

Supporting Information for

Syntheses and Characteristics of Water-Soluble, Pyridine-Based Poly(aryleneethynylene)s

Kai Seehafer,[†] Markus Bender,[†] S. Thimon Schwaebel[†] and Uwe H. F. Bunz^{*,†,‡}

[†] Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

[‡] CAM, Centre of Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 225, 69120 Heidelberg, Germany

uwe.bunz@oci.uni-heidelberg.de

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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 colouring solutions. The following colouring solutions were used for the visualization of UV-inactive substances:

KMnO₄ solution: 2.0 g KMnO₄, 10.0 g K₂CO₃, 0.3 g NaOH, 200 mL distilled water.

Cer solution: 10.0 g Ce(SO)₄, 25 g phosphomolybdic acid hydrate, 1 L distilled water, 50 mL conc. H₂SO₄.

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.¹

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

¹H 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 CDCl₃ or D₂O as indicated in each case. Chemical shifts are reported in δ units relative to the solvent residual peak (CHCl₃ in CDCl₃ at δ_H = 7.27 ppm, HDO in D₂O at δ_H = 4.79 ppm) or TMS (δ_H = 0.00 ppm).² 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.

¹³C 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_3 or D_2O as indicated in each case. Chemical shifts are reported in δ units relative to the solvent signal: CDCl_3 [$\delta_{\text{C}} = 77.16$ ppm (central line of the triplet)] or TMS ($\delta_{\text{C}} = 0.00$ ppm).

High resolution mass spectra (HR-MS) were either recorded on a Bruker ApexQe hybrid 9.4 T FT-ICR-MS (ESI^+) or a Finnigan LCQ (ESI^+) 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 anager™ 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 7 ($\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$), pH 8 (borax/ HCl), pH 9 (KH phthalate/NaOH), pH 10 (borax/ NaOH), pH 11 (boric acid/ NaOH/KCl), pH 12 ($\text{Na}_2\text{HPO}_4/\text{NaOH}$), pH 13 (glycine/ NaOH/NaCl).

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 μm particles, 10^2 -, 10^3 - and 10^5 - 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 τ 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 Φ were obtained by the absolute method described in ref.³ using an Ulbricht sphere (band widths excitation: 2 nm; band widths emission: 3 nm). Given Φ for each sample are **average** values of at least two independent measurements. Detailed informations are given in Table 1.

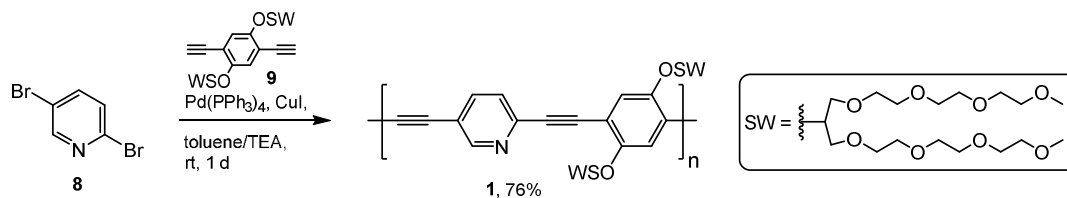
Table 1. Parameters for the determination of quantum yields Φ .

PAE	solvent	absolute absorbance at λ_{\max}	excitation [nm]	emission range [nm]	Φ
1	H ₂ O	0.087	440	430-750	0.07
	CH ₂ Cl ₂	0.083	400	390-700	0.23
2	H ₂ O	0.090	410	400-700	0.18
	CH ₂ Cl ₂	0.118	410	400-700	0.23
3	H ₂ O	0.097	450	440-750	0.17
	CH ₂ Cl ₂	0.101	420	410-700	0.42
4	H ₂ O, pH 7 ^a	0.094	420	410-750	0.10
5	H ₂ O	0.093	480	470-750	0.01
	CH ₂ Cl ₂	0.112	500	490-750	0.05
6	H ₂ O	0.111	490	480-750	0.02
	CH ₂ Cl ₂	0.103	500	490-750	0.06
7	H ₂ O	0.105	410	400-750	0.33
	CH ₂ Cl ₂	0.105	400	390-750	0.38

^abuffered (see above).

2. Synthetic Details and Analytical Data

Scheme 1. Synthesis of PAE 1

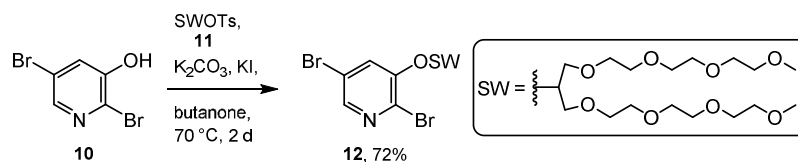


Compound **8** was purchased by Sigma-Aldrich®.

Compound 9 was synthesized according to the literature.⁴

Synthesis of 1. Monomer **8** (178 mg, 0.75 mmol) and monomer **9** (668 mg, 0.75 mmol) were dissolved in degassed toluene/NEt₃ (1.5:1, 15 mL/10 mL). Pd(PPh₃)₄ (43.3 mg, 37 μmol) and CuI (7.1 mg, 37 μmol) were added and the mixture was stirred at ambient temperature for 24 h. Brine and CH₂Cl₂ were added, the aqueous layer was separated and extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo. The crude product was dissolved in CH₂Cl₂ and slowly added to an excess of *n*-hexane. The precipitate was dissolved in H₂O and the resulting mixture was dialyzed against DI H₂O for 3 d. After freezy-drying the residue was again dissolved in CH₂Cl₂ and slowly added to an excess of *n*-hexane to gave **1** as spongy, red-brownish solid (548 mg, 76%). The *M_n* was estimated to be 2.0 x 10⁴ with a PDI of 2.5. ¹H NMR (600 MHz, CDCl₃): δ = 8.56-8.71 (m, 1 H), 7.77-7.88 (m, 1 H), 7.50-7.59 (m, 1 H), 7.23-7.31 (m, 2 H), 4.49-4.61 (m, 2 H), 3.50-3.86 (m, 56 H), 3.36 (bs, 12 H) ppm. IR (cm⁻¹): ν 2868, 1498, 1463, 1408, 1350, 1281, 1200, 1100, 947, 848. Due to low solubility, ¹³C NMR spectrum could not be obtained.

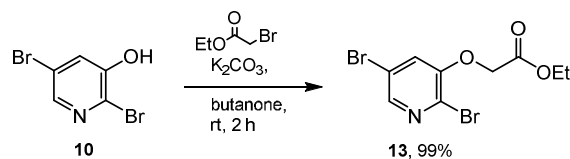
Scheme 2. Synthesis of monomer 12



Compounds **10**⁵ and **11**⁴ were synthesized according to the literature.

Synthesis of 12. A solution of compound **10** (1.00 g, 3.95 mmol), tosylate **11** (2.34 g, 4.35 mmol), K₂CO₃ (2.74 g, 19.75 mmol) and KI (32.8 mg, 0.20 mmol) in butanone (20 mL) was stirred at 70 °C for 2 days. Water and CH₂Cl₂ were added, the aqueous layer was separated and extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel [petroleum ether/ethyl acetate/CH₂Cl₂/MeOH (8/3/1.5/0.5)] to give compound **12** (1.75 g, 2.83 mmol, 72%) as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.04 (d, *J* = 2.1 Hz, 1 H), 7.67 (d, *J* = 2.1 Hz, 1 H), 4.55 (m, 1 H), 3.50-3.80 (m, 28 H), 3.36 (s, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.22, 142.64, 132.50, 126.60, 119.46, 80.82, 72.06, 71.39, 71.17, 70.77, 70.75, 70.71, 70.66, 59.17 ppm. HR-MS (ESI⁺): *m/z* calcd. for C₂₂H₃₈NO₉Br₂⁺ 620.0887 [M+H]⁺; found 620.0895. C₂₂H₃₇NO₉Br₂ (619.34): calcd. C 42.66, H 6.02, N 2.26, Br 25.80; found C 42.82, H 6.03, N 2.09, Br 25.34.

