

Deciphering the Potentiometric Properties of (Porphinato)zinc(II)-derived Supramolecular Polymers and Related Superstructures

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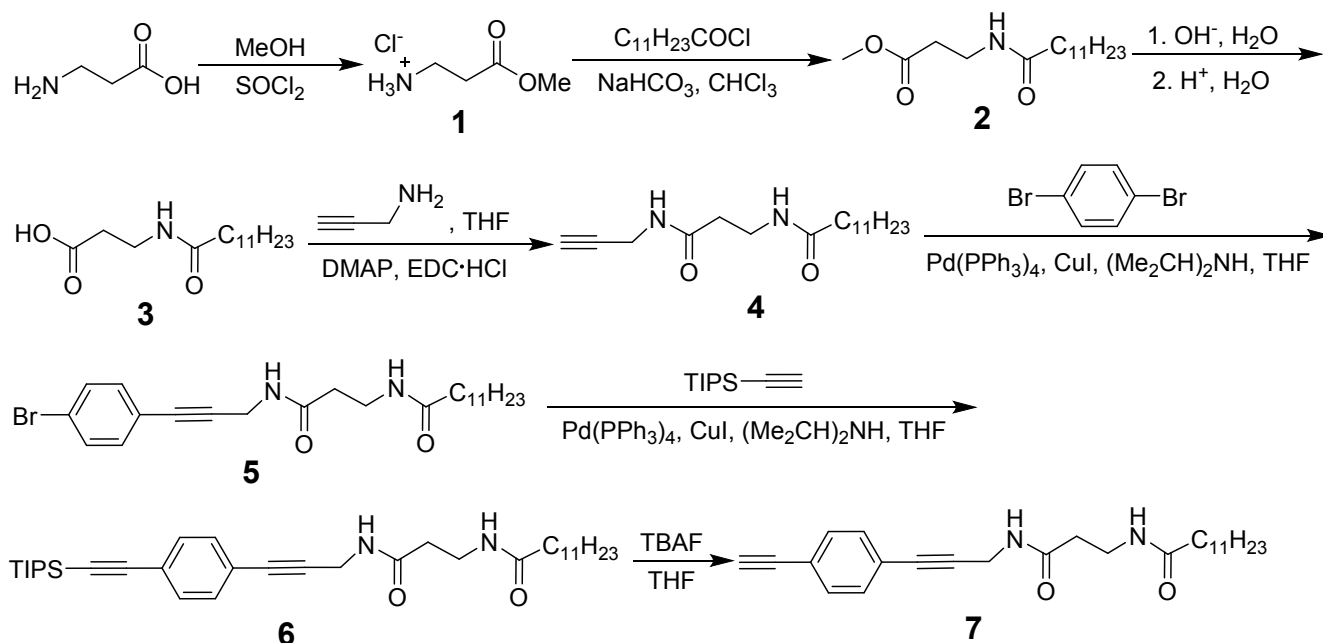
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1. Synthetic Procedures



Scheme S1: Synthesis of the BA precursor. Compounds **1** and **2** were synthesized according to previously reported procedures.¹⁻² Compound **3** was synthesized based on a procedure found in previous literature where a similar compound was synthesized.³

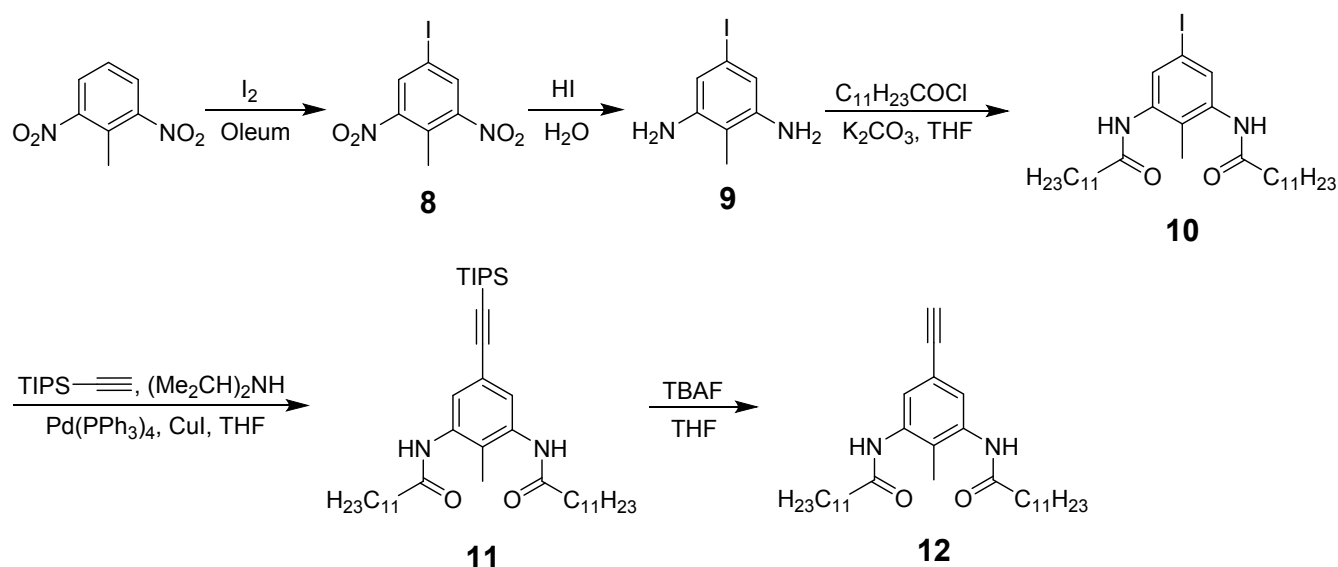
4-Aza-5-oxo-*N*-(prop-2-ynyl)hexadecanamide (4). 4-Aza-5-oxohexadecanoic acid (**7**) (5.74 g, 2.11×10^{-2} mol), *N,N*-dimethylpyridin-4-amine (6.46 g, 5.29×10^{-2} mol) and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (8.11 g, 4.23×10^{-2} mol) were dissolved in 150 mL of THF, and propargylamine (1.35 mL, 2.11×10^{-2} mol) was added to the solution. The reaction mixture was stirred at room temperature for 12 h. After solvent removal, 150 mL of CH₃OH was added, and the mixture was refluxed until all solid was dissolved and cooled to room temperature. A precipitate was collected by filtration and dried under vacuum to give the desired product as a white solid (4.70 g, 72%). ¹H NMR (400 MHz, CDCl₃) δ = 6.19 (br, 1H), 5.94 (br, 1H), 4.05 (dd, 2H, J_1 = 2.4 Hz, J_2 = 5.2 Hz), 3.54 (q, 2H, J = 5.8 Hz), 2.44 (t, 2H, J = 5.8 Hz), 2.24 (t, 2H, J = 2.6 Hz), 2.15 (t, 2H, J = 7.6 Hz), 1.61 (m, 2H), 1.4~1.2 (m, 16H), 0.88 (t, 3H, J = 6.6 Hz) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.5, 171.2, 79.2, 71.7, 36.8, 35.5, 35.2, 31.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 29.2, 25.7, 22.7, 14.1 ppm. ESI-MS m/z : 309.25 ([M+H]⁺, calcd for 309.25). FTIR: $\bar{\nu}$ = 3285, 3226, 3057, 2917, 2851, 1662, 1623, 1542 cm⁻¹.

4-Aza-*N*-[3-(4-bromophenyl)prop-2-ynyl]-5-oxohexadecanamide (5). 4-Aza-5-oxo-*N*-(prop-2-ynyl)hexadecanamide (**4**) (1.14 g, 3.70×10^{-3} mol), 1,4-dibromobenzene (0.873 g, 3.70×10^{-3} mol), CuI (35.2 mg, 1.85×10^{-4} mol) and Pd(PPh₃)₄ (300 mg, 2.59×10^{-4} mol) were added into a Schlenk flask in a glove box. After 70 mL of distilled THF and 20 mL of dry (Me₂CH)₂NH were mixed, freeze-pump-thawed and cannulated into the Schlenk flask, the reaction mixture was stirred at 60 °C for 12 h under Ar and passed through a silica plug using THF as the eluent. The solvent was evaporated, and the solid was

dissolved in 50 mL of CHCl₃, washed with 50 mL of brine twice and dried over Na₂SO₄. After solvent removal, the residue was chromatographed on silica using 20:1 CH₂Cl₂:CH₃OH as the eluent. The collected solid was dried under vacuum to give the desired product as a white solid (0.60 g, 35%). ¹H NMR (400 MHz, CDCl₃) δ = 7.44 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 2H, *J* = 7.8 Hz), 6.22 (br, 1H), 6.09 (br, 1H), 4.26 (d, 2H, *J* = 5.6 Hz), 3.55 (q, 2H, *J* = 6.0 Hz), 2.48 (t, 2H, *J* = 6.0 Hz), 2.14 (t, 2H, *J* = 7.6 Hz), 1.58 (m, 2H), 1.4~1.2 (m, 16H), 0.88 (t, 3H, *J* = 6.8 Hz) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.5, 171.1, 133.1, 131.6, 122.8, 121.3, 85.7, 82.4, 36.8, 35.6, 35.2, 31.9, 30.0, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 25.7, 22.7, 14.1 ppm. ESI-MS *m/z*: 463.19 ([*M*+*H*]⁺, calcd for 463.20). FTIR: $\bar{\nu}$ = 3270, 3063, 2916, 2848, 1634, 1544, 1464 cm⁻¹.

4-Aza-*N*-(3-{4-[4-methyl-3,3-bis(propan-2-yl)-3-silapent-1-ynyl]phenyl}prop-2-ynyl)-5-oxohexadecanamide (6). 4-Aza-*N*-[3-(4-bromophenyl)prop-2-ynyl]-5-oxohexadecanamide (**5**) (0.650 g, 1.40 × 10⁻³ mol), CuI (13.3 mg, 7.00 × 10⁻⁵ mol) and Pd(PPh₃)₄ (113 mg, 9.80 × 10⁻⁵ mol) were added into a Schlenk flask in a glove box. After triisopropylsilylacetylene (1.26 mL, 5.60 × 10⁻³ mol), 50 mL of distilled THF and 10 mL of dry (Me₂CH)₂NH were mixed, freeze-pump-thawed and cannulated into the Schlenk flask, the reaction mixture was stirred at 60 °C for 12 h under Ar and passed through a silica plug using THF as the eluent. The solvent was evaporated, and the solid was dissolved in 50 mL of CHCl₃, washed with 50 mL of brine twice and dried over Na₂SO₄. After solvent removal, the residue was chromatographed on silica using 20:1 CH₂Cl₂:CH₃OH as the eluent. The collected solid was dried under vacuum to give the desired product as a white solid (0.42 g, 53%). ¹H NMR (400 MHz, CDCl₃) δ = 7.40 (d, 2H, *J* = 8.8 Hz), 7.33 (d, 2H, *J* = 8.8 Hz), 6.20 (br, 1H), 5.94 (br, 1H), 4.28 (d, 2H, *J* = 5.2 Hz), 3.56 (q, 2H, *J* = 5.9 Hz), 2.47 (t, 2H, *J* = 6.0 Hz), 2.14 (t, 2H, *J* = 7.9 Hz), 1.60 (m, 2H), 1.4~1.2 (m, 16H), 1.12 (m, 21H), 0.88 (t, 3H, *J* = 6.8 Hz) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 174.0, 171.5, 131.9, 131.4, 123.6, 122.4, 106.4, 92.8, 86.7, 82.7, 36.7, 35.6, 35.5, 31.9, 29.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 25.8, 22.7, 18.6, 14.1, 11.3 ppm. ESI-MS *m/z*: 565.42 ([*M*+*H*]⁺, calcd for 565.42). FTIR: $\bar{\nu}$ = 3297, 3067, 2918, 2886, 2155, 1635, 1540 cm⁻¹.

4-Aza-*N*-[3-(4-ethynylphenyl)prop-2-ynyl]-5-oxododecanamide (7). 4-Aza-*N*-(3-{4-[4-methyl-3,3-bis(propan-2-yl)-3-silapent-1-ynyl]phenyl}prop-2-ynyl)-5-oxohexadecanamide (**6**) (0.300 g, 5.31 × 10⁻⁴ mol) was dissolved in 20 mL of distilled THF, and the solution was stirred at 0 °C under Ar, followed by dropwise addition of a 1 M THF solution of tetrabutylammonium fluoride (1.00 mL, 1.00 × 10⁻³ mol) to the reaction. After 20 min, a drop of H₂O was added, and the solvent was evaporated. The resulting solid was dissolved in 50 mL of CHCl₃, washed with 50 mL of brine twice and dried over Na₂SO₄. After solvent removal, the residue was chromatographed on silica using 20:1 CHCl₃:CH₃OH as the eluent. The collected solid was dried under vacuum to give the desired product as a white solid (0.11 g, 51%). ¹H NMR (400 MHz, CDCl₃) δ = 7.42 (d, 2H, *J* = 8.8 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 6.22 (br, 1H), 6.08 (br, 1H), 4.28 (d, 2H, *J* = 5.2 Hz), 3.55 (q, 2H, *J* = 6.0 Hz), 3.16 (s, 1H), 2.47 (t, 2H, *J* = 5.8 Hz), 2.14 (t, 2H, *J* = 7.6 Hz), 1.59 (m, 2H), 1.4~1.2 (m, 16H), 0.88 (t, 3H, *J* = 6.8 Hz) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.6, 171.2, 132.0, 131.6, 122.9, 122.2, 86.6, 83.0, 82.8, 79.0, 36.8, 35.5, 35.3, 31.9, 29.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 25.7, 22.7, 14.1 ppm. ESI-MS *m/z*: 409.29 ([*M*+*H*]⁺, calcd for 409.29). FTIR: $\bar{\nu}$ = 3278, 3061, 2918, 2850, 1635, 1545 cm⁻¹.



