. S4 (a) Thermal gravimetric analysis and (b) differential scanning calorimetry data recorded for polymer **2**.

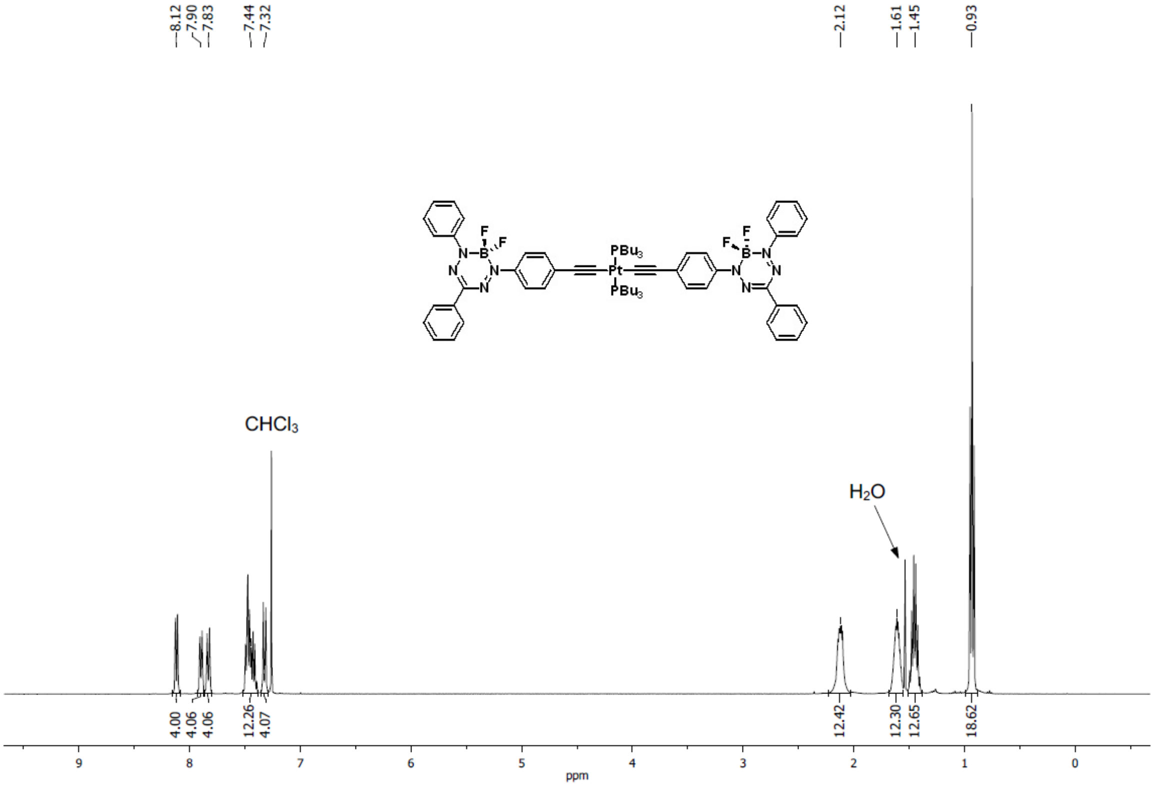

Fig. S5 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

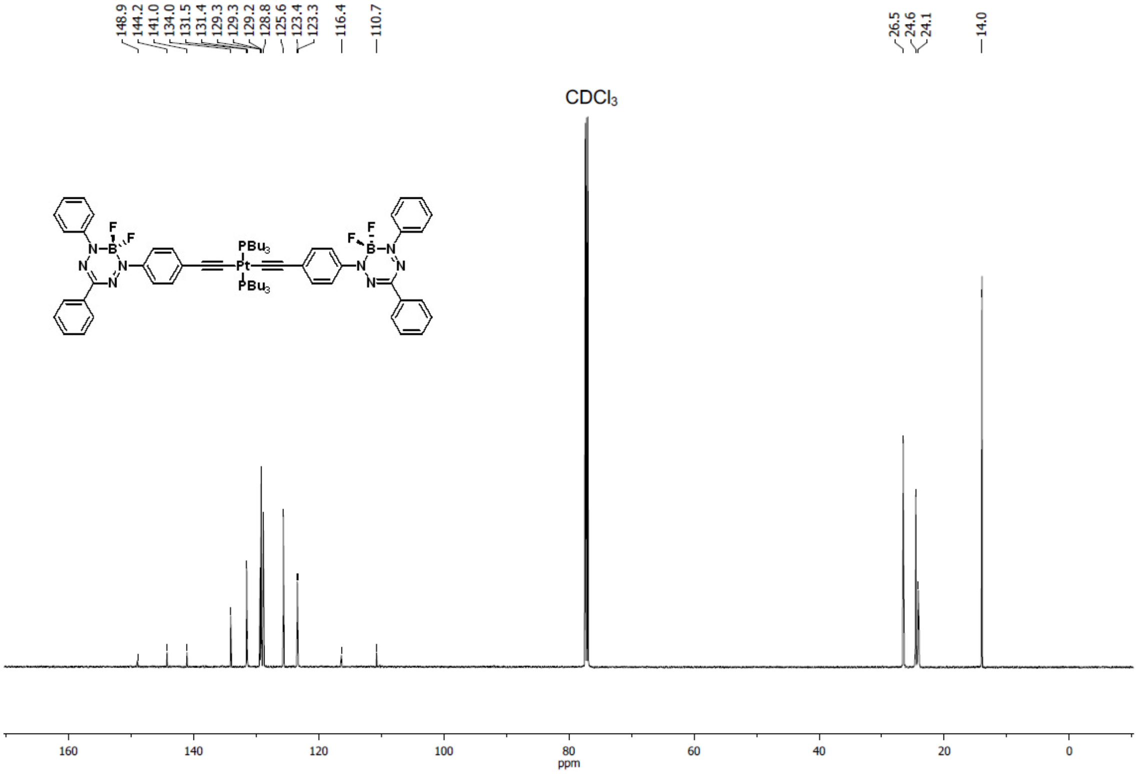

Fig. S6 $^{13}C\{^1H\}$ NMR spectrum of compound **3** in $CDCl_3$.