Scheme 3. Synthesis of monomer 13

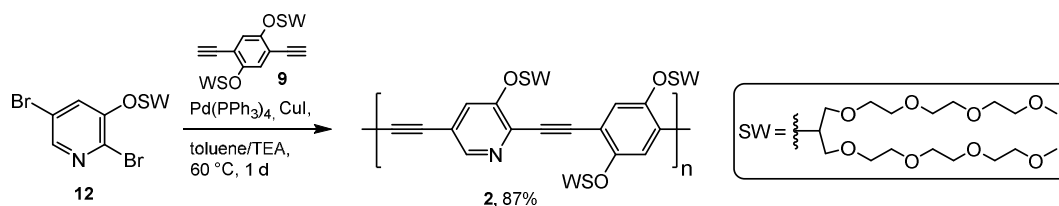


Compound **10** was synthesized according to the literature.⁵

Synthesis of 13. Ethylbromoacetate (526 μL, 4.74 mmol) was added to a solution of compound **10** (1.00 g, 3.95 mmol) and K₂CO₃ (2.74 g, 19.75 mmol) in butanone (20 mL) and was stirred at ambient temperature for 2 h. Water and CH₂Cl₂ were added, the aqueous layer was separated and extracted with CH₂Cl₂. The combined organic layers were dried over

MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel [petroleum ether/ethyl acetate (5/1)] to give compound **13** (1.33 g, 3.92 mmol, 99%) as colorless solid (m.p. 56-58 °C). ¹H NMR (600 MHz, CDCl₃): δ = 8.11 (d, *J* = 1.9 Hz, 1 H), 7.18 (d, *J* = 1.9 Hz, 1 H), 4.72 (s, 2 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 1.31 (t, *J* = 7.1 Hz, 3 H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 167.33, 151.94, 143.25, 131.71, 123.42, 119.46, 66.24, 62.13, 14.26 ppm. HR-MS (ESI⁺): *m/z* calcd. for C₉H₁₀NO₃Br₂⁺ 337.9022 [M+H]⁺; found 337.9018. C₉H₉NO₃Br₂ (338.98): calcd. C 31.89, H 2.68, N 4.13, Br 47.14; found C 31.94, H 2.73, N 4.32, Br 47.13.

Scheme 4. Synthesis of PAE 2

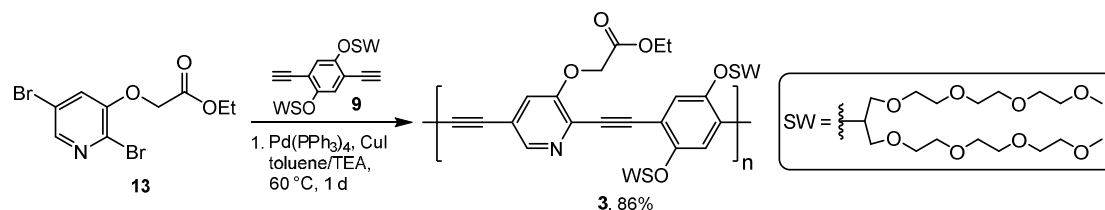


Compound **9** was synthesized according to the literature.⁴

Synthesis of 2. Monomer **12** (310 mg, 0.50 mmol) and monomer **9** (446 mg, 0.50 mmol) were dissolved in degassed toluene/NEt₃ (1.5:1, 9 mL/6 mL). Pd(PPh₃)₄ (28.9 mg, 25 μmol) and CuI (4.8 mg, 25 μmol) were added and the mixture was stirred at 60 °C for 24 h. Brine and CH₂Cl₂ were added, the aqueous layer was separated and extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo. Two times, the crude product was dissolved in CHCl₃ and slowly added to an excess of *n*-hexane. The precipitate was dissolved in H₂O, Na₂EDTA (100 mg) was added, and the resulting mixture was dialyzed against DI H₂O for 3 d. After freezy-drying the residue was again dissolved in CHCl₃ and slowly added to an excess of *n*-hexane to gave **2** as sticky, dark orange oil (588 mg, 87%). The *M_n* was estimated to be 1.5 x 10⁴ with a PDI of 2.7. ¹H NMR (600 MHz, CDCl₃): δ = 8.21-8.37 (m, 1 H), 7.51-7.79 (m, 1 H), 7.15-7.24 (m, 2 H), 4.44-4.70 (m, 3 H), 3.41-3.86 (m, 84 H), 3.34 (bs, 18 H) ppm. IR (cm⁻¹): ν 2868, 1498, 1455, 1399,

1350, 1199, 1095, 1039, 945, 850. Due to low solubility, ^{13}C NMR spectrum could not be obtained.

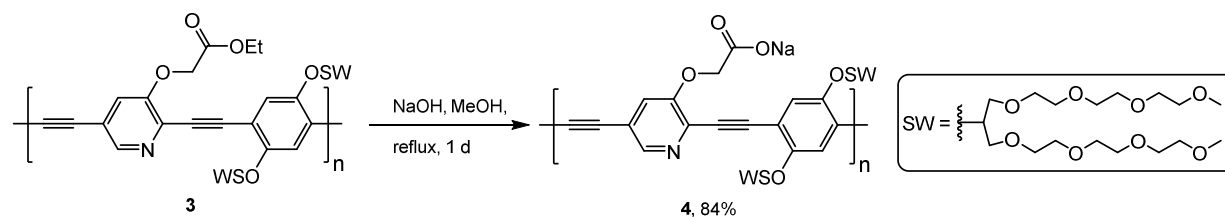
Scheme 5. Synthesis of PAE 3



Compound **9** was synthesized according to the literature.⁴

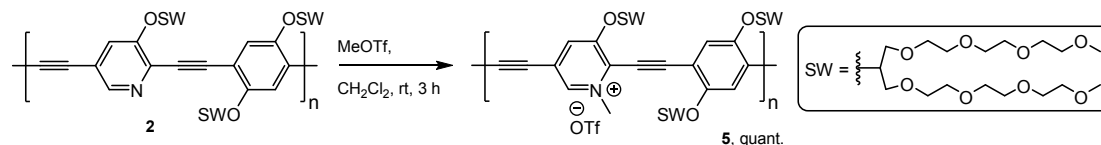
Synthesis of 3. Monomer **13** (170 mg, 0.50 mmol) and monomer **9** (446 mg, 0.50 mmol) were dissolved in degassed toluene/ NEt_3 (1.5:1, 9 mL/6 mL). $\text{Pd}(\text{PPh}_3)_4$ (28.9 mg, 25 μmol) and CuI (4.8 mg, 25 μmol) were added and the mixture was stirred at 60 $^\circ\text{C}$ for 24 h. Brine 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 CHCl_3 and slowly added to an excess of *n*-hexane. The precipitate was dissolved in H_2O , Na_2EDTA (100 mg) was added, and the resulting mixture was dialyzed against DI H_2O for 3 d. After freezy-drying, the residue was again dissolved in CHCl_3 and slowly added to an excess of *n*-hexane to give **3** as sticky, dark orange oil (459 mg, 86%). The M_n was estimated to be 1.4×10^4 with a PDI of 2.4. ^1H NMR (600 MHz, CDCl_3): δ = 8.30-8.42 (m, 1 H), 7.17-7.35 (m, 3 H), 4.82-4.91 (m, 2 H), 4.48-4.62 (m, 2 H), 4.24-4.32 (m, 2 H), 3.48-3.85 (m, 56 H), 3.35 (bs, 12 H), 1.28-1.33 (m, 3 H) ppm. IR (cm^{-1}): ν 2869, 1754, 1498, 1456, 1401, 1200, 1094, 947, 851. Due to low solubility, ^{13}C NMR spectrum could not be obtained.

Scheme 6. Synthesis of PAE 4



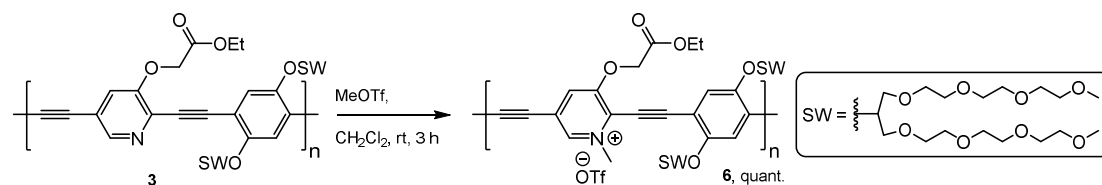
Synthesis of 4. NaOH (150 mg, 3.75 mmol) was added to a solution of polymer **3** (205 mg, 0.19 mmol) in MeOH (40 mL) and the resulting mixture was refluxed for 24 h. The solvent was reduced in vacuo, the residue was dissolved in H₂O and dialyzed against DI H₂O for 3 d. After freezy-drying, the residue was dissolved in MeOH and slowly added to an excess of Et₂O to give **4** as sticky, dark orange oil (171 mg, 84%). The *M_n* and PDI result from polymer **3**. ¹H NMR (600 MHz, D₂O): δ = 8.00-8.45 (m, 1 H), 6.95-7.83 (m, 3 H), 4.49-4.80 (m, 4 H), 3.41-4.07 (m, 56 H), 3.31 (bs, 12 H) ppm. IR (cm⁻¹): ν 2869, 1498, 1455, 1400, 1350, 1199, 1093, 945, 850. Due to low solubility, ¹³C NMR spectrum could not be obtained.