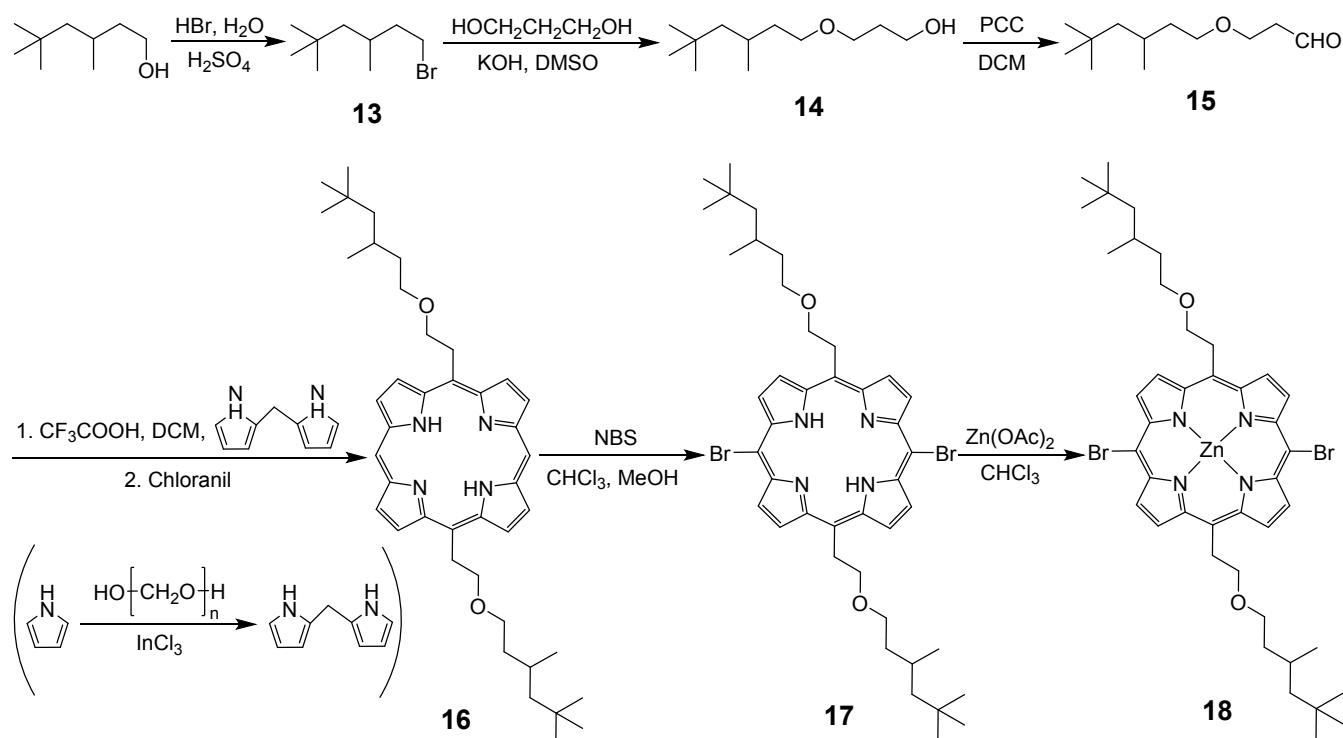
Scheme S2: Synthesis of the PBA precursor. Compounds **8** and **9** were synthesized according to previously reported procedures.⁴⁻⁵

***N,N'*-(5-Iodo-2-methyl-1,3-phenylene)didodecanamide (10).** 5-Iodo-2-methylbenzene-1,3-diamine (**9**) (0.250 g, 1.01×10^{-3} mol) and anhydrous K_2CO_3 (0.700 g, 5.06×10^{-3} mol) were added into a Schlenk flask in a glove box, and 100 mL of distilled THF was cannulated into the flask, followed by addition of dry dodecanoyl chloride (0.60 mL, 2.59×10^{-3} mol). The reaction mixture was stirred and refluxed for 20 h under Ar. The solution was concentrated to 50 mL and filtered. The collected solid was washed with 50 mL of water for three times and dissolved in 150 mL of boiling THF. The solution was cooled to 0 °C, and a precipitate was obtained by filtration and dried under vacuum to give the desired product as a white solid (0.49 g, 79%). 1H NMR (400 MHz, $CDCl_3$, 333 K) δ = 7.79 (s, 2H), 7.01 (s, 2H), 2.38 (t, 4H, J = 7.0 Hz), 2.01 (s, 3H), 1.72 (m, 4H), 1.5~1.1 (m, 32H), 0.88 (t, 6H, J = 6.8 Hz) ppm. ESI-MS m/z : 635.31 ($[M+Na]^+$, calcd for 635.31). FTIR: $\bar{\nu}$ = 3272, 2916, 2850, 1656, 1576, 1519 cm^{-1} . Note: Because of the low solubility of this compound, there were not enough signals when ^{13}C NMR was performed.

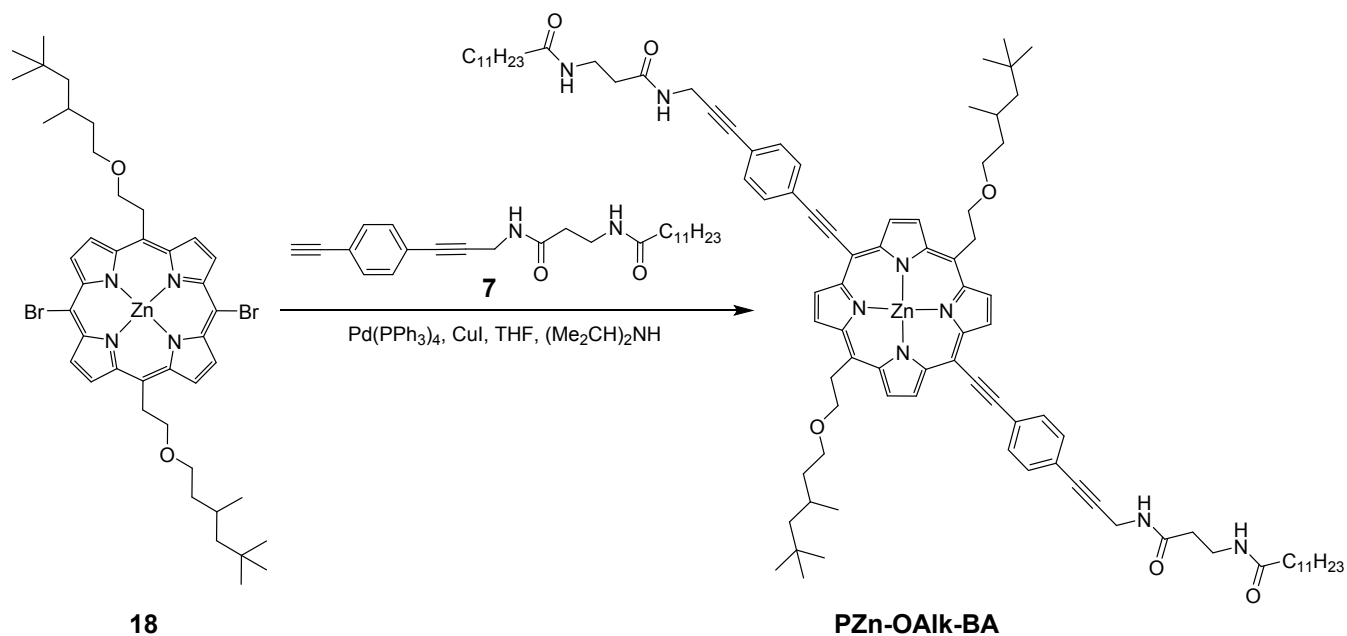
***N,N'*-(2-Methyl-5-[4-methyl-3,3-bis(propan-2-yl)-3-silapent-1-ynyl]-1,3-phenylene)didodecanamide (11).** *N,N'*-(5-iodo-2-methyl-1,3-phenylene)didodecanamide (**10**) (2.00 g, 3.27×10^{-3} mol), CuI (60.0 mg, 3.15×10^{-4} mol) and $Pd(PPh_3)_4$ (375 mg, 3.25×10^{-4} mol) were added into a Schlenk flask in a glove box. After triisopropylsilylacetylene (1.10 mL, 4.90×10^{-3} mol), 50 mL of distilled THF and 10 mL of dry $(Me_2CH)_2NH$ were mixed, freeze-pump-thawed and cannulated into the Schlenk flask, the reaction mixture was stirred at 60 °C for 12 h under Ar and passed through a silica plug using THF as the eluent. The solvent was evaporated, and the solid was dissolved in 50 mL of $CHCl_3$, washed with 50 mL of brine twice and dried over Na_2SO_4 . After solvent removal, the residue was chromatographed on silica using 20:1 $CH_2Cl_2:CH_3OH$ as the eluent. The collected solid was dried under vacuum to give the desired product as a white solid (1.57 g, 72%). 1H NMR (400 MHz, $CDCl_3$) δ = 7.55 (br, 2H), 6.93 (br, 2H), 2.38 (t, 4H, J = 6.4 Hz), 2.09 (s, 3H), 1.74 (m, 4H), 1.45~1.15 (m, 32H), 1.10 (m, 21H), 0.88 (t, 6H, J = 6.8 Hz) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.5, 135.3, 128.0, 126.9, 120.7,

106.1, 90.0, 36.6, 31.9, 29.7, 29.7, 29.7, 29.7, 29.5, 29.4, 29.4, 25.7, 22.7, 18.7, 14.1, 11.3 ppm. ESI-MS m/z : 667.56 ($[M+H]^+$, calcd for 667.56). FTIR: $\bar{\nu}$ = 3232, 3186, 3041, 2923, 2855, 2161, 1652, 1570, 1533, 1461, 1417 cm^{-1} .

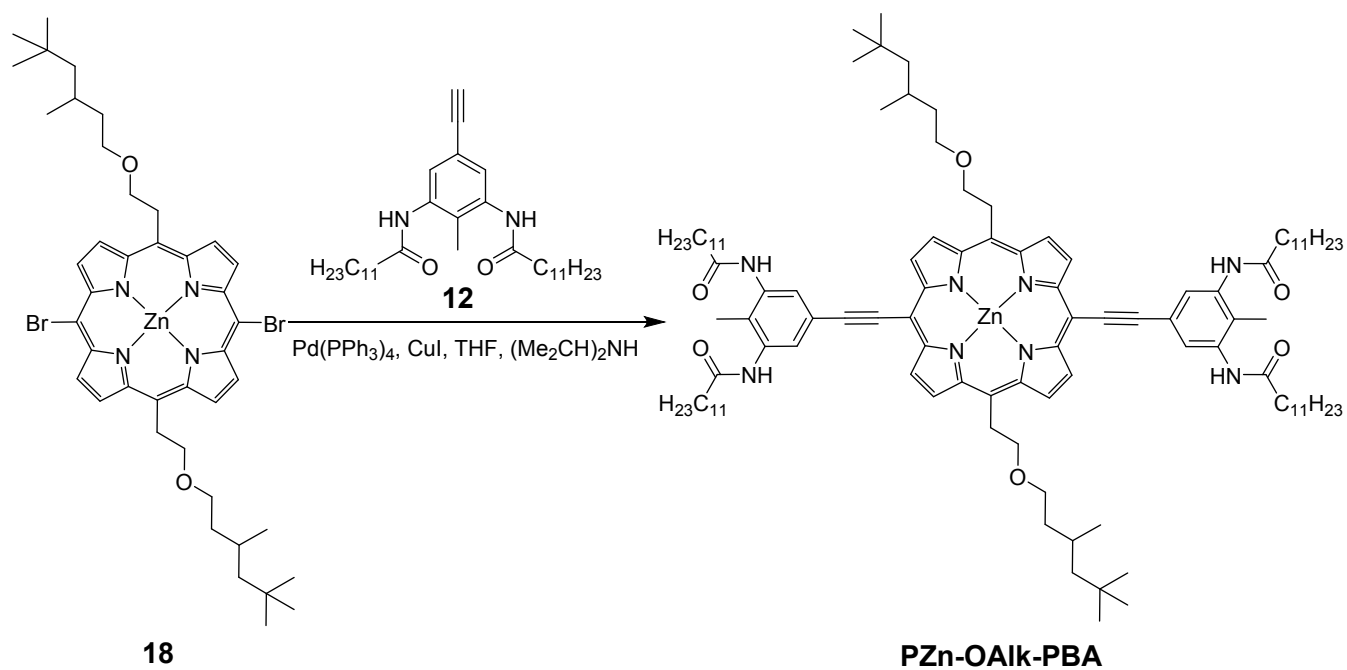
***N,N'*-(5-Ethynyl-2-methyl-1,3-phenylene)didodecanamide (12).** *N,N'*-{2-methyl-5-[4-methyl-3,3-bis(propan-2-yl)-3-silapent-1-ynyl]-1,3-phenylene}didodecanamide (**11**) (0.650 g, 9.74×10^{-4} mol) was dissolved in 20 mL of distilled THF, and the solution was stirred at 0 °C under Ar, followed by dropwise addition of a 1 M THF solution of tetrabutylammonium fluoride (1.46 mL, 1.46×10^{-3} mol) to the reaction. After 20 min, a drop of H₂O was added. After solvent removal, 70 mL of CH₃OH and 30 mL of THF were added. The mixture was refluxed for 20 min, cooled to room temperature and filtered. The collected solid was dried under vacuum to give the desired product as a white solid (0.41 g, 82%). ¹H NMR (400 MHz, CDCl₃, 333 K) δ = 7.60 (s, 2H), 6.83 (s, 2H), 3.00 (s, 1H), 2.36 (t, 4H, J = 7.6 Hz), 2.12 (s, 3H), 1.76 (m, 4H), 1.5~1.1 (m, 32H), 0.90 (t, 6H, J = 6.6 Hz) ppm. ESI-MS m/z : 533.41 ($[M+Na]^+$, calcd for 533.41). FTIR: $\bar{\nu}$ = 3278, 2917, 2850, 1648, 1573, 1521, 1461, 1416 cm^{-1} . Note: Because of the low solubility of this compound, there were not enough signals when ¹³C NMR was performed.