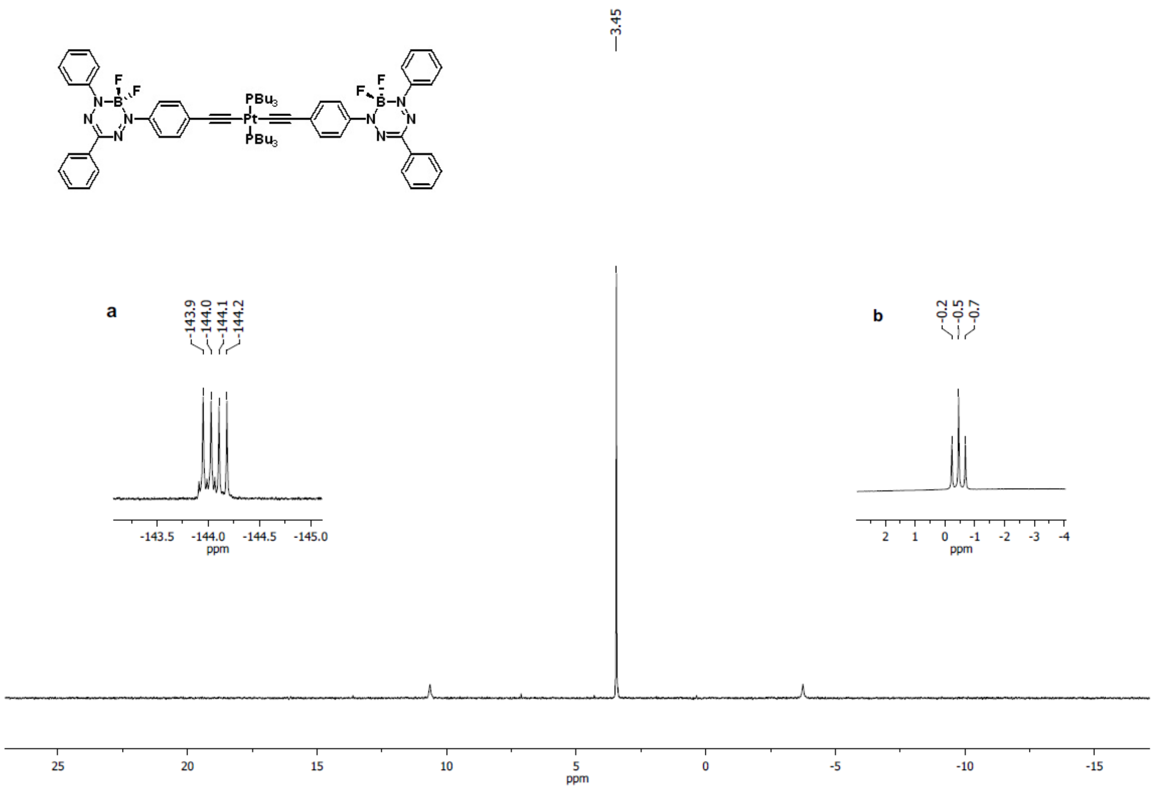

Fig. S7 $^{31}P\{^{1}H\}$, ^{19}F (inset a) and ^{11}B (inset b) NMR spectra of