Scheme 7. Synthesis of PAE 5



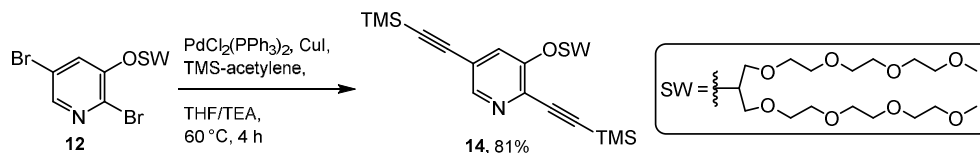
Synthesis of 5. Methyl trifluoromethanesulfonate (6.3 μL, 55.7 μmol) was added to a solution of polymer **2** (37.2 mg, 27.6 μmol) in CH₂Cl₂ (1 mL) and the resulting mixture was stirred at ambient temperature for 3 h. The solvent and MeOTf were evaporated in vacuo to give **5** as red solid (42 mg, quant.). The *M_n* and PDI result from polymer **2**. ¹H NMR (600 MHz, D₂O): δ = 8.48-8.93 (m, 2 H), 7.54-7.64 (m, 2 H), 5.10-5.19 (bs, 1 H), 4.84-4.95 (bs, 2 H), 4.44-4.63 (m, 3 H), 3.50-4.00 (m, 84 H), 3.30-3.34 (m, 18 H) ppm. IR (cm⁻¹): ν 2872, 1272, 1223, 1097, 1030, 948, 850, 637. Due to low solubility, ¹³C NMR spectrum could not be obtained.

Scheme 8. Synthesis of PAE 6



Synthesis of 6. Methyl trifluoromethanesulfonate (42.6 μL , 0.38 mmol) was added to a solution of polymer **3** (201 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) and the resulting mixture was stirred at ambient temperature for 3 h. The solvent and MeOTf were evaporated in vacuo to give **6** as red solid (232 mg, quant.). The M_n and PDI result from polymer **3**. ^1H NMR (600 MHz, D_2O): δ = 8.46-8.92 (m, 1 H), 7.25-7.92 (m, 3 H), 5.14-5.40 (m, 2 H), 4.85-5.00 (bs, 2 H), 4.21-4.72 (m, 5 H), 3.37-4.18 (m, 56 H), 3.18-3.33 (m, 12 H), 1.28-1.49 (m, 3 H) ppm. IR (cm^{-1}): ν 2872, 1749, 1262, 1220, 1093, 1029, 851, 636. Due to low solubility, ^{13}C NMR spectrum could not be obtained.

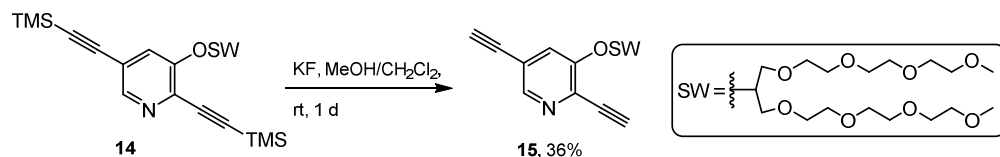
Scheme 9. Synthesis of compound 14



Synthesis of 14. Compound **12** (500 mg, 0.81 mmol) was dissolved in degassed toluene/piperidine (1:1, 2 mL/2 mL). $\text{PdCl}_2(\text{PPh}_3)_2$ (28.3 mg, 40 μmol) and CuI (8.0 mg, 40 μmol) were added. Subsequently TMS-acetylene was added dropwise and the resulting mixture was stirred at 70 $^\circ\text{C}$ for 4 h. The reaction mixture was quenched by the addition of aqueous NH_4Cl (15 mL). 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 purified by flash chromatography on silica gel [petroleum ether/ethyl acetate/ CH_2Cl_2 /MeOH (7/1/1/0.5)] to give compound **14** (427 mg, 0.65 mmol, 81%) as brown oil. ^1H NMR (600 MHz, CDCl_3): δ = 8.25 (d, J = 1.5 Hz, 1 H), 7.49 (d, J = 1.5 Hz, 1 H), 4.56

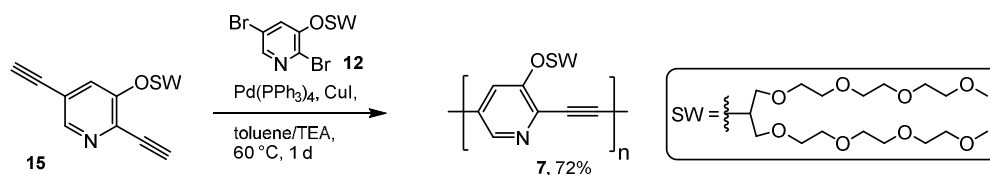
(m, 1 H), 3.53-3.80 (m, 28 H), 3.38 (s, 6 H), 0.27 (s, 18 H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 155.82, 145.43, 133.67, 125.26, 120.13, 101.15, 100.99, 100.39, 99.71, 79.61, 71.90, 71.28, 70.83, 70.63, 70.60, 70.56, 70.51, 59.03, 0.24 ppm. HR-MS (ESI^+): m/z calcd. for $\text{C}_{32}\text{H}_{56}\text{NO}_9\text{Si}_2^+$ 654.3488 $[\text{M}+\text{H}]^+$; found 654.3495. $\text{C}_{32}\text{H}_{55}\text{NO}_9\text{Si}_2$ (653.96): calcd. C 58.77, H 8.48, N 2.14; found C 58.95, H 8.40, N 2.15.

Scheme 10. Synthesis of monomer 15



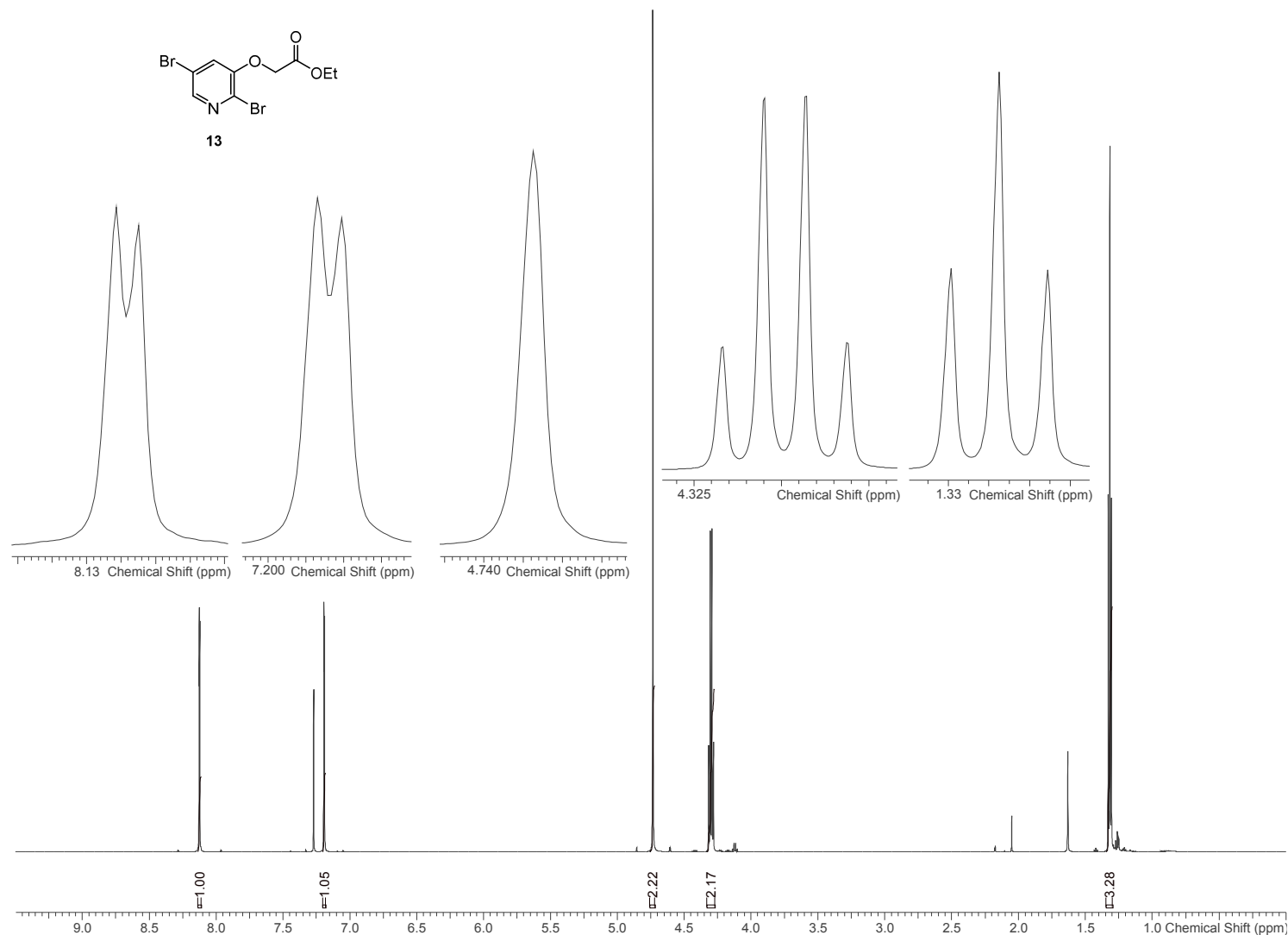
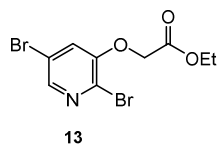
Synthesis of 15. Compound **14** (409 mg, 0.62 mmol) was dissolved in MeOH (10 mL). KF (145 mg, 2.50 mmol) in Methanol (10 mL) was added and stirred at ambient temperature overnight. The reaction mixture was quenched by the addition of SiO_2 , filtrated and concentrated in vacuo. Flash chromatography on silica gel [petroleum ether/ethyl acetate/ CH_2Cl_2 /MeOH (5/3/1/1)] of the crude product afforded compound **15** (114 mg, 0.22 mmol, 36%) as yellow oil. ^1H NMR (300 MHz, CDCl_3): δ = 8.29 (d, J = 1.4 Hz, 1 H), 7.60 (d, J = 1.4 Hz, 1 H), 4.58 (m, 1 H), 3.53-3.82 (m, 28 H), 3.46 (s, 1 H), 3.38 (s, 6 H), 3.29 (s, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 156.22, 145.44, 133.35, 125.26, 119.52, 82.99, 81.88, 80.02, 79.74, 79.49, 71.92, 71.25, 70.94, 70.63, 70.56, 70.51, 59.01 ppm. HR-MS (ESI^+): m/z calcd. for $\text{C}_{26}\text{H}_{40}\text{NO}_9^+$ 510.2698 $[\text{M}+\text{H}]^+$; found 510.2699. $\text{C}_{26}\text{H}_{39}\text{NO}_9$ (509.60): calcd. C 61.28, H 7.71, N 2.75; found C 61.01, H 7.81, N 2.83.

