

## Supporting Information for

# Pyridine-Based Poly(aryleneethynylene)s: A Study on Anionic Side Chain Density and Their Influence on Optical Properties and Metallocromicity

Markus Bender,<sup>†</sup> Kai Seehafer,<sup>†</sup> Marlene Findt<sup>†</sup> and Uwe H. F. Bunz<sup>\*,†,‡</sup>

<sup>†</sup> Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

<sup>‡</sup>CAM, Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 225, 69120 Heidelberg, Germany

[uwe.bunz@oci.uni-heidelberg.de](mailto:uwe.bunz@oci.uni-heidelberg.de)

## Contents

<b>1. General Informations</b>	<b>2</b>
<b>2. Synthetic Details and Analytical Data</b>	<b>5</b>
<b>3. <sup>1</sup>H NMR Spectra</b>	<b>23</b>
<b>4. UV/VIS Spectra</b>	<b>44</b>
<b>5. Metall Sensing Data</b>	<b>44</b>
<b>6. pH-Titration Data</b>	<b>44</b>
<b>7. Evaluation of Stern-Volmer Constants</b>	<b>47</b>
<b>8. Supplemental References</b>	<b>55</b>

## 1. General Informations

**Analytical thin layer chromatography (TLC)** was performed on Macherey & Nagel Polygram® SIL G/UV254 precoated plastic sheets. Components were visualized by observation under UV light (254 nm or 365 nm) or in the case of UV-inactive substances by using the suitably coloring solutions. The following coloring solutions were used for the visualization of UV-inactive substances:

KMnO<sub>4</sub> solution: 2.0 g KMnO<sub>4</sub>, 10.0 g K<sub>2</sub>CO<sub>3</sub>, 0.3 g NaOH, 200 mL distilled water.

Cer solution: 10.0 g Ce(SO)<sub>4</sub>, 25 g phosphomolybdic acid hydrate, 1 L distilled water, 50 mL conc. H<sub>2</sub>SO<sub>4</sub>.

**Flash column chromatography** was carried out using silica gel S (0.032 mm-0.062 mm), purchased from Sigma Aldrich, according to G. Nill, unless otherwise stated.<sup>1</sup>

**Dialysis** was realized with regenerated cellulose tubular membranes (ZelluTrans, Carl Roth®) with a molecular weight cut-off of 3500 Da against deionized (DI) water.

**Melting points** (m. p.) were determined in open glass capillaries on a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK) and are not corrected.

**<sup>1</sup>H NMR spectra** were recorded at room temperature on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance III 400 (400 MHz) and Bruker Avance III 600 (600 MHz). The data were interpreted in first order spectra. The spectra were recorded in CDCl<sub>3</sub> or D<sub>2</sub>O as indicated in each case. Chemical shifts are reported in δ units relative to the solvent residual peak (CHCl<sub>3</sub> in CDCl<sub>3</sub> at δ<sub>H</sub> = 7.27 ppm, HDO in D<sub>2</sub>O at δ<sub>H</sub> = 4.79 ppm) or TMS (δ<sub>H</sub> = 0.00 ppm).<sup>2</sup> The following abbreviations are used to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), etc., bs (broad signal), m (multiplet). All NMR spectra were integrated and processed using ACD/Spectrum Processor.

**<sup>13</sup>C NMR spectra** were recorded at room temperature on the following spectrometers: Bruker Avance III 300 (75 MHz), Bruker Avance III 400 (100 MHz) and Bruker Avance III 600 (150 MHz). The spectra were recorded in CDCl<sub>3</sub> or D<sub>2</sub>O as indicated in each case. Chemical shifts are reported in  $\delta$  units relative to the solvent signal: CDCl<sub>3</sub> [ $\delta_C = 77.16$  ppm (central line of the triplet)] or TMS ( $\delta_C = 0.00$  ppm).

**High resolution mass spectra (HR-MS)** were either recorded on a Bruker ApexQe hybrid 9.4 T FT-ICR-MS (ESI<sup>+</sup>, DART<sup>+</sup>), a Finnigan LCQ (ESI<sup>+</sup>) or a JEOL JMS-700 (EI<sup>+</sup>) mass spectrometer at the Organisch-Chemisches Institut der Universität Heidelberg.

**IR spectra** were recorded on a JASCO FT/IR-4100. Substances were applied as a film, solid or in solution. The obtained data was processed with the software JASCO Spectra Manager™ II.

**Elemental analyses** were carried out at the Organisch-Chemisches Institut der Universität Heidelberg.

Used **buffer solutions**: pH 1 (HCl/KCl), pH 2 (KH phthalate/HCl), pH 3 (citric acid/NaOH/NaCl), pH 4 (citric acid/NaOH/NaCl), pH 5 (citric acid/NaOH), pH 6 (citric acid/NaOH), , pH 8 (borax/HCl), pH 9 (KH phthalate/NaOH), pH 10 (borax/NaOH), pH 11 (boric acid/NaOH/KCl), pH 12 (Na<sub>2</sub>HPO<sub>4</sub>/NaOH), pH 13 (glycine/NaOH/NaCl). All commercially available at Sigma Aldrich. Buffer pH 7 [PIPES (c = 0.05 M)/KClO<sub>4</sub> (c = 0.1 M)] was made with PIPES (1,4-piperazinediethanesulfonic acid) commercially available at Sigma Aldrich.

**Gel Permeation Chromatography (GPC)**: Number- ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights and polydispersities (PDI,  $M_w/M_n$ ) were determined by GPC versus polystyrene standards. Measurements were carried out at room temperature in chloroform with PSS-SDV columns (8.0 mm x 30.0 mm, 5  $\mu$ m particles, 10<sup>2</sup>-, 10<sup>3</sup>- and 10<sup>5</sup>- Å pore size) on a Jasco PU-2050 GPC unit equipped with a Jasco UV-2075 UV- and a Jasco RI-2031 RI-detector.

All **absorption and emission spectra** were recorded using a Jasco V660 and Jasco FP6500 spectrometer.

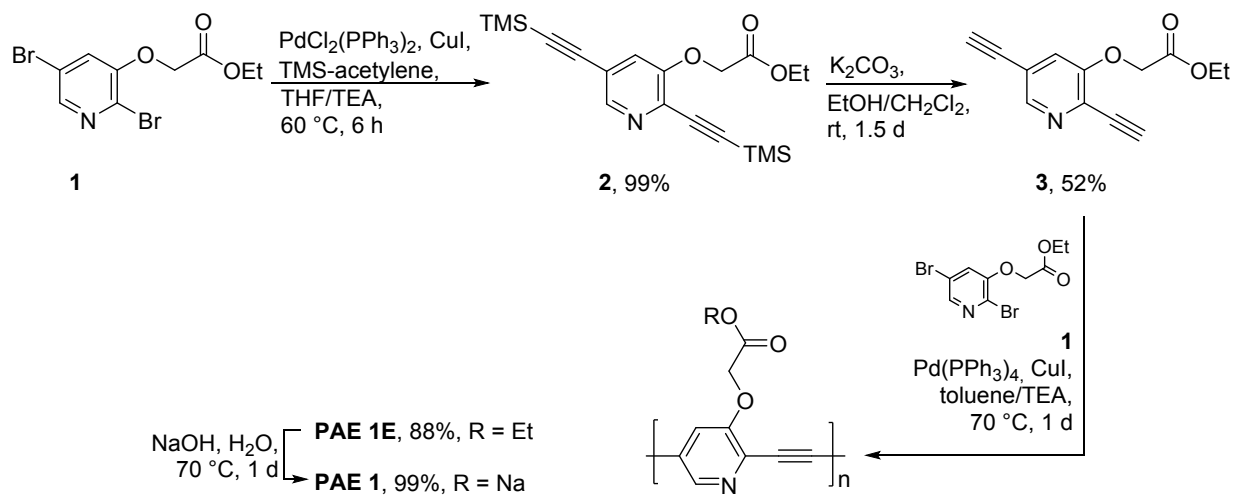
**Pictures** were taken with a Canon EOS 7D camera equipped with an EF-S 60mm F/2.8 Macro lens.

**Fluorescence lifetimes  $\tau$**  were acquired by an exponential fit according to the least mean square with commercially available software HORIBA Scientific Decay Data Analyses 6 (DAS6) version 6.4.4. The luminescence decays were recorded with a HORIBA Scientific Fluorocube single photon counting system operated with HORIBA Scientific DataStation version 2.2.

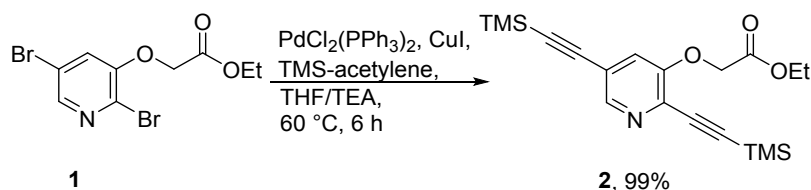
**Quantum yields  $\Phi$**  were measured by using the comparative method with quinine sulfate in 0.1 N sulfuric acid as a reference ( $\Phi = 0.54$ ) according to the literature.<sup>3</sup>

## 2. Synthetic Details and Analytical Data

### Scheme 1. Route to PAEs 1



### Scheme 2. Synthesis of 2

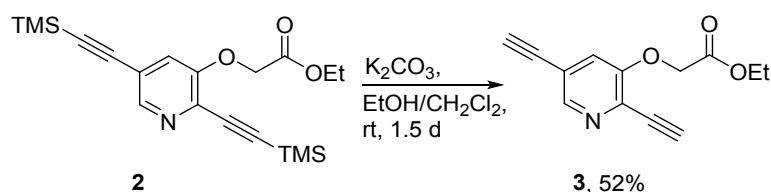


Compound 1 was synthesized according to the literature.<sup>4</sup>

**Synthesis of 2.** Compound 1 (350 mg, 1.03 mmol) was dissolved in a degassed mixture of THF/ $\text{NEt}_3$  (2:1, 4 mL/2 mL).  $\text{PdCl}_2(\text{PPh}_3)_2$  (36 mg, 52  $\mu\text{mol}$ ) and CuI (10 mg, 52  $\mu\text{mol}$ ) were added, then TMS-acetylene (370  $\mu\text{L}$ , 2.60 mmol) was added dropwise and the resulting mixture was stirred for 6 h at 60 °C. Saturated aqueous  $\text{NH}_4\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel [petroleum ether/ethyl acetate (10/1)] to give compound 2 (380 mg, 1.02 mmol, 99%) as colorless solid (m. p. 77 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.29 (d,  $J$  = 1.6 Hz, 1 H), 7.16 (d,  $J$  = 1.6 Hz, 1 H), 4.70 (s, 2 H), 4.29 (q,  $J$  = 7.1 Hz, 2 H), 1.31 (t,  $J$  = 7.1 Hz, 3 H), 0.29 (s, 9 H), 0.26 (s, 9 H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.96,

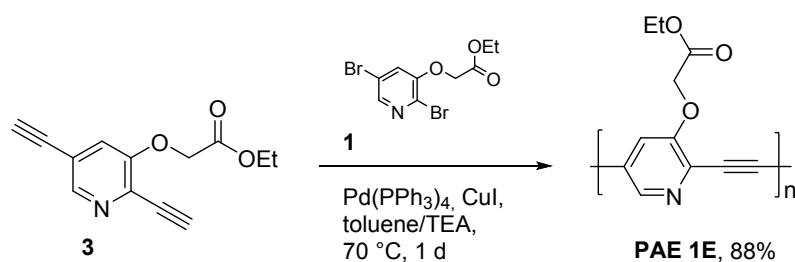
155.04, 146.15, 133.38, 123.16, 120.21, 102.47, 101.03, 100.47, 99.28, 66.43, 61.78, 14.30, -0.11, -0.13 ppm. IR (cm<sup>-1</sup>):  $\nu$  2957, 2898, 2163, 1769, 1581, 1454, 1403, 1270, 1246, 1212, 1157, 1113, 1078, 1024, 996, 861, 835, 755, 697, 627, 594, 575, 543, 502, 485, 459, 417. HR-MS (DART<sup>+</sup>):  $m/z$  calcd. for C<sub>38</sub>H<sub>55</sub>N<sub>2</sub>O<sub>6</sub>Si<sub>4</sub><sup>+</sup> 747.3132 [M<sub>2</sub>+H]<sup>+</sup>; found 747.3188. C<sub>19</sub>H<sub>27</sub>NO<sub>3</sub>Si<sub>2</sub> (373.60): calcd. C 61.08, H 7.28, N 3.75, found C 60.61, H 7.29, N 3.60.

### Scheme 3. Synthesis of 3



**Synthesis of 3.** Compound **2** (380 mg, 1.02 mmol) was dissolved in a mixture of EtOH/CH<sub>2</sub>Cl<sub>2</sub> (1:1, 10 mL/10 mL). K<sub>2</sub>CO<sub>3</sub> (1.41 g, 10.2 mmol) was added and the resulting mixture was stirred for 1.5 d at ambient temperature. Water and CH<sub>2</sub>Cl<sub>2</sub> were added, the aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel [petroleum ether/ethyl acetate (3/1)] to give compound **3** (122 mg, 0.53 mmol, 52%) as colorless solid (m. p. 122 °C). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.34 (d,  $J$  = 1.5 Hz, 1 H), 7.18 (d,  $J$  = 1.4 Hz, 1 H), 4.74 (s, 2 H), 4.28 (q,  $J$  = 7.1 Hz, 2 H), 3.51 (s, 1 H), 3.30 (s, 1 H), 1.30 (t,  $J$  = 7.1 Hz, 3 H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 167.77, 155.21, 146.08, 132.88, 122.58, 119.70, 83.86, 82.53, 79.83, 79.02, 65.99, 61.96, 14.26 ppm. IR (cm<sup>-1</sup>):  $\nu$  3249, 3167, 2982, 2107, 1753, 1582, 1541, 1465, 1455, 1409, 1382, 1297, 1242, 1213, 1143, 1097, 1059, 1013, 980, 905, 877, 861, 810, 754, 712, 695, 680, 626, 604, 557, 484, 473, 418. HR-MS (DART<sup>+</sup>):  $m/z$  calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub><sup>+</sup> 459.1551 [M<sub>2</sub>+H]<sup>+</sup>; found 459.1547. C<sub>13</sub>H<sub>11</sub>NO<sub>3</sub> (229.24): calcd. C 68.11, H 4.84, N 6.11, found C 67.93, H 5.03, N 5.93.

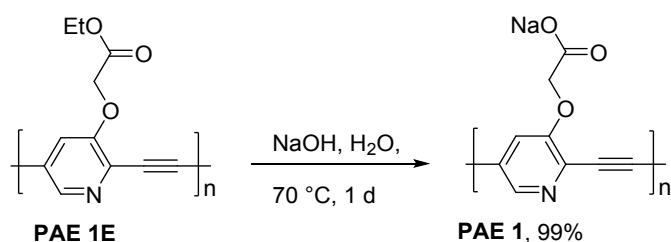
#### Scheme 4. Synthesis of PAE 1E



Compound **1** was synthesized according to the literature.<sup>4</sup>

**Synthesis of PAE 1E.** Monomer **1** (172 mg, 0.51 mmol) and monomer **3** (116 mg, 0.51 mmol) were dissolved in a mixture of degassed toluene/ $\text{NEt}_3$  (1.5:1, 9 mL/6 mL).  $\text{Pd}(\text{PPh}_3)_4$  (29 mg, 25  $\mu\text{mol}$ ) and  $\text{CuI}$  (4.8 mg, 25  $\mu\text{mol}$ ) were added and the mixture was stirred at  $70^\circ\text{C}$  for 24 h. Saturated aqueous  $\text{NH}_4\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. Two times, the crude product was dissolved in a small amount of  $\text{CHCl}_3$  and slowly added to an excess of  $\text{MeOH}$  to give PAE 1E as orange solid (178 mg, 88%). The  $M_n$  was estimated to be  $3.2 \times 10^3$  with a PDI of 1.2.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.17\text{-}8.60$  (m, 1 H),  $7.29\text{-}7.75$  (m, 1 H),  $4.63\text{-}5.05$  (m, 2 H),  $4.17\text{-}4.43$  (m, 2 H),  $1.23\text{-}1.29$  (m, 3 H) ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  3060, 2979, 2931, 2364, 2194, 2159, 2033, 1746, 1577, 1560, 1532, 1478, 1434, 1401, 1296, 1194, 1111, 1096, 1061, 1018, 895, 857, 753, 694, 620, 589, 566, 542, 534, 518, 509, 499, 493, 485, 476, 466, 457, 453, 435, 426, 419, 407. Due to low solubility,  $^{13}\text{C NMR}$  spectrum could not be obtained.

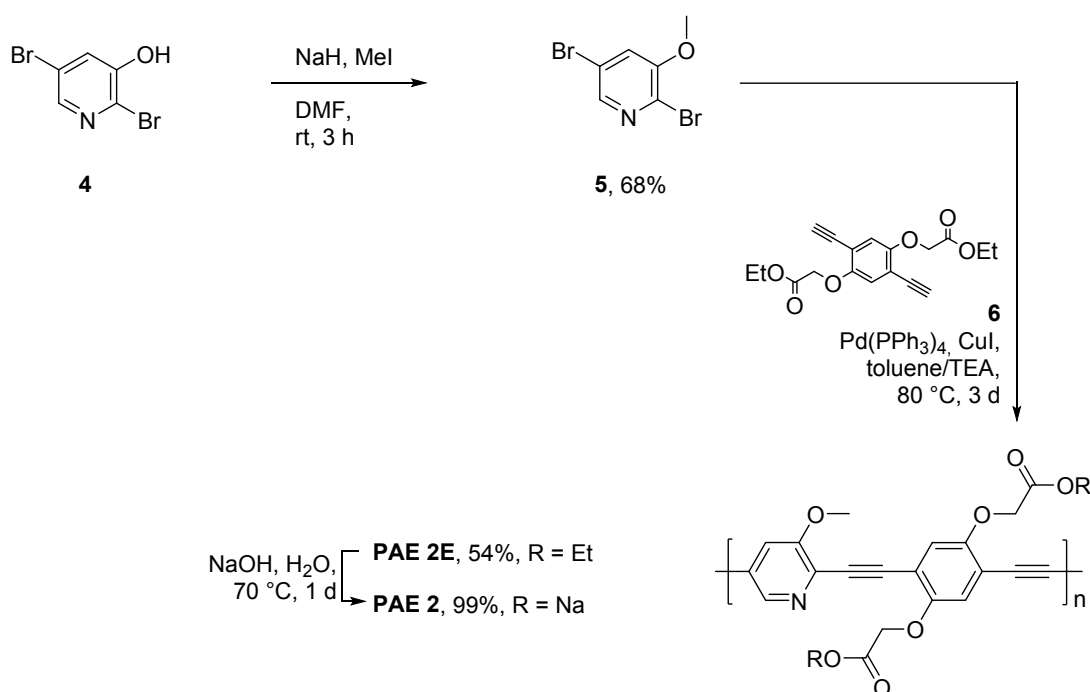
#### Scheme 5. Synthesis of PAE 1



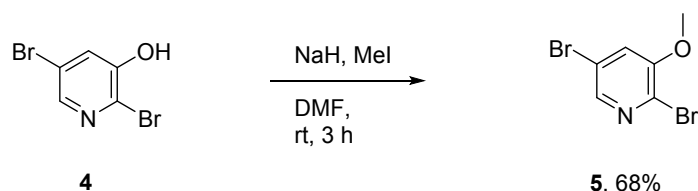
**Synthesis of PAE 1.** To a mixture of PAE 1E (70 mg, 0.34 mmol) and water (20 mL),  $\text{NaOH}$  (272 mg, 6.8 mmol) was added and the resulting mixture was stirred at  $70^\circ\text{C}$  for 24 h. After

adjusting a pH of 7 (HCl) the aqueous mixture was dialyzed against DI H<sub>2</sub>O for 3 d. Freeze-drying gave **PAE 1** as spongy, dark orange solid (59 mg, 99%). The  $M_n$  and PDI result from **PAE 1E**. <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O): δ 6.80-8.38 (m, 2 H), 3.81-3.88 (s, 2 H) ppm. IR (cm<sup>-1</sup>): ν 3361, 3243, 3007, 2852, 1606, 1481, 1393, 1357, 1322, 1275, 1229, 1204, 1093, 1048, 955, 911, 862, 806, 687, 621, 527, 476, 464, 432, 413. Due to low solubility, <sup>13</sup>C NMR spectrum could not be obtained.

### Scheme 6. Route to PAEs 2



### Scheme 7. Synthesis of 5



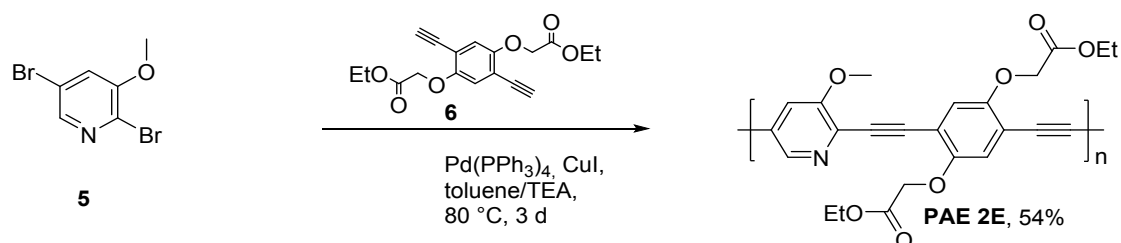
*Compound 4 was synthesized according to the literature.<sup>5,6</sup>*

**Synthesis of 5.** To a solution of compound **4** (1.13 g, 4.47 mmol) in DMF (20 mL), NaH (118 mg, 4.92 mmol) was added. After the hydrogen generation was finished, MeI (306 μL, 4.92 mmol) was added and the resulting mixture was stirred for 3 h at ambient temperature. Water



and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel [petroleum ether/ethyl acetate (8/1)] to give compound **5** (812 mg, 3.04 mmol, 68%) as yellowish solid (m. p. 74-75 °C).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.07 (d,  $J$  = 1.9 Hz, 1 H), 7.26 (d,  $J$  = 1.9 Hz, 1 H), 3.93 (s, 3 H) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.45, 141.96, 131.25, 121.68, 119.83, 56.65 ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  3063, 3045, 3001, 2943, 2857, 1772, 1754, 1557, 1539, 1462, 1441, 1412, 1387, 1304, 1270, 1251, 1199, 1186, 1175, 1111, 1055, 1003, 930, 904, 886, 862, 789, 742, 719, 684, 577, 502. HR-MS (ESI<sup>+</sup>):  $m/z$  calcd. for  $\text{C}_6\text{H}_6\text{NO}^{79}\text{Br}^{81}\text{Br}^+$  267.8790 [M+H]<sup>+</sup>; found 267.8796.  $\text{C}_6\text{H}_5\text{NOBr}_2$  (266.92): calcd. C 27.00, H 1.89, N 5.25, Br 59.87, found C 27.24, H 2.01, N 5.27, Br 59.68.

### Scheme 8. Synthesis of PAE 2E

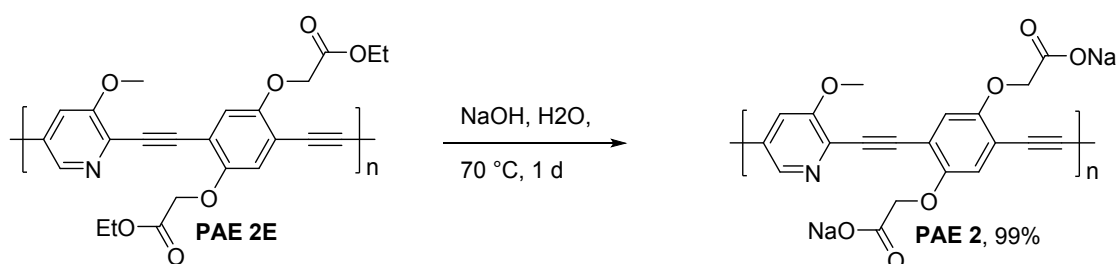


Compound **6** was synthesized according to the literature.<sup>7</sup>

**Synthesis of PAE 2E.** Monomer **5** (200 mg, 0.75 mmol) and monomer **6** (248 mg, 0.75 mmol) were dissolved in a mixture of degassed toluene/ $\text{NEt}_3$  (1.5:1, 15 mL/10 mL).  $\text{Pd}(\text{PPh}_3)_4$  (43 mg, 37  $\mu\text{mol}$ ) and  $\text{CuI}$  (7.0 mg, 37  $\mu\text{mol}$ ) were added and the mixture was stirred at 80 °C for 3 d. Saturated aqueous  $\text{NH}_4\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. Two times, the crude product was dissolved in a small amount of  $\text{CHCl}_3$  and slowly added to an excess of pentene to give **PAE 2E** as dark orange solid (176 mg, 54%). The  $M_n$  was estimated to be  $5.8 \times 10^3$  with a PDI of 1.5.  $^1\text{H}$

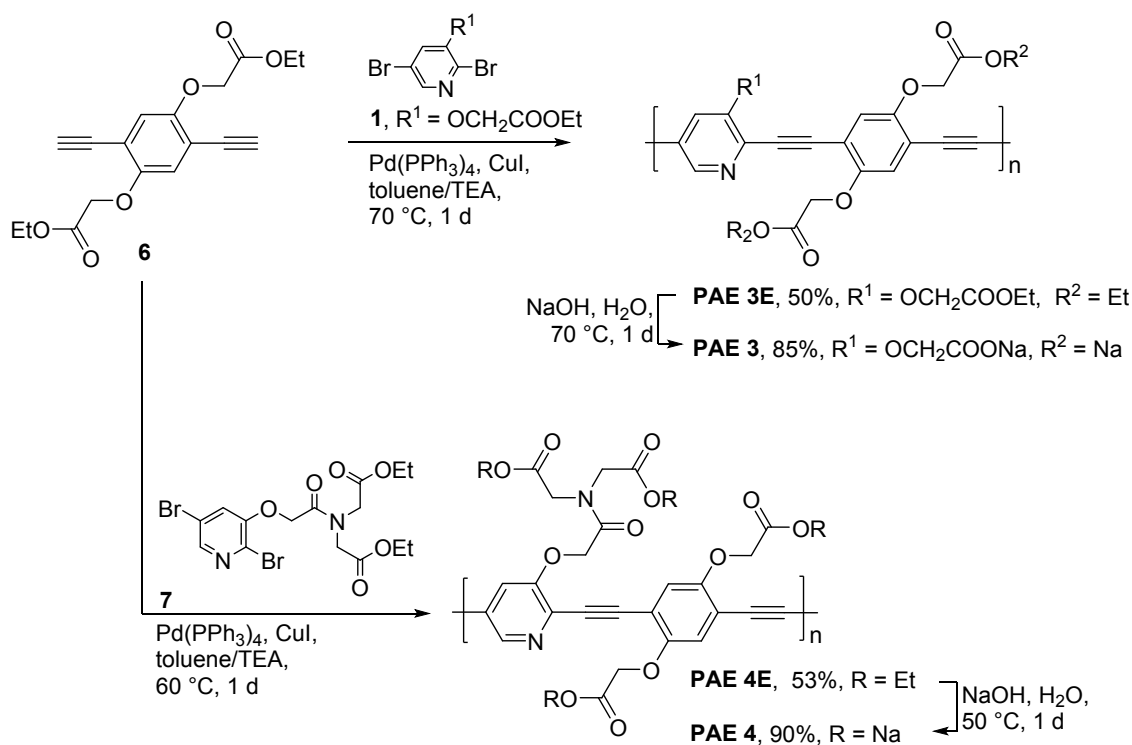
NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.13-8.52 (m, 1 H), 7.31-7.73 (m, 2 H), 6.99-7.14 (m, 1 H), 3.78-4.92 (m, 8 H), 3.06-3.18 (m, 3 H), 1.29-1.41 (m, 6 H) ppm. IR (cm<sup>-1</sup>):  $\nu$  3407, 2979, 2938, 2605, 2499, 1750, 1733, 1578, 1503, 1444, 1394, 1265, 1238, 1180, 1071, 1017, 852, 807, 754, 694, 623, 610, 580, 541, 521, 495, 429, 424, 416, 409. Due to low solubility, <sup>13</sup>C NMR spectrum could not be obtained.