compound **3** in $CDCl_3$.

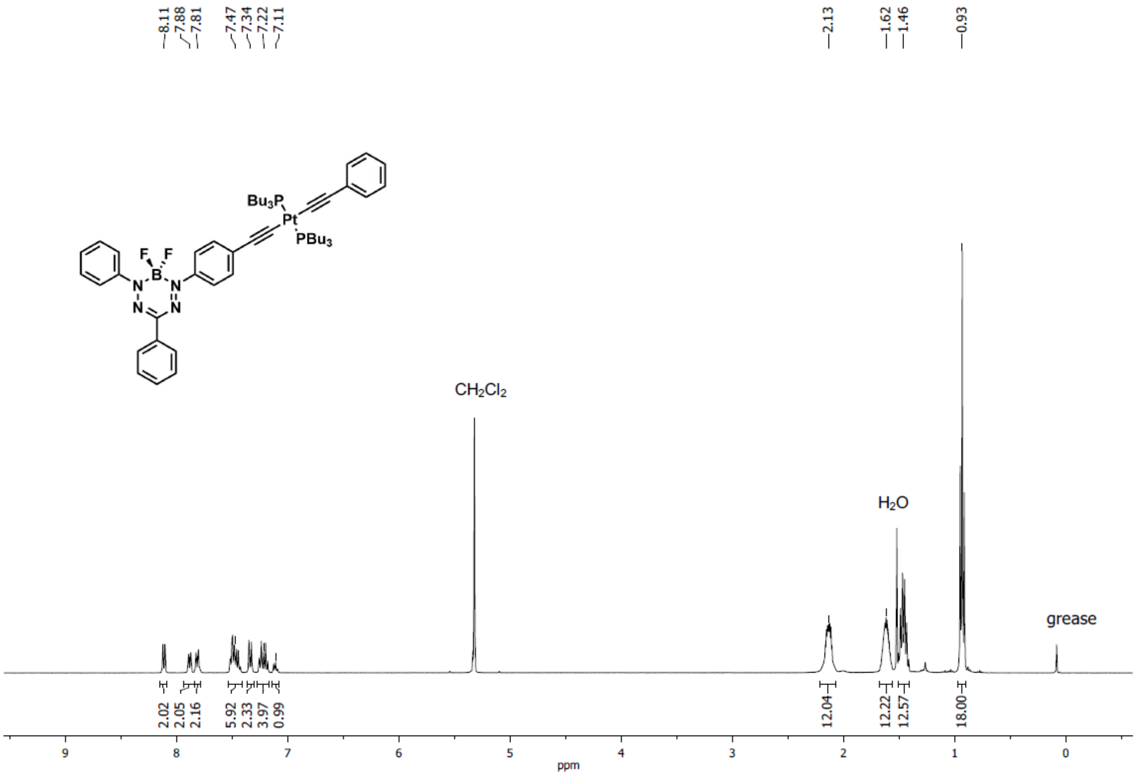

Fig. S8 ^{1}H NMR spectrum of compound **4** in CD_2Cl_2.