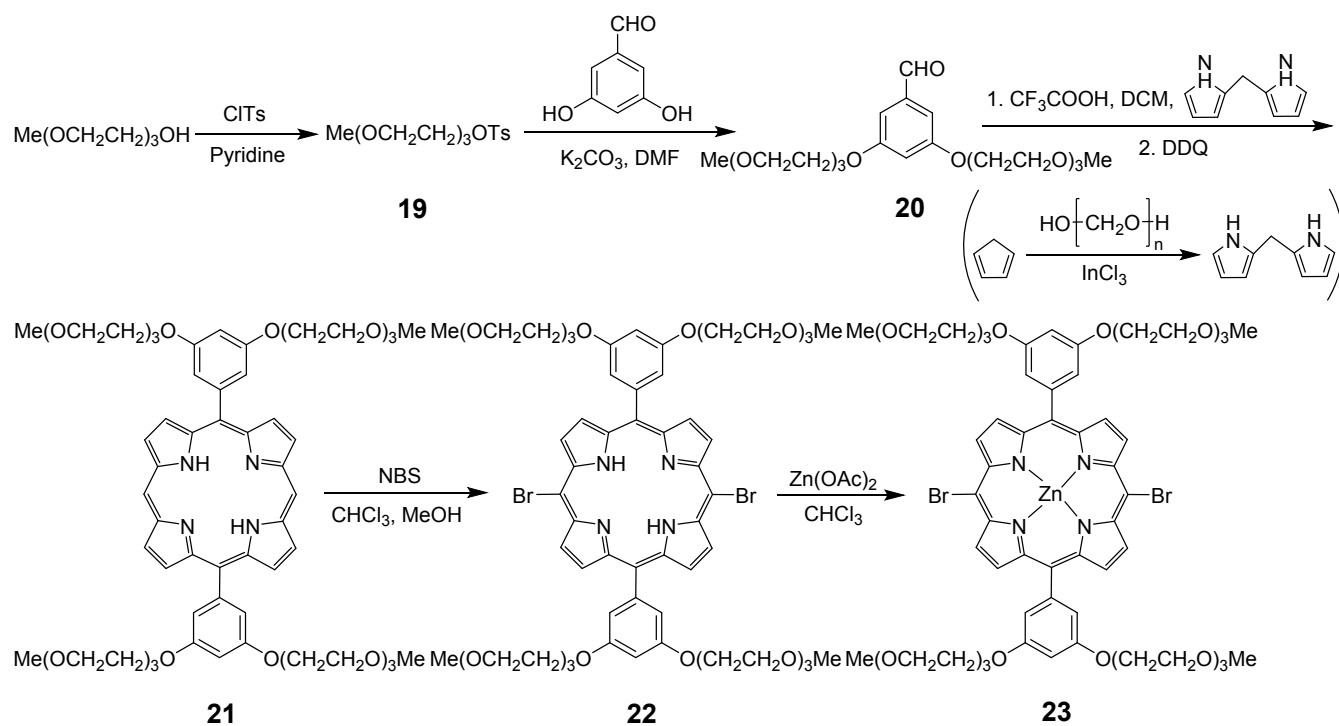
Scheme S3: Synthesis of the PZn-OAlk core. Compounds **13**, **14**, **15**, **16**, **17** and **18** were synthesized according to previously reported procedures.⁶



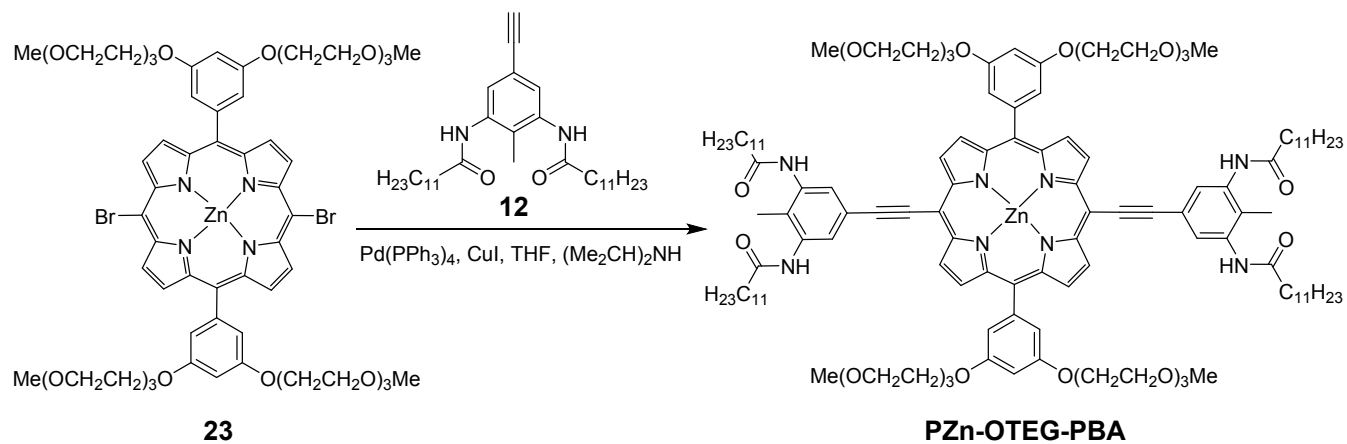
Scheme S4: Synthesis of **PZn-OAlk-BA**.



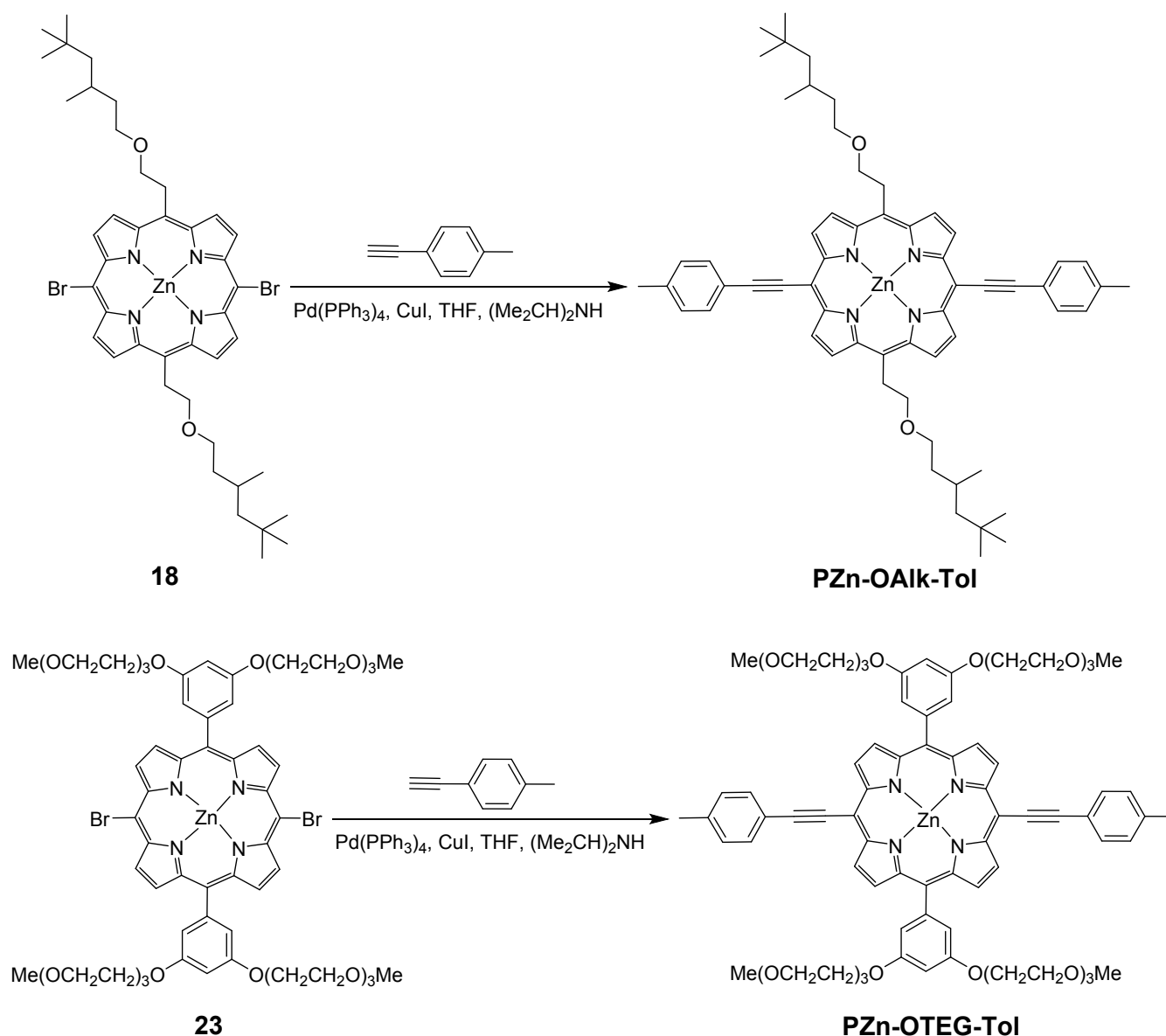
Scheme S5: Synthesis of **PZn-OAlk-PBA**.



Scheme S6: Synthesis of the **PZn-OTEG** core. Compounds **19**, **20**, **21**, **22** and **23** were synthesized according to previously reported procedures.⁷



Scheme S7: Synthesis of **PZn-OTEG-PBA**.



Scheme S8: Synthesis of control **PZn-OAlk-Tol** and **PZn-OTEG-Tol** building blocks.

{5,15-Bis[2-(4-methylphenyl)ethynyl]-10,20-bis[2-(3,5,5-trimethylhexyloxy)ethyl]porphinato}zinc(II).

{5,15-Dibromo-10,20-bis[2-(3,5,5-trimethylhexyloxy)ethyl]porphinato}zinc(II) (18) (0.075 g, 8.60×10^{-5} mol), CuI (1.60 mg, 8.40×10^{-6} mol) and Pd(PPh₃)₄ (15.0 mg, 1.30×10^{-5} mol) were added into a Schlenk flask in a glove box. After 4-ethynyltoluene (0.0440 mL, 3.47×10^{-4} mol), 50 mL of distilled THF and 10 mL of dry (Me₂CH)₂NH were mixed, freeze-pump-thawed and cannulated into the Schlenk flask, the reaction mixture was stirred at 60 °C for 12 h under Ar and passed through a silica plug using THF as the eluent. After solvent removal, the residue was chromatographed first on silica using CHCl₃ as the eluent, then on a size exclusion column using THF as the eluent, and finally on silica again using CHCl₃ as the eluent. The collected solid was dried under vacuum to give the desired product as a green solid (0.041 g, 50%). ¹H NMR (400 MHz, CDCl₃ with a drop of pyridine-D₅) δ = 9.75 (d, 4H, *J* = 4.0 Hz), 9.49 (d, 4H, *J* = 3.6 Hz), 7.94 (d, 4H, *J*

= 7.2 Hz), 7.38 (d, 4H, J = 7.2 Hz), 5.19 (t, 4H, J = 6.8 Hz), 4.43 (t, 4H, J = 6.8 Hz), 3.61 (t, 4H, J = 6.2 Hz), 2.50 (s, 6H), 2.0~1.0 (m, 10H), 1.0~0.8 (m, 24H) ppm. ^{13}C NMR (101 MHz, CDCl_3 with a drop of pyridine- D_5) δ = 151.3, 150.3, 138.4, 131.4, 131.2, 129.5, 129.2, 121.4, 117.1, 100.3, 96.0, 92.9, 76.4, 69.7, 51.3, 39.2, 36.6, 35.9, 31.2, 30.0, 26.3, 22.9, 21.7 ppm. MALDI-MS m/z : 940.42 ($[\text{M}+\text{H}]^+$, calcd for 940.46).

{5,15-Bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)-10,20-bis[2-(4-methylphenyl)ethynyl]porphinato}zinc(II).

[5,15-Bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)-10,20-dibromoporphinato]zinc(II) (**23**) (0.075 g, 5.63×10^{-5} mol), CuI (1.00 mg, 5.25×10^{-6} mol) and $\text{Pd}(\text{PPh}_3)_4$ (10.0 mg, 8.67×10^{-6} mol) were added into a Schlenk flask in a glove box. After 4-ethynyltoluene (0.0290 mL, 2.29×10^{-4} mol), 50 mL of distilled THF and 10 mL of dry $(\text{Me}_2\text{CH})_2\text{NH}$ were mixed, freeze-pump-thawed and cannulated into the Schlenk flask, the reaction mixture was stirred at 60 °C for 12 h under Ar and passed through a silica plug using THF as the eluent. After solvent removal, the residue was chromatographed first on silica using CHCl_3 as the eluent, then on a size exclusion column using THF as the eluent, and finally on silica again using CHCl_3 as the eluent. The collected solid was washed with hexane and dried under vacuum to give the desired product as a green solid (0.050 g, 64%). ^1H NMR (400 MHz, CDCl_3 with a drop of pyridine- D_5) δ = 9.68 (d, 4H, J = 4.8 Hz), 8.92 (d, 4H, J = 4.8 Hz), 7.92 (d, 4H, J = 8.0 Hz), 7.38 (d, 4H, J = 2.4 Hz), 7.36 (d, 4H, J = 7.6 Hz), 6.94 (t, 2H, J = 2.2 Hz), 4.32 (t, 8H, J = 4.6 Hz), 3.94 (t, 8H, J = 4.6 Hz), 3.77 (m, 8H), 3.69 (m, 8H), 3.63 (m, 8H), 3.50 (m, 8H), 3.32 (s, 12H), 2.49 (s, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3 with a drop of pyridine- D_5) δ = 157.8, 152.0, 149.6, 144.6, 138.4, 132.4, 131.5, 130.6, 129.4, 122.0, 121.3, 114.8, 101.1, 101.0, 96.3, 92.7, 71.9, 70.9, 70.7, 70.6, 69.9, 67.8, 59.0 ppm. MALDI-MS m/z : 1401.48 ($[\text{M}+\text{H}]^+$, calcd for 1401.56).

2. Supramolecular Polymerization Mechanism

2.a. Estimation of the Degree of Aggregation (α_{agg})

The fraction of aggregated molecules (α_{agg}) at a given temperature can be calculated from equation S1:⁷

$$\alpha_{agg} = 1 - \left(\frac{\varepsilon(t) - \varepsilon(agg)}{\varepsilon(mono) - \varepsilon(agg)} \right) \quad (S1)$$

Where $\varepsilon(mono)$ and $\varepsilon(agg)$ stand for the extinction coefficient of the monomer and the fully aggregated state respectively, and $\varepsilon(t)$ represents the extinction coefficient at the given temperature (t).