### Scheme 9. Synthesis of PAE 2

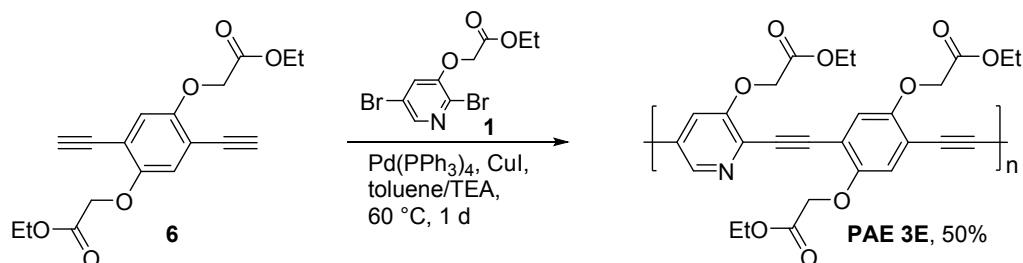


**Synthesis of PAE 2.** To a mixture of **PAE 2E** (100 mg, 0.23 mmol) and water (20 mL), NaOH (184 mg, 4.6 mmol) was added and the resulting mixture was stirred at 70 °C for 24 h. After adjusting a pH of 7 (HCl) the aqueous mixture was dialyzed against DI H<sub>2</sub>O for 3 d. Freeze-drying gave **PAE 2** as spongy, orange solid (86 mg, 99%). The  $M_n$  and PDI result from **PAE 2E**. <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O):  $\delta$  = 6.75-7.84 (m, 4 H), 3.01-3.20 (m, 7 H) ppm. IR (cm<sup>-1</sup>):  $\nu$  3208, 2925, 2868, 2211, 1584, 1505, 1397, 1327, 1245, 1119, 1053, 936, 666, 583, 449, 409. Due to low solubility, <sup>13</sup>C NMR spectrum could not be obtained.

### Scheme 10. Route to PAEs 3 and PAEs 4



### Scheme 11. Synthesis of PAE 3E



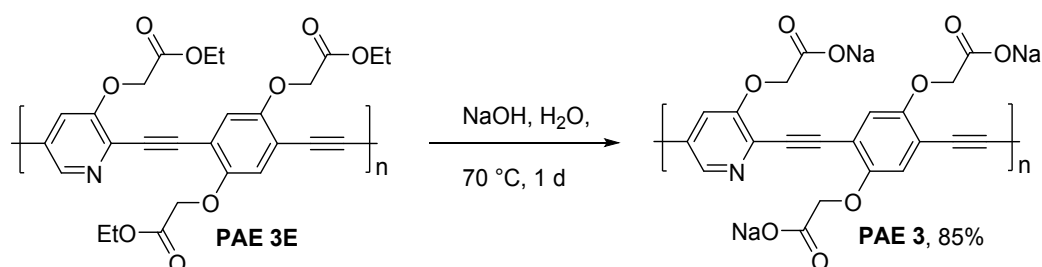
Compound **1** was synthesized according to the literature.<sup>4</sup>

Compound **6** was synthesized according to the literature.<sup>7</sup>

**Synthesis of PAE 3E.** Monomer **1** (270 mg, 0.80 mmol) and monomer **6** (263 mg, 0.80 mmol) were dissolved in a mixture of degassed toluene/ $\text{NEt}_3$  (2:1, 20 mL/10 mL).  $\text{Pd(PPh}_3)_4$  (46 mg, 40  $\mu\text{mol}$ ) and  $\text{CuI}$  (8.0 mg, 40  $\mu\text{mol}$ ) were added and the mixture was stirred at 70  $^\circ\text{C}$  for 24 h. Saturated aqueous  $\text{NH}_4\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. Two times, the crude product was dissolved in a small amount of  $\text{CHCl}_3$  and slowly added to an excess of  $\text{MeOH}$  to give **PAE 3E** as a red solid (202 mg, 50%).

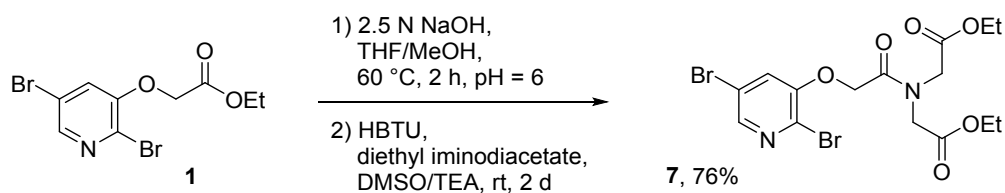
The  $M_n$  was estimated to be  $5.8 \times 10^3$  with a PDI of 1.5.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.24\text{-}8.63$  (m, 1 H),  $7.53\text{-}7.73$  (m, 1 H),  $7.32\text{-}7.48$  (m, 1 H),  $6.98\text{-}7.17$  (m, 1 H),  $4.70\text{-}4.91$  (m, 2 H),  $4.24\text{-}4.32$  (m, 2 H),  $3.57\text{-}3.67$  (m, 4 H),  $3.07\text{-}3.14$  (m, 4 H),  $1.34\text{-}1.45$  (m, 9 H) ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  3365, 3038, 2979, 2941, 2738, 2623, 2604, 2531, 2497, 2208, 1748, 1622, 1579, 1505, 1464, 1439, 1396, 1282, 1072, 1026, 945, 895, 852, 804, 753, 721, 694, 622, 594, 541. Due to low solubility,  $^{13}\text{C NMR}$  spectrum could not be obtained.

### Scheme 12. Synthesis of PAE 3



**Synthesis of PAE 3.** To a mixture of **PAE 3E** (100 mg, 0.20 mmol) and water (20 mL), NaOH (160 mg, 2.0 mmol) was added and the resulting mixture was stirred at 70 °C for 24 h. After adjusting a pH of 7 (HCl) the aqueous mixture was dialyzed against DI  $\text{H}_2\text{O}$  for 3 d. Freeze-drying gave **PAE 3** as spongy, dark orange solid (72 mg, 85%). The  $M_n$  and PDI result from **PAE 3E**.  $^1\text{H NMR}$  (600 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 6.62\text{-}8.37$  (m, 4 H),  $3.00\text{-}3.96$  (m, 6 H) ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  3396, 3220, 3059, 2926, 2877, 2650, 2203, 1726, 1604, 1588, 1504, 1402, 1282, 1191, 1064, 963, 915, 887, 465, 455, 444, 431, 417. Due to low solubility,  $^{13}\text{C NMR}$  spectrum could not be obtained

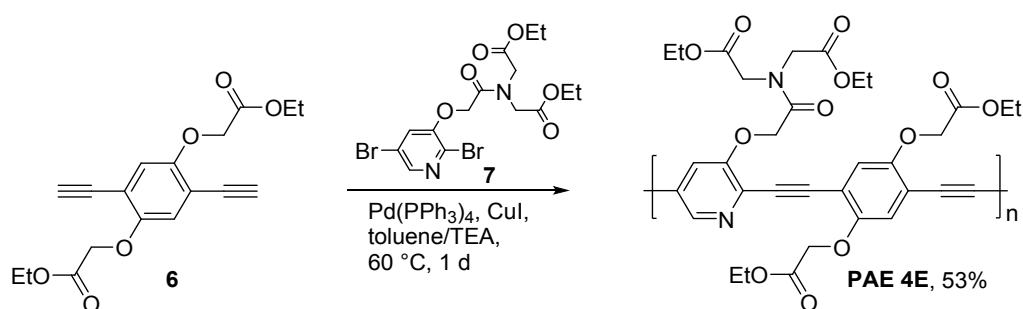
### Scheme 13. Synthesis of 7



*Compound 1 was synthesized according to the literature.<sup>4</sup>*

**Synthesis of 7.** To a solution of **1** (3.00 g, 8.85 mmol) in mixture of THF/MeOH (2:1, 60 mL/30 mL) was added 2.5 N NaOH<sub>aq</sub> (33 mL) and heated at 60 °C for 2 h. After cooling down to ambient temperature, the pH value was adjusted to 6.0. The solution was filtered and the solvent was removed under reduced pressure. The resulting white solid was solved in DMSO (30 mL) and TEA (5 mL), before diethyliminodiacetate (2.0 mL, 10.6 mmol) was added. The reaction was stirred for 2 d at room temperature. The solution was diluted with ethyl acetate, washed with H<sub>2</sub>O and NaCl<sub>aq</sub>. The organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated in vacuo. The resulting yellow oil was purified by flash chromatography on silica gel [petroleum ether/ethyl acetate (1/1)] to give compound **7** (3.24 g, 6.72 mmol, 76%) as colorless solid (m. p. 100-102 °C). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.11 (d, *J* = 1.9 Hz, 1 H), 7.39 (d, *J* = 1.9 Hz, 1 H), 4.88 (s, 2 H), 4.28 (s, 2 H), 4.19-4.25 (m, 4 H), 4.18 (s, 2 H), 1.25-1.30 (m, 6 H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 168.44, 168.30, 167.04, 151.74, 143.10, 130.99, 123.53, 119.66, 67.97, 62.18, 61.61, 49.74, 48.48, 14.10 ppm. IR (cm<sup>-1</sup>): ν 2964, 1736, 1665, 1561, 1546, 1475, 1450, 1417, 1398, 1372, 1351, 1299, 1271, 1248, 1214, 1190, 1124, 1088, 1051, 1024, 960, 867, 826, 743, 713, 687, 602, 576, 502, 425. HR-MS (EI<sup>+</sup>): *m/z* calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>6</sub>Br<sub>2</sub><sup>+</sup> 482.5989 [M+H]<sup>+</sup>; found 482.9577. C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Br<sub>2</sub> (482.13): calcd. C 37.37, H 3.76, N 5.81, Br 33.15, found C 37.13, H 3.74, N 5.65, Br 32.96.

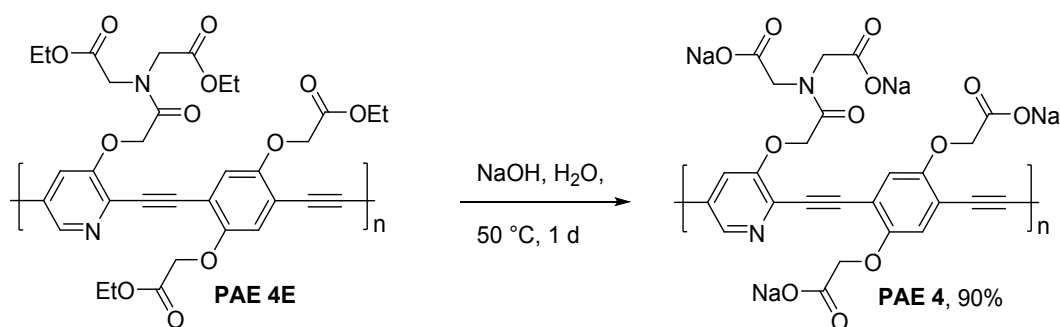
#### Scheme 14. Synthesis of PAE 4E



Compound **6** was synthesized according to the literature.<sup>7</sup>

**Synthesis of PAE 4E.** Monomer **6** (138 mg, 0.42 mmol) and monomer **7** (202 mg, 0.42 mmol) were dissolved in mixture of degassed toluene/ $\text{NEt}_3$  (1.5:1, 8.4 mL/5.6 mL).  $\text{Pd}(\text{PPh}_3)_4$  (24 mg, 21  $\mu\text{mol}$ )  $\text{CuI}$  (4 mg, 21  $\mu\text{mol}$ ) were added and the mixture was stirred at 60 °C for 24 h. Water and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. Two times, the crude product was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  and slowly added to an excess of pentane. **PAE 4E** was purified by gel permeation chromatography ( $\text{CHCl}_3$ ) to give an orange powder (152 mg, 53%). The  $M_n$  was estimated to be  $6.6 \times 10^3$  with a PDI of 2.6.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.29-8.48 (m, 1 H), 7.49-7.60 (m, 1 H), 6.99-7.22 (m, 2 H), 5.05-5.13 (m, 2 H), 4.69-4.80 (m, 4 H), 4.38-4.52 (m, 2 H), 4.27-4.35 (m, 4 H), 4.06-4.20 (m, 6 H), 1.24-1.36 (m, 9 H), 1.07-1.13 (m, 3 H) ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  2161, 1742, 1681, 1504, 1400, 1187, 1077, 1023, 861, 457, 434, 425, 414. Due to low solubility,  $^{13}\text{C}$  NMR spectrum could not be obtained.

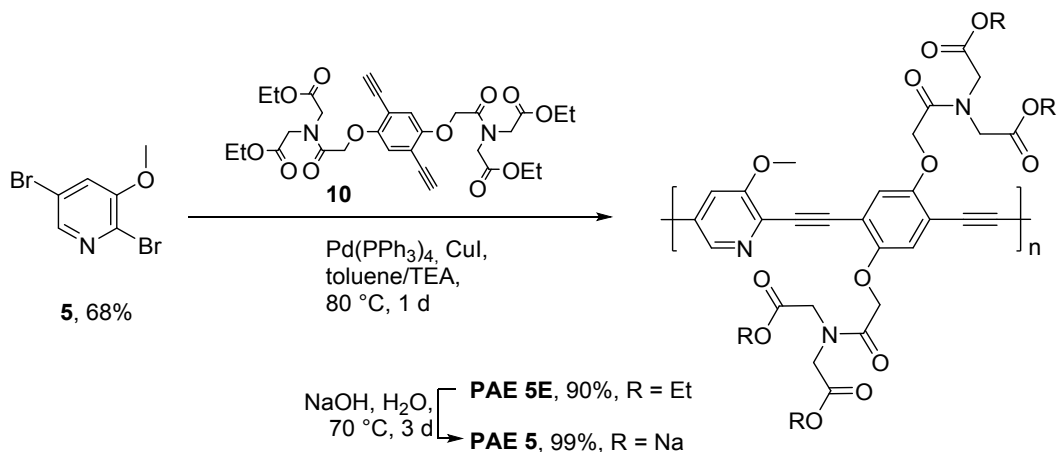
#### Scheme 15. Synthesis of PAE 4



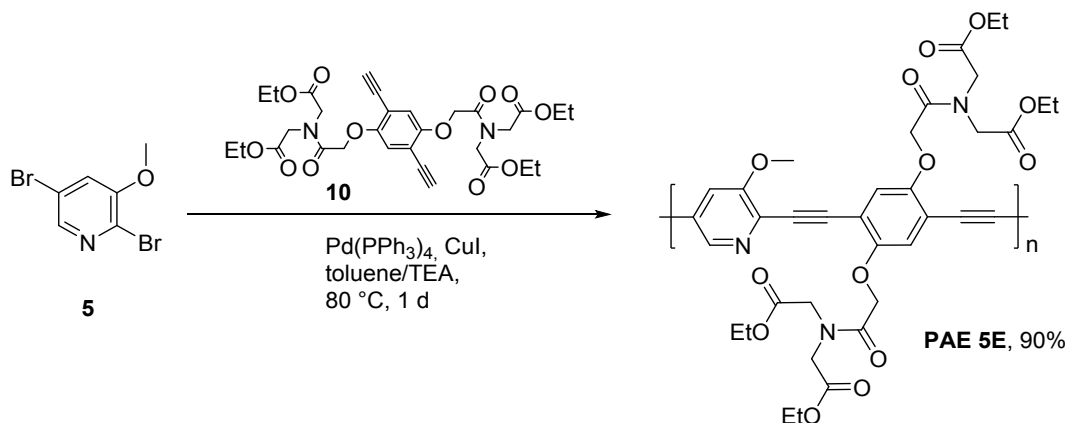
**Synthesis of PAE 4.** **PAE 4E** (70 mg, 0.10 mmol) was suspended in 2.5 N  $\text{NaOH}$  (2 mL) and refluxed at 50 °C for 24 h. After adjusting a pH of 7 ( $\text{HCl}$ ) the aqueous mixture was dialyzed against DI  $\text{H}_2\text{O}$  for 3 d. Freeze-drying gave **PAE 4** as fluffy, orange solid (58 mg, 90%). The  $M_n$  and PDI result from **PAE 4E**.  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 8.21-8.40 (m, 1 H), 7.62-7.74 (m, 1 H), 6.94-7.23 (m, 2 H), 4.96-5.21 (m, 2 H), 4.53-4.65 (m, 4 H), 3.93-4.12 (m, 4 H)

ppm. IR (cm<sup>-1</sup>):  $\nu$  2359, 1605, 1506, 1400, 1205, 1033, 868, 619, 486, 444, 418. Due to low solubility, <sup>13</sup>C NMR spectrum could not be obtained.

### Scheme 16. Route to PAEs 5



### Scheme 17. Synthesis of PAE 5E



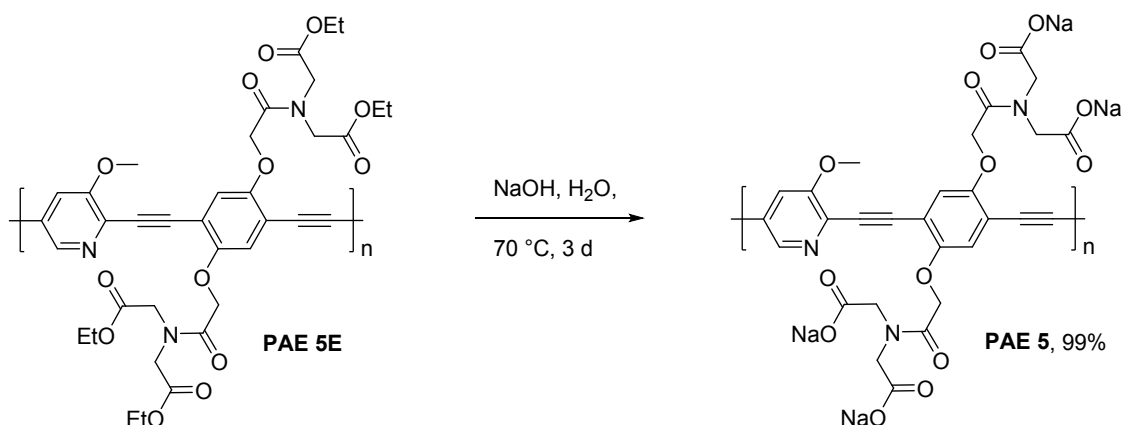
*Synthesis of compound 5 see above.*

*Synthesis of 10 see below.*

**Synthesis of PAE 5E.** Monomer **5** (130 mg, 0.49 mmol) and monomer **10** (300 mg, 0.49 mmol) were dissolved in a mixture of degassed toluene/NEt<sub>3</sub> (1.5:1, 9 mL/7 mL). Pd(PPh<sub>3</sub>)<sub>4</sub> (28 mg, 24  $\mu$ mol) and CuI (4.5 mg, 24  $\mu$ mol) were added and the mixture was stirred at 80 °C for 24 h. Saturated aqueous NH<sub>4</sub>Cl and CHCl<sub>3</sub> were added, the aqueous layer was separated and extracted with CHCl<sub>3</sub>. The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. Two times, the crude product was dissolved in a small amount of

CHCl<sub>3</sub> and slowly added to an excess of pentene to give **PAE 5E** as yellow/orange solid (318 mg, 90%). The  $M_n$  was estimated to be  $1.1 \times 10^4$  with a PDI of 1.9. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.21-8.44 (m, 1 H), 7.47-7.71 (m, 1 H), 7.09-7.22 (m, 2 H), 4.68-5.01 (m, 4 H), 4.05-4.47 (m, 16 H), 3.91-4.03 (m, 3 H), 1.14-1.30 (m, 12 H) ppm. IR (cm<sup>-1</sup>):  $\nu$  3129, 2983, 2947, 2806, 1735, 1663, 1578, 1502, 1446, 1397, 1374, 1297, 1181, 1093, 1020, 969, 867, 747, 678, 667, 573, 514, 504. Due to low solubility, <sup>13</sup>C NMR spectrum could not be obtained.

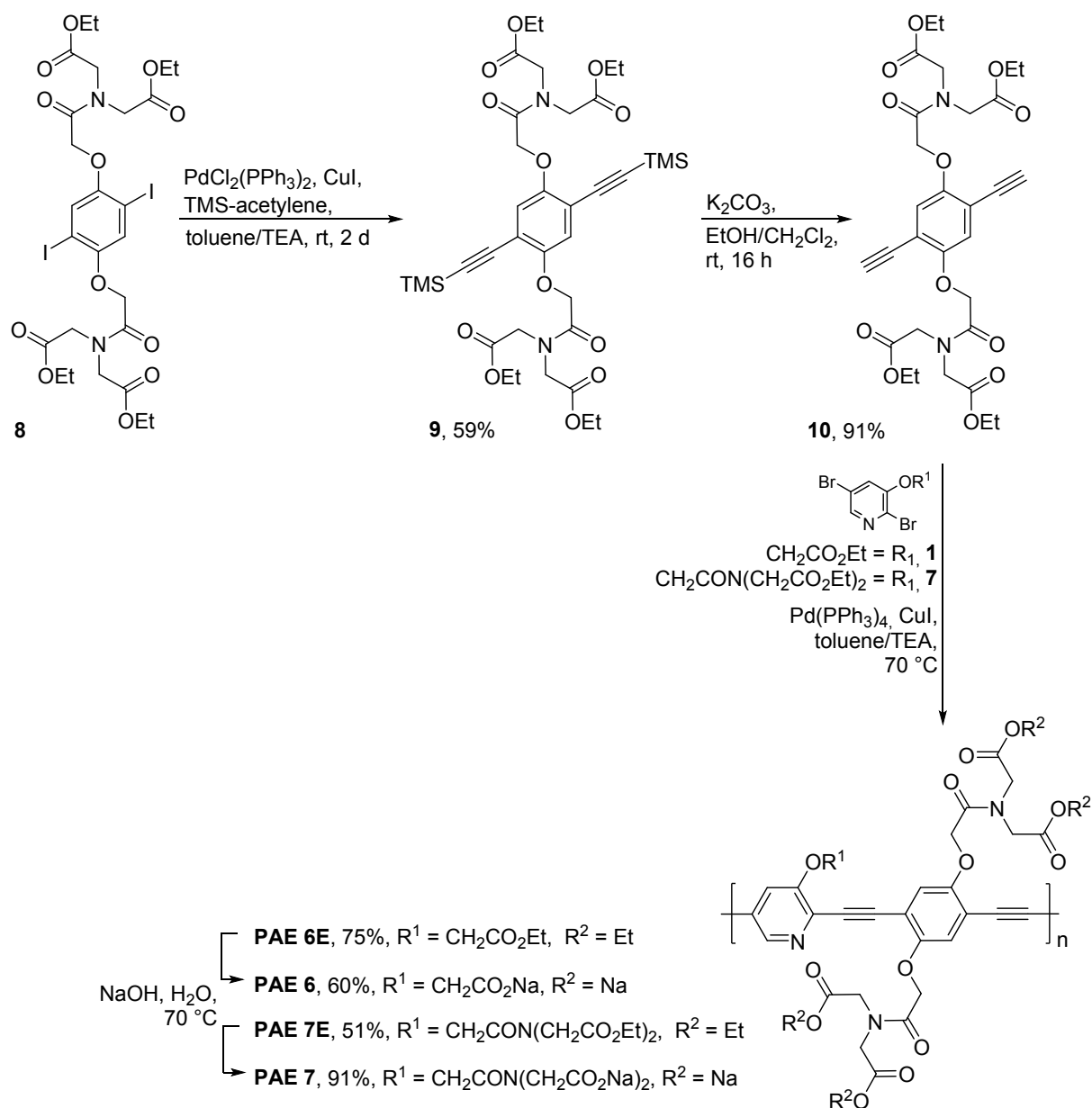
### Scheme 18. Synthesis of PAE 5



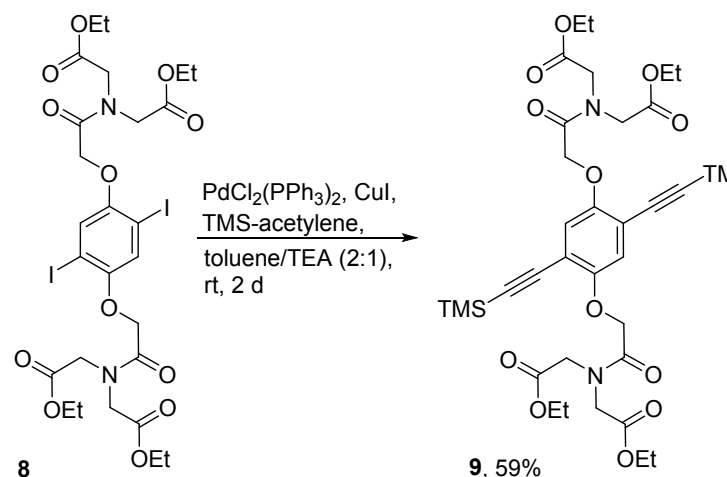
**Synthesis of PAE 5.** To a mixture of **PAE 5E** (195 mg, 0.27 mmol) and water (40 mL), NaOH (216 mg, 5.4 mmol) was added and the resulting mixture was stirred at 70 °C for 3 d. After adjusting a pH of 7 (HCl) the aqueous mixture was dialyzed against DI H<sub>2</sub>O for 3 d. Freeze-drying gave **PAE 5** as spongy, yellow solid (187 mg, 99%). The  $M_n$  and PDI result from **PAE 5E**. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.08-8.43 (m, 4 H), 4.93-5.07 (m, 2 H), 2.96-4.12 (m, 13 H) ppm. IR (cm<sup>-1</sup>):  $\nu$  3352, 1591, 1503, 1395, 1316, 1061, 972, 792, 720, 545, 448. Due to low solubility, <sup>13</sup>C NMR spectrum could not be obtained.