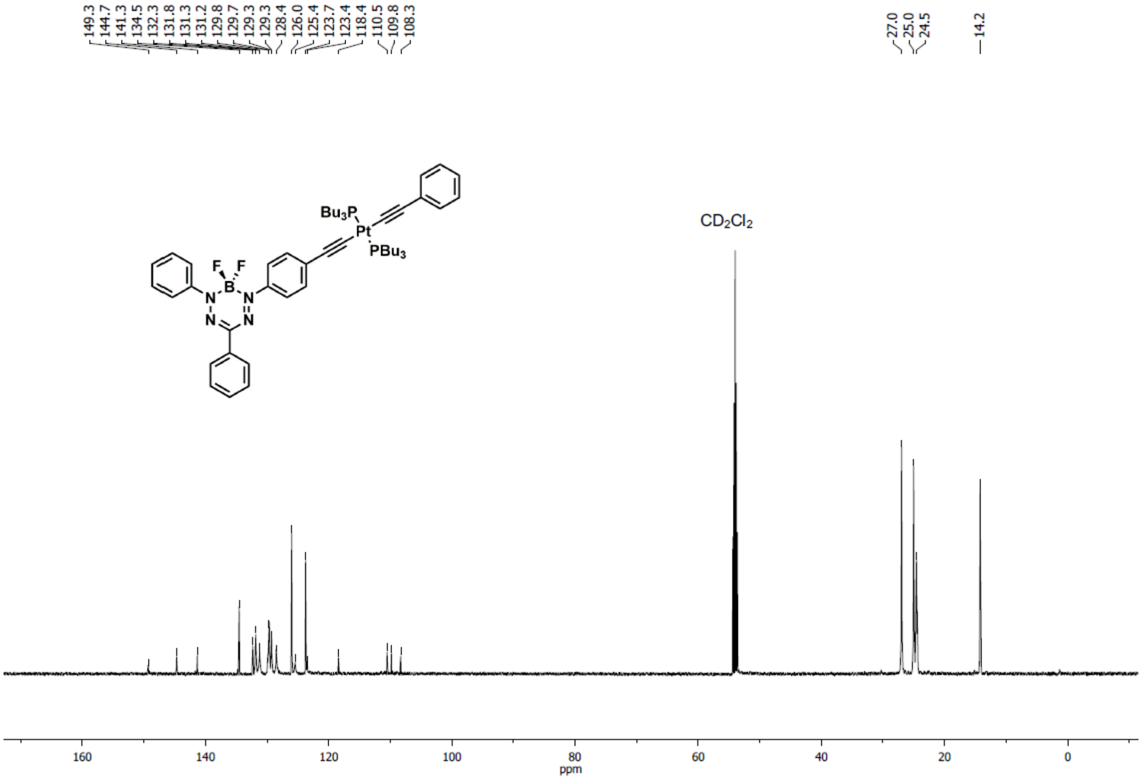

Fig. S9 $^{13}C\{^1H\}$ NMR spectrum of compound **4** in CD_2Cl_2.