Scheme 11. Synthesis of PAE 7



Synthesis of 7. Monomer **15** (230 mg, 0.45 mmol) and monomer **12** (451 mg, 0.45 mmol) were dissolved in degassed toluene/ NEt_3 (1.5:1, 9 mL/6 mL). $\text{Pd(PPh}_3)_4$ (26.1 mg, 23 μmol) and CuI (4.3 mg, 23 μmol) were added and the mixture was stirred at 60 $^\circ\text{C}$ for 24 h. Brine 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. Two times, the crude product was dissolved in CHCl_3 and slowly added to an excess of *n*-hexane. The precipitate was dissolved in H_2O , Na_2EDTA (100 mg) was added, and the resulting mixture was dialyzed against DI H_2O for 3 d. After freezy-drying the residue was again dissolved in CHCl_3 and slowly added to an excess of *n*-hexane to gave **2** as sticky, dark brown oil (316 mg, 72%). The M_n was estimated to be 1.4×10^4 with a PDI of 3.1. ^1H NMR (600 MHz, CDCl_3): δ = 8.26-8.40 (m, 1 H), 7.62-7.80 (m, 1 H), 4.62-4.69 (m, 1 H), 3.45-3.86 (m, 28 H), 3.34 (bs, 6 H) ppm. IR (cm^{-1}): ν 2871, 1720, 1578, 1471, 1404, 1351, 1233, 1198, 1095, 940, 849, 756, 542, 446, 404. Due to low solubility, ^{13}C NMR spectrum could not be obtained.

3. ^1H NMR-Spectra



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PROCNO 1

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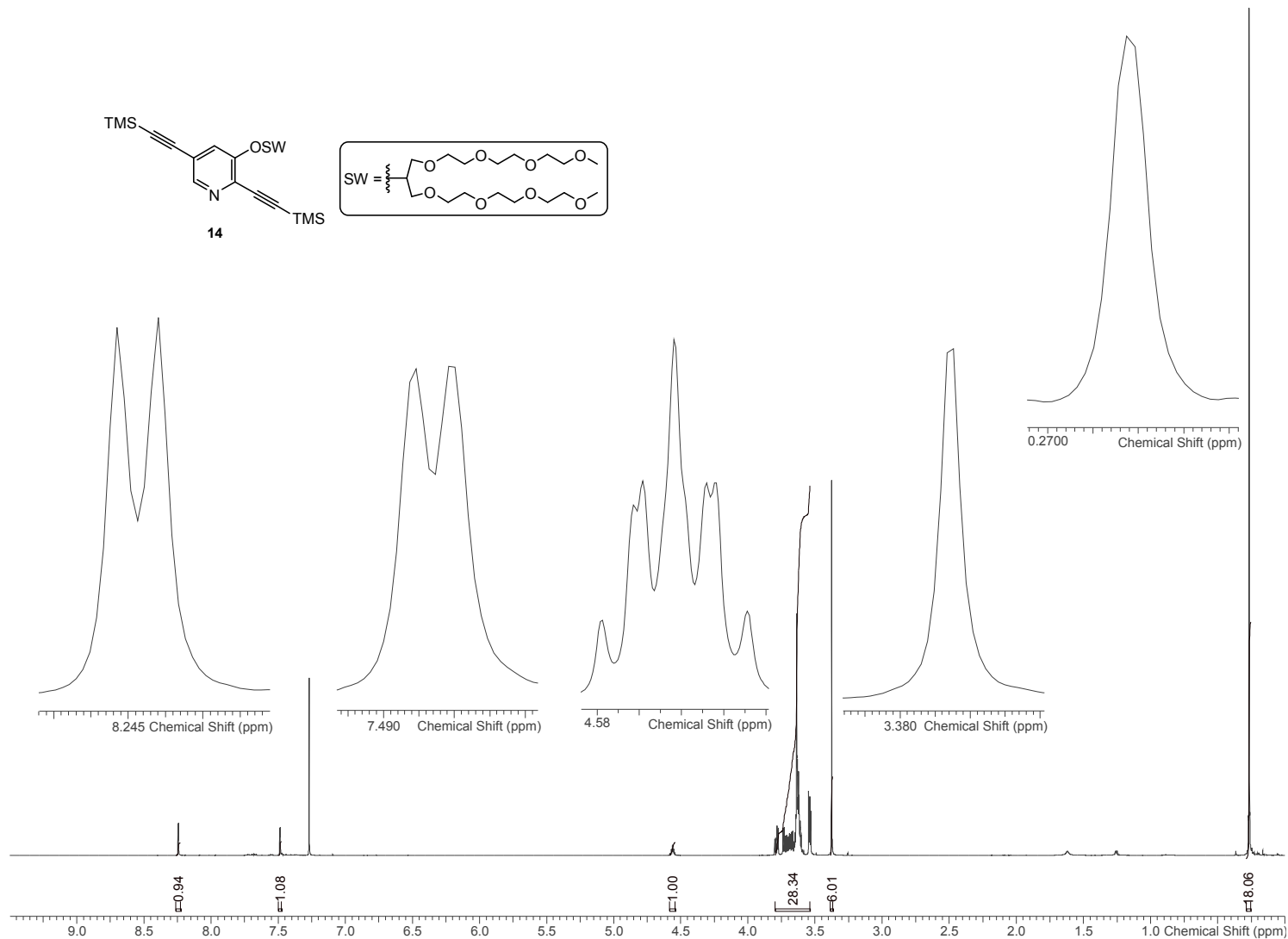
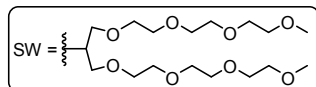
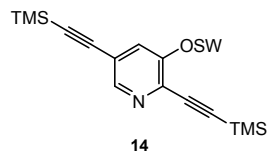
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LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters

NAME e140225ubmb.03
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

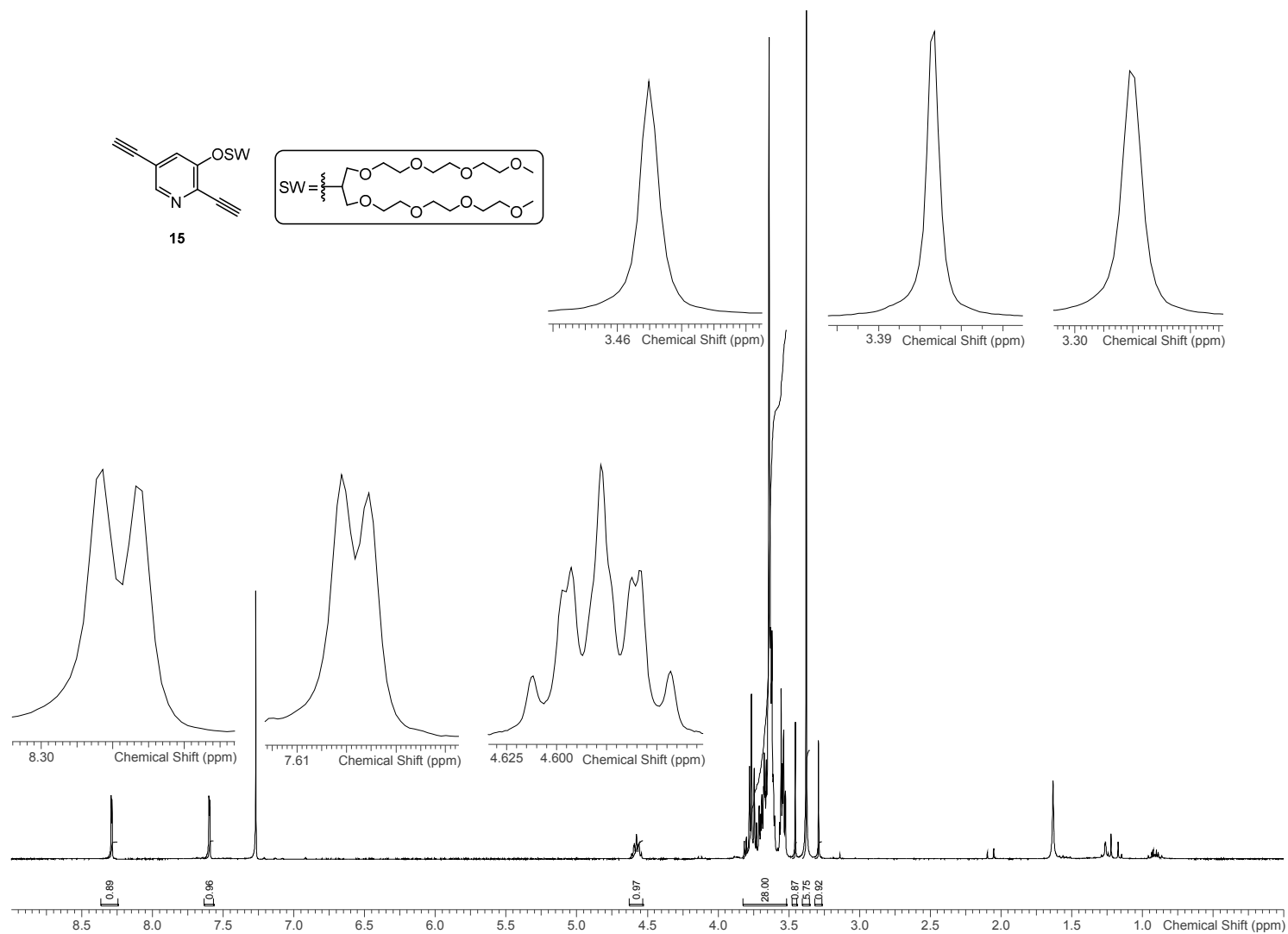
Date 20140225
Time 10.53
INSTRUM spect
PROBHD 5 mm CPQCI-1H-
PULPROG zg30
TD 131072
SOLVENT CDCl₃
NS 128
DS 2
SWH 18028.846 Hz
FIDRES 0.137549 Hz
AQ 3.6350634 sec
RG 15.35
DW 27.733 usec
DE 12.00 usec
TE 295 K
D1 0.1000000 sec
TD0 16

===== CHANNEL f1 =====

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

F2 - Processing parameters

SI 65536
SF 600.2439367 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters

NAME b140221ubmb.01
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

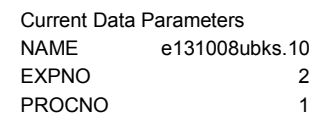
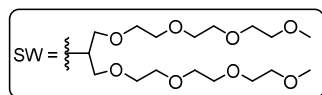
Date 20140222
Time 9.12
INSTRUM spect
PROBHD 5 mm PATXO 31P
PULPROG zg30
TD 65536
SOLVENT CDCl_3
NS 128
DS 2
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 574.7
DW 55.600 usec
DE 6.00 usec
TE 298.2 K
D1 0.1000000 sec
TD0 16

===== CHANNEL f1 =====

NUC1 ^1H
P1 11.50 usec
PL1 -3.00 dB
SFO1 300.1315007 MHz

F2 - Processing parameters

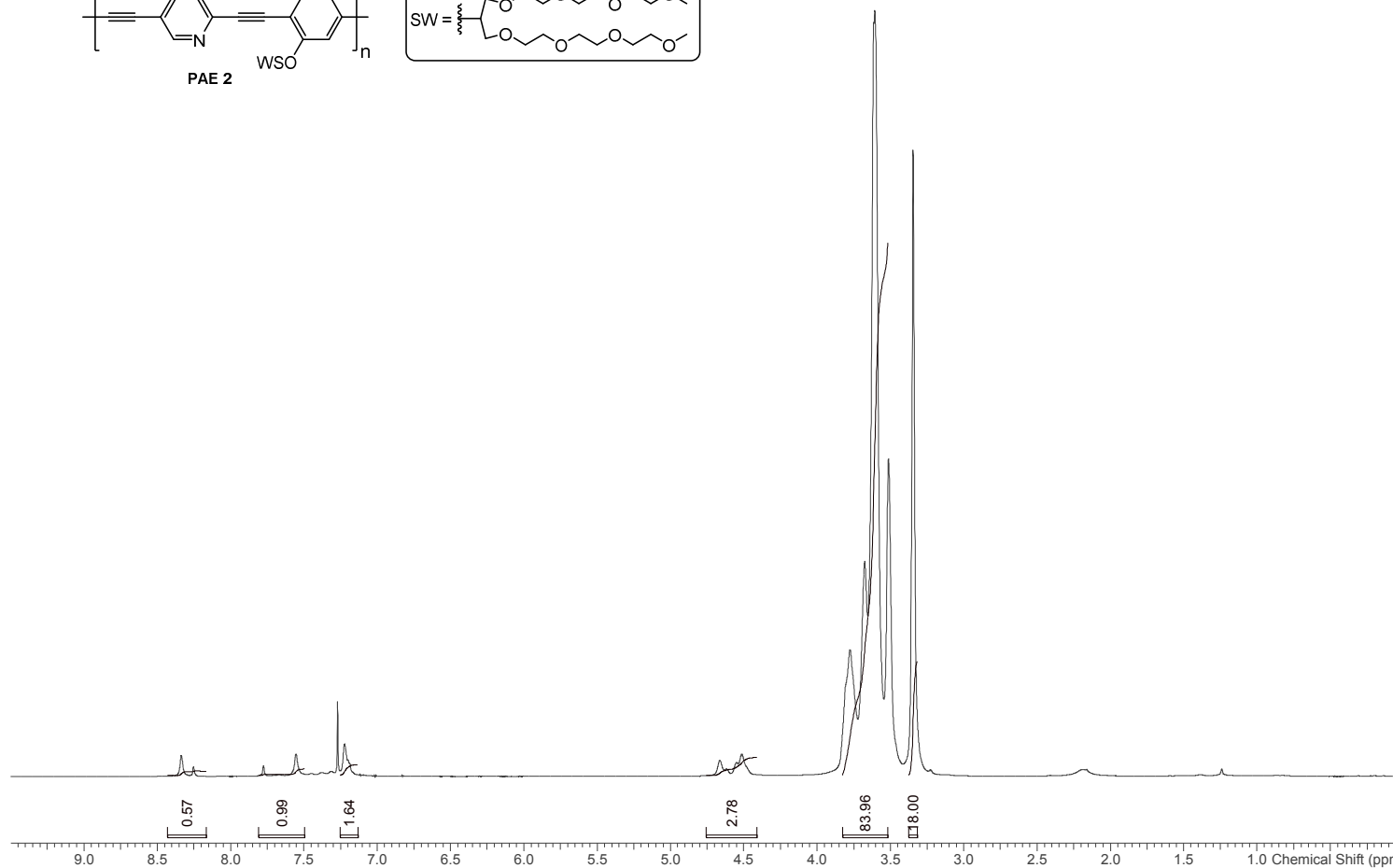
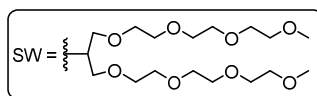
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Date	20131009
Time	6.04
INSTRUM	spect
PROBH	5 mm CPQCI-1H-
PULPROG	zg30
TD	131072
SOLVENT	CDCl ₃
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