**Scheme 19. Route to PAEs 6 and PAEs 7**



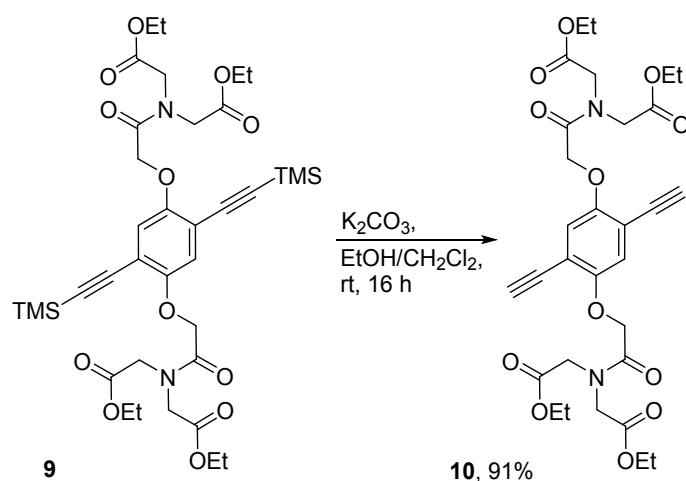
## Scheme 20. Synthesis of 9



Compound **8** was synthesized according to the literature.<sup>8</sup>

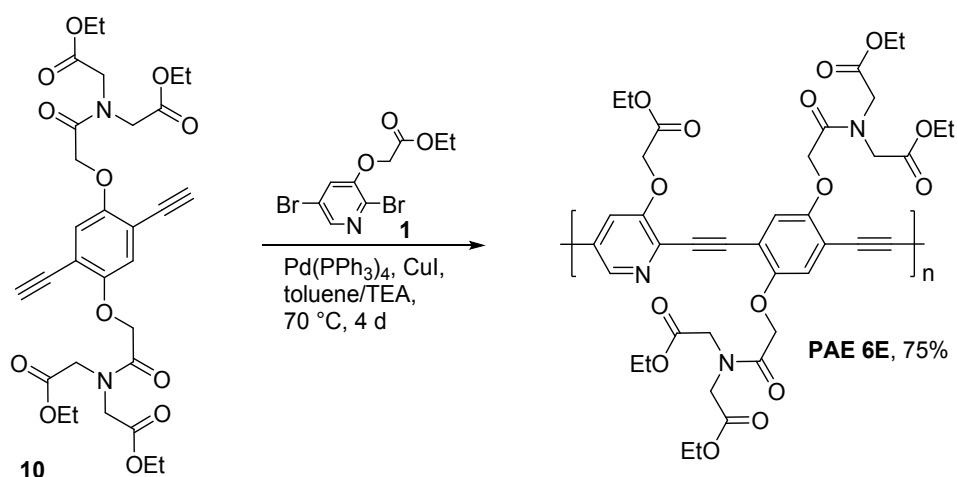
**Synthesis of 9.** Compound **8** (2.00 g, 2.44 mmol) was dissolved in a degassed mixture of toluene/ $\text{NEt}_3$  (2:1, 15 mL/7.5 mL).  $\text{PdCl}_2(\text{PPh}_3)_2$  (86 mg, 122  $\mu\text{mol}$ ) and  $\text{CuI}$  (23 mg, 122  $\mu\text{mol}$ ) were added, then TMS-acetylene (867  $\mu\text{L}$ , 2.60 mmol) was added dropwise and the resulting mixture was stirred for 2 d at room temperature. Saturated aqueous  $\text{NH}_4\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel [petroleum ether/ethyl acetate (5/2)] to give compound **9** (1.10 g, 1.45 mmol, 59%) as grizzly solid (m. p. 120 - 122  $^\circ\text{C}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.98 (s, 2 H), 4.76 (s, 4 H), 4.39 (s, 4 H), 4.13-4.21 (m, 12 H), 1.19-1.27 (m, 12 H), 0.26 (s, 18 H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.81, 168.79, 168.49, 153.51, 118.76, 114.82, 101.71, 99.97, 69.41, 61.87, 49.98, 48.75, 14.27, 14.26, -0.01 ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  2987, 2960, 2900, 2160, 2153, 1741, 1666, 1502, 1491, 1464, 1446, 1433, 1407, 1374, 1351, 1291, 1248, 1183, 1117, 1088, 1046, 1021, 1013, 973, 876, 858, 840, 762, 731, 704. HR-MS (DART<sup>+</sup>):  $m/z$  calcd. for  $\text{C}_{36}\text{H}_{56}\text{N}_3\text{O}_{12}\text{Si}_2^+$  778.3397 [ $\text{M}+\text{NH}_4$ ]<sup>+</sup>; found 778.3402.  $\text{C}_{36}\text{H}_{52}\text{N}_2\text{O}_{12}\text{Si}_2$  (760.98): calcd. C 56.82, H 6.89, N 3.68; found C 56.80, H 6.59, N 3.54.

### Scheme 21. Synthesis of 10



**Synthesis of 10.** Compound **9** (1.10 g, 1.45 mmol) was dissolved in a mixture of  $EtOH/CH_2Cl_2$  (1:1, 15 mL/15 mL).  $K_2CO_3$  (2.00 g, 14.5 mmol) was added and the resulting mixture was stirred for 16 h at ambient temperature. Water and  $CH_2Cl_2$  were added, the aqueous layer was separated and extracted with  $CH_2Cl_2$ . The combined organic layers were dried over  $MgSO_4$ , filtered and concentrated in vacuo. The crude product was dissolved in  $CH_2Cl_2$  and filtered again and concentrated in vacuo to give compound **10** (812 mg, 1.32 mmol, 91%) as yellowish solid (m. p. 190 °C decomposition).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.03 (s, 2 H), 4.78 (s, 4 H), 4.34 (s, 4 H), 4.13-4.23 (m, 12 H), 3.34 (s, 2 H), 1.21-1.30 (m, 12 H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 168.85, 168.69, 168.31, 153.77, 118.78, 114.01, 83.81, 78.92, 69.18, 61.95, 61.55, 49.93, 48.64, 14.28, 14.25 ppm. IR ( $cm^{-1}$ ):  $\nu$  3242, 2982, 2942, 1743, 1658, 1506, 1472, 1431, 1403, 1373, 1354, 1311, 1292, 1274, 1249, 1193, 1118, 1094, 1046, 1022, 1010, 971, 927, 889, 872, 821, 796, 762, 731, 633. HR-MS (DART<sup>+</sup>):  $m/z$  calcd. for  $C_{30}H_{40}N_3O_{12}^+$  634.2607  $[M+NH_4]^+$ ; found 634.2583.  $C_{30}H_{36}N_2O_{12}$  (616.62): calcd. C 58.44, H 5.88, N 4.54, found C 57.94, H 5.84, N 4.50.

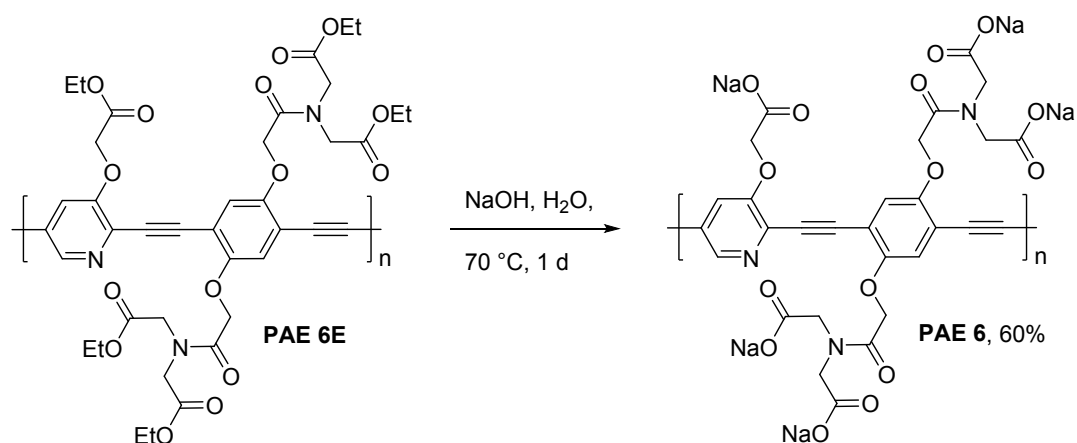
## Scheme 22. Synthesis of PAE 6E



Compound **1** was synthesized according to the literature.<sup>4</sup>

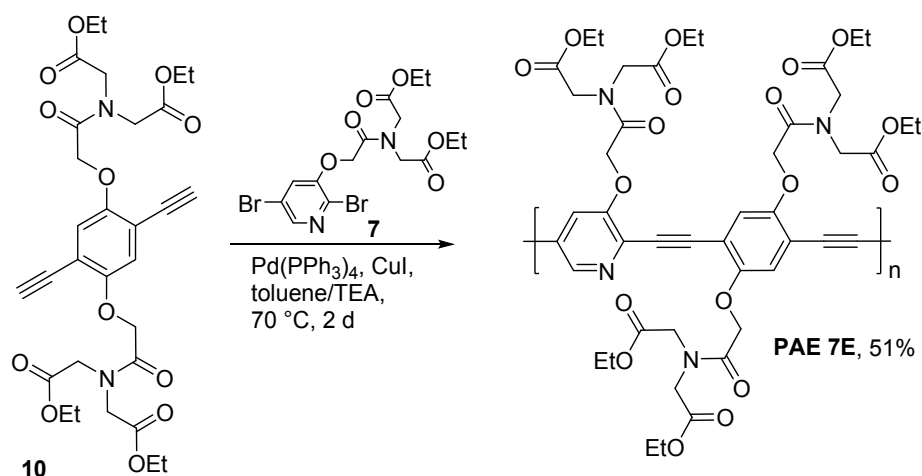
**Synthesis of PAE 6E.** Monomer **1** (200 mg, 0.59 mmol) and monomer **10** (304 mg, 0.59 mmol) were dissolved in a mixture of degassed toluene/ $\text{NEt}_3$  (1.5:1, 12 mL/8 mL).  $\text{Pd}(\text{PPh}_3)_4$  (34 mg, 30  $\mu\text{mol}$ ) and  $\text{CuI}$  (5.7 mg, 30  $\mu\text{mol}$ ) were added and the mixture was stirred at  $70^\circ\text{C}$  for 4 d. Saturated aqueous  $\text{NH}_4\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , filtered again and concentrated in vacuo. Two times, the crude product was dissolved in a small amount of  $\text{CHCl}_3$  and slowly added to an excess of pentene to give **PAE 6E** as yellow solid (353 mg, 75%). The  $M_n$  was estimated to be  $8.4 \times 10^3$  with a PDI of 1.2.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.26\text{-}8.52$  (m, 1 H), 7.30-7.49 (m, 1 H), 7.00-7.23 (m, 2 H), 4.80-4.94 (m, 4 H), 4.07-4.51 (m, 20 H), 1.15-1.32 (m, 15 H) ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  2983, 2939, 2909, 2871, 1737, 1668, 1561, 1498, 1464, 1404, 1373, 1351, 1264, 1183, 1094, 1021, 970, 932, 909, 858, 830, 810, 788, 750, 721, 650, 588. Due to low solubility,  $^{13}\text{C}$  NMR spectrum could not be obtained.

### Scheme 23. Synthesis of PAE 6



**Synthesis of PAE 6.** To a mixture of **PAE 6E** (100 mg, 0.13 mmol) and water (20 mL), NaOH (104 mg, 2.6 mmol) was added and the resulting mixture was stirred at 70 °C for 1 d. After adjusting a pH of 7 (HCl) the aqueous mixture was dialyzed against DI H<sub>2</sub>O for 3 d. Freeze-drying gave **PAE 6** as spongy, orange solid (59 mg, 60%). The  $M_n$  and PDI result from **PAE 6E**. <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O):  $\delta$  = 6.85-8.37 (m, 4 H), 4.86-5.03 (m, 2 H), 3.89-4.36 (m, 12 H) ppm. IR (cm<sup>-1</sup>):  $\nu$  3399, 3065, 2947, 2643, 1722, 1651, 1607, 1498, 1401, 1320, 1187, 1087, 1044, 971, 884, 792, 579, 458, 411. Due to low solubility, <sup>13</sup>C NMR spectrum could not be obtained

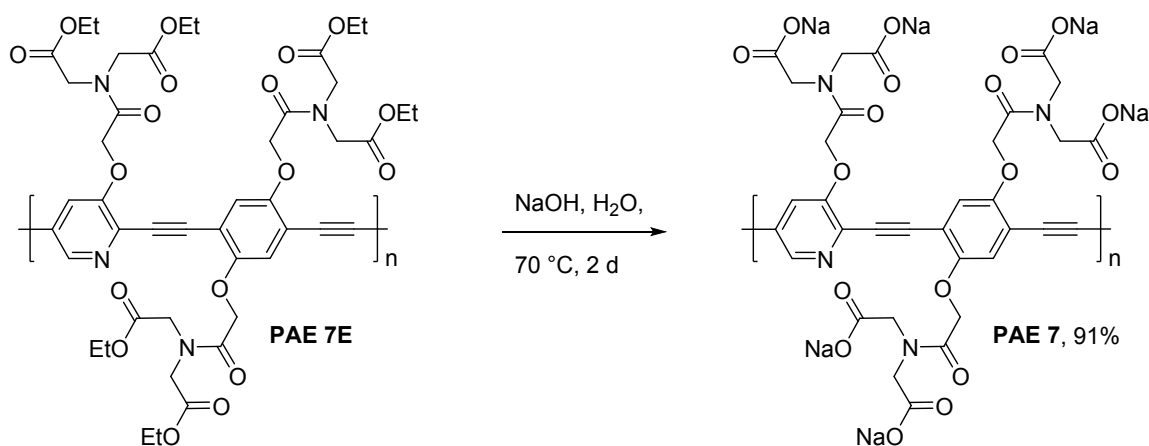
### Scheme 24. Synthesis of PAE 7E



**Synthesis of PAE 7E.** Monomer 7 (250 mg, 0.52 mmol) and monomer 10 (320 mg, 0.52 mmol) were dissolved in a mixture of degassed toluene/NEt<sub>3</sub> (1.5:1, 9 mL/7 mL). Pd(PPh<sub>3</sub>)<sub>4</sub>

(30 mg, 26  $\mu\text{mol}$ ) and CuI (5.0 mg, 26  $\mu\text{mol}$ ) were added and the mixture was stirred at 70 °C for 2 d. Saturated aqueous  $\text{NH}_4\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  were added, the aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , filtered again and concentrated in vacuo. Two times, the crude product was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  and slowly added to an excess of pentene to give **PAE 7E** as yellow solid (256 mg, 51%). The  $M_n$  was estimated to be  $1.1 \times 10^4$  with a PDI of 1.5.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.28\text{-}8.47$  (m, 1 H), 7.46-7.60 (m, 1 H), 7.02-7.24 (m, 2 H), 4.75-5.12 (m, 6 H), 4.06-4.45 (m, 24 H), 1.10-1.32 (m, 18 H) ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  2983, 2939, 2905, 2875, 1738, 1661, 1575, 1560, 1503, 1464, 1402, 1373, 1352, 1260, 1094, 1021, 970, 863, 752, 698, 651, 623, 589, 520. Due to low solubility,  $^{13}\text{C}$  NMR spectrum could not be obtained.

#### Scheme 25. Synthesis of PAE 7

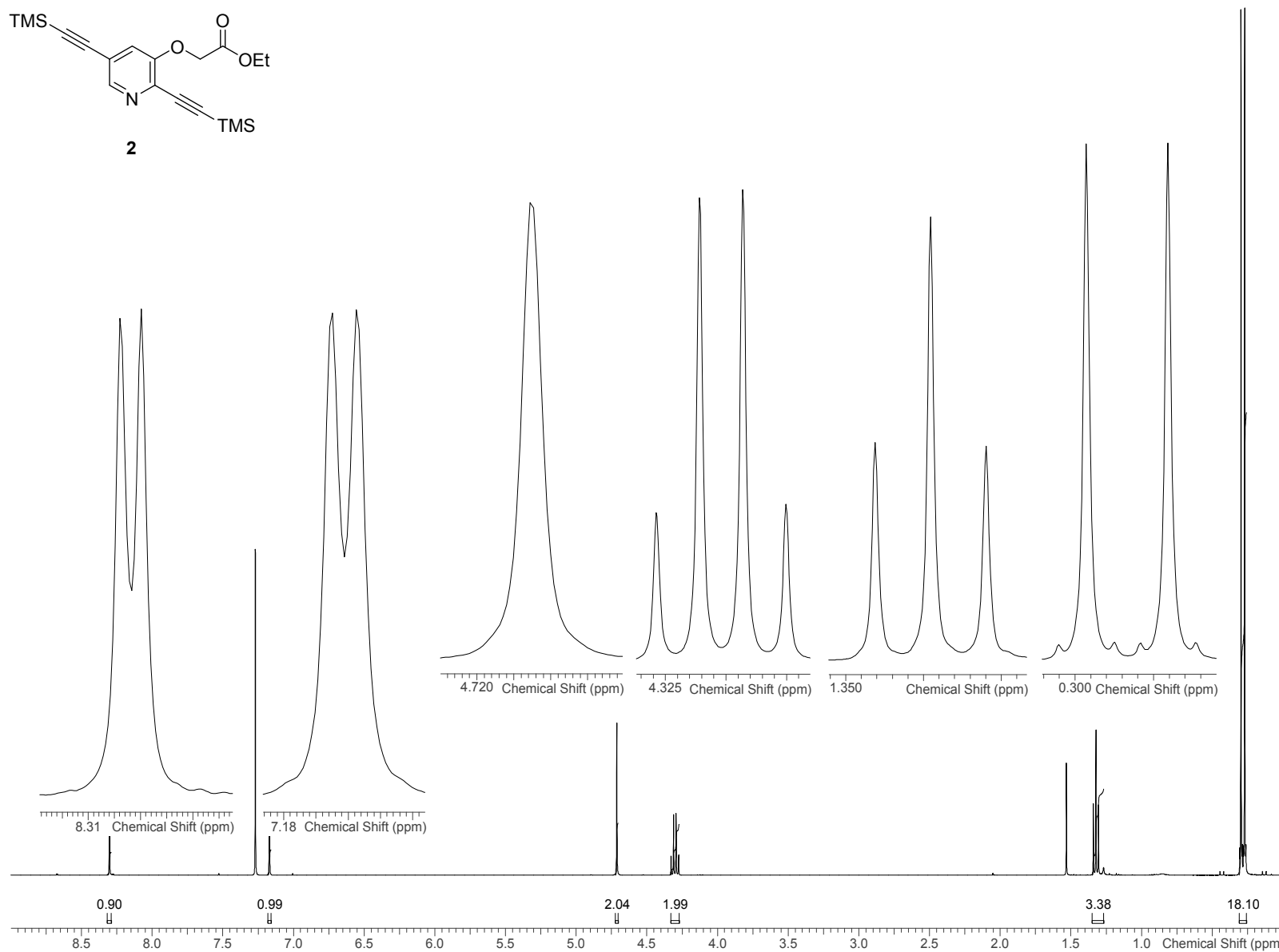
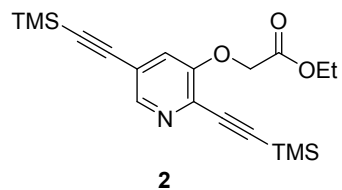


**Synthesis of PAE 7.** To a mixture of **PAE 7E** (100 mg, 0.11 mmol) and water (20 mL), NaOH (88 mg, 2.2 mmol) was added and the resulting mixture was stirred at 70 °C for 2 d. After adjusting a pH of 7 (HCl) the aqueous mixture was dialyzed against DI  $\text{H}_2\text{O}$  for 3 d. Freeze-drying gave **PAE 7** as spongy, orange solid (77 mg, 91%). The  $M_n$  and PDI result from **PAE 7E**.  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 8.22\text{-}8.30$  (m, 1 H), 7.63-7.75 (m, 1 H), 7.04-7.33 (m, 2 H), 4.95-5.10 (m, 4 H), 3.96-4.14 (m, 14 H) ppm. IR ( $\text{cm}^{-1}$ ):  $\nu$  3384, 3263, 3068, 2996, 2950, 2643, 1715, 1642, 1598, 1502, 1478, 1396, 1319, 1294, 1193, 1140, 1091, 1038,

974, 915, 877, 844, 658, 548, 519, 457, 428, 413 Due to low solubility,  $^{13}\text{C}$  NMR spectrum could not be obtained.