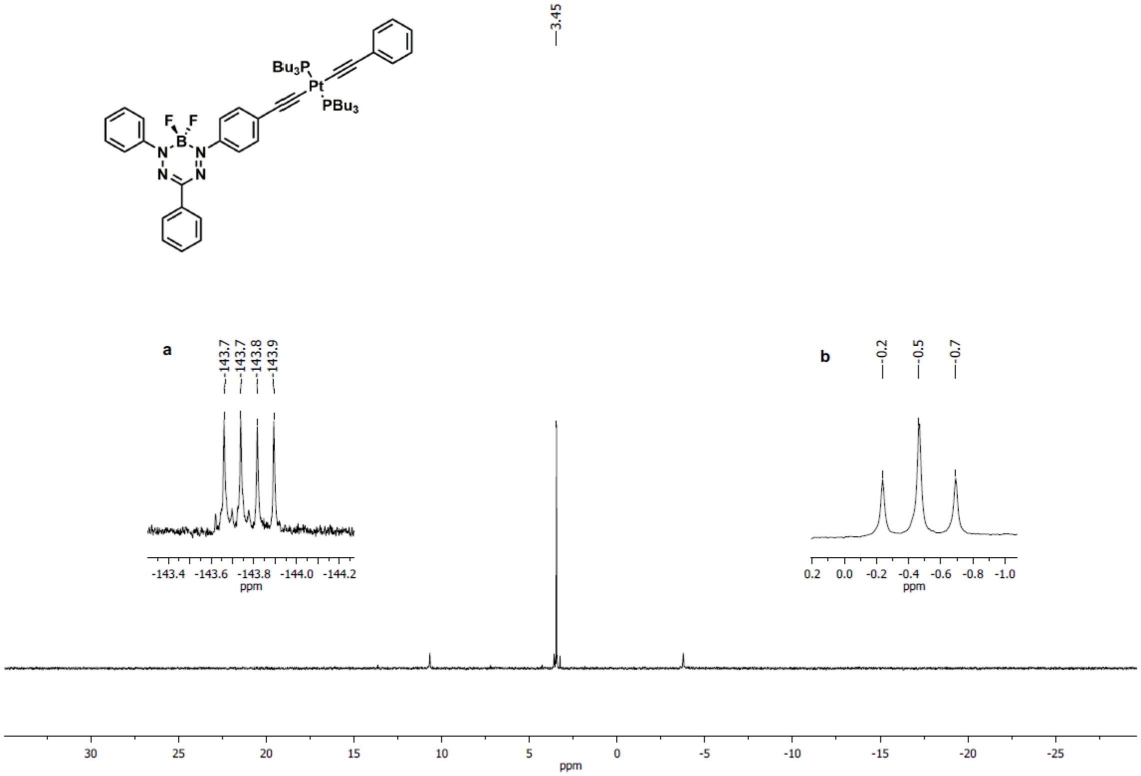

Fig. S10 $^{31}P\{^1H\}$, ^{19}F (inset a) and ^{11}B (inset b) NMR spectra of compound **4** in CD_2Cl_2.