2.b. Isodesmic Model

The fraction of aggregated species (α_{agg}) as a function of temperature can be fit using non-linear least squares regression method based on equation S2:⁸

$$\alpha_{agg} = 1 - \frac{1}{1 + \exp\left(-0.908 \Delta H \frac{T - T_m}{R T_m}\right)} \quad (S2)$$

Elongation constant K_e can be calculated from equation S3:⁸

$$\frac{1}{\sqrt{1 - \alpha(T)}} = \frac{1}{2} + \frac{1}{2} \sqrt{4K_e(T)C_T + 1} \quad (S3)$$

2.c. Cooperative Model

Supramolecular polymerization that operates following a cooperative mechanism can be dissociated into two regimes: 1) a nucleation process during which a nucleus formed by n repeating units is formed, and 2) an elongation process during which the nucleus grows toward bigger superstructures that feature n repeating units at a given temperature.⁹⁻¹¹

As proposed in the model developed by van der Schoot, the fraction of aggregated species (α) as a function of temperature in the elongation regime is governed by the following equation:

$$\alpha_{agg} = \alpha_{sat} \left(1 - \exp \left[\frac{-\Delta H_e}{RT_e^2} (T - T_e) \right] \right) \quad (S4)$$

Using non-linear least squares regression method based on equation S2 to fit the degree of aggregation as a function of temperature, the enthalpy associated to the elongation process ΔH_e , the elongation temperature T_e , and the correction factor α_{sat} can be estimated. Please note that α_{sat} is introduced in this equation to prevent that $\alpha_{agg}/\alpha_{sat}$ exceeds unity. It is also worth noting that equation S4 can *only* be used below the elongation temperature T_e .

The parameters ΔH_e , α_{sat} , and T_e calculated from equation S4 can then be utilized to estimate the fraction of aggregated building blocks using equation S5:

$$\alpha_{agg} = \alpha_{sat} \left(\sqrt[3]{K_a} \exp \left[\left(\frac{2}{3\sqrt[3]{K_a}} - 1 \right) \frac{\Delta H_e}{RT_e^2} (T - T_e) \right] \right) \quad (S5)$$

Please note that K_a in equation S5 is a dimensionless equilibrium constant of the activation step at the elongation temperature.

The degree of polymerization $\langle N_n \rangle$ as a function of temperature can be calculated using equation S6:

$$\langle N_n \rangle = \frac{1}{\sqrt[3]{K_a}} \frac{\alpha_{agg}}{\alpha_{sat} - \alpha_{agg}} \quad (S6)$$

Please note that n represents the number of building blocks that comprise the aggregate under investigation.

To calculate the size of the aggregate at the elongation temperature, equation S7 was utilized.

$$\langle N_n(T_e) \rangle = \frac{1}{\sqrt[3]{K_a}} \quad (S7)$$

3. Ground State Electronic Absorption Spectra

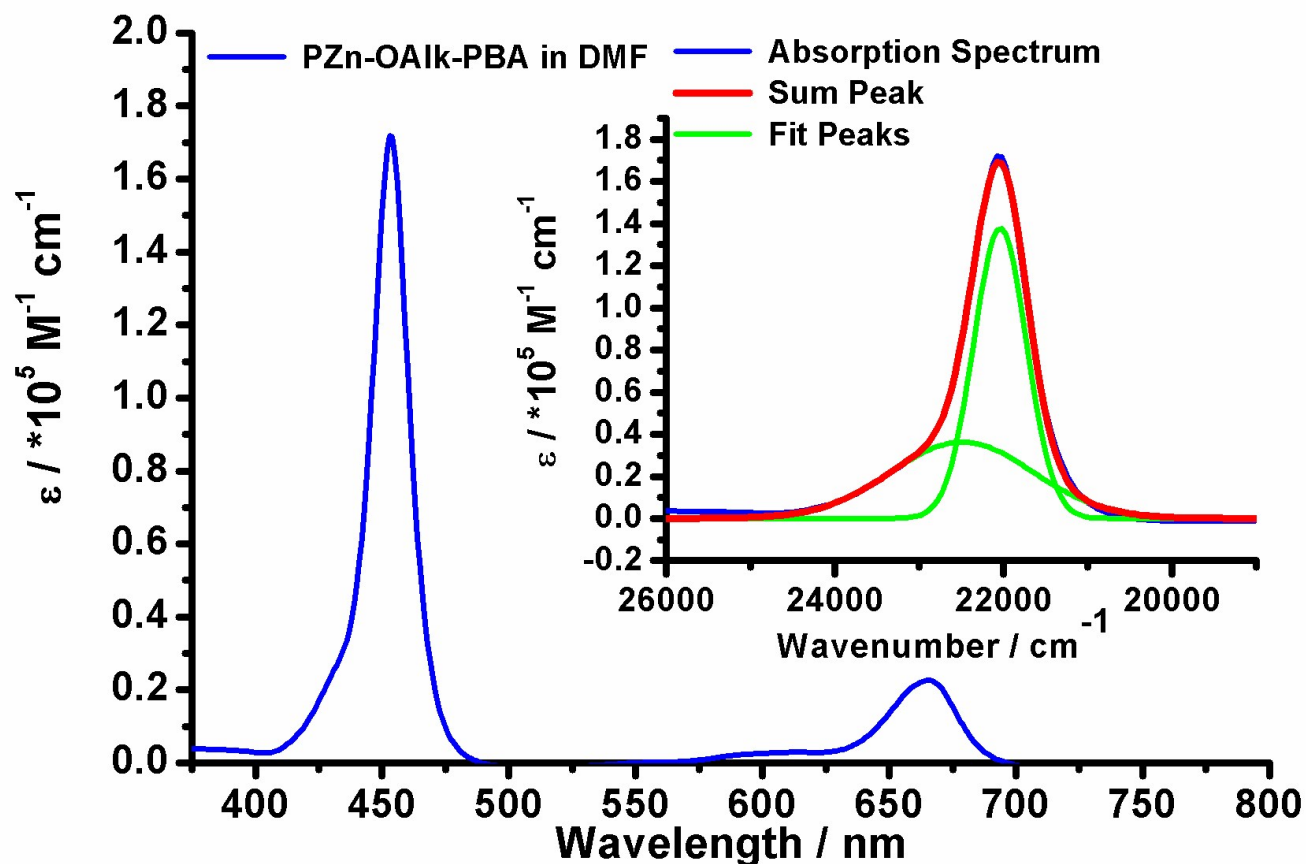


Figure S1: Electronic absorption spectrum recorded at room temperature for **PZn-OAlk-PBA** in DMF ($c = 5.4 * 10^{-5} \text{ M}$). Please note that this spectrum has been acquired after ramping the solution to 110°C to ensure that all molecular building blocks are fully individualized. Inset illustrates the deconvoluted spectra of the B-band transition used to calculate the oscillator strength.

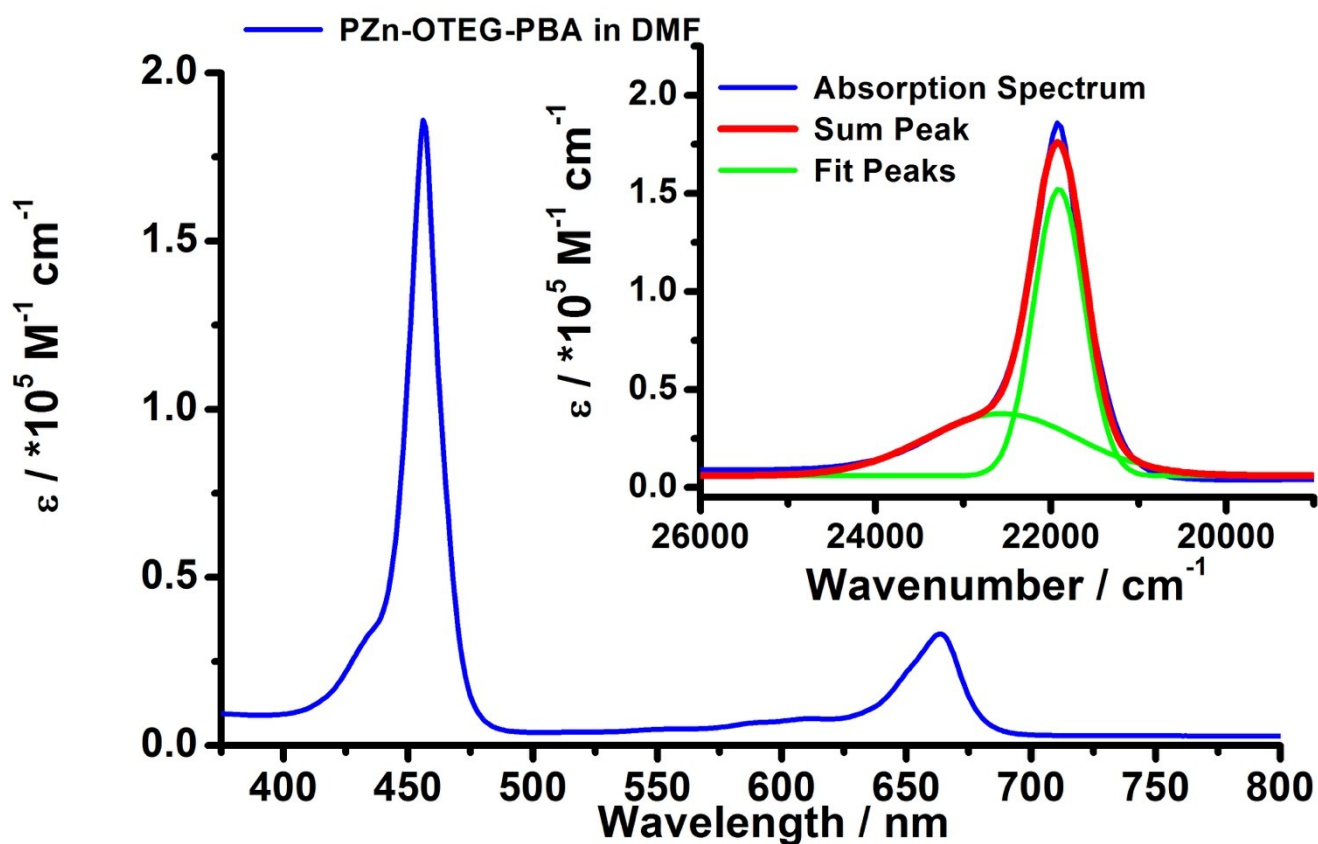


Figure S2: Electronic absorption spectrum recorded at room temperature for **PZn-OTEG-PBA** in DMF ($c = 5.8 * 10^{-5} \text{ M}$). Please note that this spectrum has been acquired at room temperature after ramping the solution to 110°C to ensure that all molecular building blocks are fully individualized. Inset illustrates the deconvoluted spectra of the B-band transition used to calculate the oscillator strength.

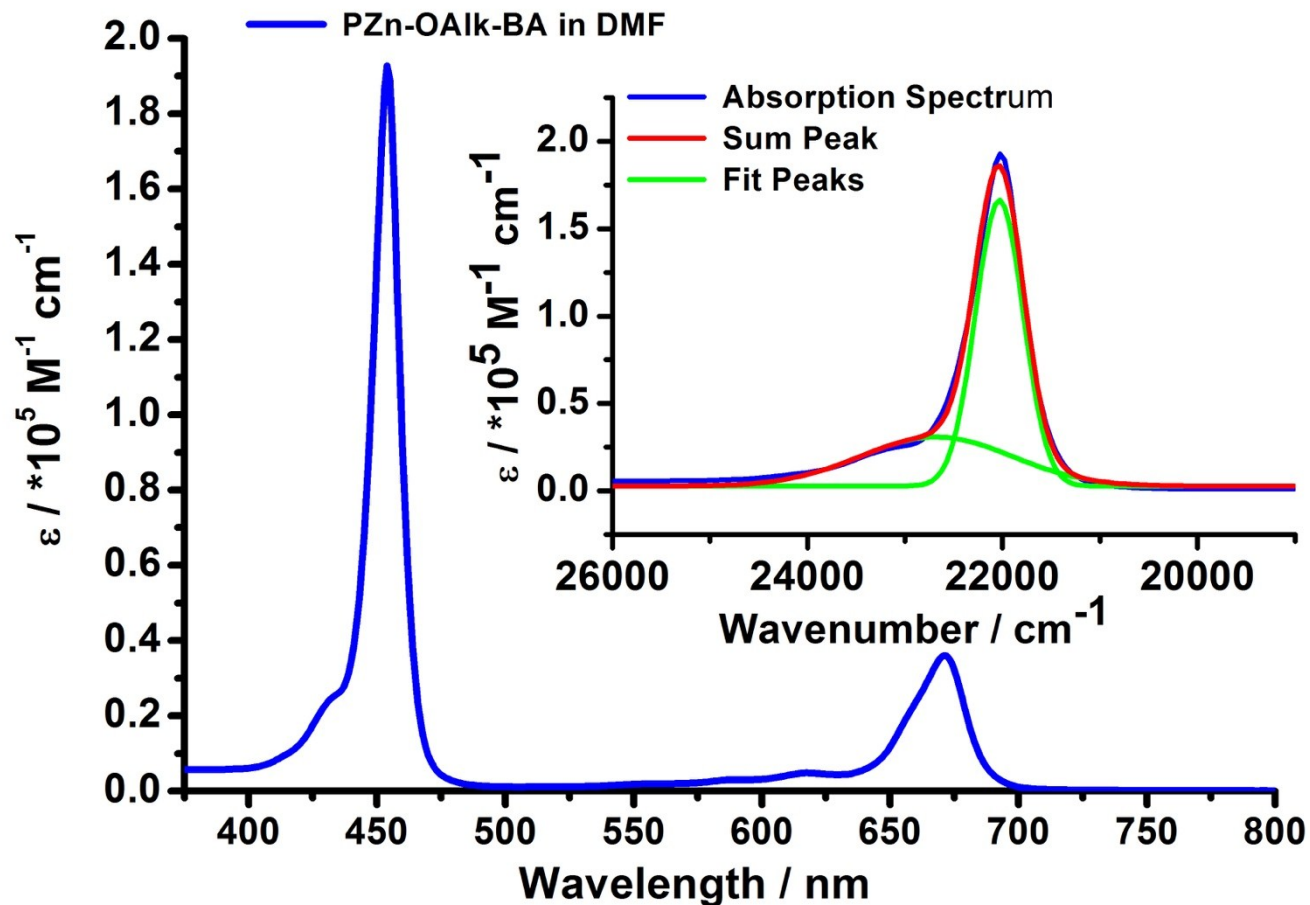


Figure S3: Electronic absorption spectrum recorded at room temperature for **PZn-OAlk-BA** in DMF ($c = 5.1 * 10^{-5} \text{ M}$). Please note that this spectrum has been acquired at room temperature after ramping the solution to 110°C to ensure that all molecular building blocks are fully individualized. Inset illustrates the deconvoluted spectra of the B-band transition used to calculate the oscillator strength.