### 3. $^1\text{H}$ NMR Spectra



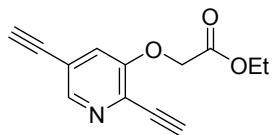


Current Data Parameters  
 NAME c140325submb.11  
 EXPNO 2  
 PROCNO 1

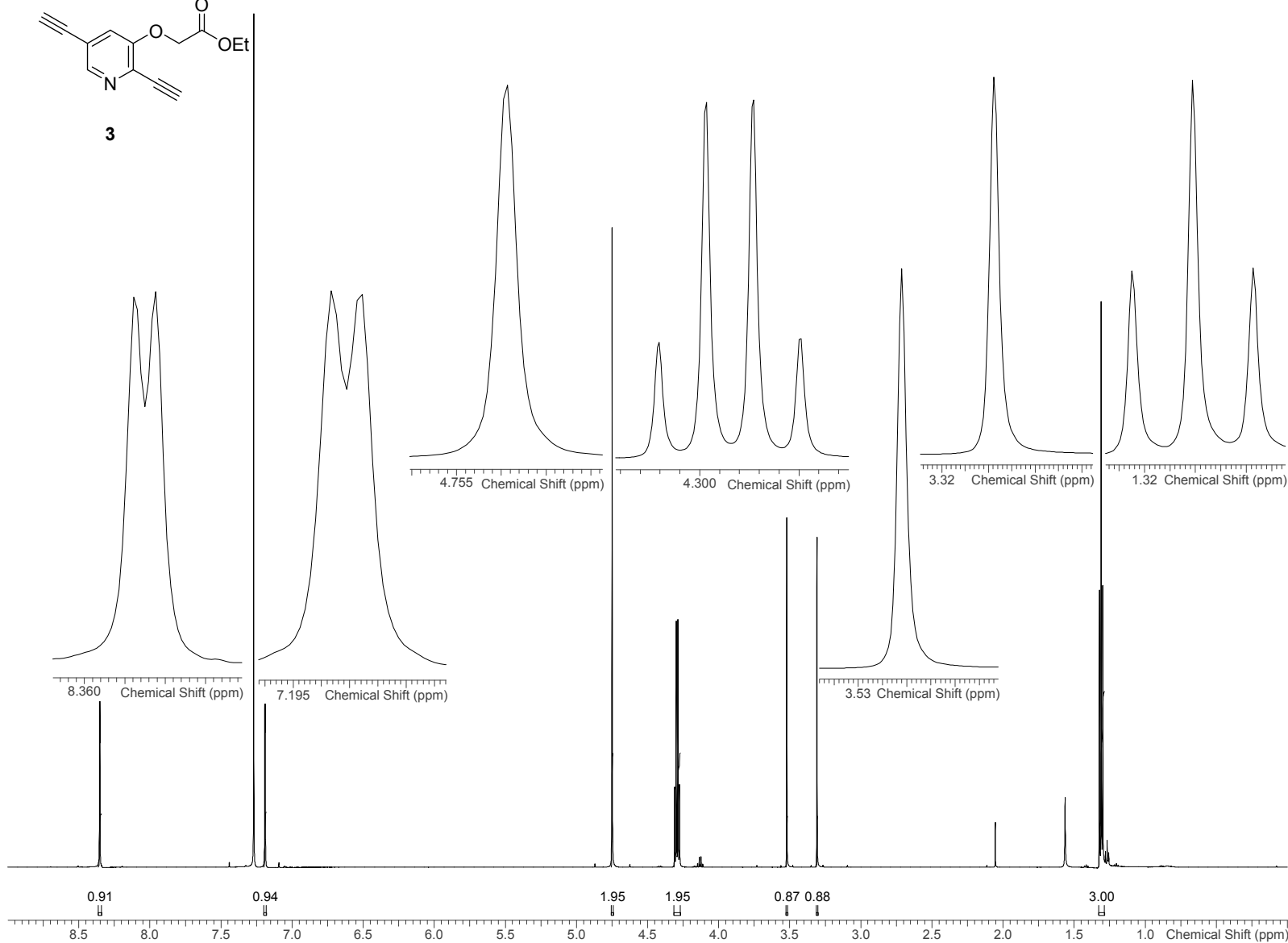
F2 - Acquisition Parameters  
 Date 20140325  
 Time 16.17  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 12019.230 Hz  
 FIDRES 0.183399 Hz  
 AQ 2.7262976  
 RG 2050  
 DW 41.600 usec  
 DE 12.00 usec  
 TE 298.2 K  
 D1 0.50000000 sec  
 TD0 16

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 11.50 usec  
 PLW1 10.00000000 W  
 SFO1 400.3320009 MHz

F2 - Processing parameters  
 SI 65536  
 SF 400.3300620 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



3

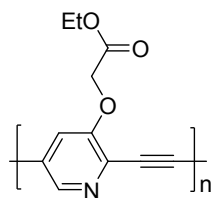


Current Data Parameters  
 NAME e140409ubmb.14  
 EXPNO 2  
 PROCNO 1

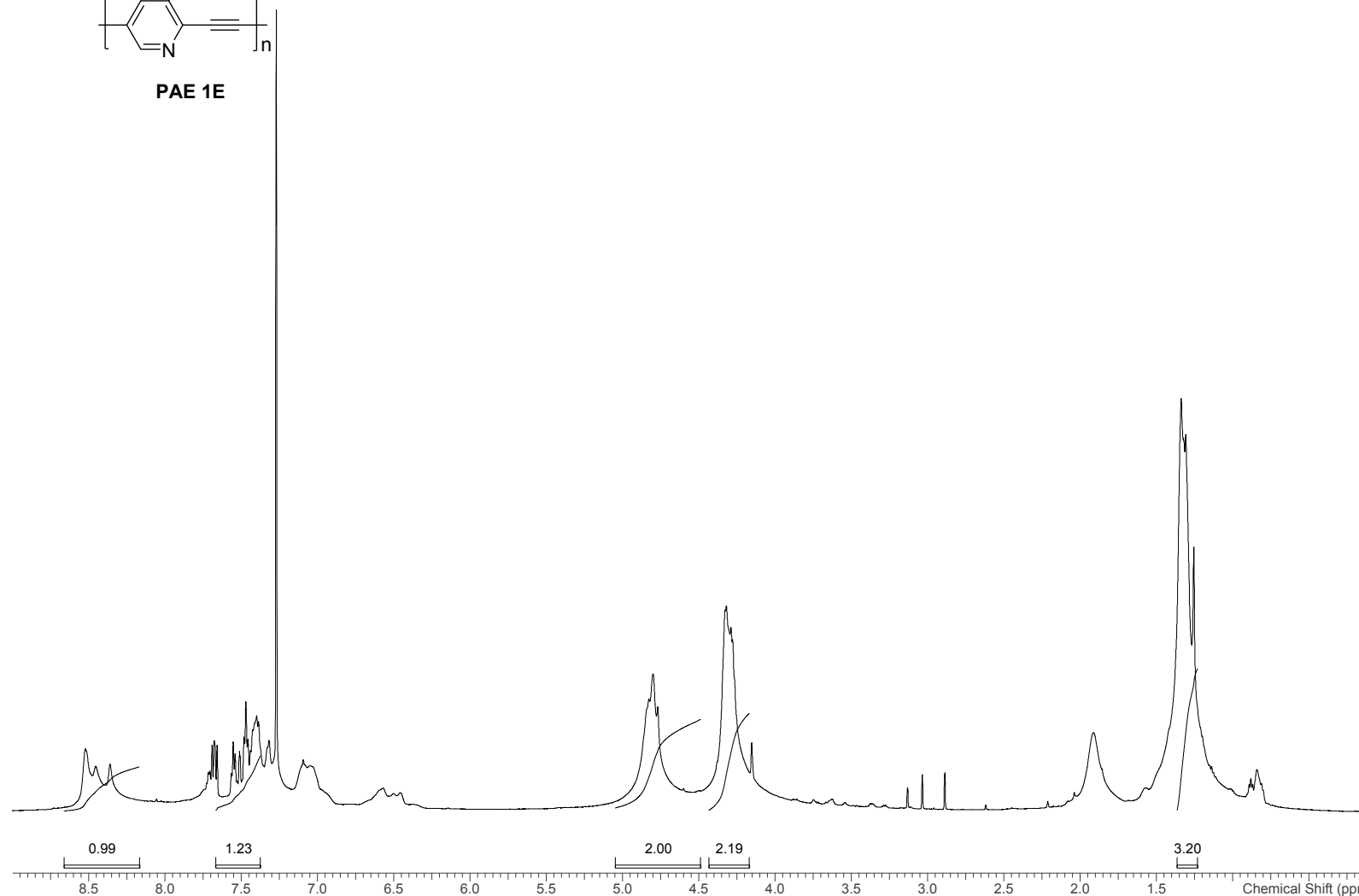
F2 - Acquisition Parameters  
 Date 20140410  
 Time 5.55  
 INSTRUM spect  
 PROBHD 5 mm CPQCI 1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 80  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 12.19  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 10

==== CHANNEL f1 ====  
 NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



PAE 1E

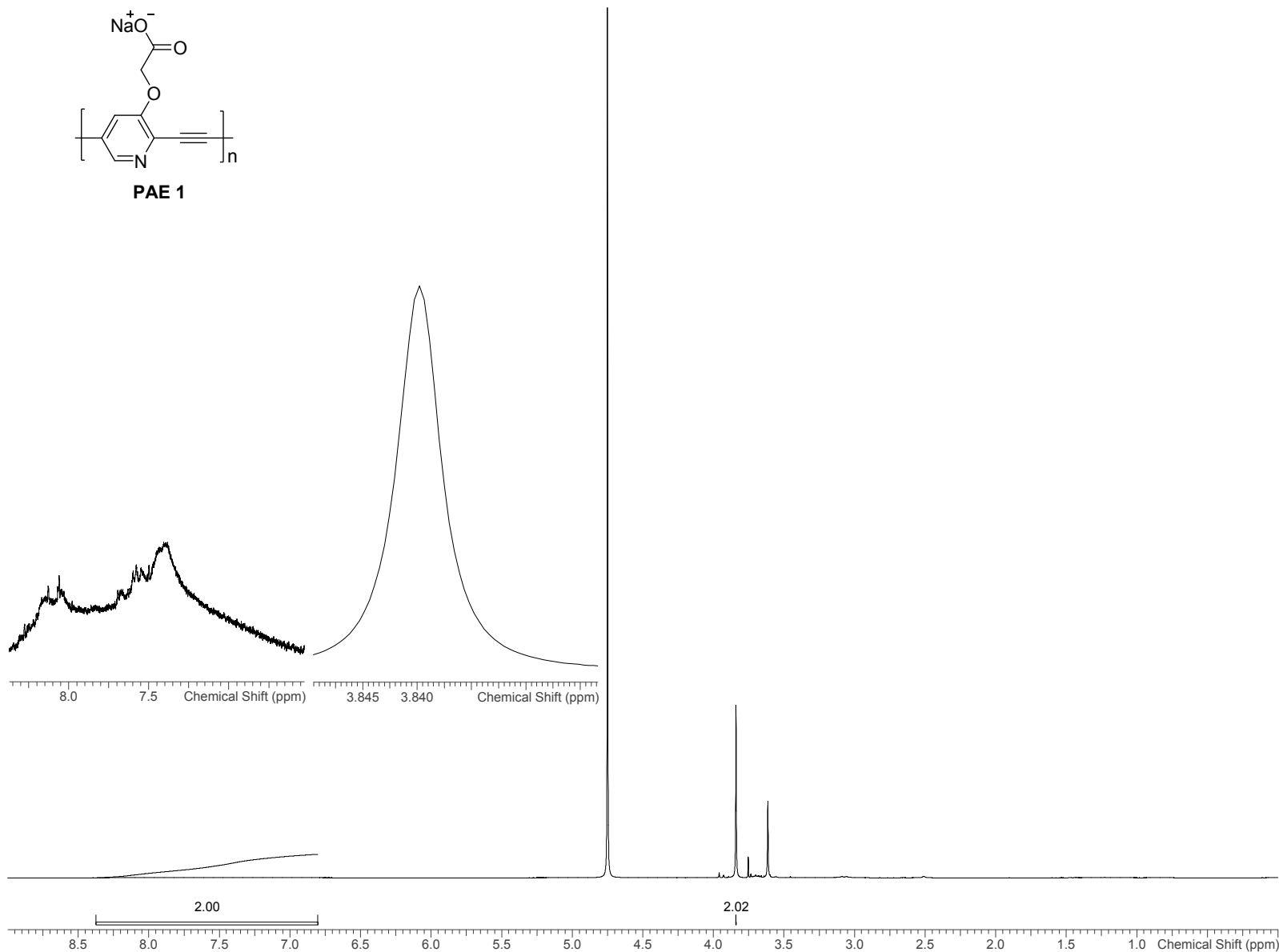
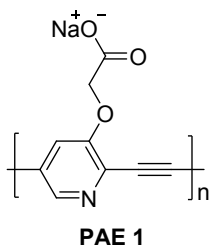


Current Data Parameters  
 NAME e140513ubmb.29  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date 20140514  
 Time 23.21  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 15.35  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.2438802 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters

NAME e150505submb.31  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

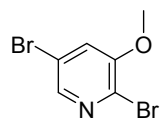
Date 20150505  
 Time 13.01  
 INSTRUM spect  
 PROBHD Z132808\_0001 (  
 PULPROG zg30  
 TD 131072  
 SOLVENT D<sub>2</sub>O  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 18.85  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====

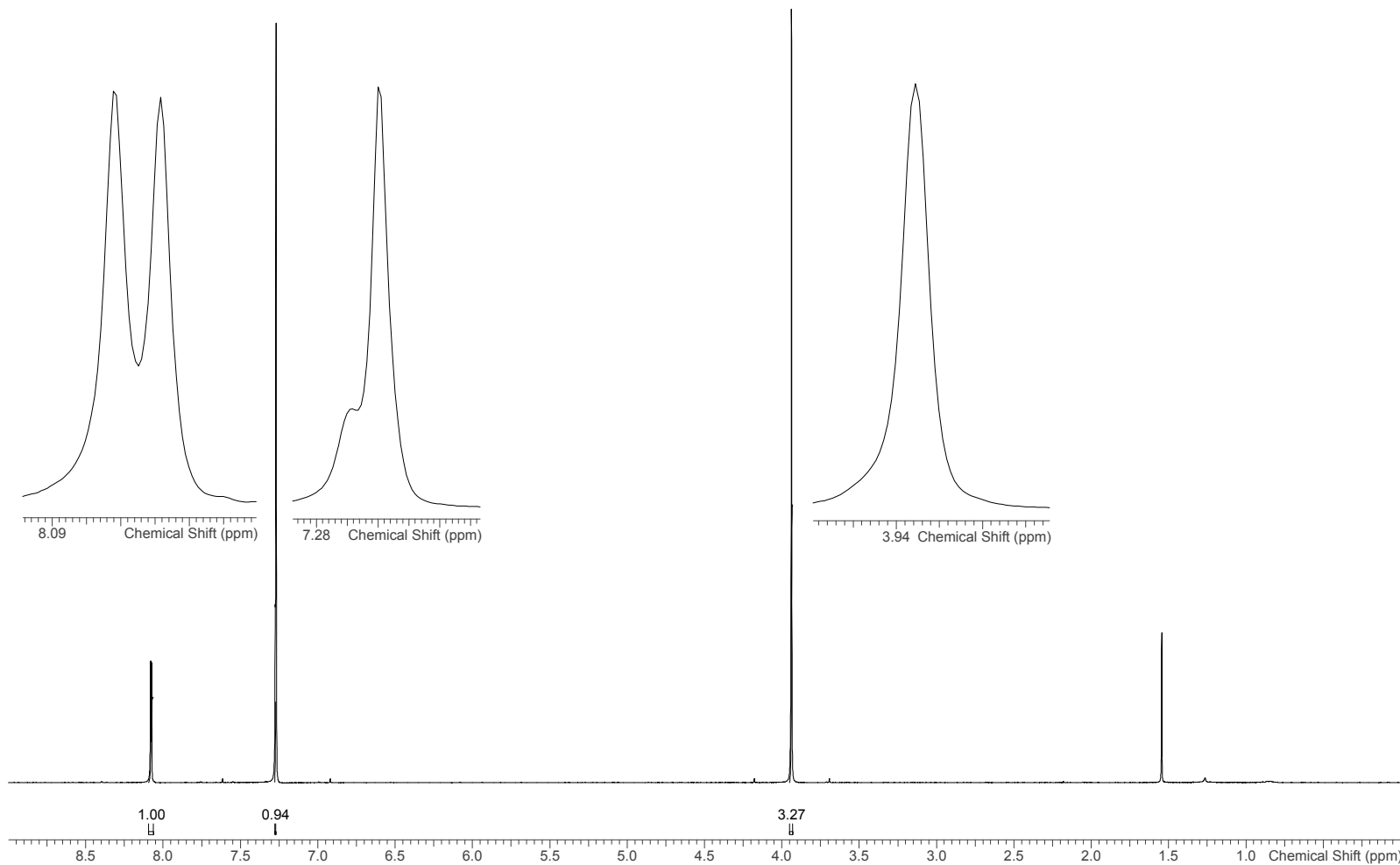
NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



5



Current Data Parameters

NAME e141121ubmb.106  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

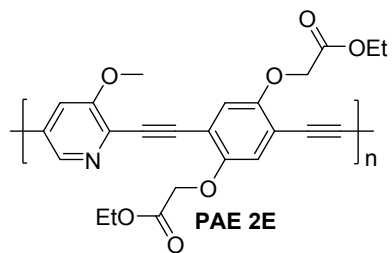
Date 20141125  
 Time 1.00  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl3  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 15.35  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====

NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.3468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters

NAME e150506ubmb.119  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

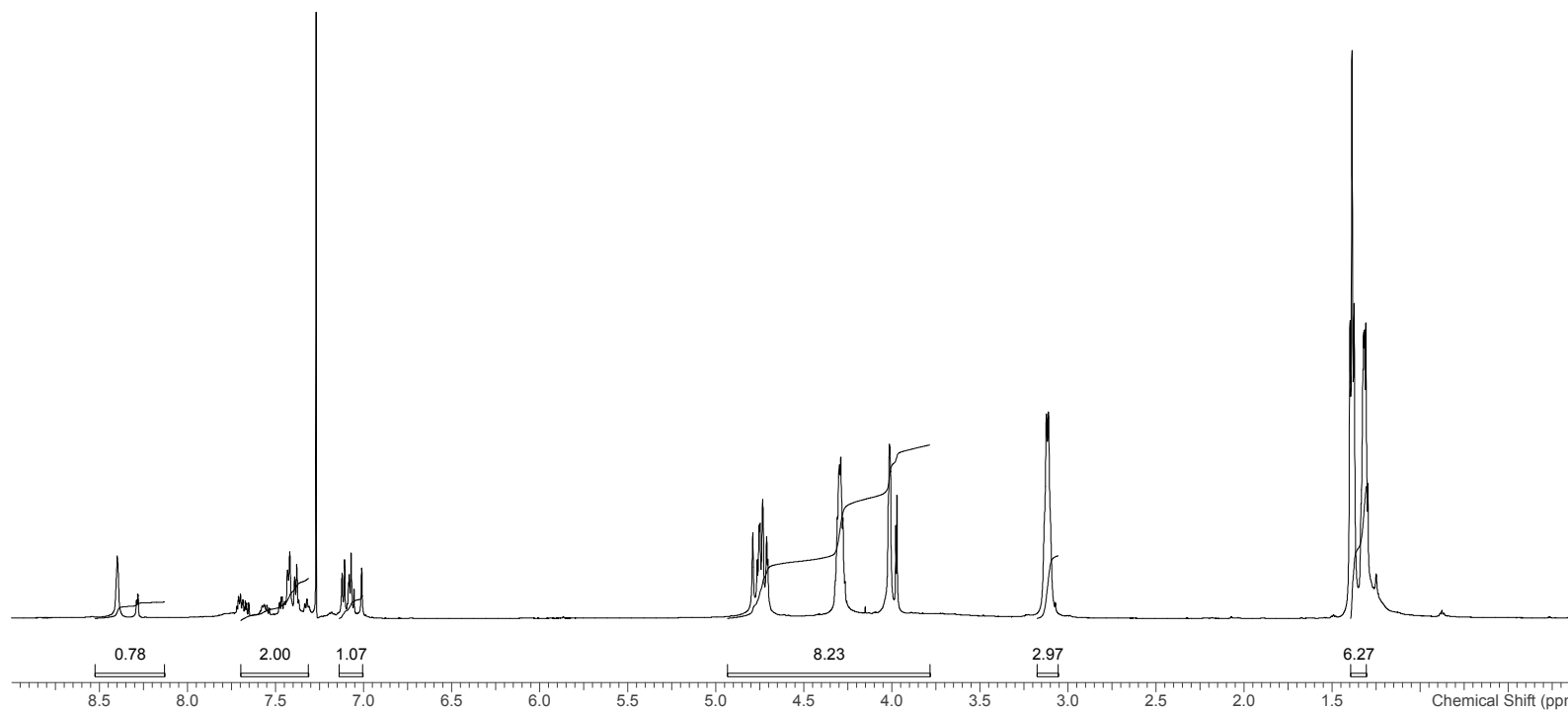
Date 20150506  
 Time 14.26  
 INSTRUM spect  
 PROBHD Z132808\_0001 (  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 13.85  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

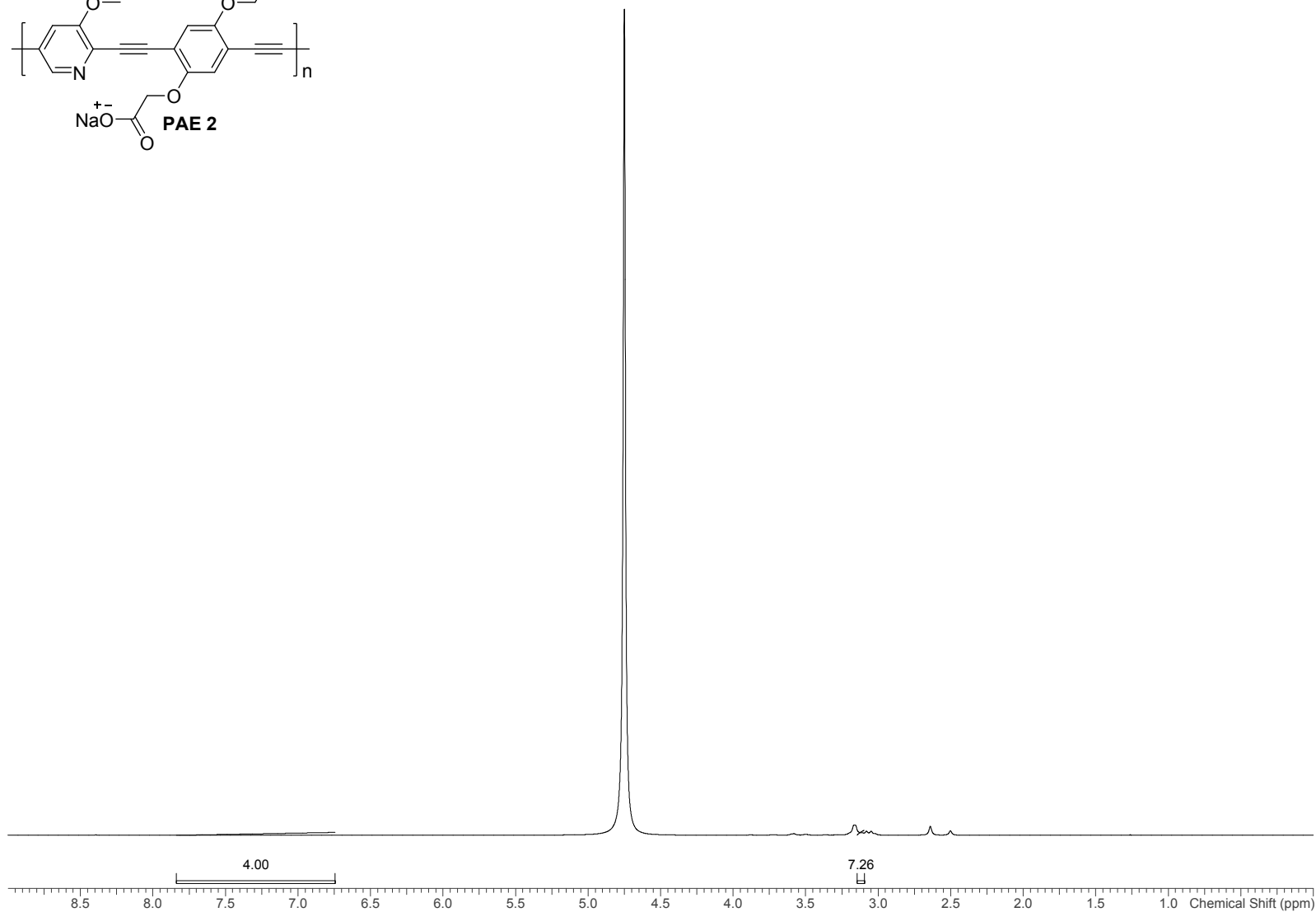
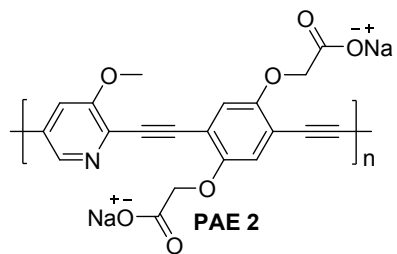
==== CHANNEL f1 =====

NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00





Current Data Parameters

NAME e150408submb.143  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

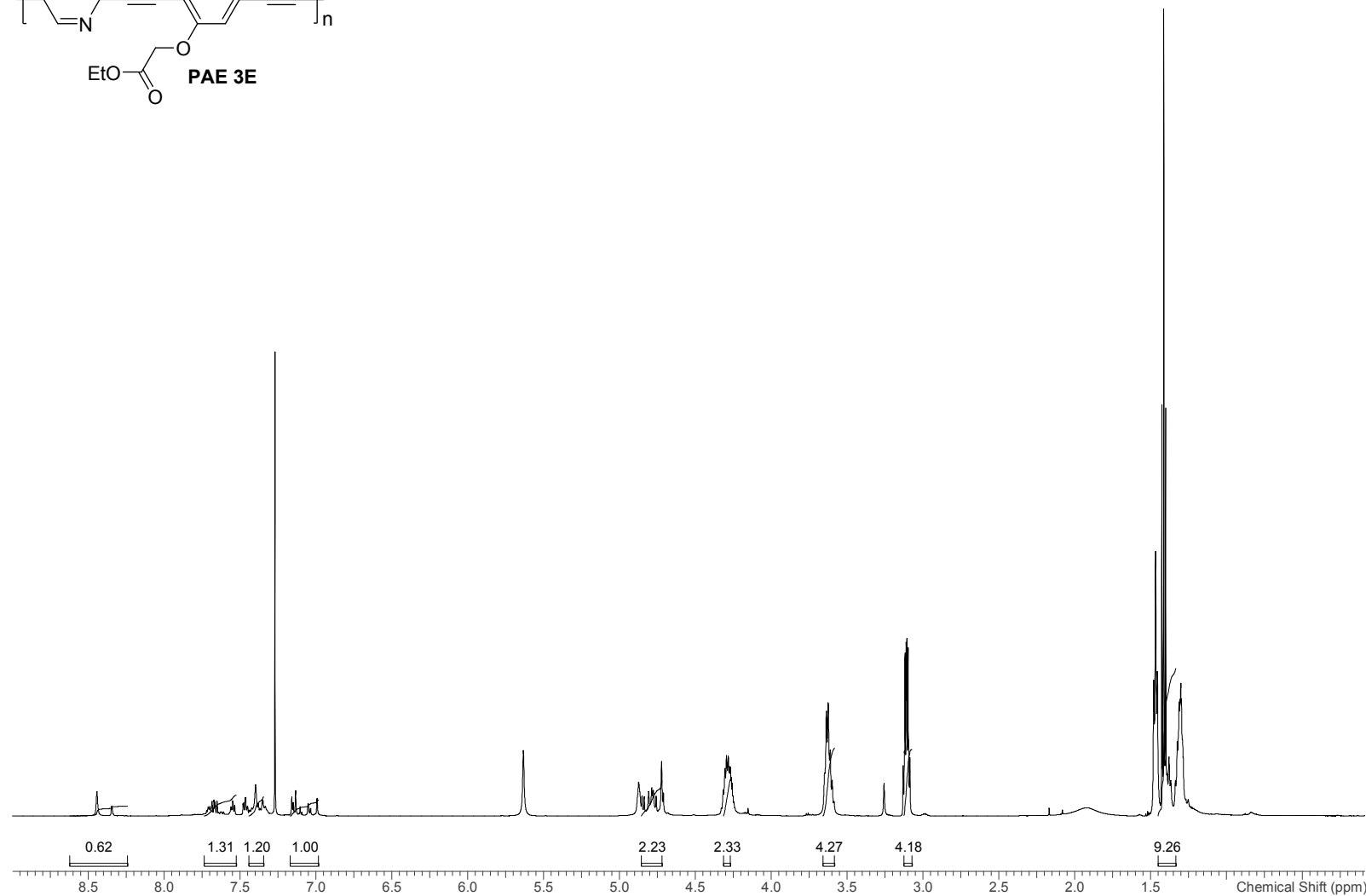
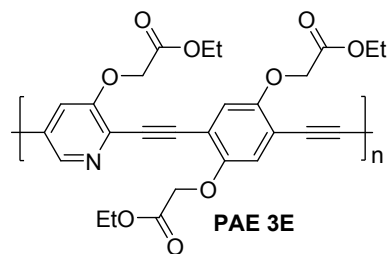
Date 20150408  
 Time 17.13  
 INSTRUM spect  
 PROBHD Z132808\_0001 (  
 PULPROG zg30  
 TD 131072  
 SOLVENT D<sub>2</sub>O  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 18.85  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====