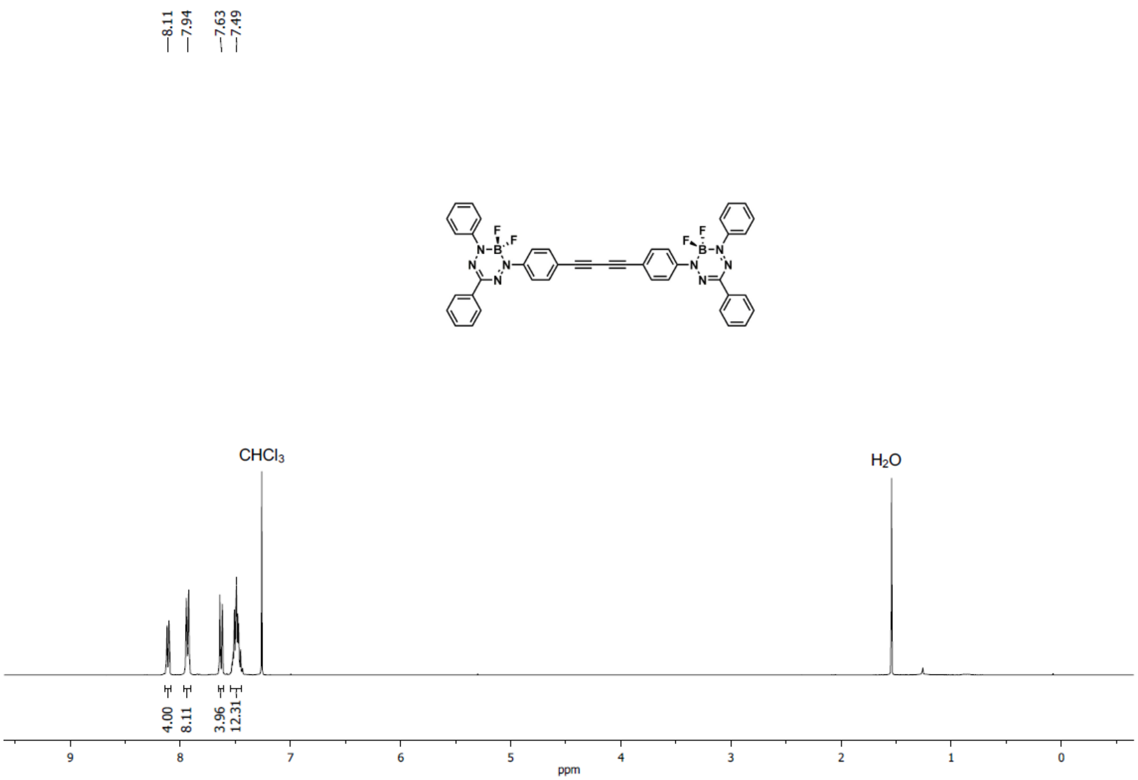

Fig. S11 ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

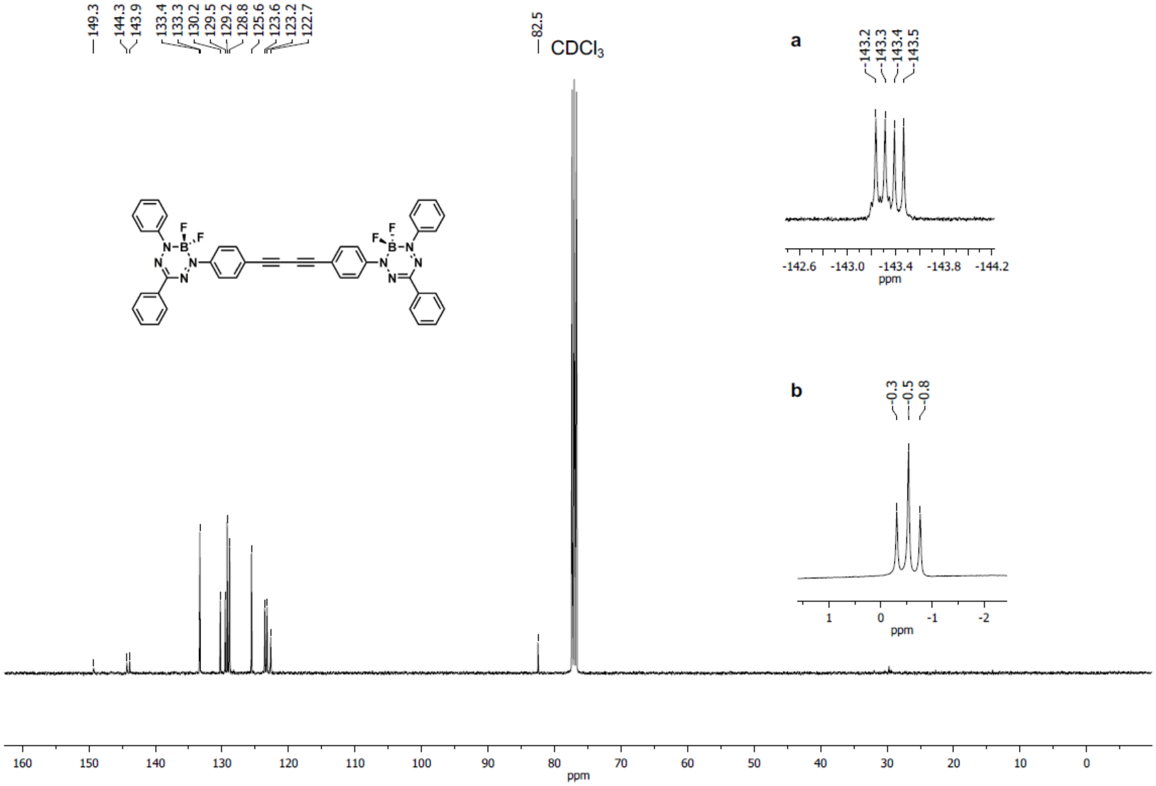

Fig. S12 $^{13}C\{^1H\}$, ^{19}F (inset a) and ^{11}B (inset b) NMR spectra of compound **5** in $CDCl_3$.