NUC1	1H
P1	7.63 usec
PLW1	7.50000000 W
SFO1	600.3468302 MHz

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

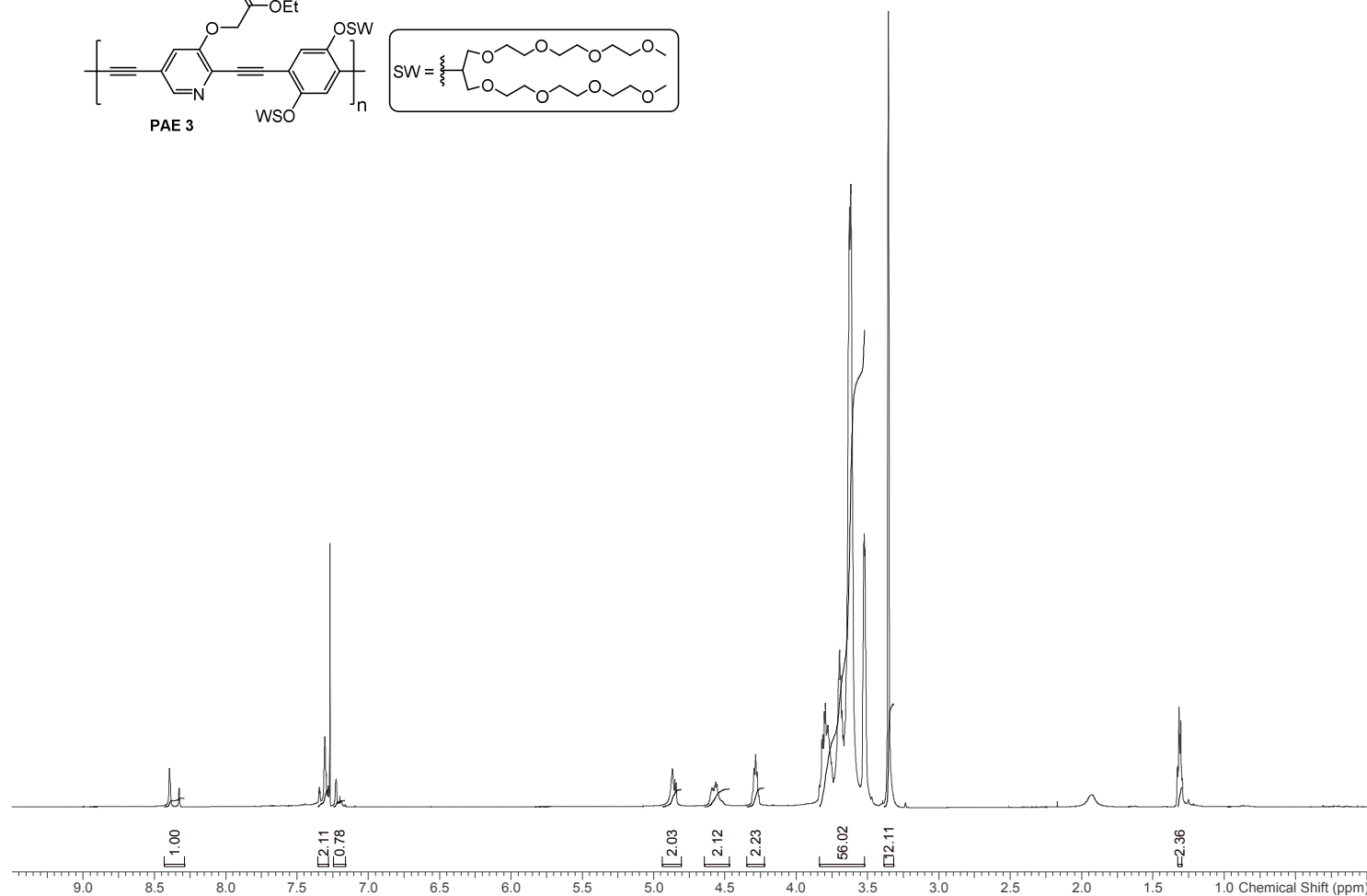


```
NAME          e131004ubks.18
EXPNO          2
PROCNO         1
```

Date	20131029
Time	18.18
INSTRUM	spect
PROBH	5 mm CPQCI-1H-
PULPROG	zg30
TD	131072
SOLVENT	CDCl ₃
NS	128
DS	2
SWH	18028.846 Hz
FIDRES	0.137549 Hz
AQ	3.6350634 sec
RG	7.02
DW	27.733 usec
DE	12.00 usec
TE	295 K
D1	0.10000000 sec
TD0	16

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

SI	65536
SF	600.2439196 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



GB	0
BC	1.00

Current Data Parameters

NAME e131106ubks.19
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

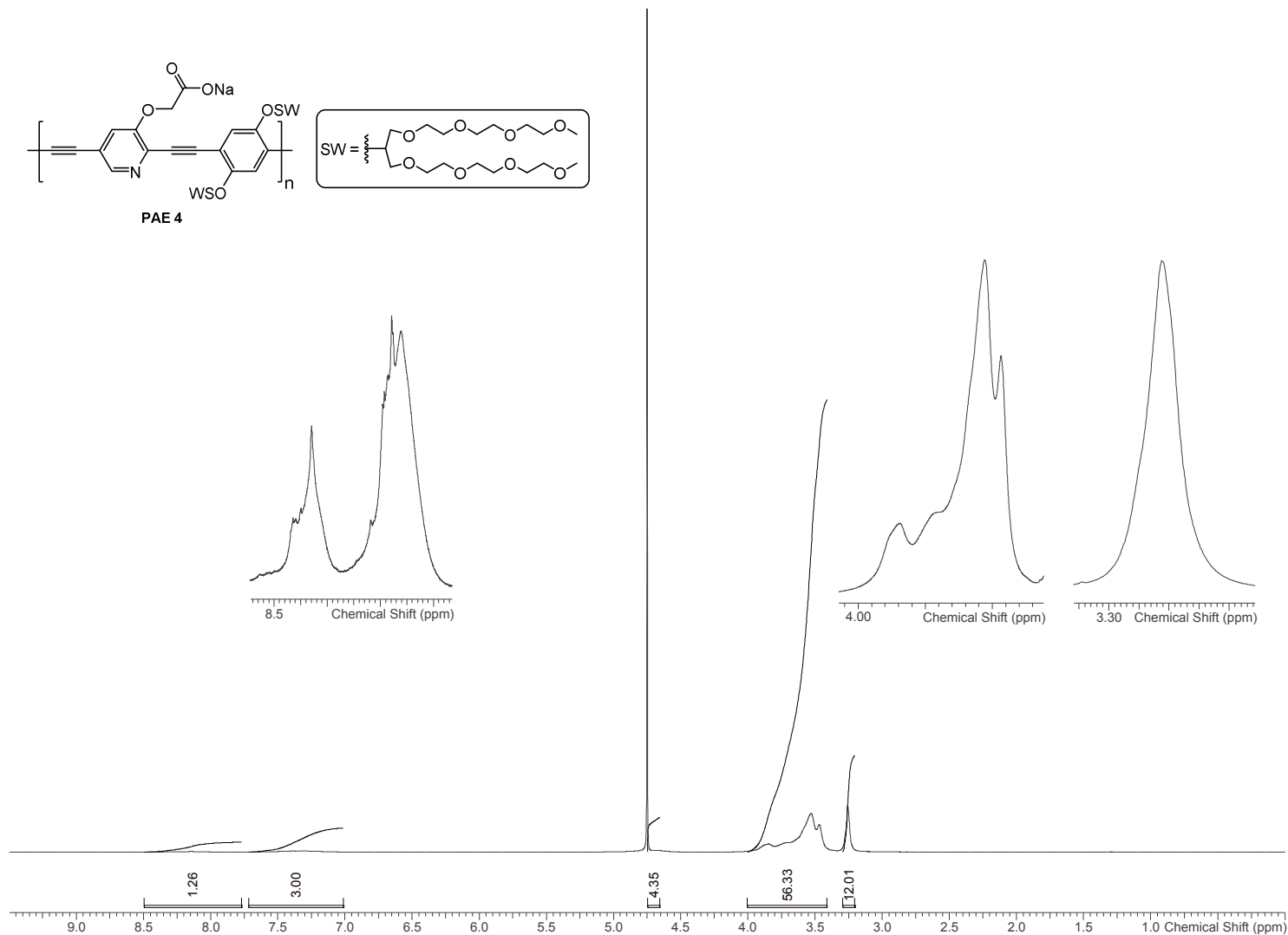
Date 20131107
Time 1.13
INSTRUM spect
PROBHD 5 mm CPQCI-1H-
PULPROG zg30
TD 131072
SOLVENT D₂O
NS 128
DS 2
SWH 18028.846 Hz
FIDRES 0.137549 Hz
AQ 3.6350634 sec
RG 7.02
DW 27.733 usec
DE 12.00 usec
TE 295 K
D1 0.10000000 sec
TD0 16