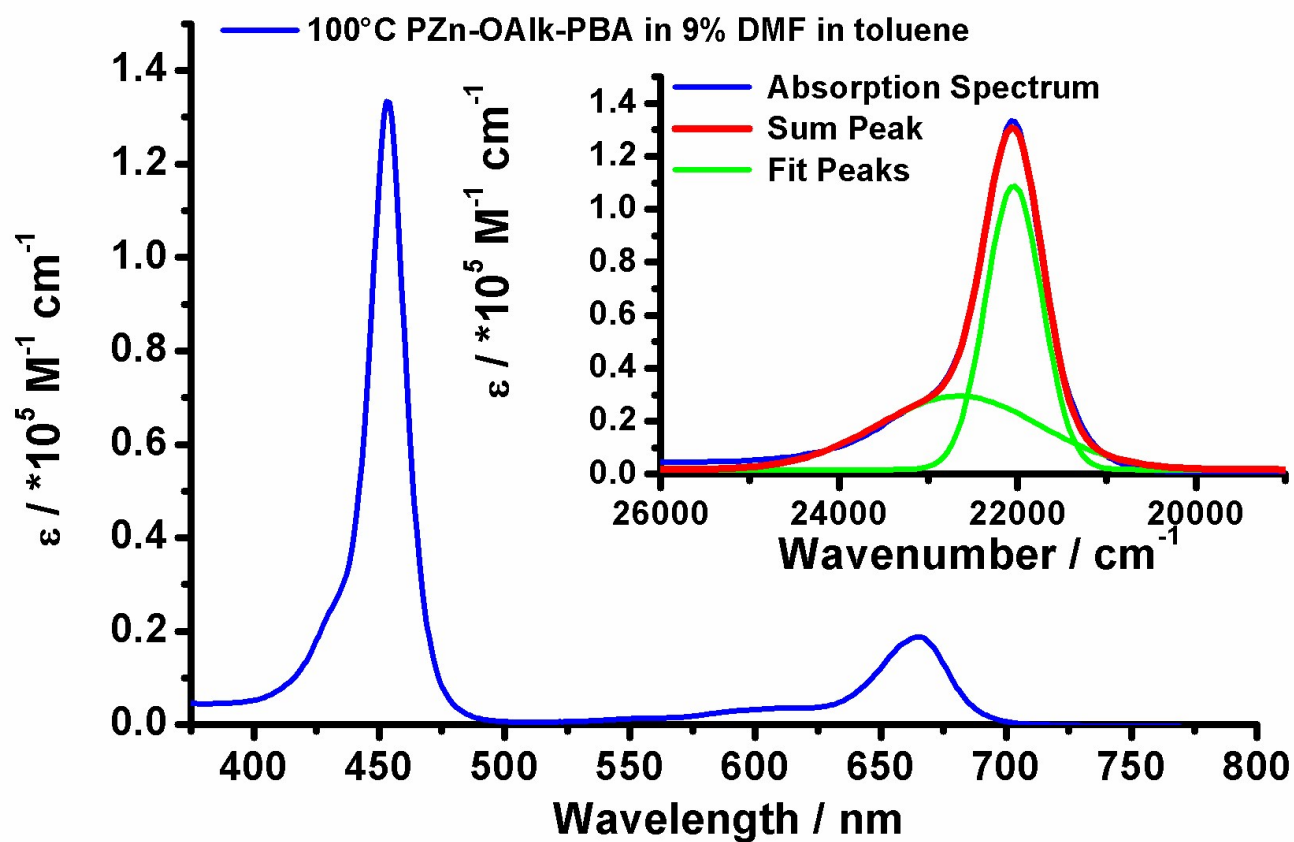


Figure S4: Electronic absorption spectrum recorded at room temperature for **PZn-OAlk-PBA** in 9% DMF in toluene ($c = 5.7 * 10^{-5} \text{ M}$). Please note that this spectrum has been acquired at 110°C to ensure that all molecular building blocks are fully individualized. Inset illustrates the deconvoluted spectra of the B-band transition used to calculate the oscillator strength.

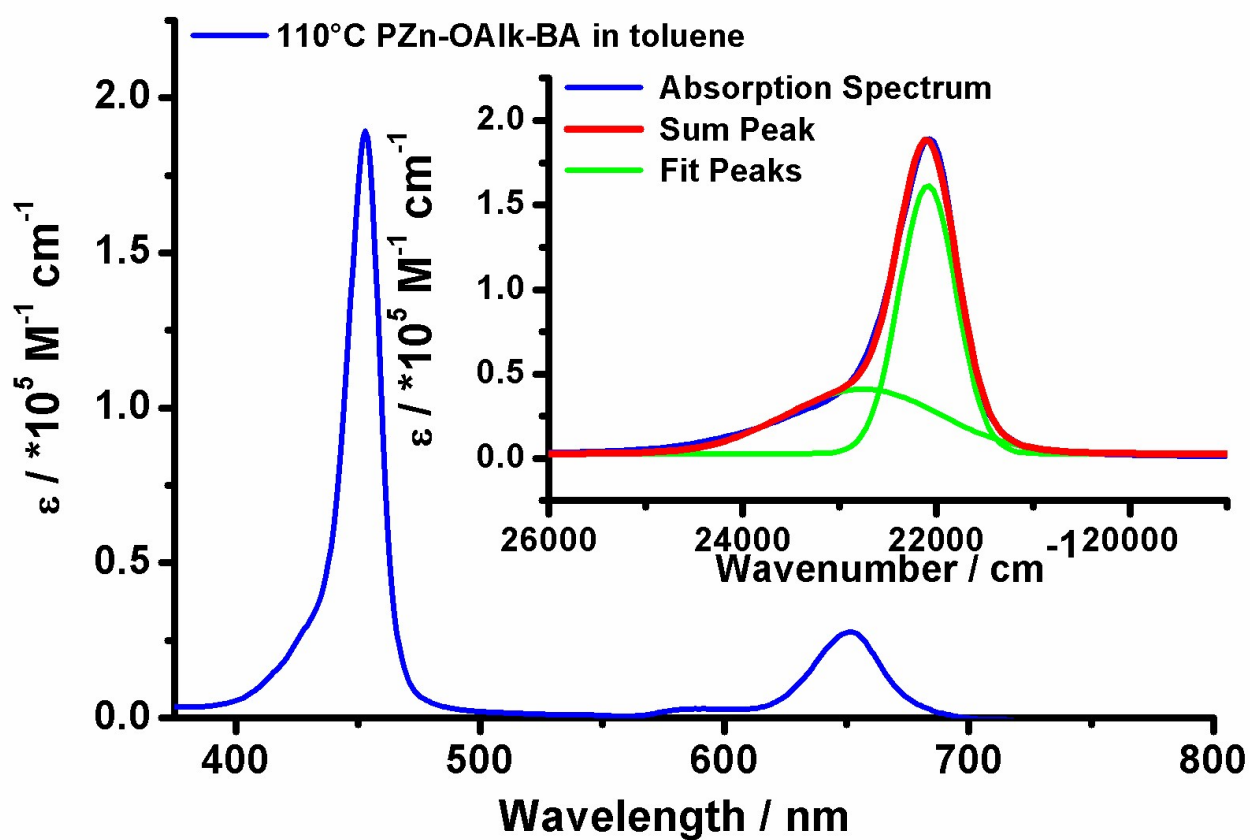


Figure S5: Electronic absorption spectrum recorded at room temperature for **PZn-OAlk-BA** in toluene ($c = 6.50 * 10^{-6} \text{ M}$). Please note that this spectrum has been acquired at 110°C to ensure that all molecular building blocks are fully individualized. Inset illustrates the deconvoluted spectra of the B-band transition used to calculate the oscillator strength.

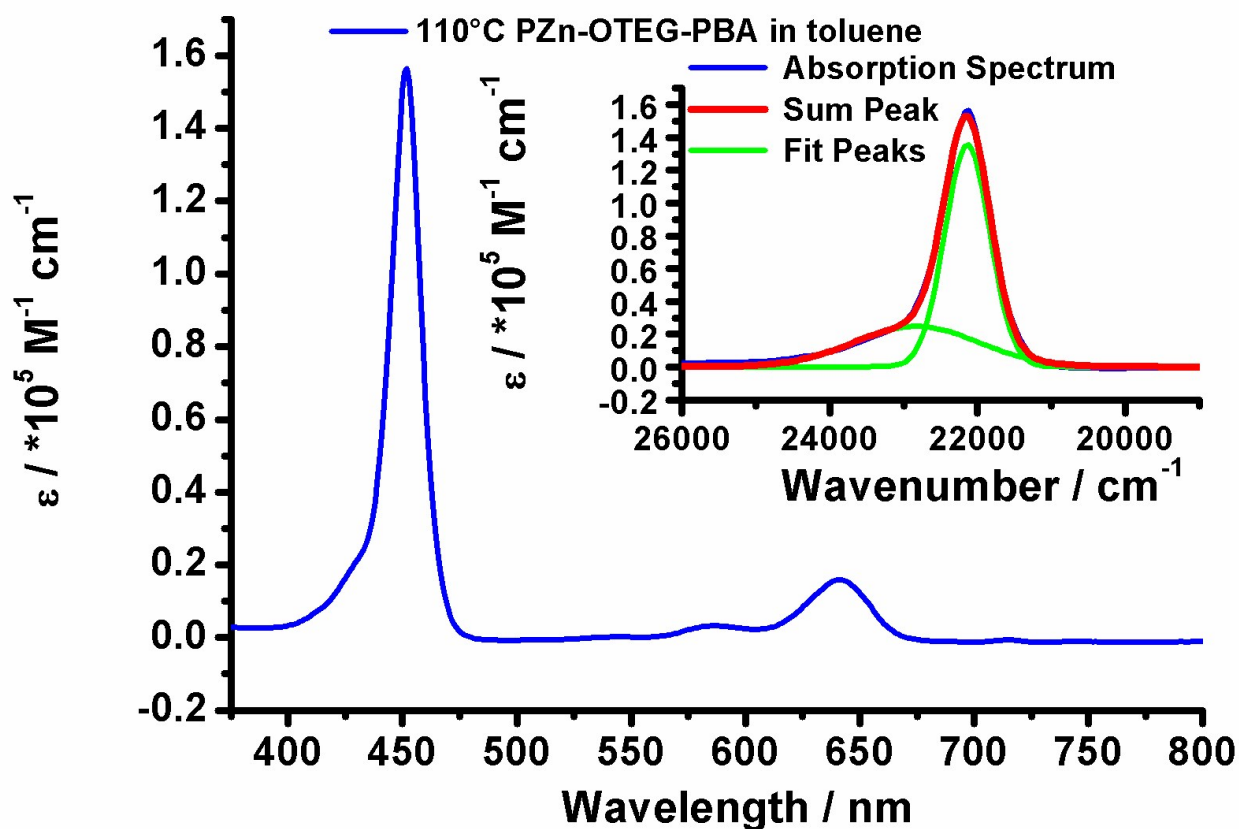


Figure S6: Electronic absorption spectrum recorded at room temperature for **PZn-OTEG-PBA** in toluene ($c = 4.70 * 10^{-5} \text{ M}$). Please note that this spectrum has been acquired at 110°C to ensure that all molecular building blocks are fully individualized. Inset illustrates the deconvoluted spectra of the B-band transition used to calculate the oscillator strength.

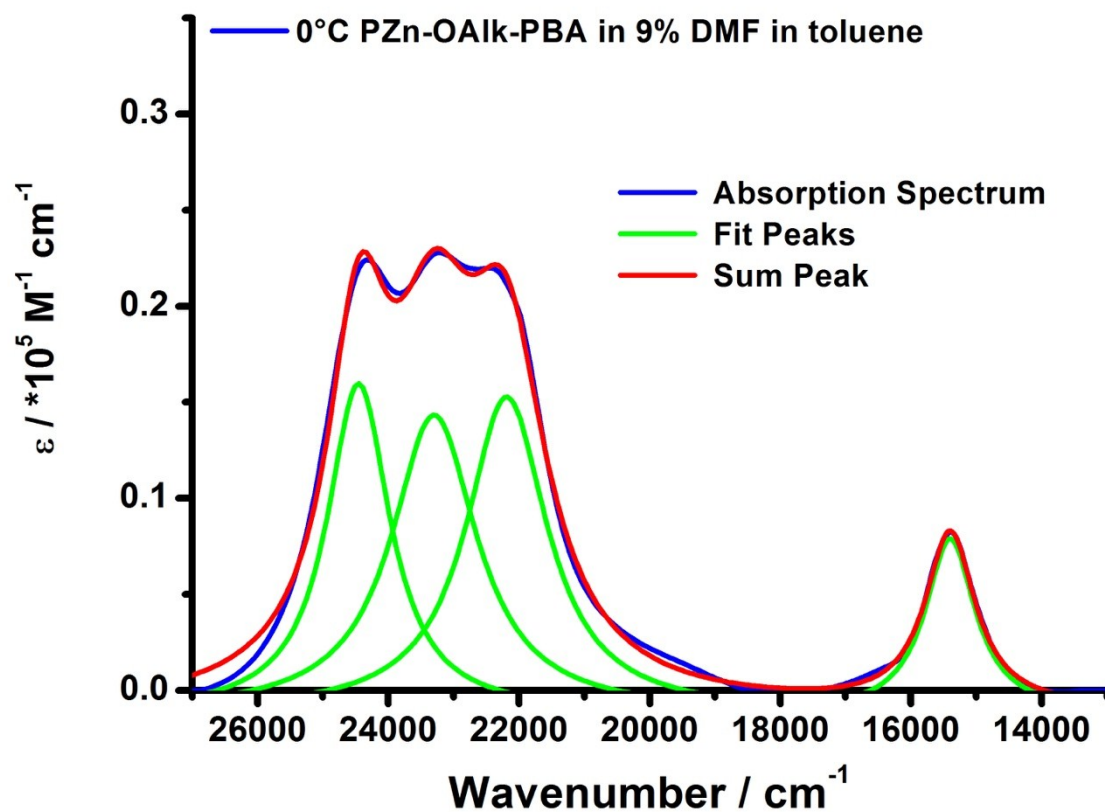


Figure S7: Electronic absorption spectrum recorded at room temperature for **PZn-OAlk-PBA** in 9% DMF in toluene ($c = 5.7 * 10^{-5} \text{ M}$). Please note that this spectrum has been acquired at 0°C, temperature at which building blocks are mainly aggregated.