NUC1 1H  
 P1 7.63 usec  
 PLW1 7.50000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 NAME e140623ubmb.38  
 EXPNO 2  
 PROCNO 1

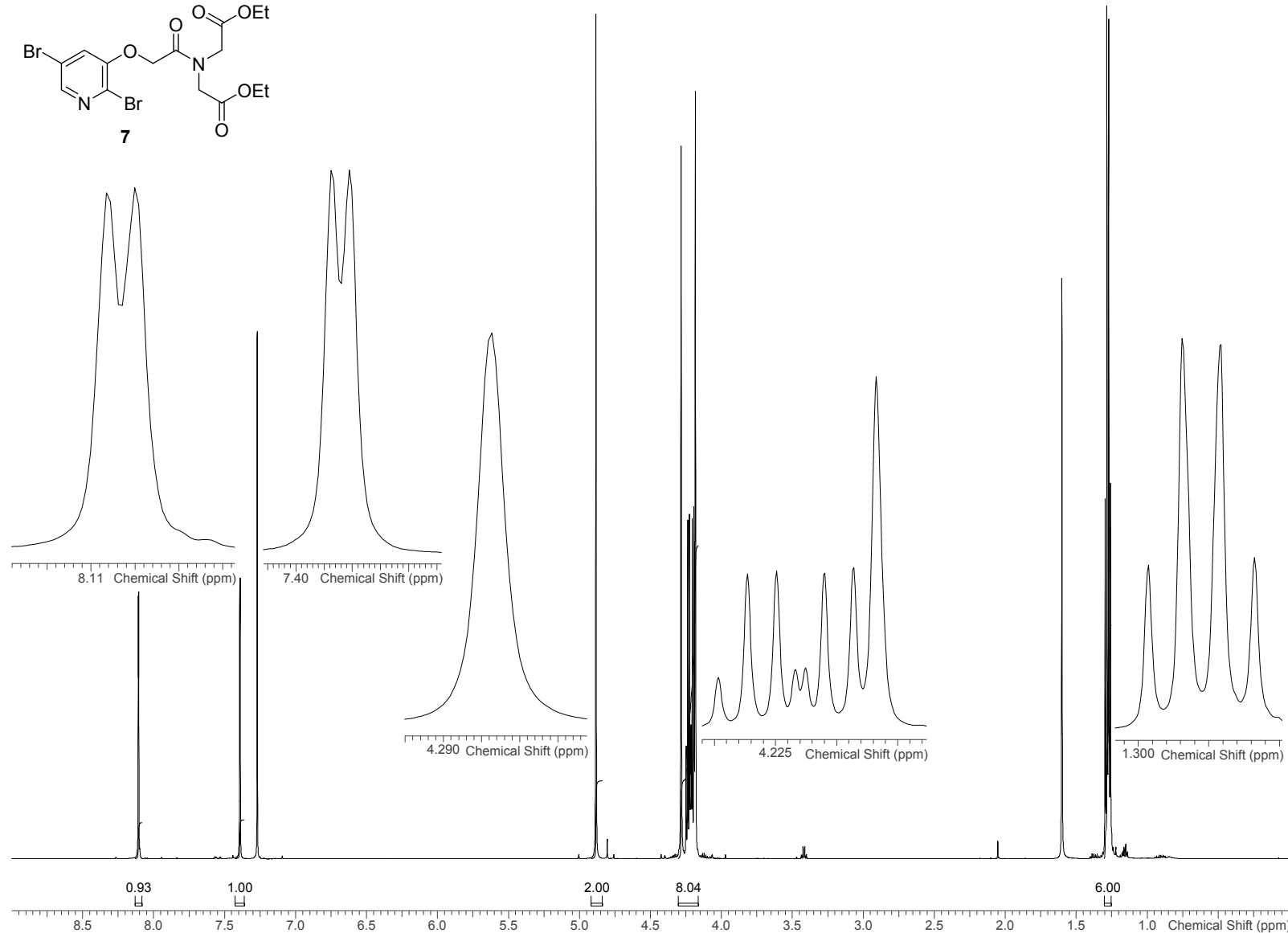
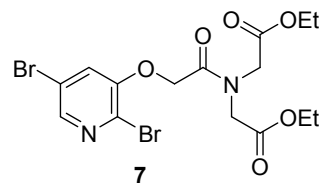
F2 - Acquisition Parameters  
 Date 20140624  
 Time 6.44  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 13.85  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 298.1 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.2438788 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00







Current Data Parameters

NAME e140408ubMmf.32  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

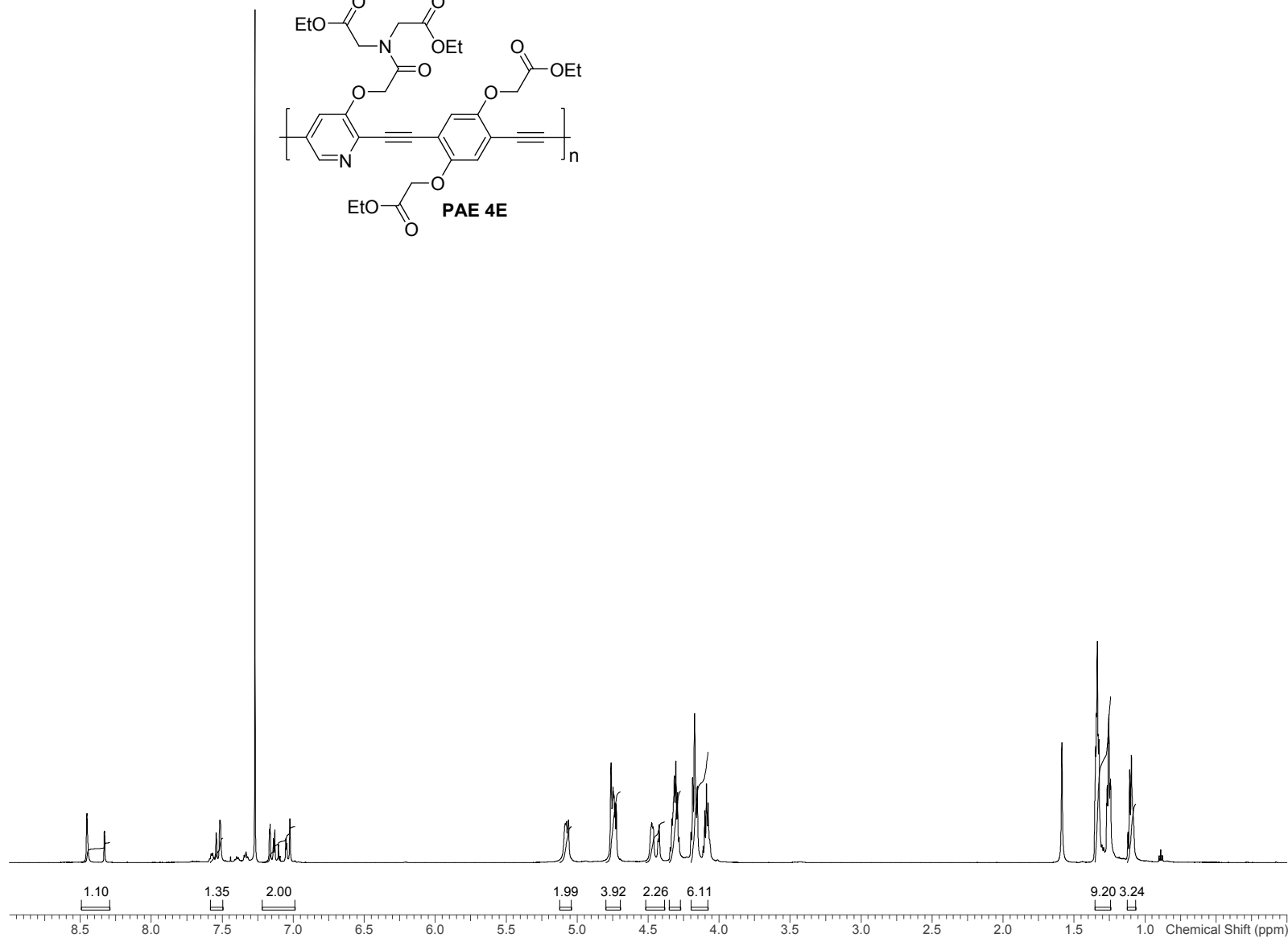
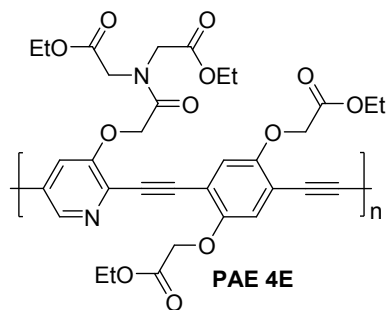
Date 20140408  
 Time 11.24  
 INSTRUM spect  
 PROBHD 5 mm CPQCI 1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 15.35  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====

NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters

NAME e140417ubmf.36  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

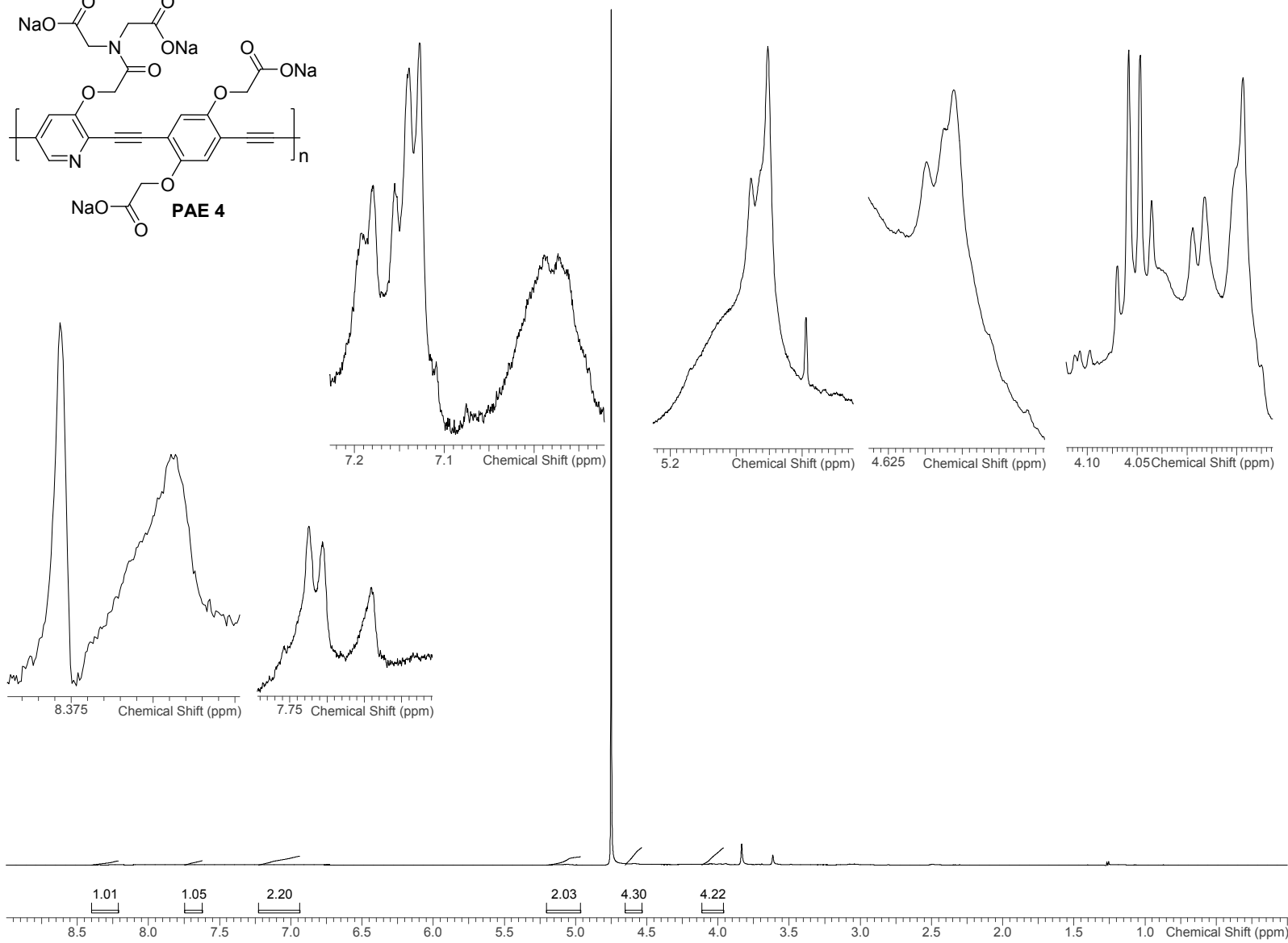
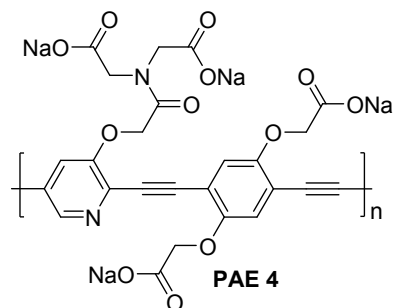
Date 20140418  
 Time 16.31  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 10.93  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====

NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters

NAME e140516ubmf.40  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

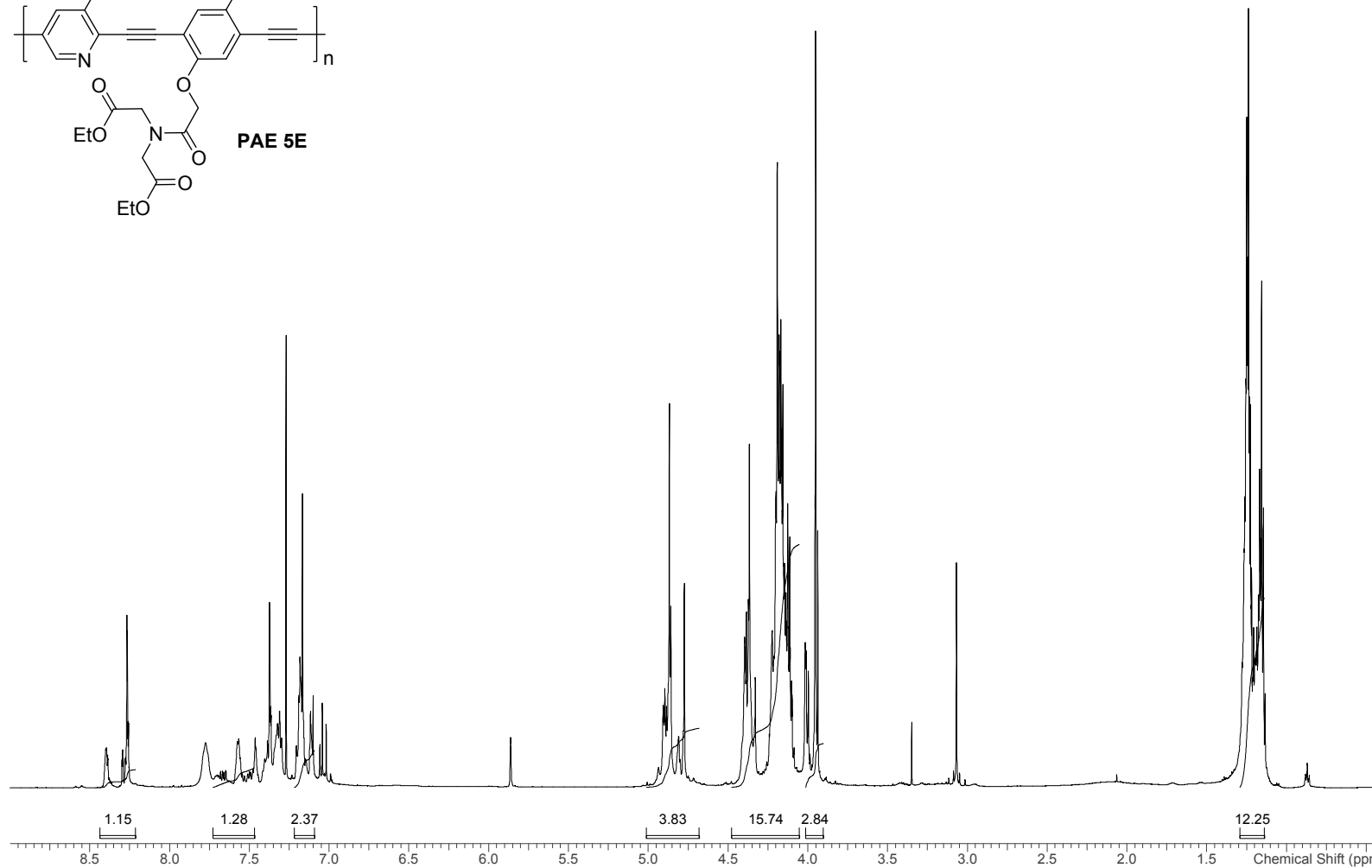
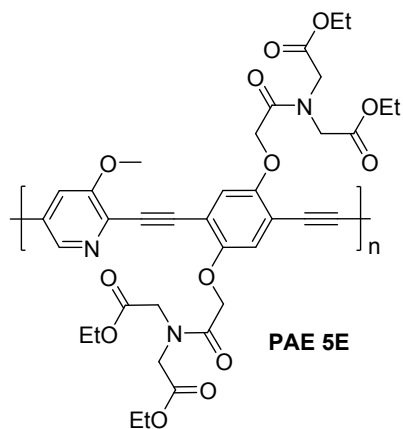
Date 20140517  
 Time 9.14  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT D<sub>2</sub>O  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 18.85  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 ====

NUC1 1H  
 P1 7.63 usec  
 PLW1 7.50000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438015  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

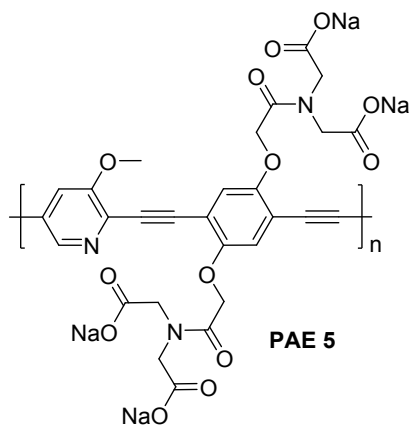


Current Data Parameters  
 NAME e150505submb.136  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date 20150506  
 Time 8.51  
 INSTRUM spect  
 PROBHD Z132808\_0001 (  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 10.93  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters

NAME e150408submb.139  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

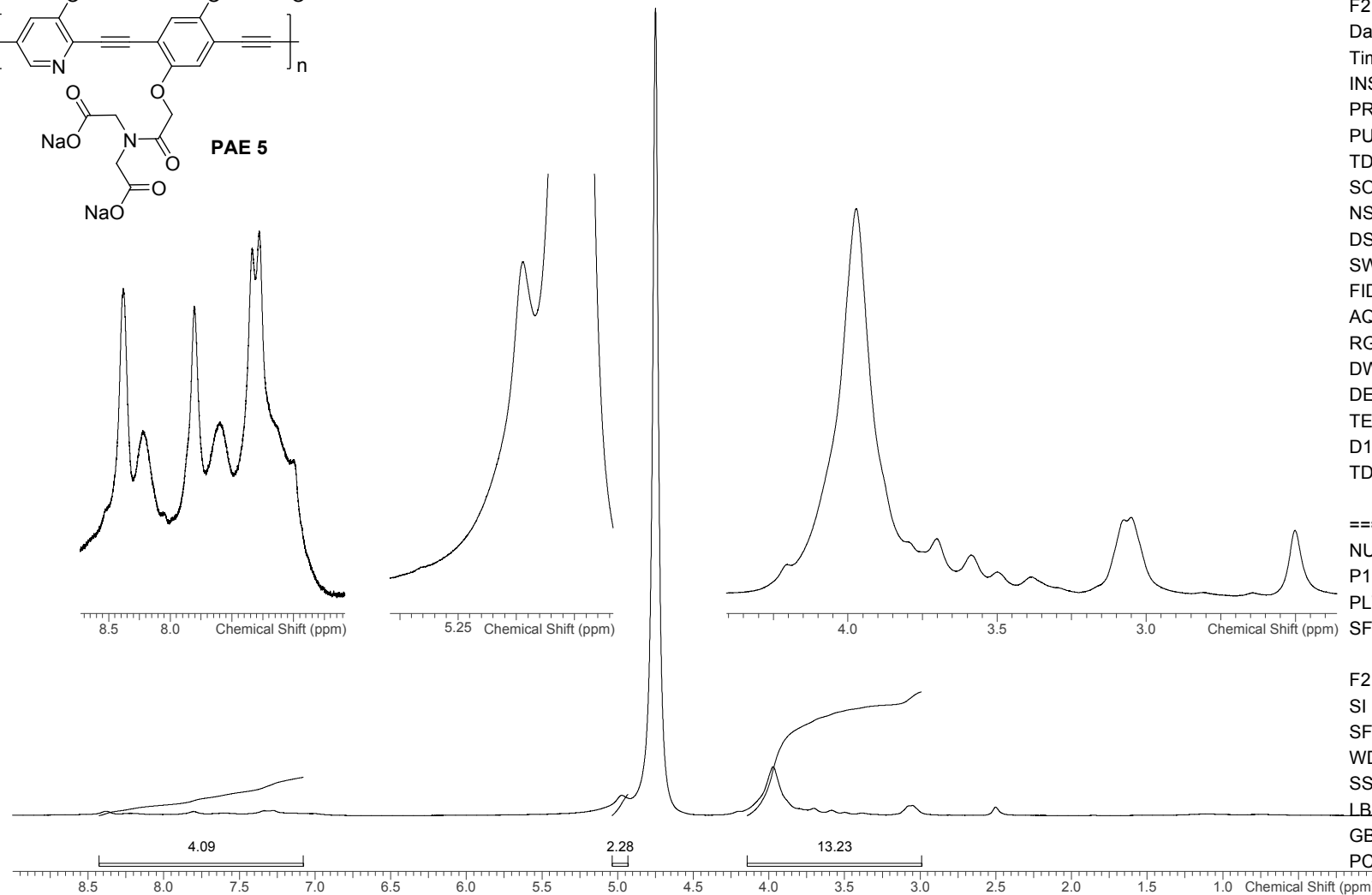
Date 20150408  
 Time 13.24  
 INSTRUM spect  
 PROBHD Z132808\_0001 (  
 PULPROG zg30  
 TD 131072  
 SOLVENT D<sub>2</sub>O  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 15.35  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