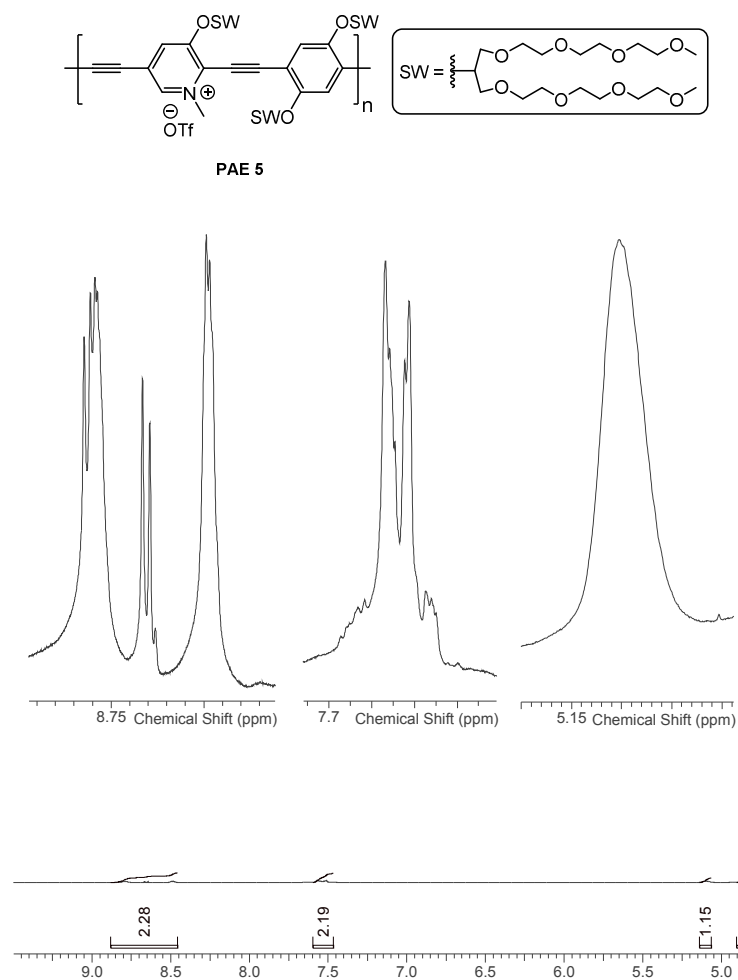
===== CHANNEL f1 =====

NUC1 1H
P1 7.63 usec
PLW1 7.50000000 W
SFO1 600.2468302

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 e140221ubks.35
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

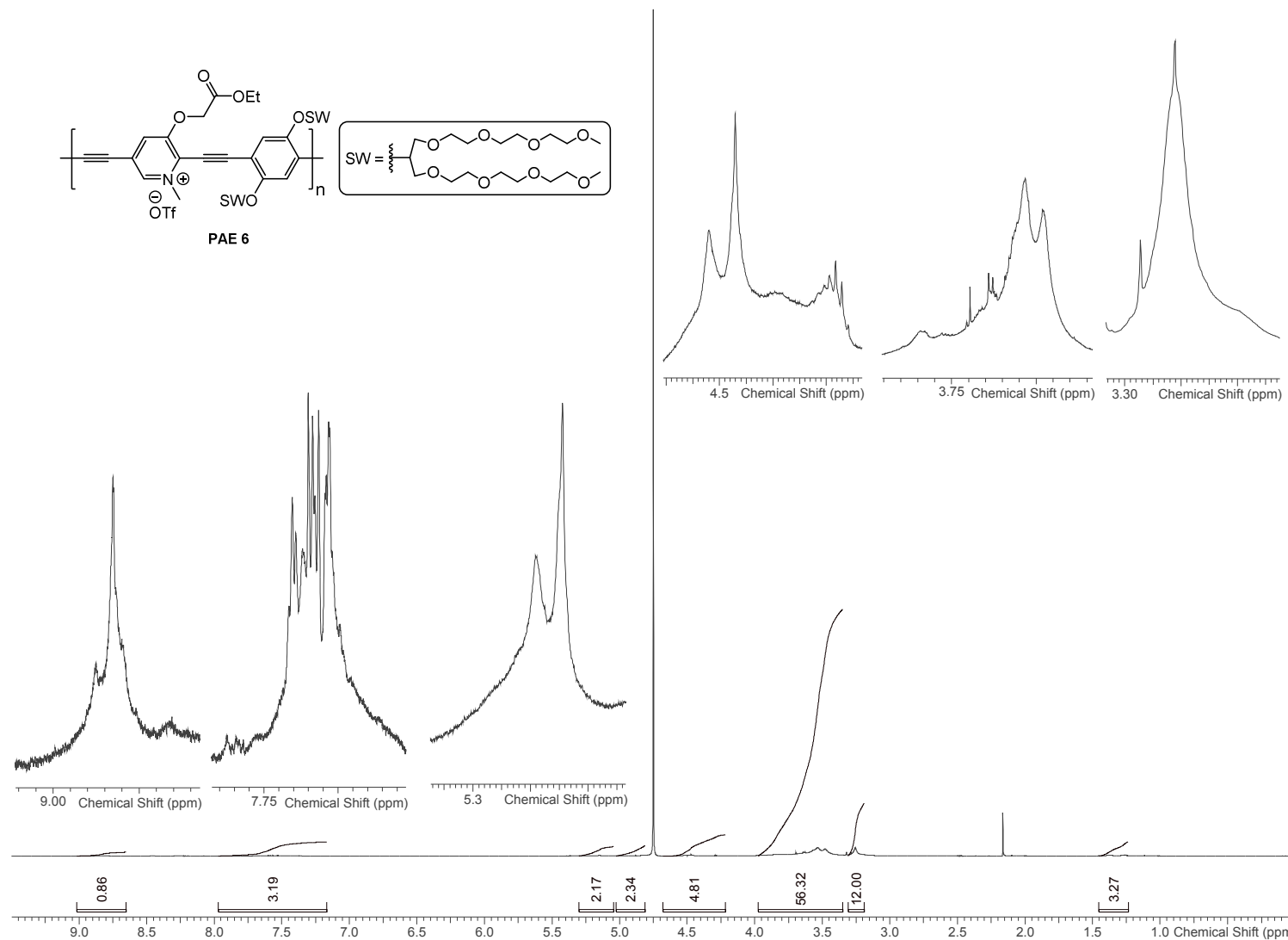
Date 20140222
Time 19.20
INSTRUM spect
PROBHD 5 mm CPQCI-1H-
PULPROG zg30
TD 131072
SOLVENT D₂O
NS 128
DS 2
SWH 18028.846 Hz
FIDRES 0.137549 Hz
AQ 3.6350634 sec
RG 13.85
DW 27.733 usec
DE 12.00 usec
TE 295 K
D1 0.1000000 sec
TD0 16

===== CHANNEL f1 =====

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

F2 - Processing parameters

SI 65536
SF 600.2438579 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters

NAME e140221ubks.34
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

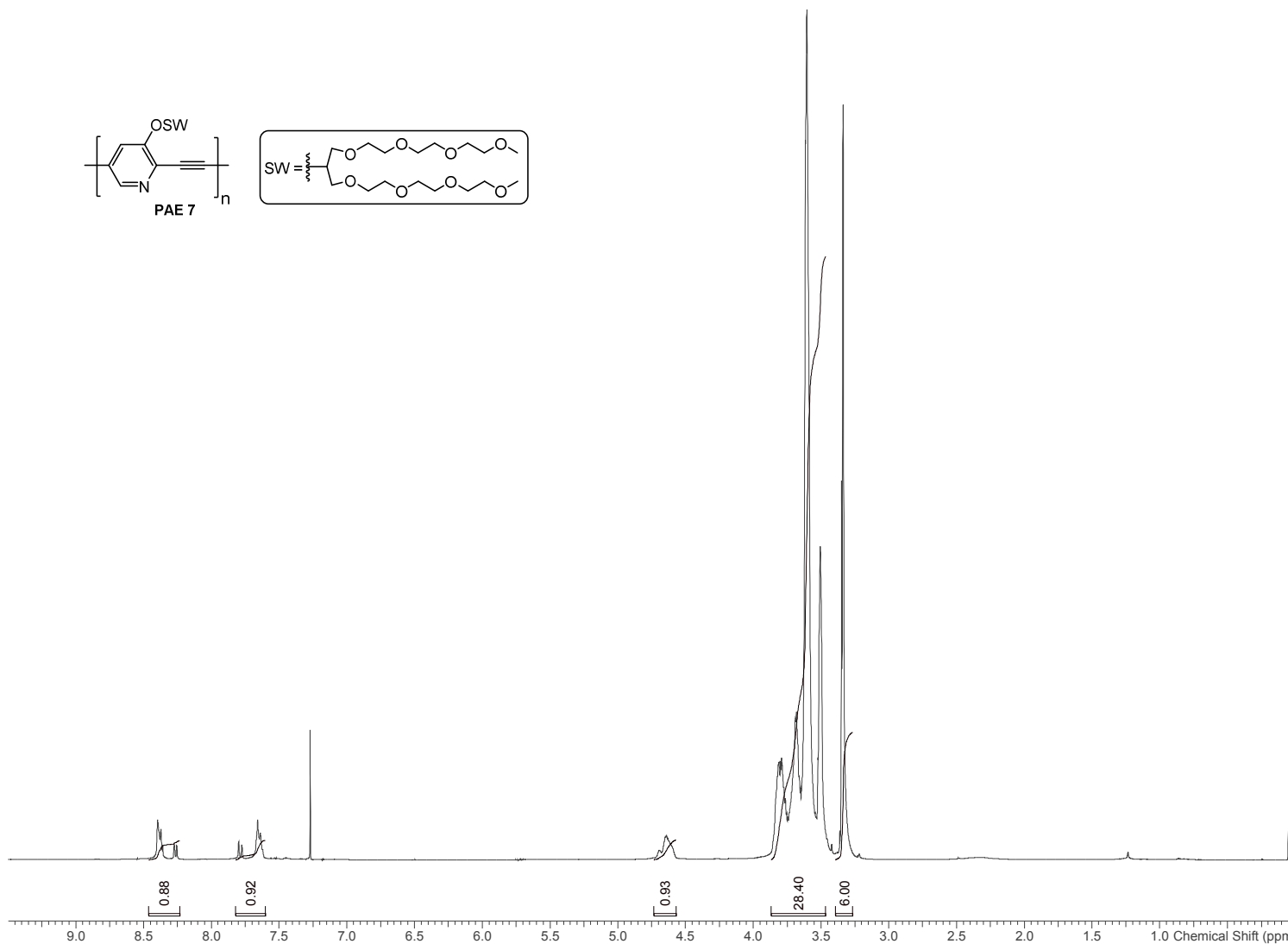
Date 20140221
Time 19.26
INSTRUM spect
PROBHD 5 mm CPQCI-1H-
PULPROG zg30
TD 131072
SOLVENT D₂O
NS 128
DS 2
SWH 18028.846 Hz
FIDRES 0.137549 Hz
AQ 3.6350634 sec
RG 16.84
DW 27.733 usec
DE 12.00 usec
TE 295 K
D1 0.1000000 sec
TD0 16