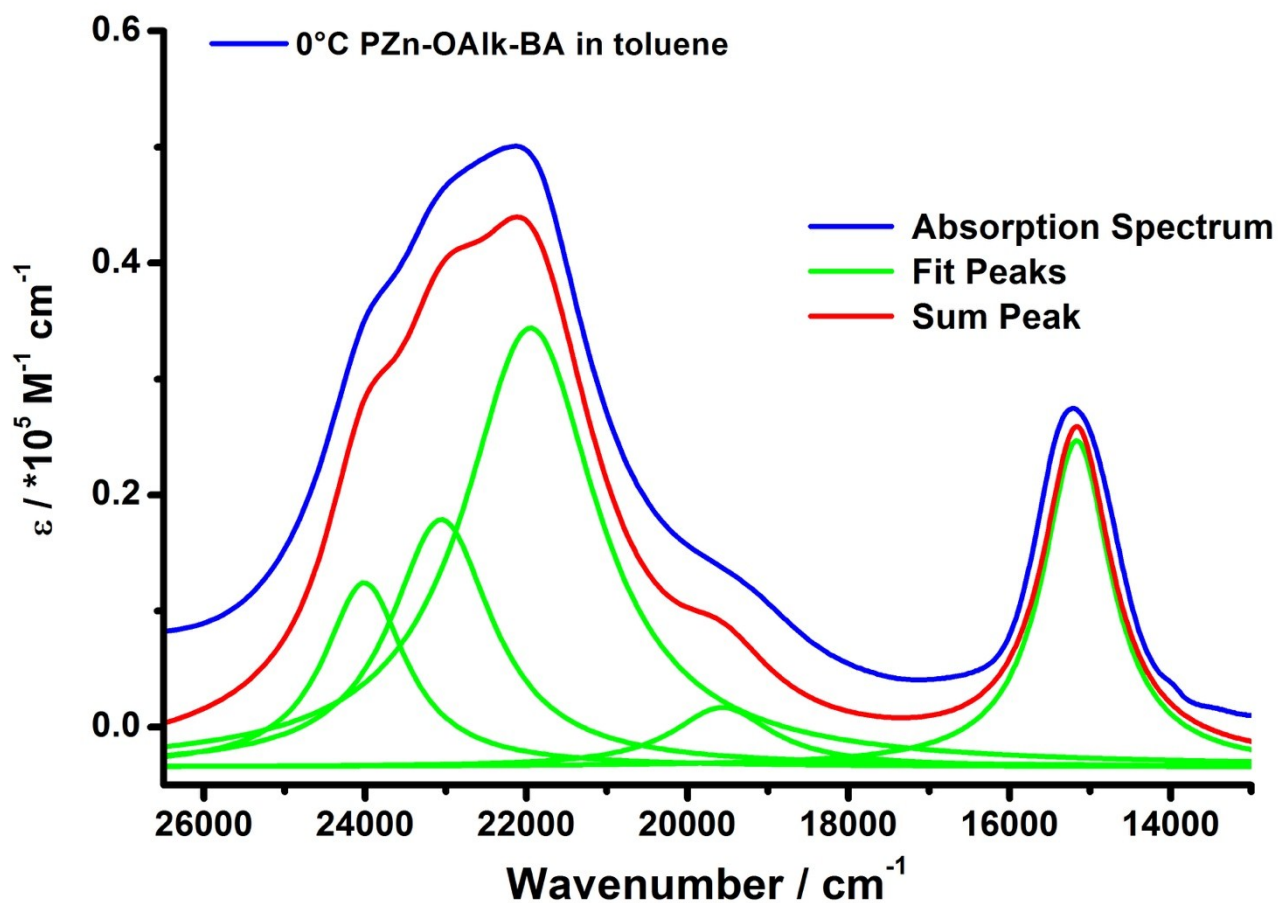


Figure S8: Electronic absorption spectrum recorded at room temperature for **PZn-OAlk-BA** in toluene ($c = 6.5 * 10^{-6} \text{ M}$). Please note that this spectrum has been acquired at 0°C, temperature at which building blocks are mainly aggregated.

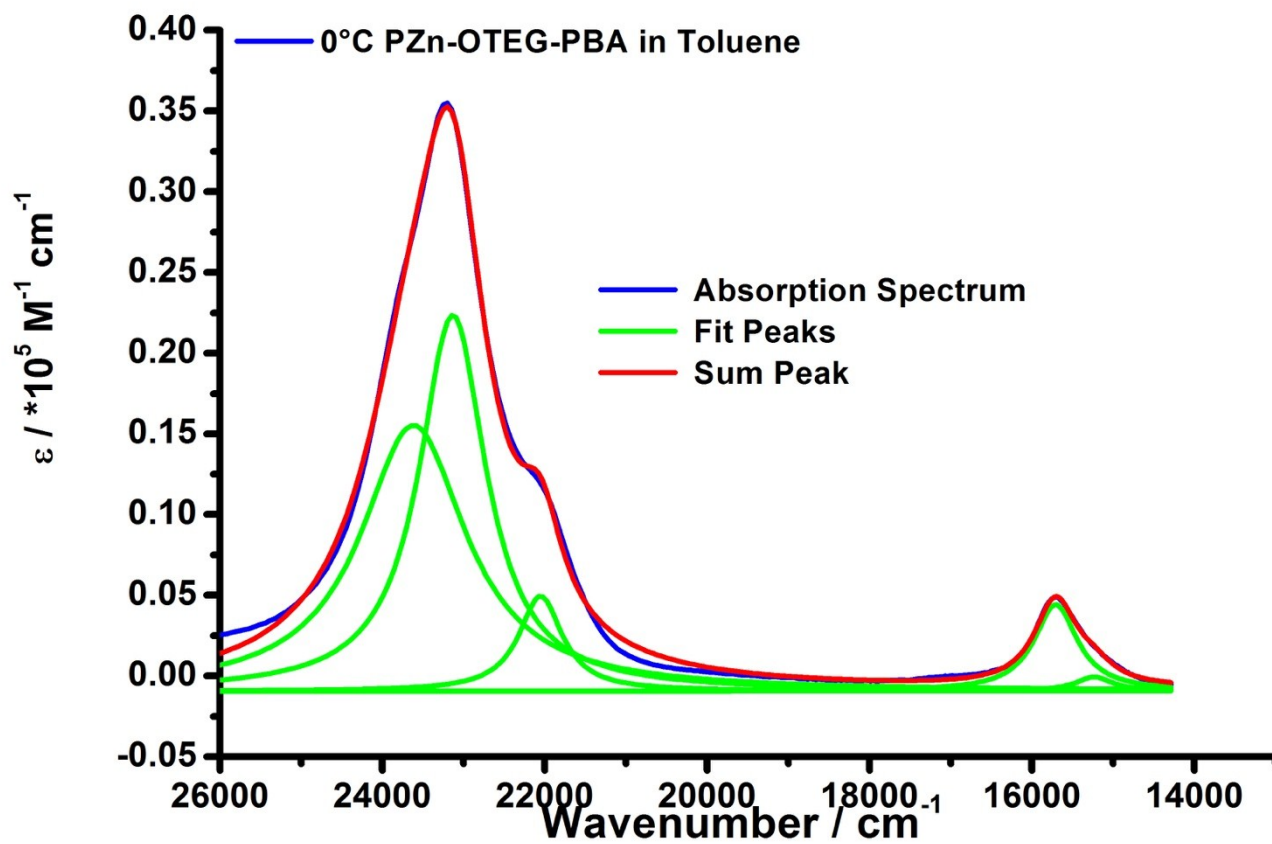


Figure S9: Electronic absorption spectrum recorded at room temperature for **PZn-OTEG-PBA** in toluene ($c = 4.7 \times 10^{-6} \text{ M}$). Please note that this spectrum has been acquired at 20°C, temperature at which building blocks are mainly aggregated.

4. Atomic Force Microscopy Images

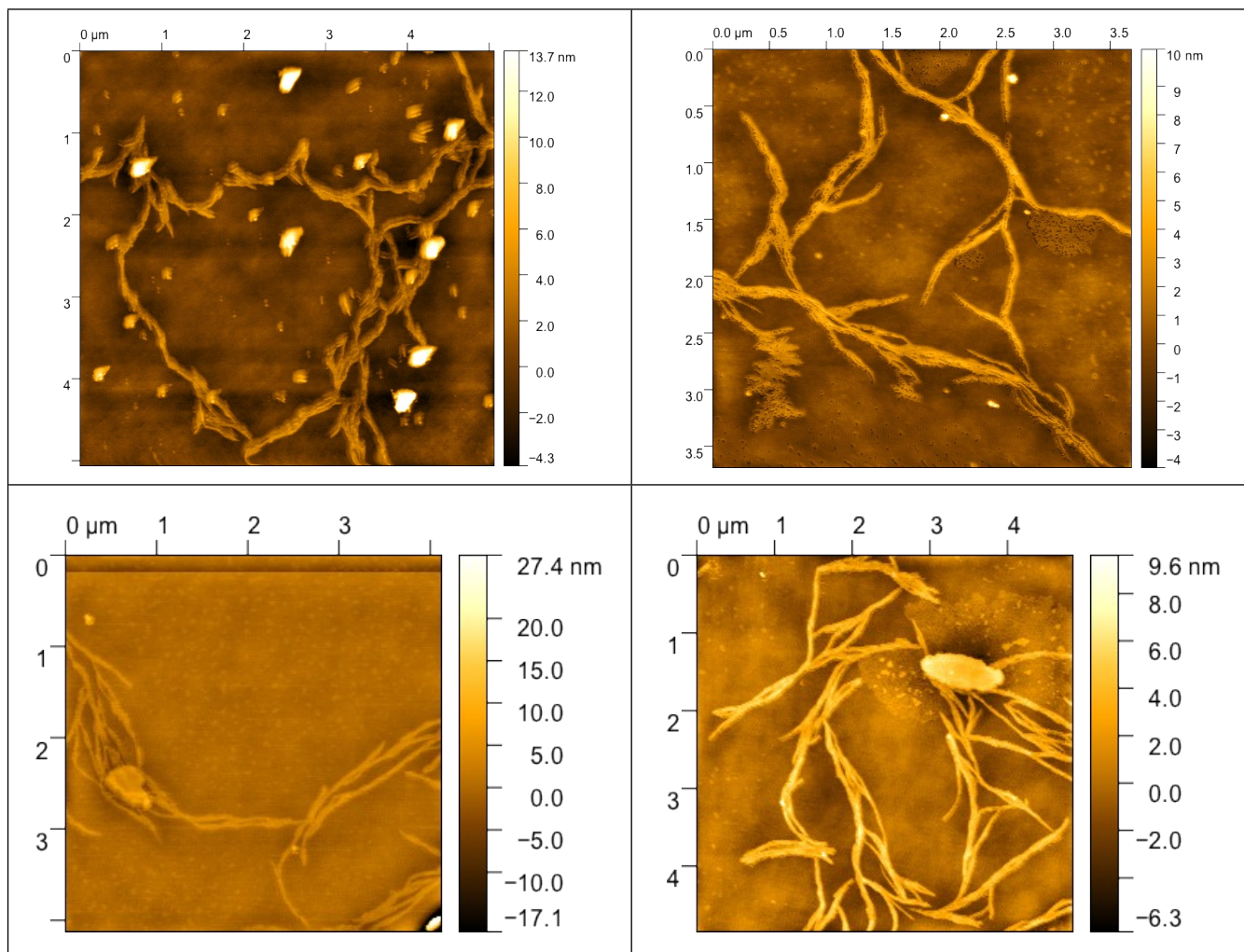


Figure S10: Topographic intermittent contact mode AFM images of [PZn-OAlk-PBA]_{Fib} from a temperature treated 9% DMF in toluene suspension drop-casted on a Si surface.