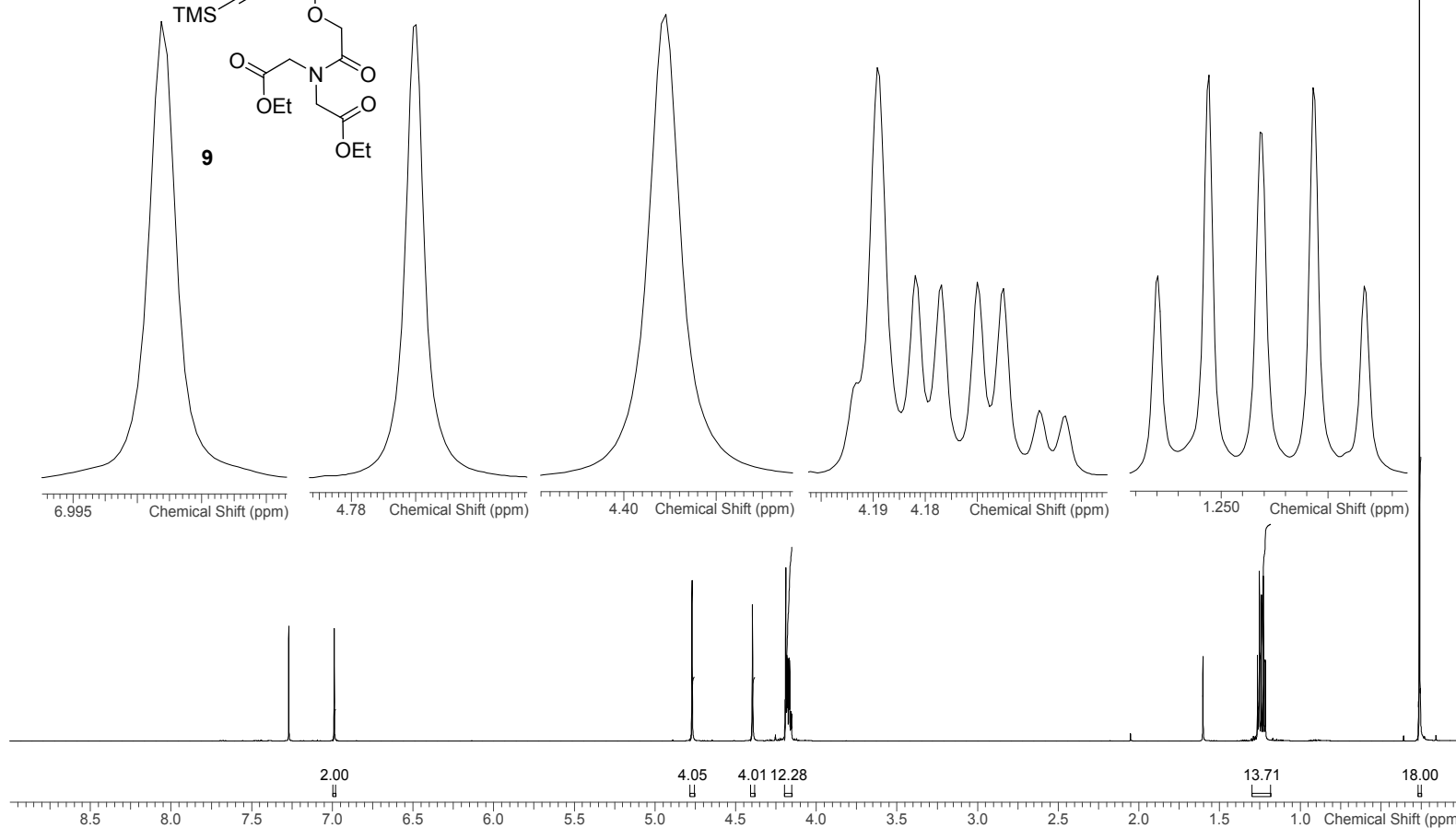
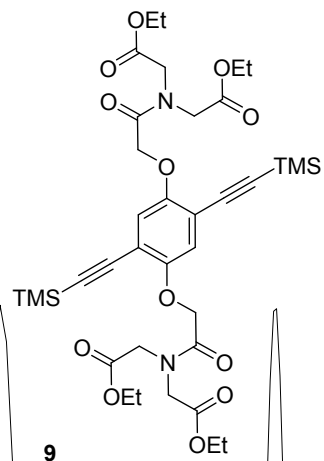
==== CHANNEL f1 ====

NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00





Current Data Parameters

NAME c140804ubmb.55  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

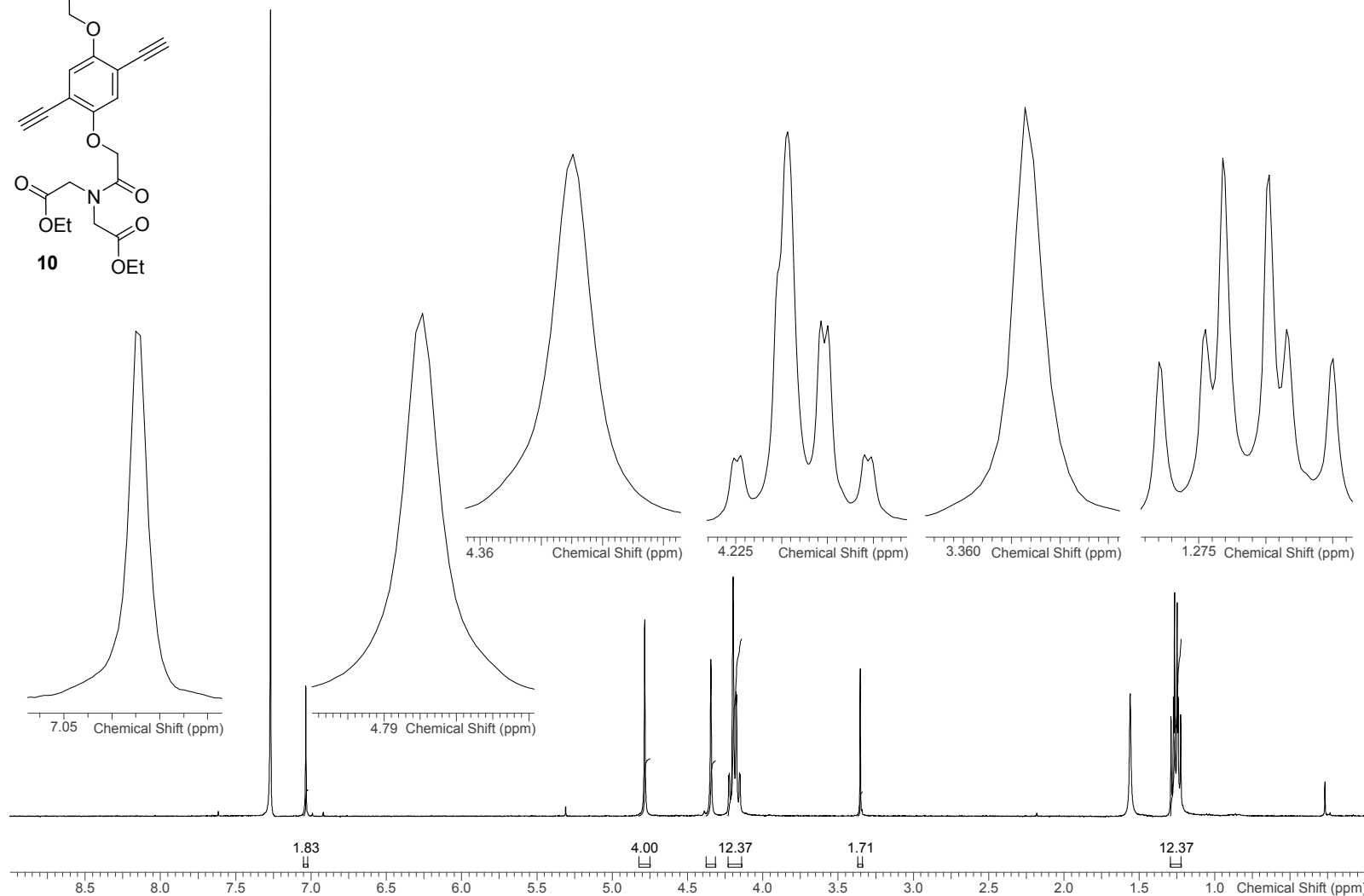
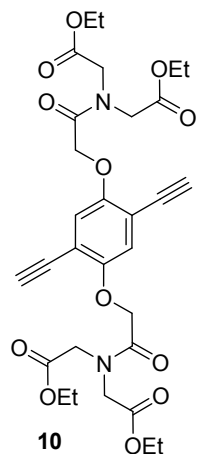
Date 20140805  
 Time 5.32  
 INSTRUM spect  
 PROBHD 5 mm CPPBBO BB  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 12019.230 Hz  
 FIDRES 0.183399 Hz  
 AQ 2.7262976 sec  
 RG 456  
 DW 41.600 usec  
 DE 12.00 usec  
 TE 298.0 K  
 D1 0.50000000 sec  
 TD0 16

==== CHANNEL f1 ====

NUC1 1H  
 P1 11.50 usec  
 PLW1 10.00000000 W  
 SFO1 400.3320009 MHz

F2 - Processing parameters

SI 65536  
 SF 400.3300974 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



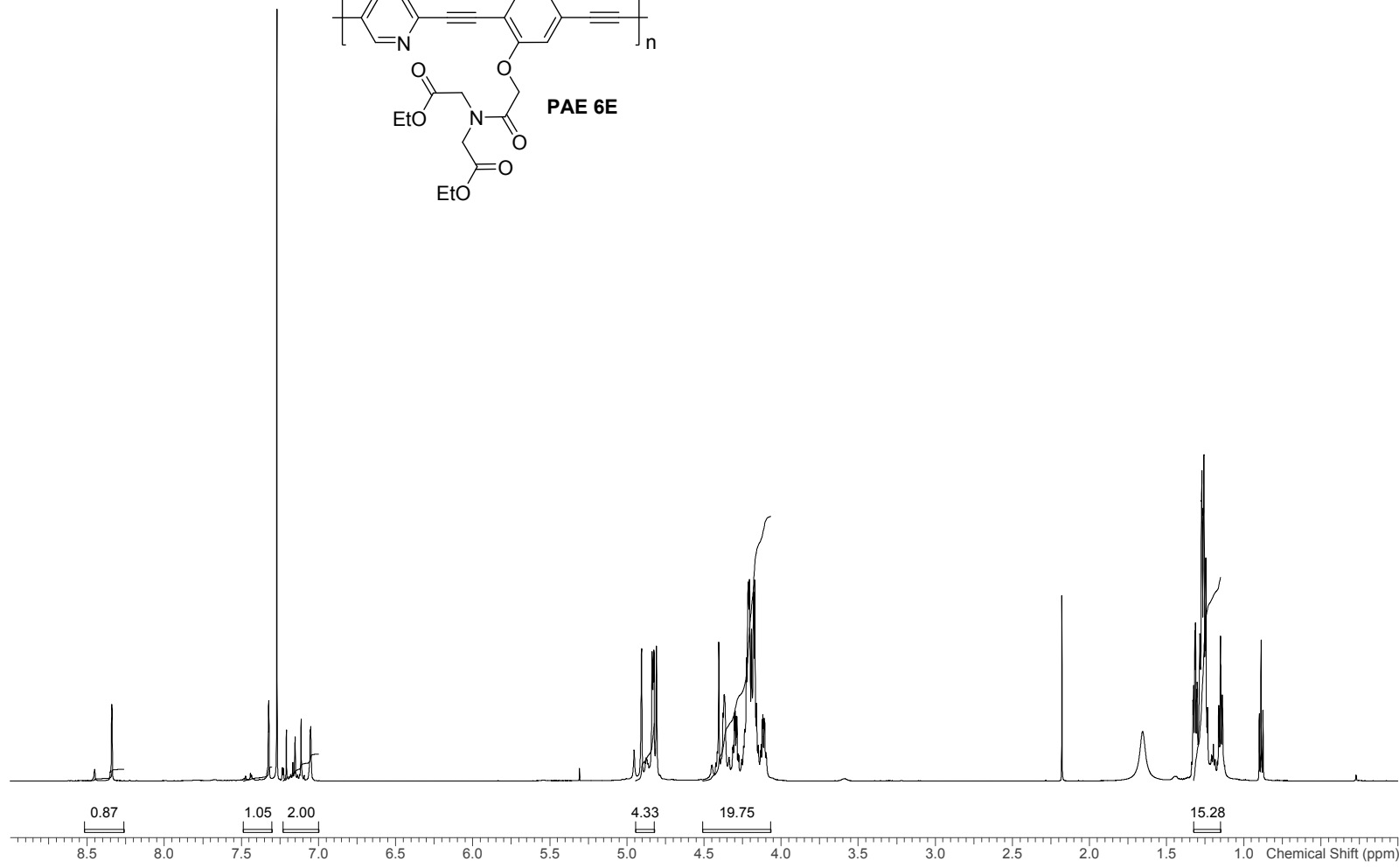
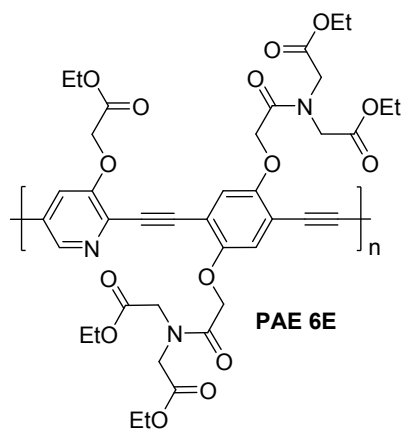
Current Data Parameters  
 NAME b140813ubmb.61  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date 20140813  
 Time 20.33  
 INSTRUM spect  
 PROBHD 5 mm PATXO 31P  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 8992.806 Hz  
 FIDRES 0.137219 Hz  
 AQ 3.6438515 sec  
 RG 574.7  
 DW 55.600 usec  
 DE 6.00 usec  
 TE 298.2 K  
 D1 0.10000000 sec  
 TD0 16

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 11.50 usec  
 PL1 -3.00 dB  
 SFO1 300.1315007 MHz

F2 - Processing parameters  
 SI 32768  
 SF 300.1300734 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



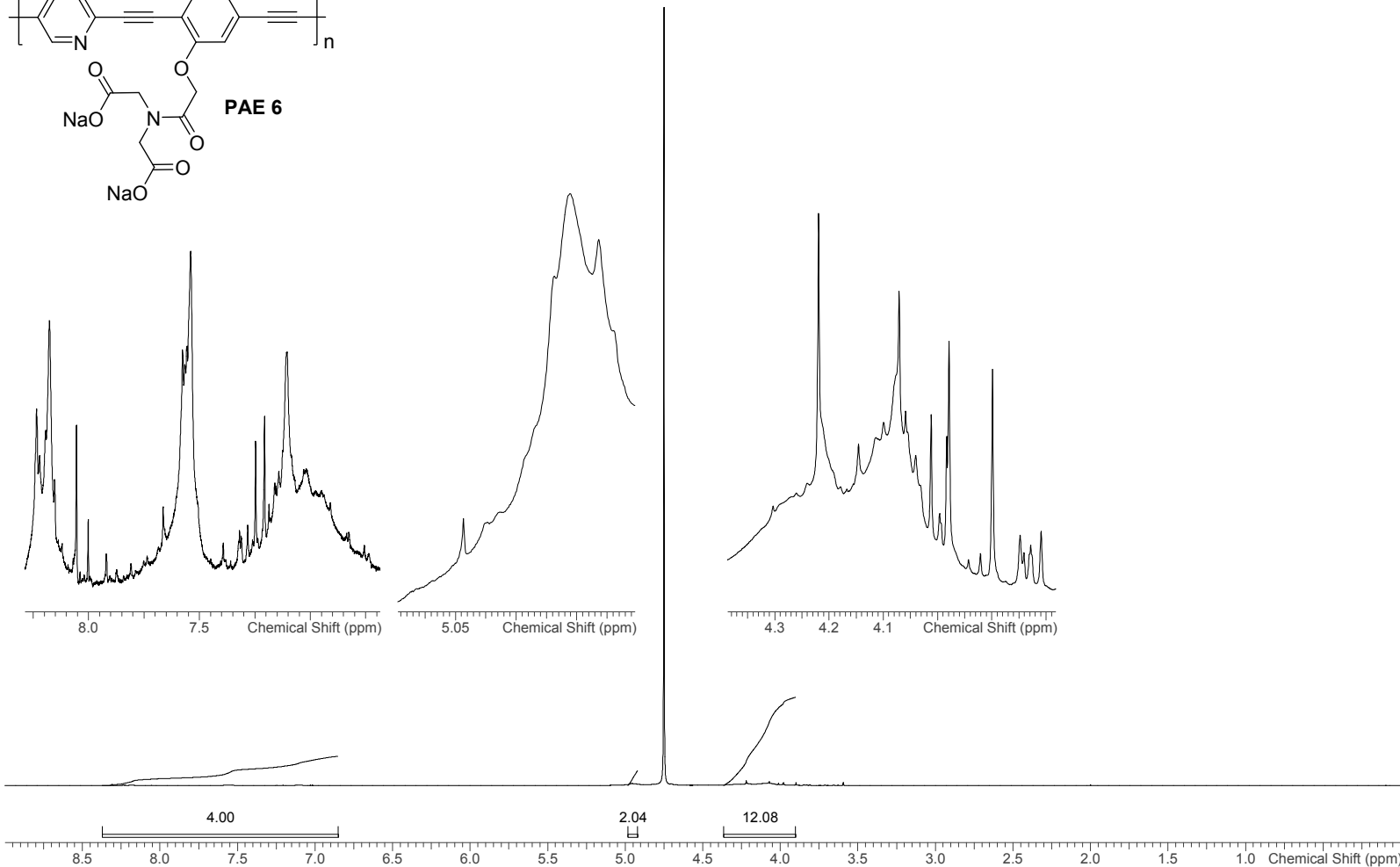
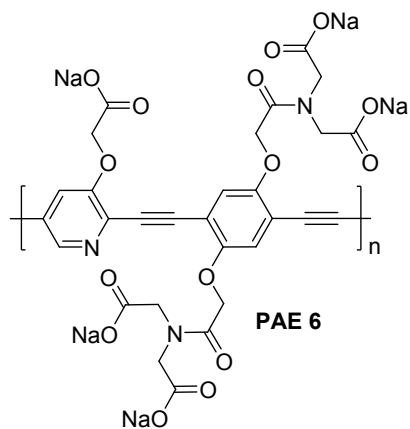


Current Data Parameters  
 NAME e140916ubmb.68  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date 20140916  
 Time 22.18  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 15.35  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters

NAME e150116ubmb.075  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

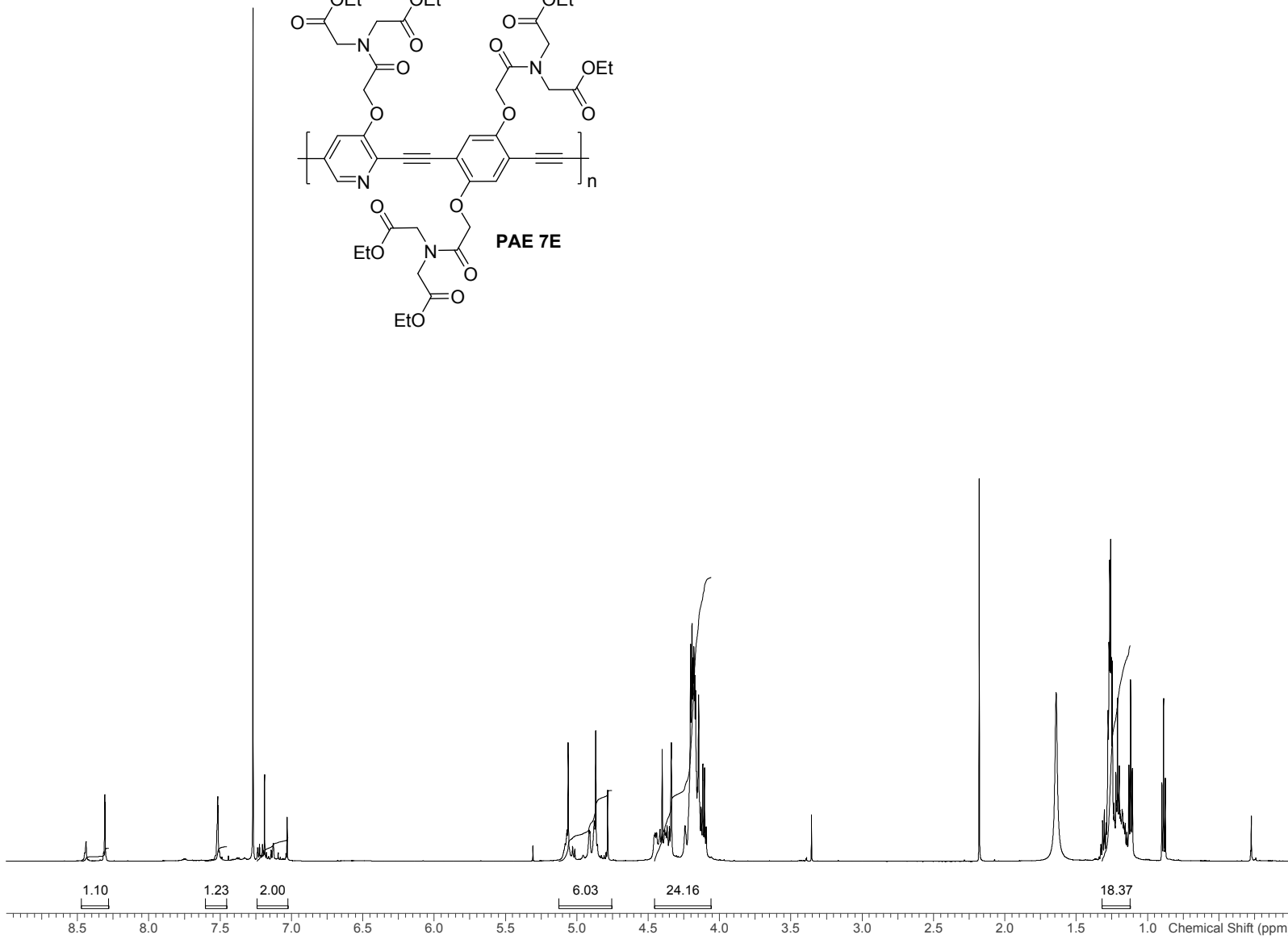
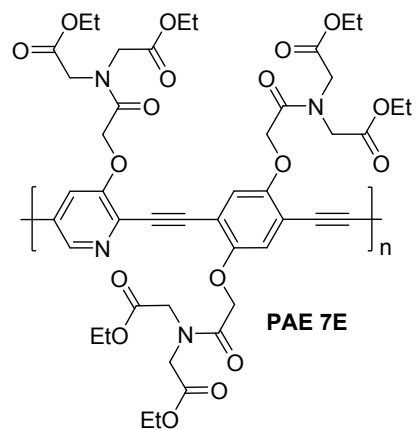
Date 20150117  
 Time 7.12  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT  $\text{D}_2\text{O}$   
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 16.84  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====

NUC1  $^1\text{H}$   
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

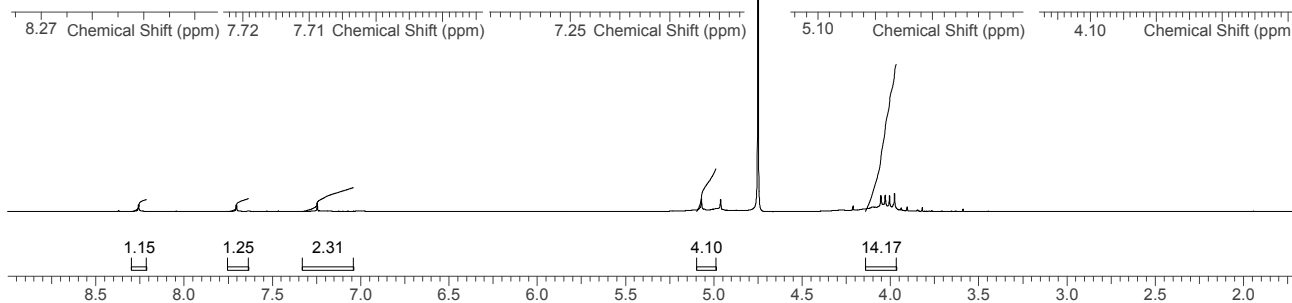
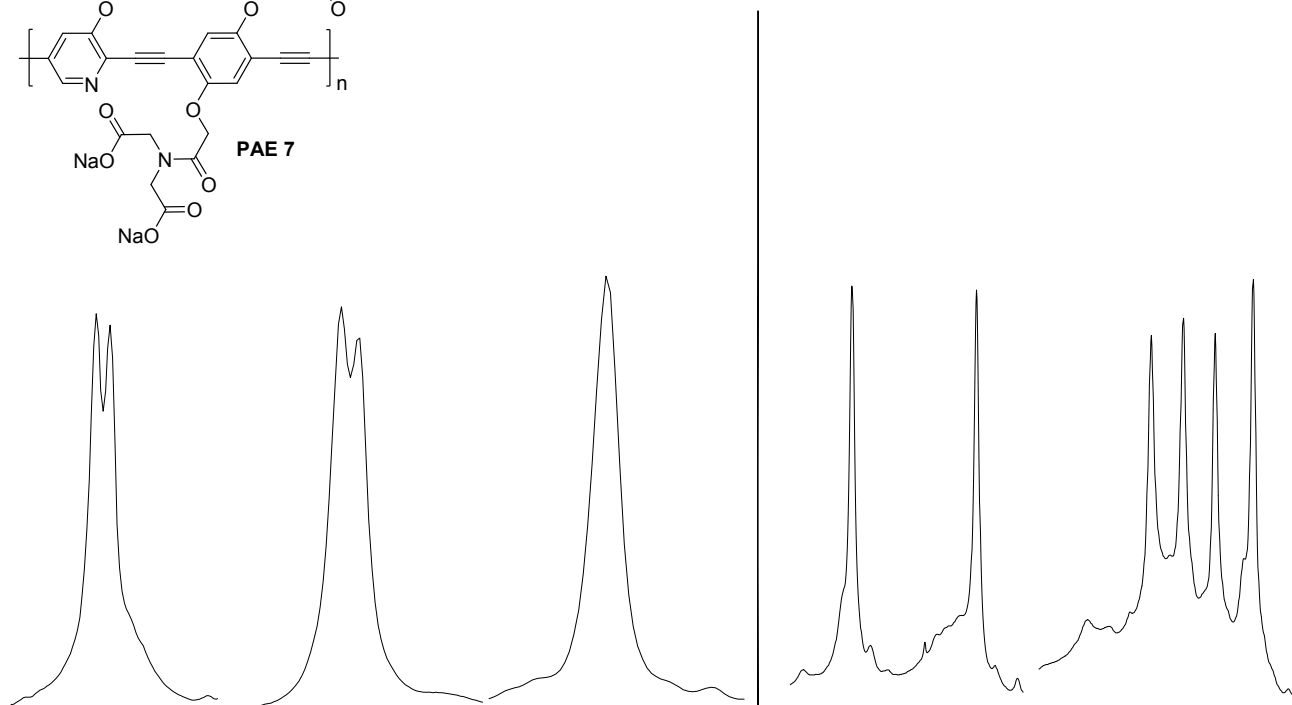
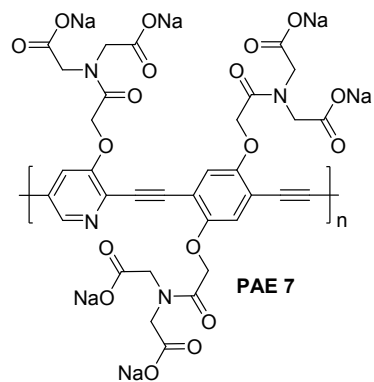