===== CHANNEL f1 =====

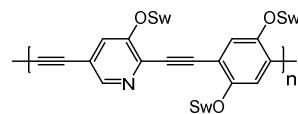
NUC1 1H
P1 7.63 usec
PLW1 7.5000000 W
SFO1 600.2468302

F2 - Processing parameters

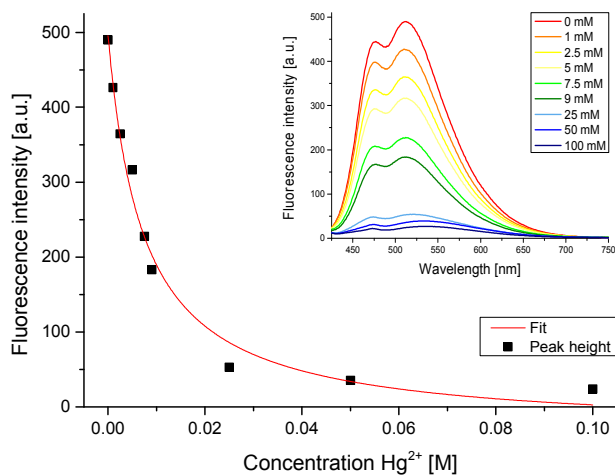
SI 65536
SF 600.2438015
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

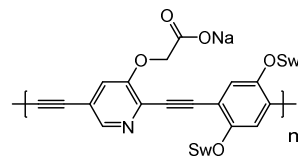


1.00

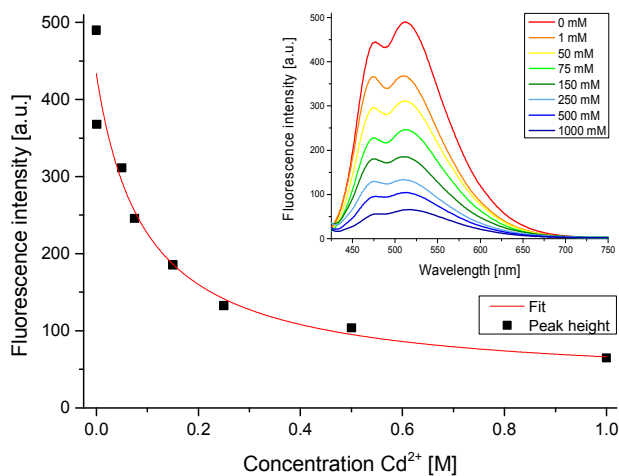
$$K_{SV} = 58.63 \pm 15.34$$
$$\log K_{SV} = 1.79 \pm 0.15$$


$$c(\text{Polymer}) = 6.14 \times 10^{-6} \text{ mol L}^{-1}$$


$$K_{SV} = 137.58 \pm 24.69$$

$$\log K_{SV} = 2.13 \pm 0.08$$


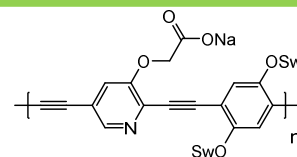
$$c(\text{Polymer}) = 2.31 \times 10^{-6} \text{ mol L}^{-1}$$



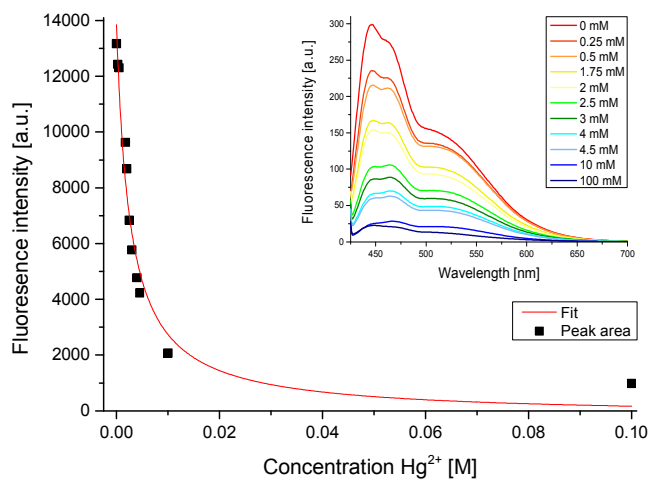
Quencher: $\text{Cd}(\text{Cl})_2$

$$K_{SV} = 10.64 \pm 4.28$$

$$\log K_{SV} = 1.02 \pm 0.39$$



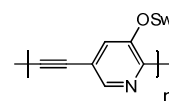
$$c(\text{Polymer}) = 2.31 \times 10^{-6} \text{ mol L}^{-1}$$



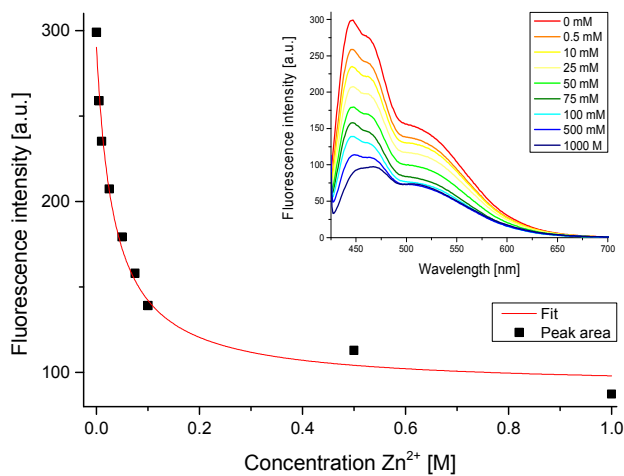
Quencher: $\text{Hg}(\text{OAc})_2$

$$K_{SV} = 378.09 \pm 80.75$$

$$\log K_{SV} = 2.58 \pm 0.08$$



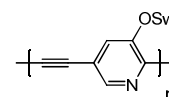
$$c(\text{Polymer}) = 4.14 \times 10^{-6} \text{ mol L}^{-1}$$



Quencher: $\text{Zn}(\text{Cl})_2$

$$K_{SV} = 29.16 \pm 5.03$$

$$\log K_{SV} = 1.46 \pm 0.12$$



$$c(\text{Polymer}) = 4.14 \times 10^{-6} \text{ mol L}^{-1}$$

5. Supplemental References

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- (2) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2012**, *29*, 2176-2179.
- (3) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. *Nat. Protoc.* **2013**, *8*, 1535-1550.
- (4) (a) Kim, I.-B.; Phillips, R.; Bunz, U. H. F. *Macromolecules* **2007**, *40*, 5290-5293. (b) Khan, A.; Müller, S.; Hecht, S. *Chem. Commun.* **2005**, 584-586. (c) Lauter, U.; Meyer, W. H.; Eukelmann, V.; Wegner, G. *Macromolecules* **1998**, *199*, 2129-2140.
- (5) (a) Haydon, D. J.; Bennett, J. M.; Brown, B.; Collins, I.; Galbraith, G.; Lancett, P.; Macdonald, R.; Stokes, N. R.; Chauhan, P. K.; Sutariya, J. K.; Nayal, N.; Srivastava, A.; Beanland, J.; Hall, R.; Henstock, V.; Noola, C.; Rockley, C.; Czaplowski, L. *J. Med Chem.* **2010**, *53*, 3927-3936. (b) Berrie, A. H.; Newbold, G. T.; Spring, F. S. *J. Chem. Soc.* **1952**, 2042-2046.