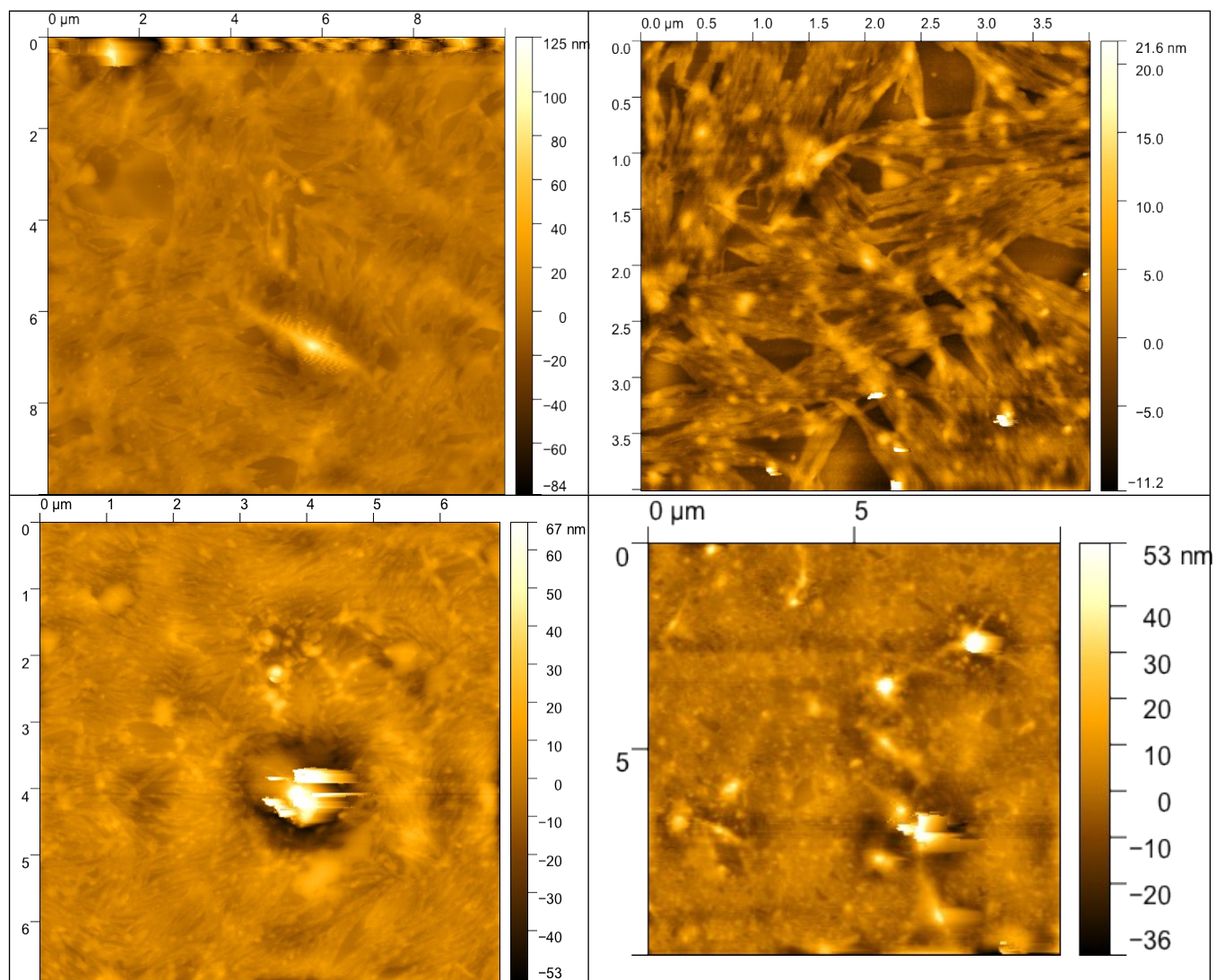


Figure S11: Topographic intermittent contact mode AFM images of $[\text{PZn-OAlk-PBA}]_{\text{Agg}}$ from a temperature treated DMF suspension drop-casted on a Si surface.

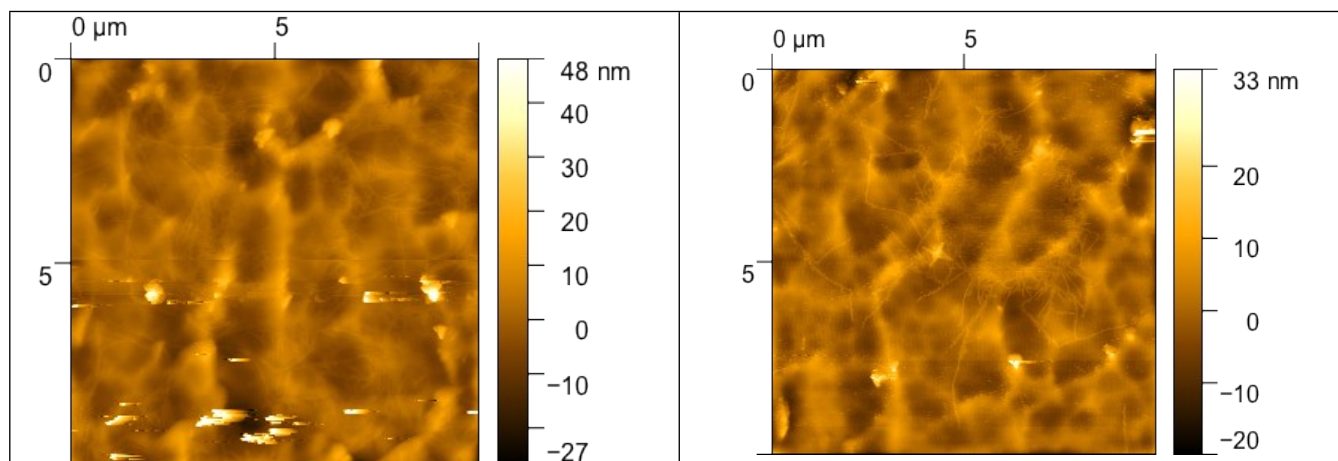


Figure S12. Topographic intermittent contact mode AFM images of [PZn-OAlk-BA]_{NW} from a temperature treated DMF suspension drop-casted on a Si surface.

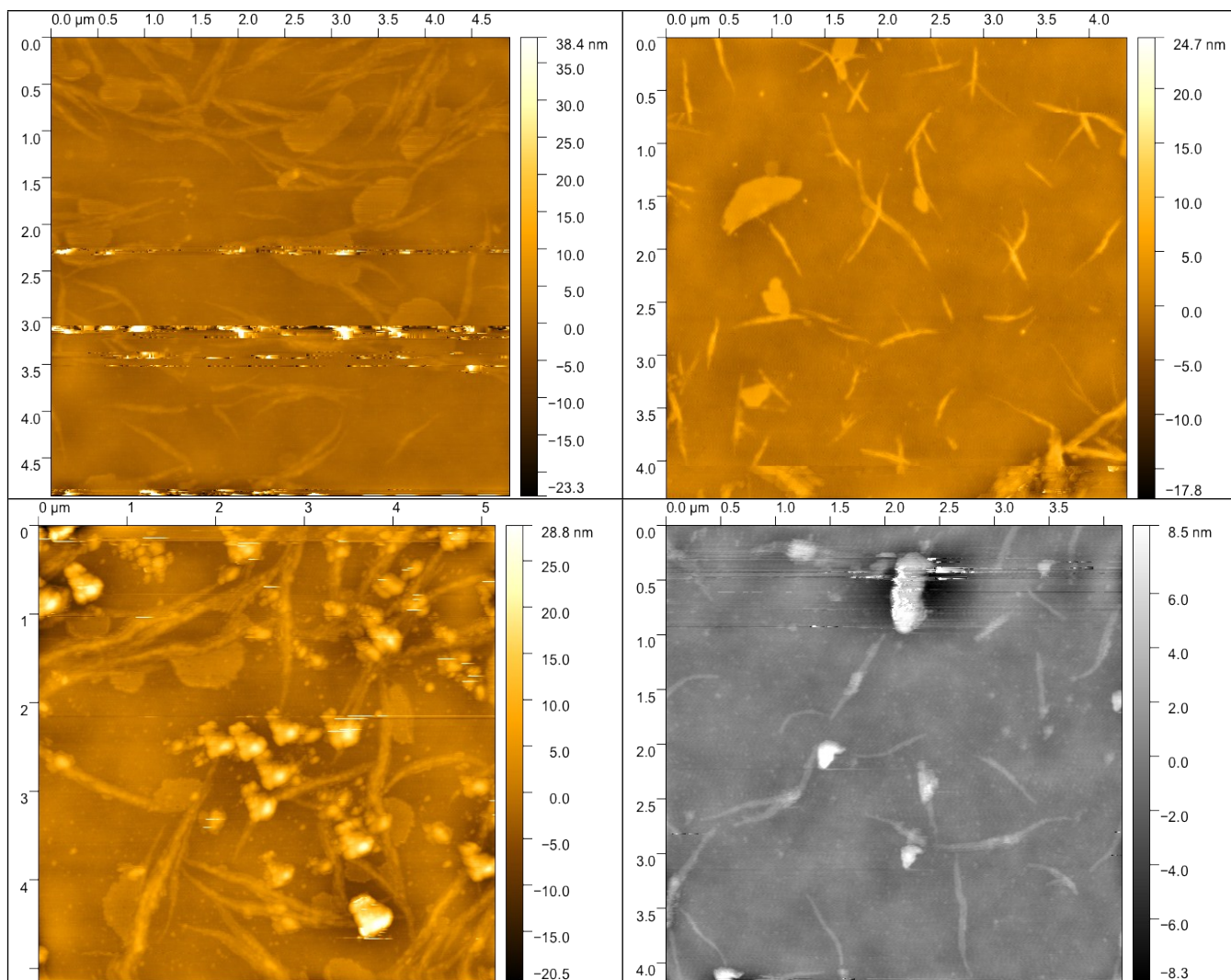


Figure S13: Topographic intermittent contact mode AFM images of [PZn-OAlk-BA]_{NS} from a temperature treated toluene suspension drop-casted on a Si surface.

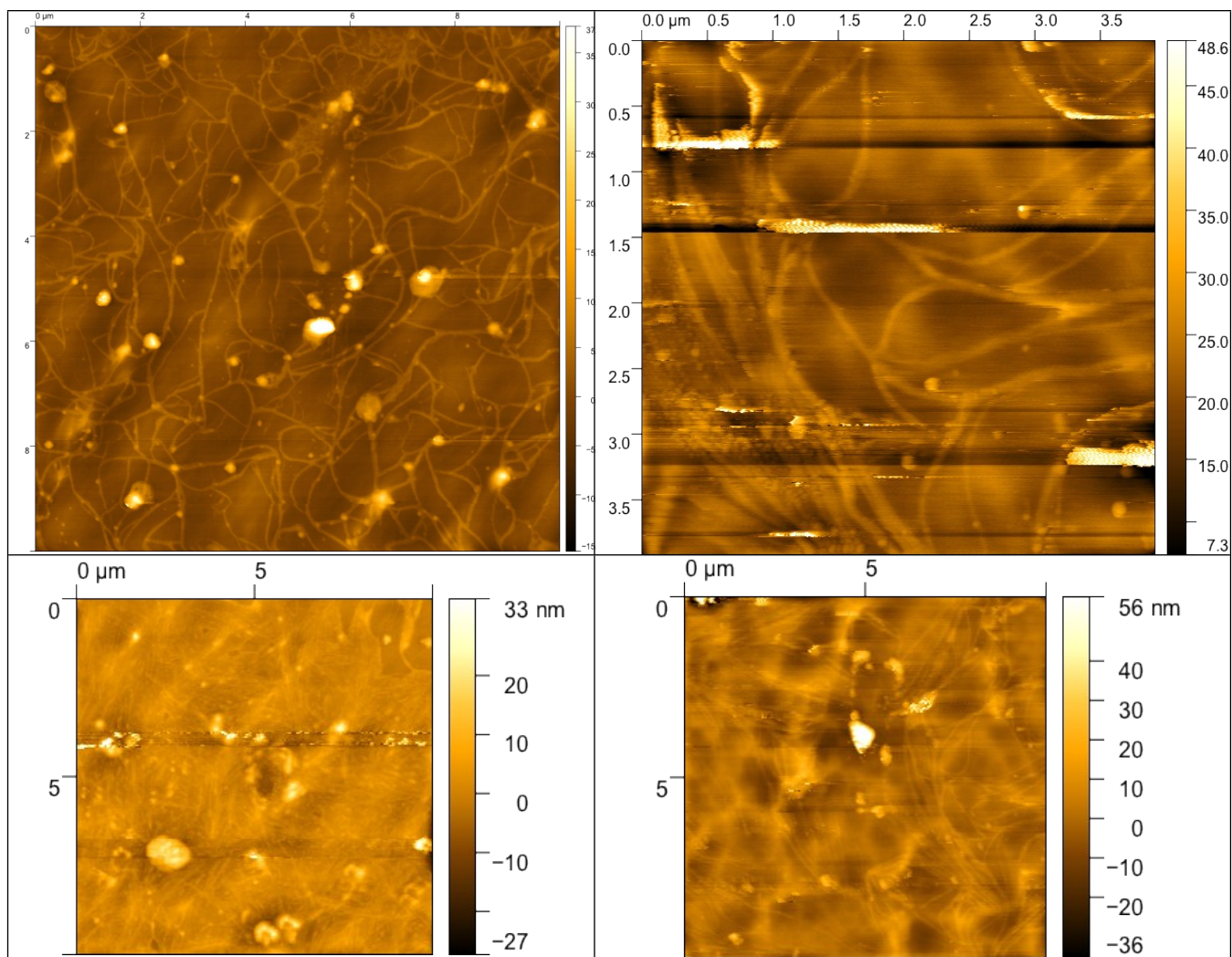


Figure S14: Topographic intermittent contact mode AFM images of [PZn-OTEG-PBA]_{NW} from a temperature treated DMF suspension drop-casted on a Si surface.

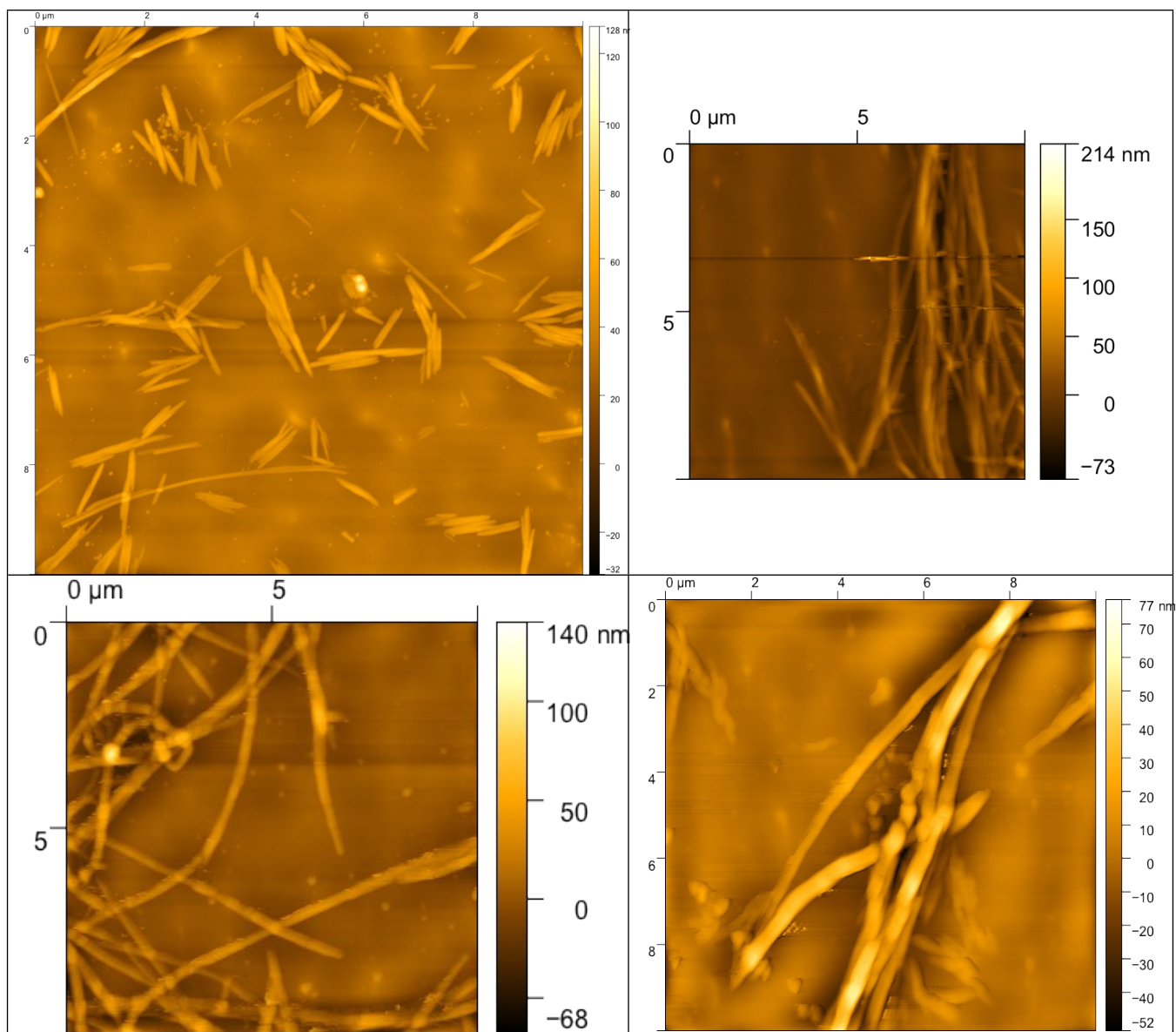


Figure S15: Topographic intermittent contact mode AFM images of [PZn-OTEG-PBA]_{Fib} from a temperature treated toluene suspension drop-casted on a Si surface.