Current Data Parameters  
 NAME e140917ubmb.69  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date 20140918  
 Time 11.33  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 15.35  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters  
 SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters

NAME e150116ubmb.076  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters

Date 20150117  
 Time 16.20  
 INSTRUM spect  
 PROBHD 5 mm CPQCI-1H-  
 PULPROG zg30  
 TD 131072  
 SOLVENT D<sub>2</sub>O  
 NS 128  
 DS 2  
 SWH 18028.846 Hz  
 FIDRES 0.137549 Hz  
 AQ 3.6350634 sec  
 RG 18.85  
 DW 27.733 usec  
 DE 12.00 usec  
 TE 295.0 K  
 D1 0.10000000 sec  
 TD0 16

==== CHANNEL f1 =====

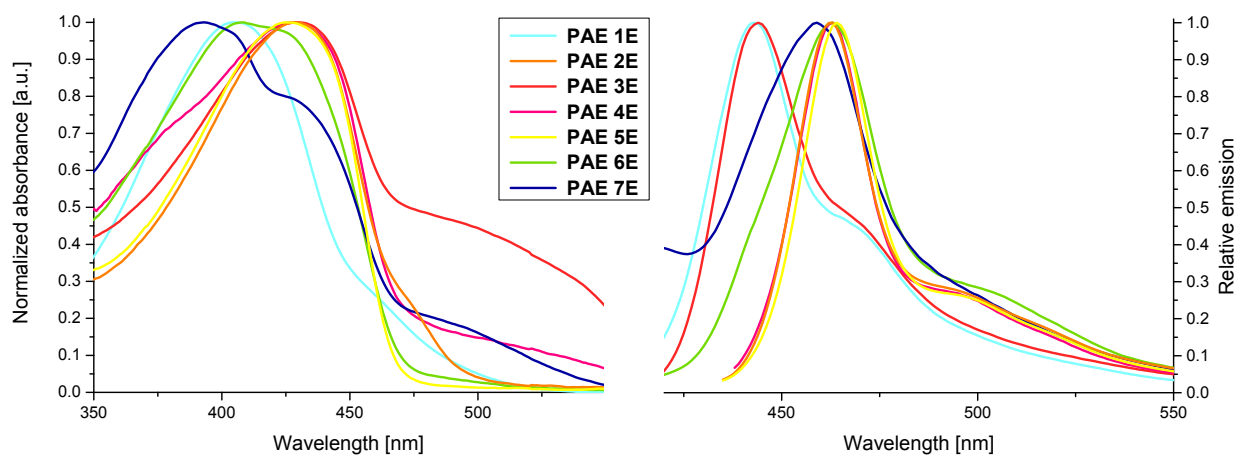
NUC1 1H  
 P1 7.63 usec  
 PLW1 7.5000000 W  
 SFO1 600.2468302 MHz

F2 - Processing parameters

SI 65536  
 SF 600.2438290 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

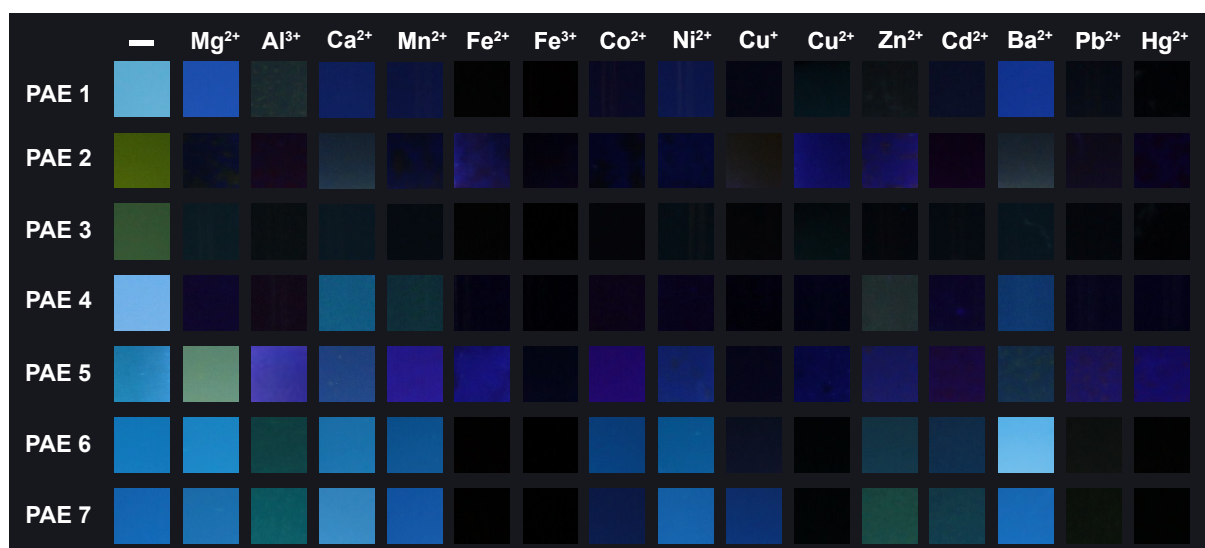
## 4. UV/VIS Spectra

Normalized UV/VIS spectra of the unsaponified polymer precursors is shown in the graphic below.



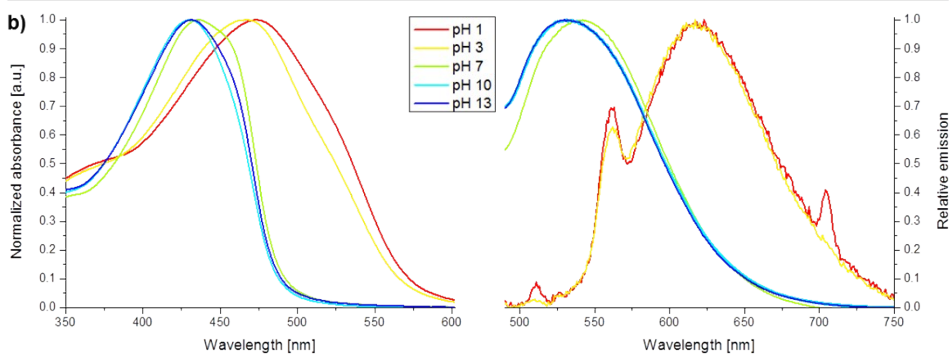
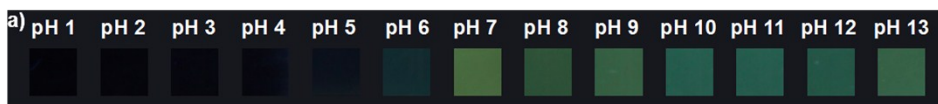
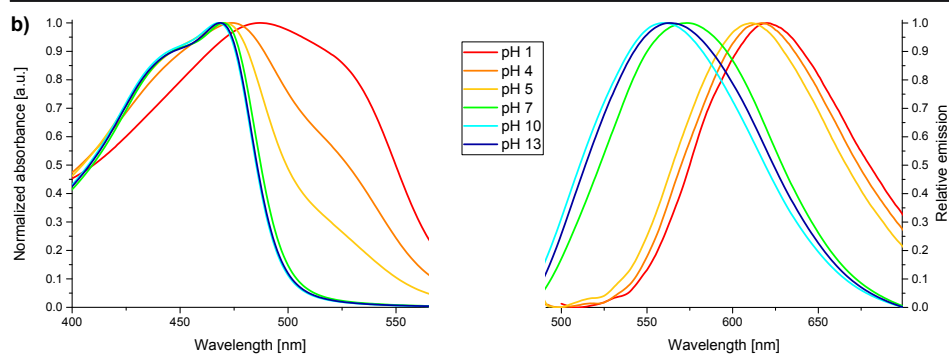
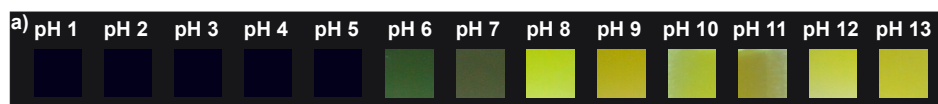
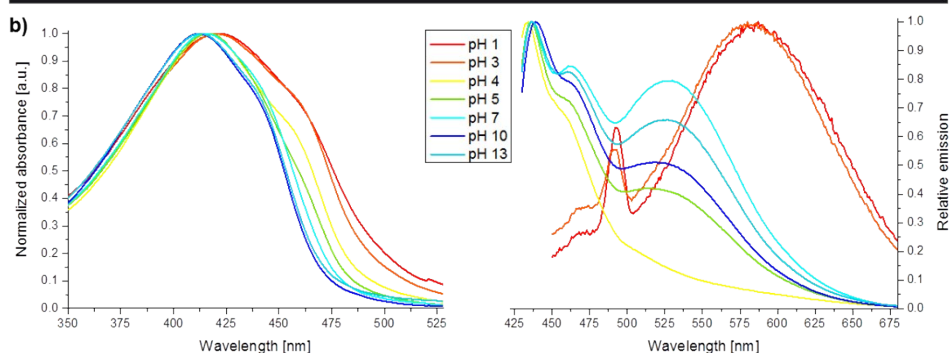
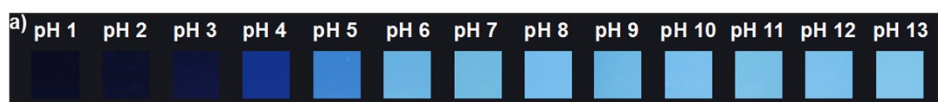
## 5. Metall Sensing Data

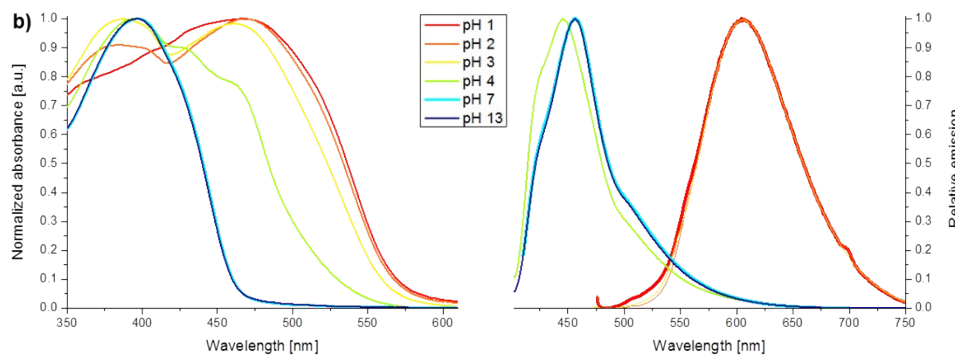
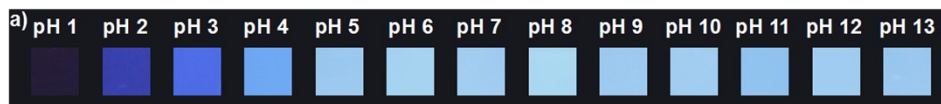
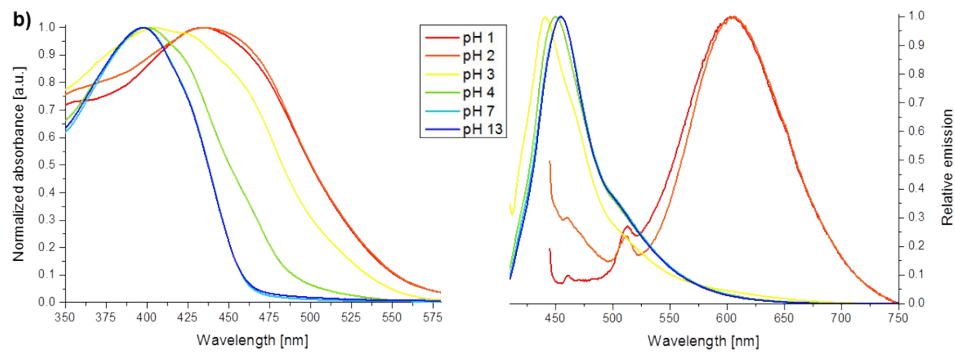
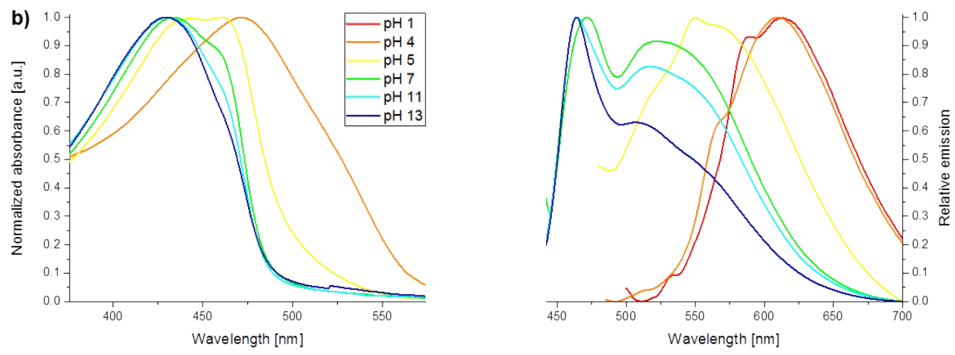
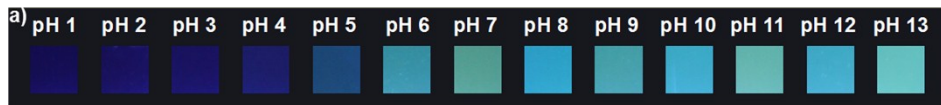
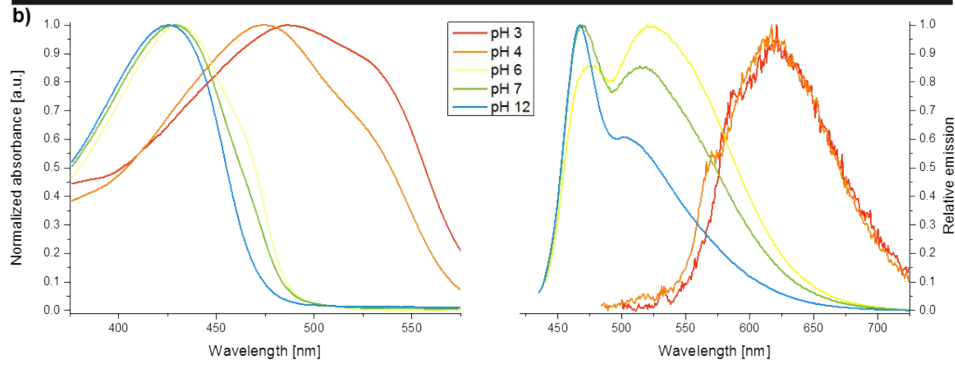
The picture below shows PAEs 1-7 in H<sub>2</sub>O (c = 5 µg/mL) with different metal cations (added as perchlorates and CuI) under a hand-held black light with illumination at 365 nm. Since solely Pb<sup>2+</sup> and Hg<sup>2+</sup> show quenching effects for all synthesized PAEs, we chose these cases for a detailed Stern-Volmer analysis.



## 6. pH-Titrations

All titrations were performed in buffer solutions as stated above. Under a) the corresponding photographs of the resulting solutions ( $c(\text{PAE}) = 2.5 \mu\text{g/mL}$ ) illuminated under a hand-held blacklight at 365 nm are shown. The corresponding normalized absorption and emission spectra are shown under b). The molecular structure belonging to the measurements is shown on the right.





## 7. Evaluation of Stern-Volmer Constants

All metal titrations were performed at pH 7 in PIPES buffer ( $c = 0.050$  M) and  $\text{KClO}_4$  ( $c = 0.1$  M). The gathered emission data is shown in the inset of the following graphs. The fitting was done using a modified Stern-Volmer equation, by either using the decreasing peak height or the decreasing peak area under the emission curve.

$$I_q = I_0 + \frac{I_{final} - I_0}{2} \times \left\{ 1 + \frac{[Q]}{[F]} + \frac{1}{K_{SV}[F]} - \left[ \left( 1 + \frac{[Q]}{[F]} + \frac{1}{K_{SV}[F]} \right)^2 - 4 \frac{[Q]}{[F]} \right]^{1/2} \right\}$$

$I_0$  = initial fluorescence intensity of the fluorophore

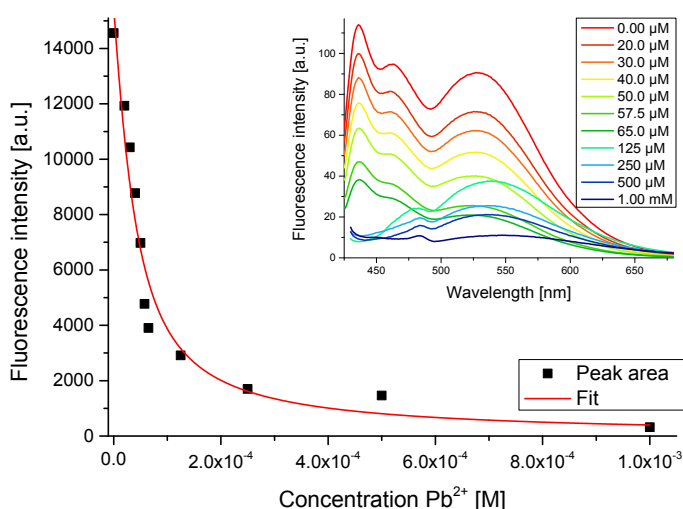
$I_{final}$  = final fluorescence intensity of the fluorophore

$I_q$  = fluorescence intensity by a given quencher concentration

$[F]$  = concentration of the fluorophore

$[Q]$  = concentration of the quencher

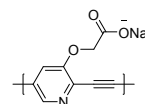
$K_{SV}$  = Stern-Volmer constant.



Quencher:  $\text{Pb}(\text{NO}_3)_2$

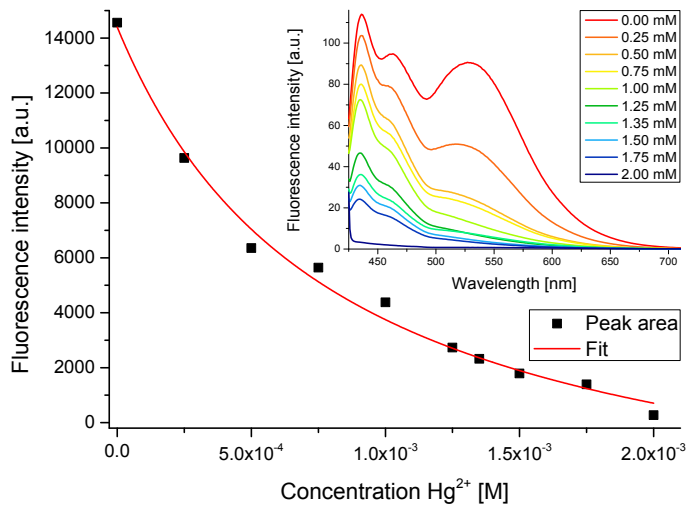
$$K_{SV} = 38165.96 \pm 11298.55$$

$$\log K_{SV} = 4.58 \pm 0.13$$



$$c(\text{Polymer}) = 2.85 \times 10^{-5} \text{ molL}^{-1}$$

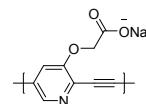




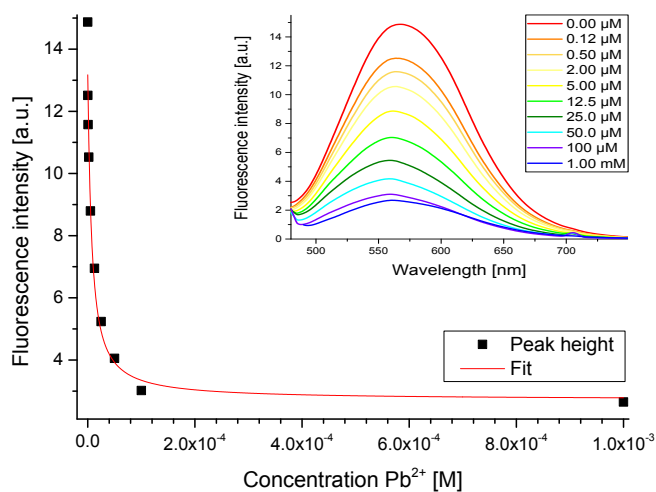
Quencher:  $\text{Hg}(\text{OAc})_2$

$$K_{SV} = 1283.89 \pm 221.14$$

$$\log K_{SV} = 3.11 \pm 0.07$$



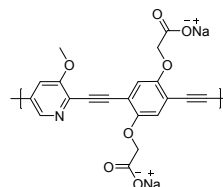
$$c(\text{Polymer}) = 2.85 \times 10^{-5} \text{ molL}^{-1}$$



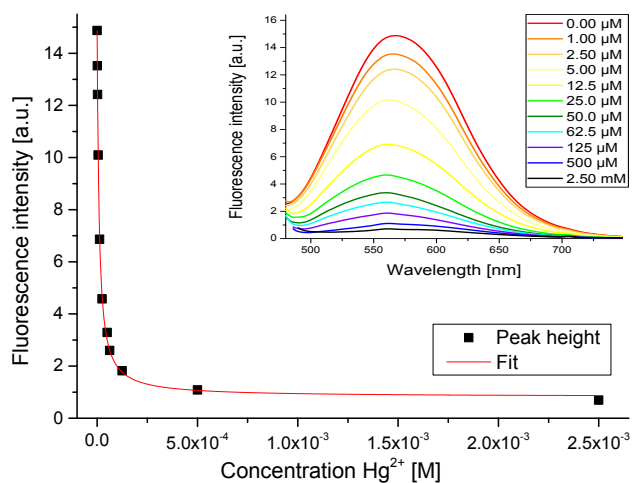
Quencher:  $\text{Pb}(\text{NO}_3)_2$

$$K_{SV} = 158989.88 \pm 50851.44$$

$$\log K_{SV} = 4.23 \pm 0.11$$



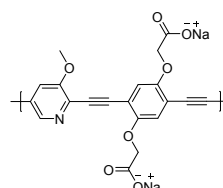
$$c(\text{Polymer}) = 1.85 \times 10^{-6} \text{ molL}^{-1}$$



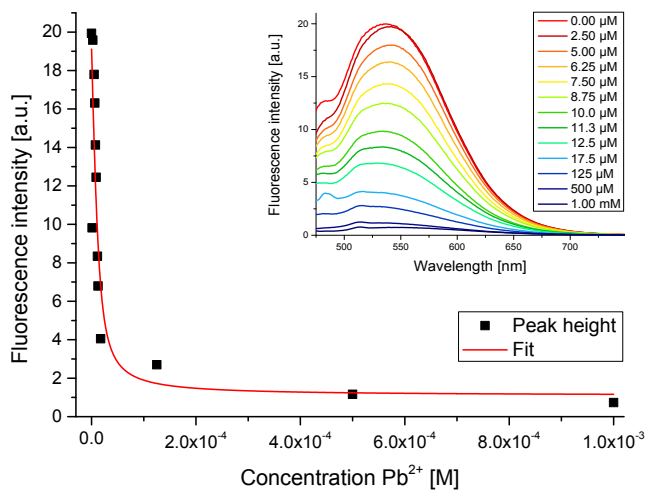
Quencher:  $\text{Hg}(\text{OAc})_2$

$$K_{SV} = 112161.96 \pm 5357.46$$

$$\log K_{SV} = 4.48 \pm 0.20$$



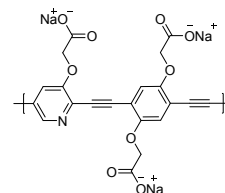
$$c(\text{Polymer}) = 1.85 \times 10^{-6} \text{ molL}^{-1}$$



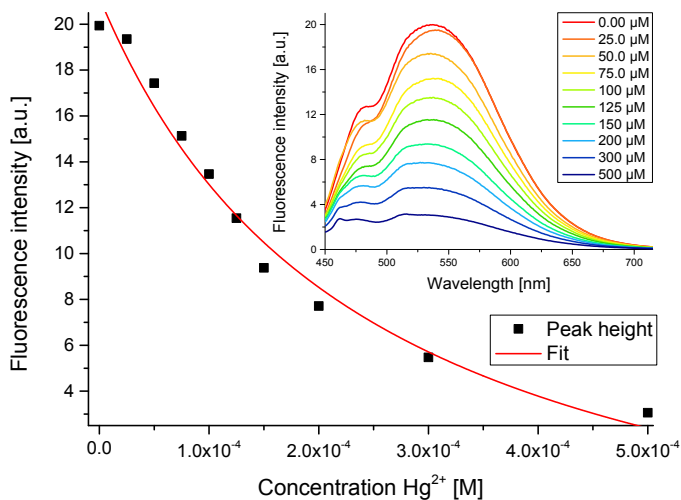
Quencher:  $\text{Pb}(\text{NO}_3)_2$

$$K_{SV} = 241691.06 \pm 218086.79$$

$$\log K_{SV} = 5.38 \pm 0.39$$



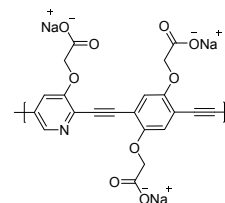
$$c(\text{Polymer}) = 1.26 \times 10^{-5} \text{ molL}^{-1}$$