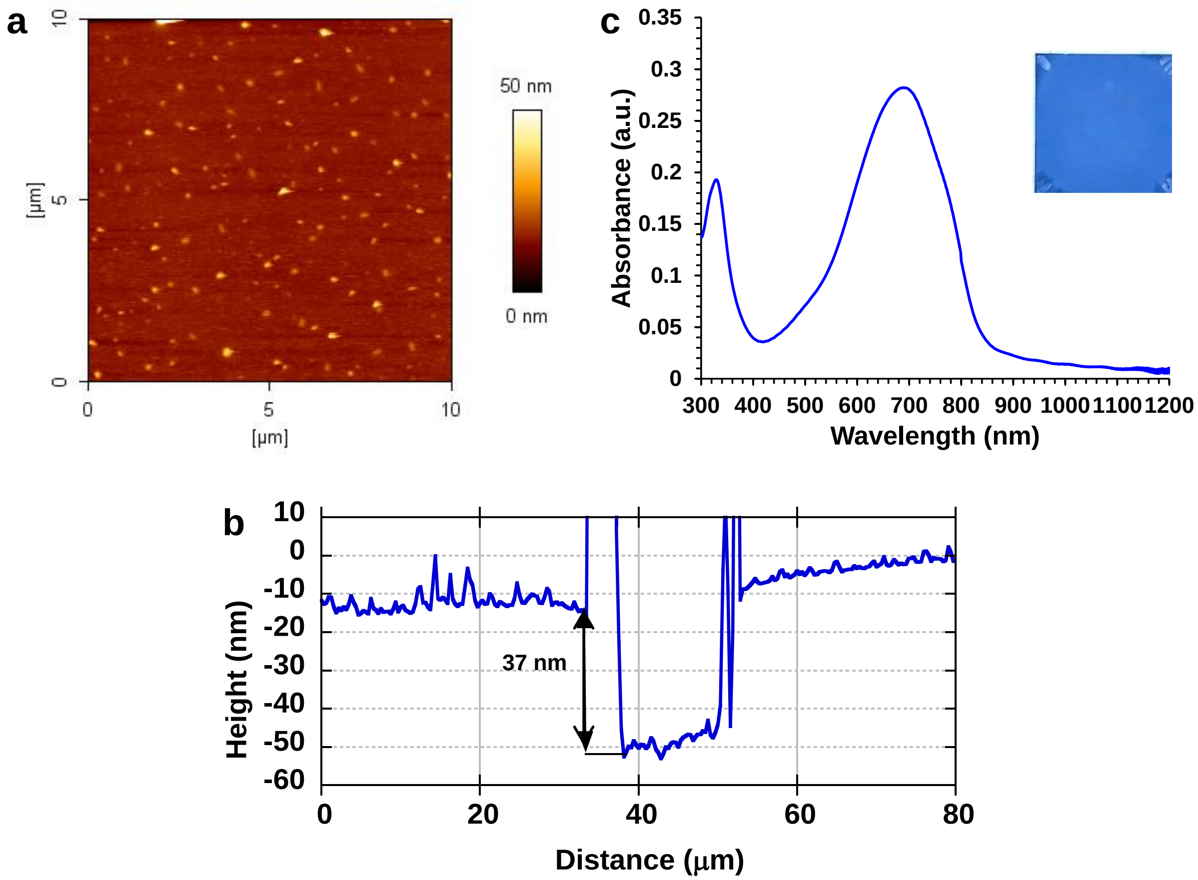

Fig. S13 (a) Atomic force microscopy topography of a 40 ± 5 nm thick film of polymer **2**. (b) Cross section used to determine the thickness and (c) UV-vis absorption spectrum and photograph (inset) of the same film. The RMS roughness of the film presented in panel (a) is 1.74 nm.

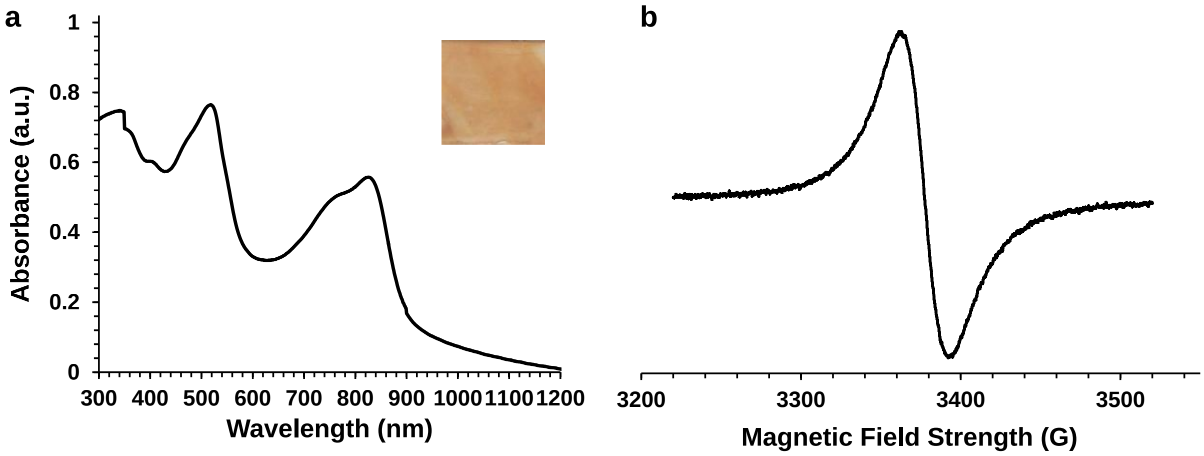

Fig. S14 (a) UV-vis absorption spectrum and photograph (inset) of a film of the reduced form of polymer **2** (1.5 equiv. of cobaltocene). (b) EPR spectrum (g = 2.0042) recorded for a solution of the reduced form of polymer **2** (1.5 equiv. of cobaltocene) in a 1:20 (v/v) mixture of CH_3CN and CH_2Cl_2 (290 µM).

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