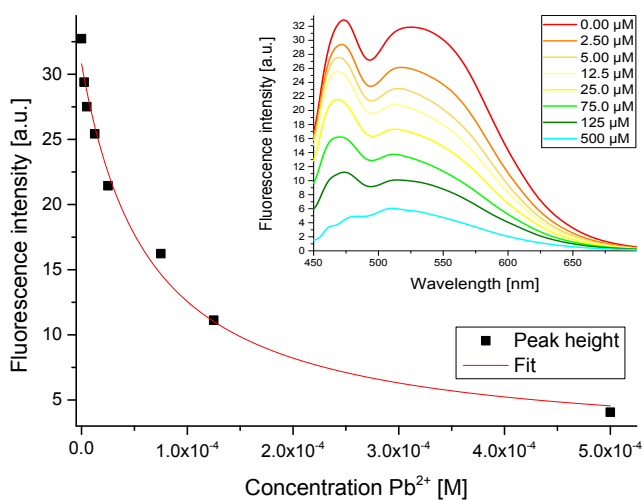
Quencher:  $\text{Hg}(\text{OAc})_2$

$$K_{SV} = 4364.94 \pm 1140.32$$

$$\log K_{SV} = 3.64 \pm 0.11$$



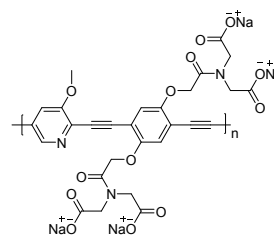
$$c(\text{Polymer}) = 1.26 \times 10^{-5} \text{ molL}^{-1}$$



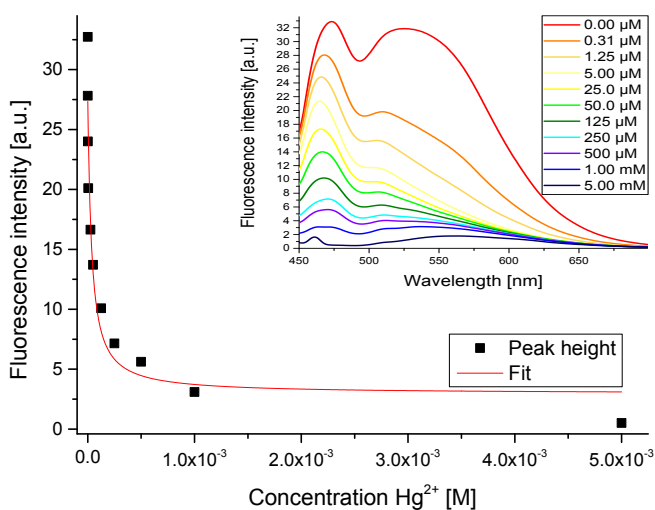
Quencher:  $\text{Pb}(\text{NO}_3)_2$

$$K_{SV} = 17103.86 \pm 4165.57$$

$$\log K_{SV} = 5.20 \pm 0.14$$



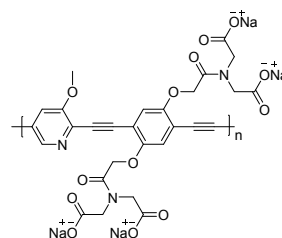
$$c(\text{Polymer}) = 6.56 \times 10^{-6} \text{ molL}^{-1}$$



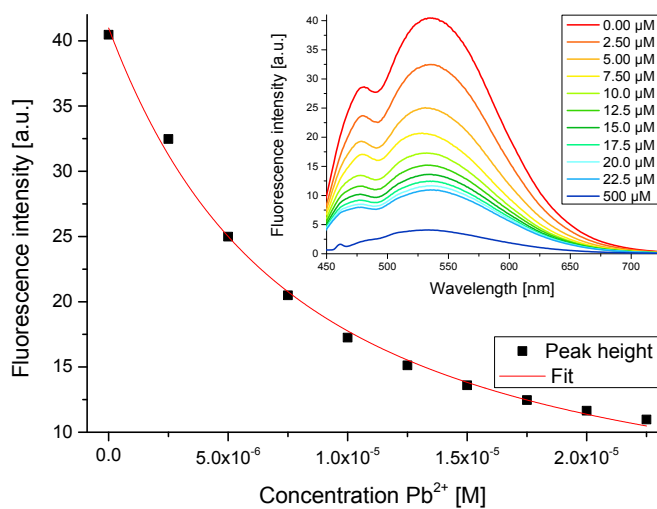
Quencher:  $\text{Hg}(\text{OAc})_2$

$$K_{SV} = 30507.07 \pm 13731.05$$

$$\log K_{SV} = 5.02 \pm 0.02$$



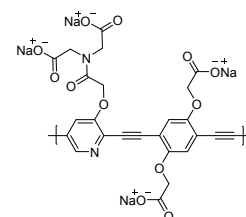
$$c(\text{Polymer}) = 6.56 \times 10^{-6} \text{ molL}^{-1}$$



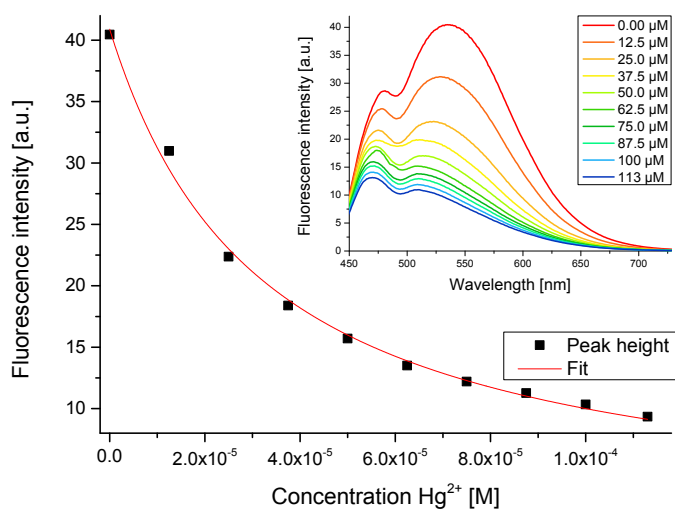
Quencher:  $\text{Pb}(\text{NO}_3)_2$

$$K_{SV} = 158645.66 \pm 17020.17$$

$$\log K_{SV} = 5.20 \pm 0.05$$



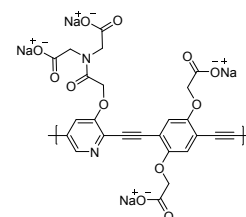
$$c(\text{Polymer}) = 1.84 \times 10^{-5} \text{ molL}^{-1}$$



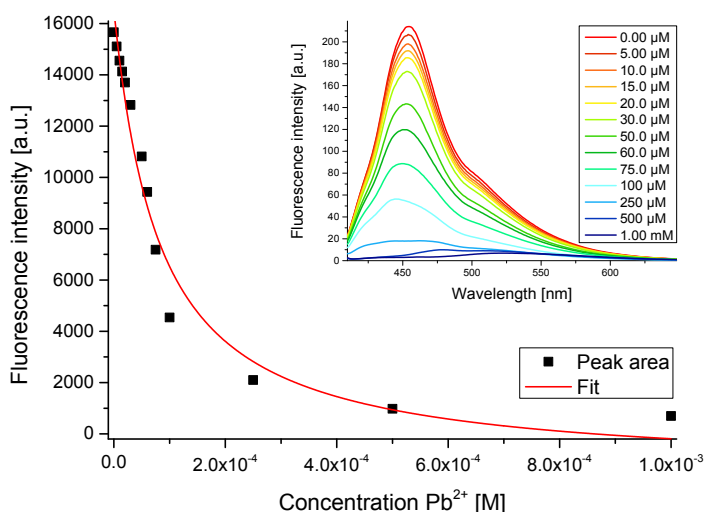
Quencher:  $\text{Hg}(\text{OAc})_2$

$$K_{SV} = 32782.94 \pm 3414.56$$

$$\log K_{SV} = 4.52 \pm 0.05$$



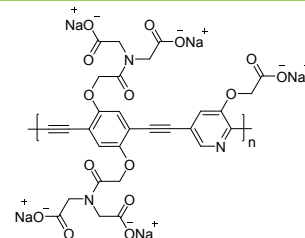
$$c(\text{Polymer}) = 1.84 \times 10^{-5} \text{ molL}^{-1}$$



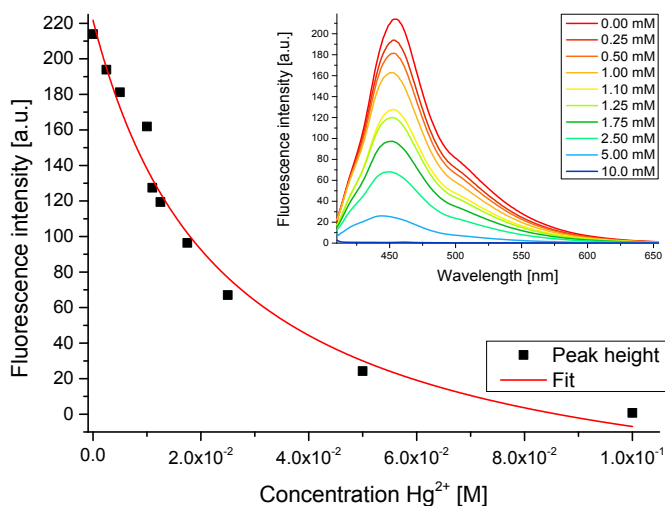
Quencher:  $\text{Pb}(\text{NO}_3)_2$

$$K_{SV} = 13065.18 \pm 2730.01$$

$$\log K_{SV} = 4.12 \pm 0.09$$



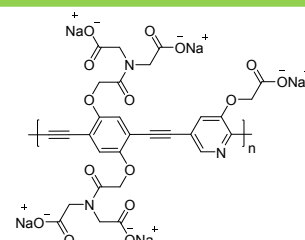
$$c(\text{Polymer}) = 7.65 \times 10^{-6} \text{ molL}^{-1}$$



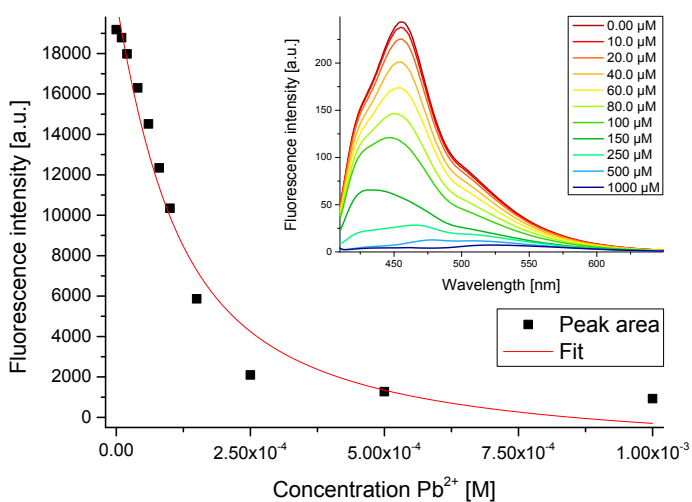
Quencher:  $\text{Hg}(\text{OAc})_2$

$$K_{SV} = 41.90 \pm 9.08$$

$$\log K_{SV} = 1.62 \pm 0.09$$



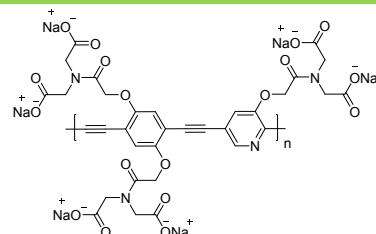
$$c(\text{Polymer}) = 7.65 \times 10^{-6} \text{ molL}^{-1}$$



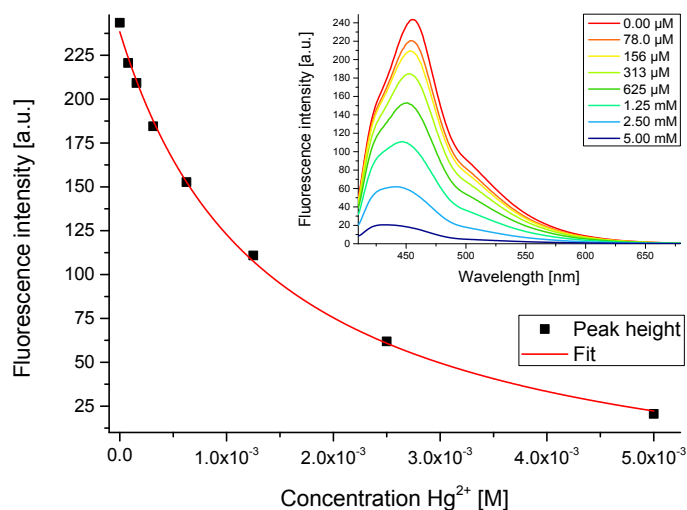
Quencher:  $\text{Pb}(\text{NO}_3)_2$

$$K_{SV} = 12842.89 \pm 3800.12$$

$$\log K_{SV} = 4.11 \pm 0.13$$



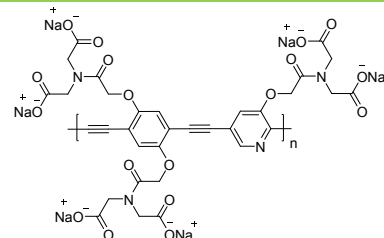
$$c(\text{Polymer}) = 6.51 \times 10^{-6} \text{ molL}^{-1}$$



Quencher:  $\text{Hg}(\text{OAc})_2$

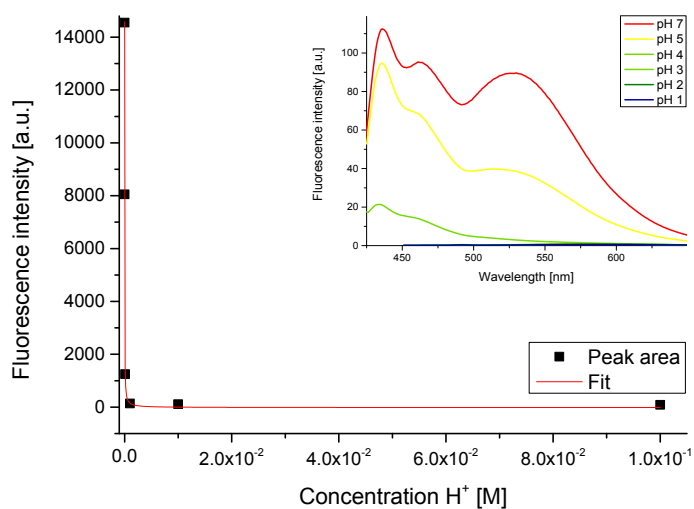
$$K_{SV} = 721.63 \pm 60.05$$

$$\log K_{SV} = 2.86 \pm 0.04$$



$$c(\text{Polymer}) = 6.51 \times 10^{-6} \text{ molL}^{-1}$$

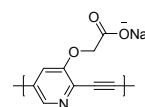
The emission data gathered during pH-titration was also fitted using the modified Stern-Volmer equation stated above. The obtained Stern-Volmer constants represent a roughly direction of the quenching behavior towards  $\text{H}^+$ . Since there is a remarkably bathochromic shift in emission wavelength only the decreasing peak area under the emission curve was used for fitting. The analyzed emission data is shown in the inset of the following graphs.



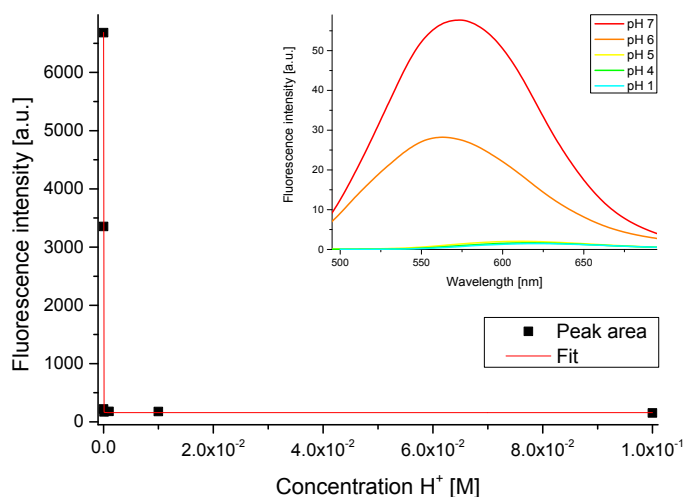
Quencher:  $\text{H}^+$

$$K_{SV} = 86226.68 \pm 5248.24$$

$$\log K_{SV} = 4.94 \pm 0.03$$



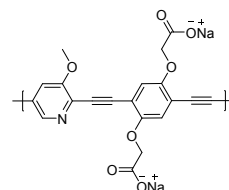
$$c(\text{Polymer}) = 2.85 \times 10^{-5} \text{ molL}^{-1}$$



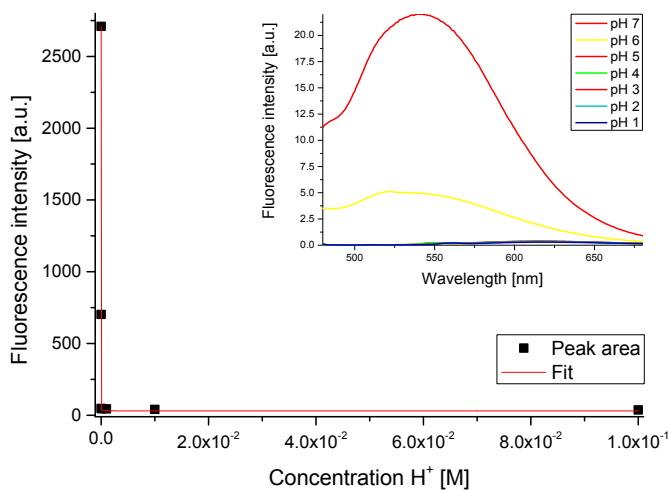
Quencher:  $H^+$

$$K_{SV} = 8034610 \pm 498304$$

$$\log K_{SV} = 6.90 \pm 0.03$$



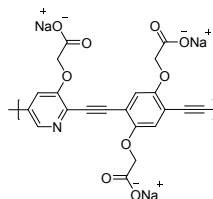
$$c(\text{Polymer}) = 1.85 \times 10^{-6} \text{ molL}^{-1}$$



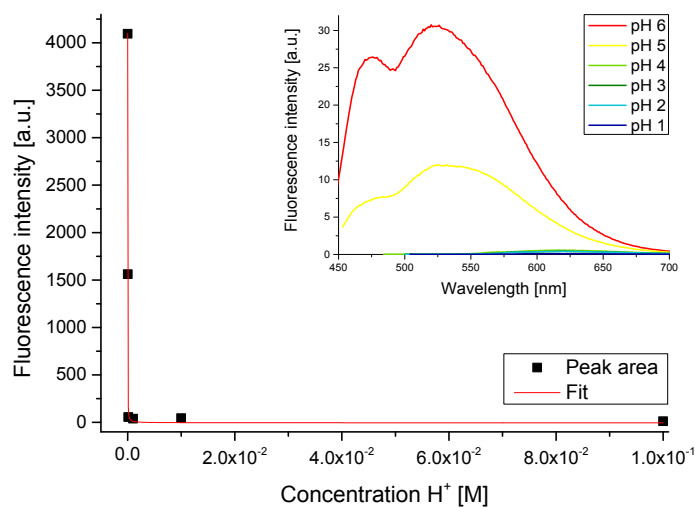
Quencher:  $H^+$

$$K_{SV} = 5438960 \pm 329568$$

$$\log K_{SV} = 6.74 \pm 0.03$$



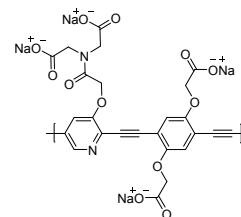
$$c(\text{Polymer}) = 1.26 \times 10^{-5} \text{ molL}^{-1}$$



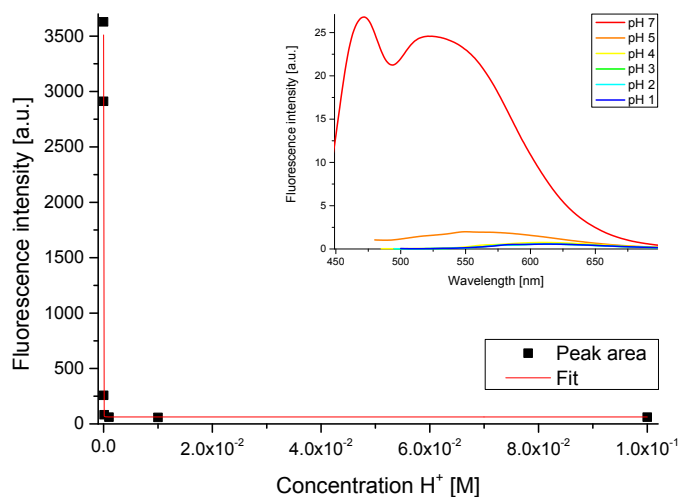
Quencher:  $H^+$

$$K_{SV} = 283207.47 \pm 27497.64$$

$$\log K_{SV} = 5.45 \pm 0.04$$



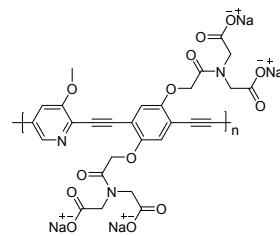
$$c(\text{Polymer}) = 1.84 \times 10^{-5} \text{ molL}^{-1}$$



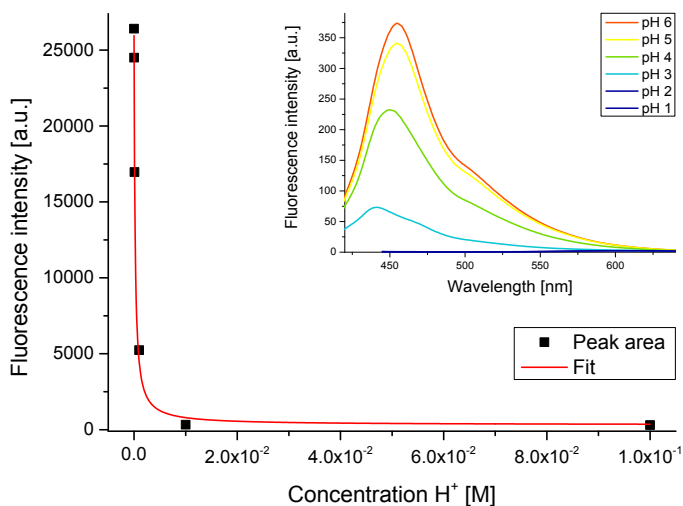
Quencher:  $H^+$

$$K_{SV} = 4829480 \pm 3104070$$

$$\log K_{SV} = 6.68 \pm 0.03$$



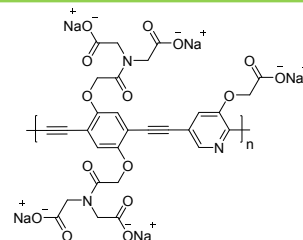
$$c(\text{Polymer}) = 6.56 \times 10^{-6} \text{ molL}^{-1}$$



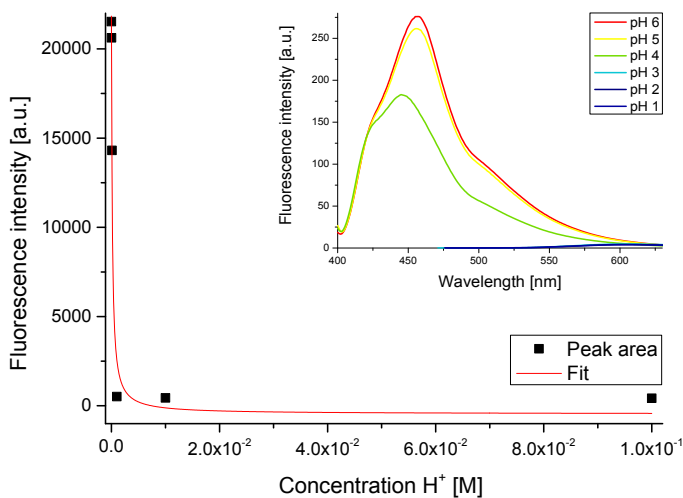
Quencher:  $H^+$

$$K_{SV} = 5258.23 \pm 687.95$$

$$\log K_{SV} = 3.72 \pm 0.06$$



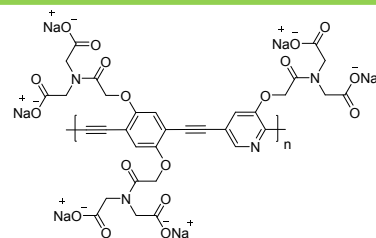
$$c(\text{Polymer}) = 7.65 \times 10^{-6} \text{ molL}^{-1}$$



Quencher:  $H^+$

$$K_{SV} = 6450.56 \pm 2080.16$$

$$\log K_{SV} = 3.81 \pm 0.14$$



$$c(\text{Polymer}) = 6.51 \times 10^{-6} \text{ molL}^{-1}$$

## 8. Supplemental References

- (1) G. Helmchen, G. Nill, D. Flockerzi, W. Schühle and M.S.K. Youssef, *Angew. Chem.* **1979**, *91*, 64-65; *Angew. Chem. Int. Ed. Engl.*, **1979**, *18*, 62-63
- (2) G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179
- (3) W. Melhuish, *J. Phys. Chem.*, **1961**, *65*, 229-235.
- (4) K. Seehafer, M. Bender and U. H. Bunz, *Macromolecules*, **2014**, *47*, 922-927.
- (5) D. J. Haydon, J. M. Bennett, D. Brown, I. Collins, G. Galbraith, P. Lancett, R. Macdonald, N. R. Stokes, P. K. Chauhan and J. K. Sutariya, *J. Med. Chem.*, **2010**, *53*, 3927-3936.
- (6) A. H. Berrie, G. T. Gewbold and F. S. Spring, *J. Chem. Soc.*, **1952**, 2042-2046.
- (7) I.-B. Kim, A. Dunkhorst, J. Gilbert and U. H. Bunz, *Macromolecules*, **2005**, *38*, 4560-4562.
- (8) I.-B. Kim, R. Phillips and U. H. Bunz, *Macromolecules*, **2007**, *40*, 5290-5293.