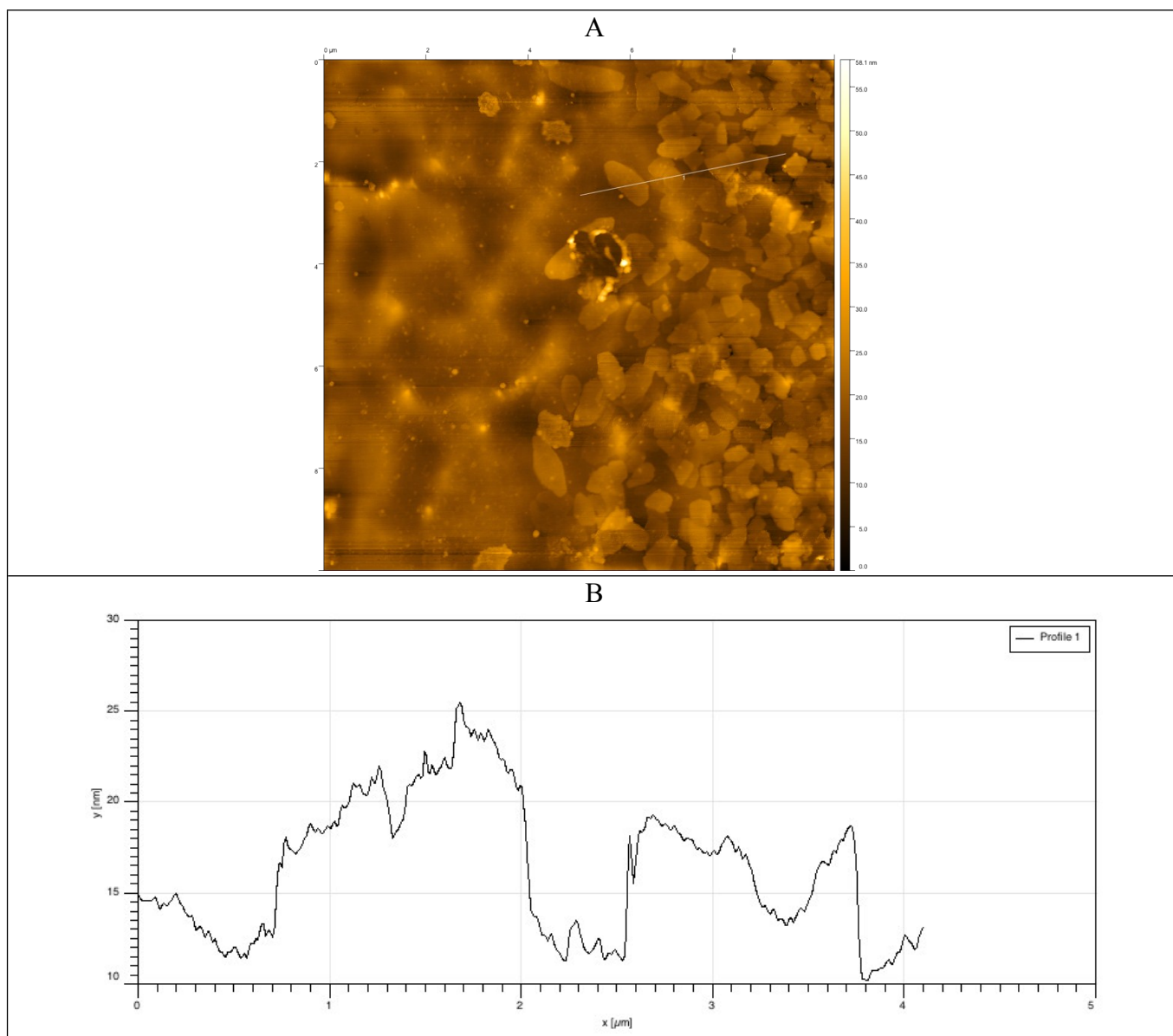


Figure S16: Topographic intermittent contact mode AFM image of $[\text{PZn-OAlk-Tol}]_{\text{Agg}}$ from a temperature treated DMF suspension drop-casted on a Si surface. The height profile corresponds to the white line in the AFM image.

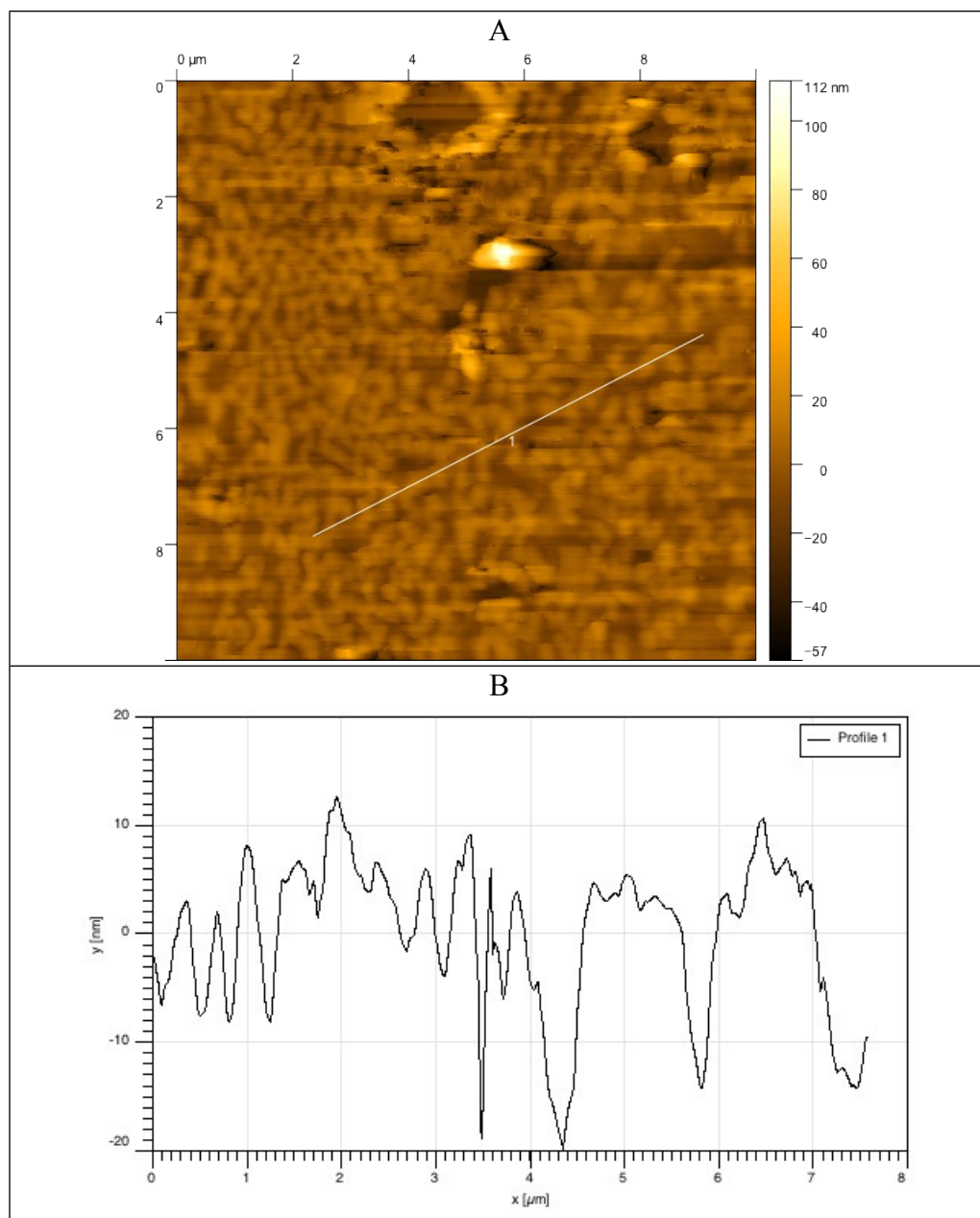


Figure S17: Topographic intermittent contact mode AFM image of $[\text{PZn-OTEG-Tol}]_{\text{Agg}}$ from a temperature treated DMF suspension drop-casted on a Si surface. The height profile corresponds to the white line in the AFM image.

5. Cyclic Voltammetry Measurements

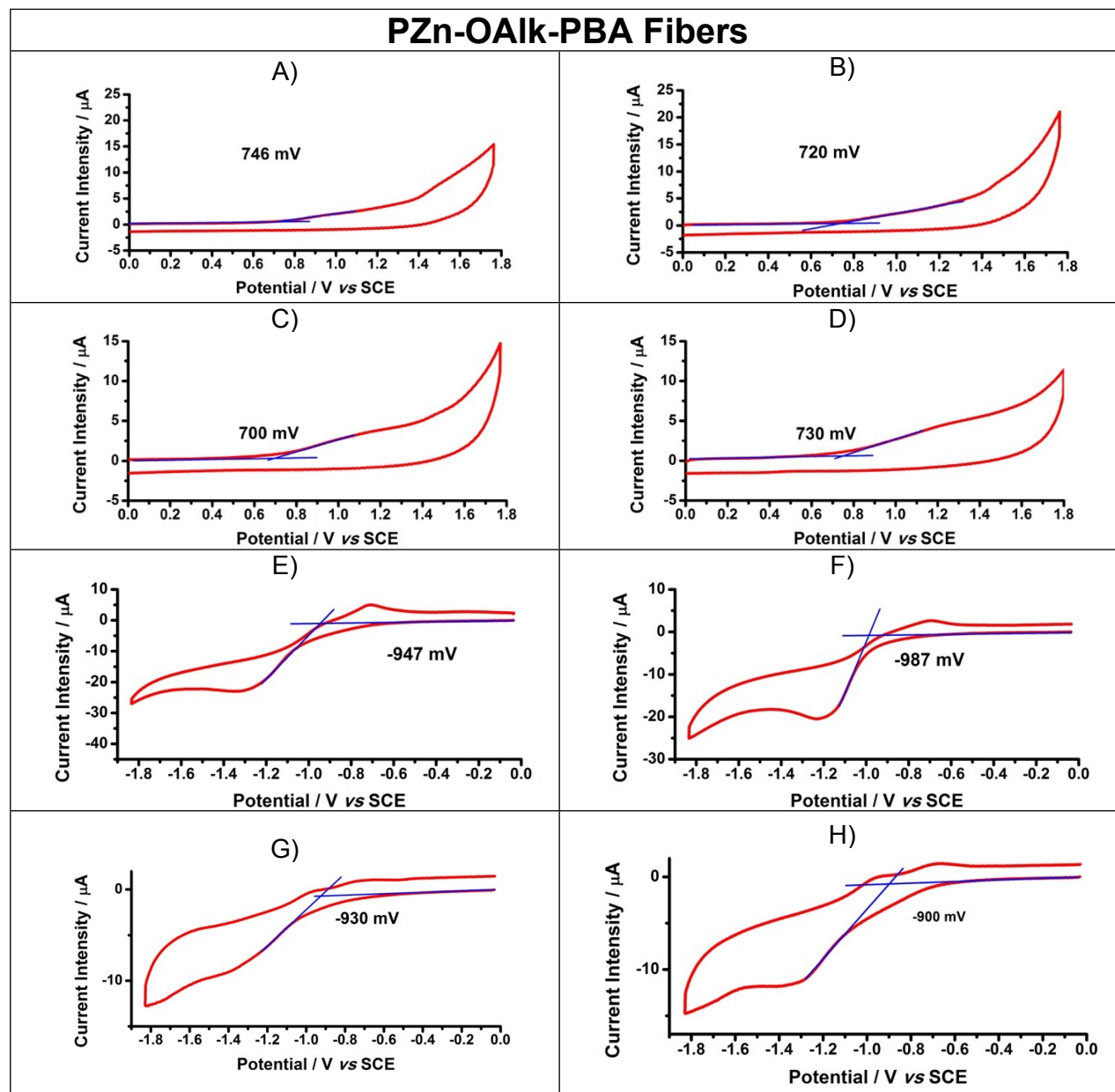


Figure S18: Cyclic voltammetry responses of **PZn-OAlk-PBA** fibers recorded in acetonitrile solvent showing the anodic (A-D) and cathodic (E-H) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40 \text{ V vs SCE}$ in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of supramolecular **PZn-OAlk-PBA** polymers drop-casted on the working electrode from parent 9% DMF in toluene solution.

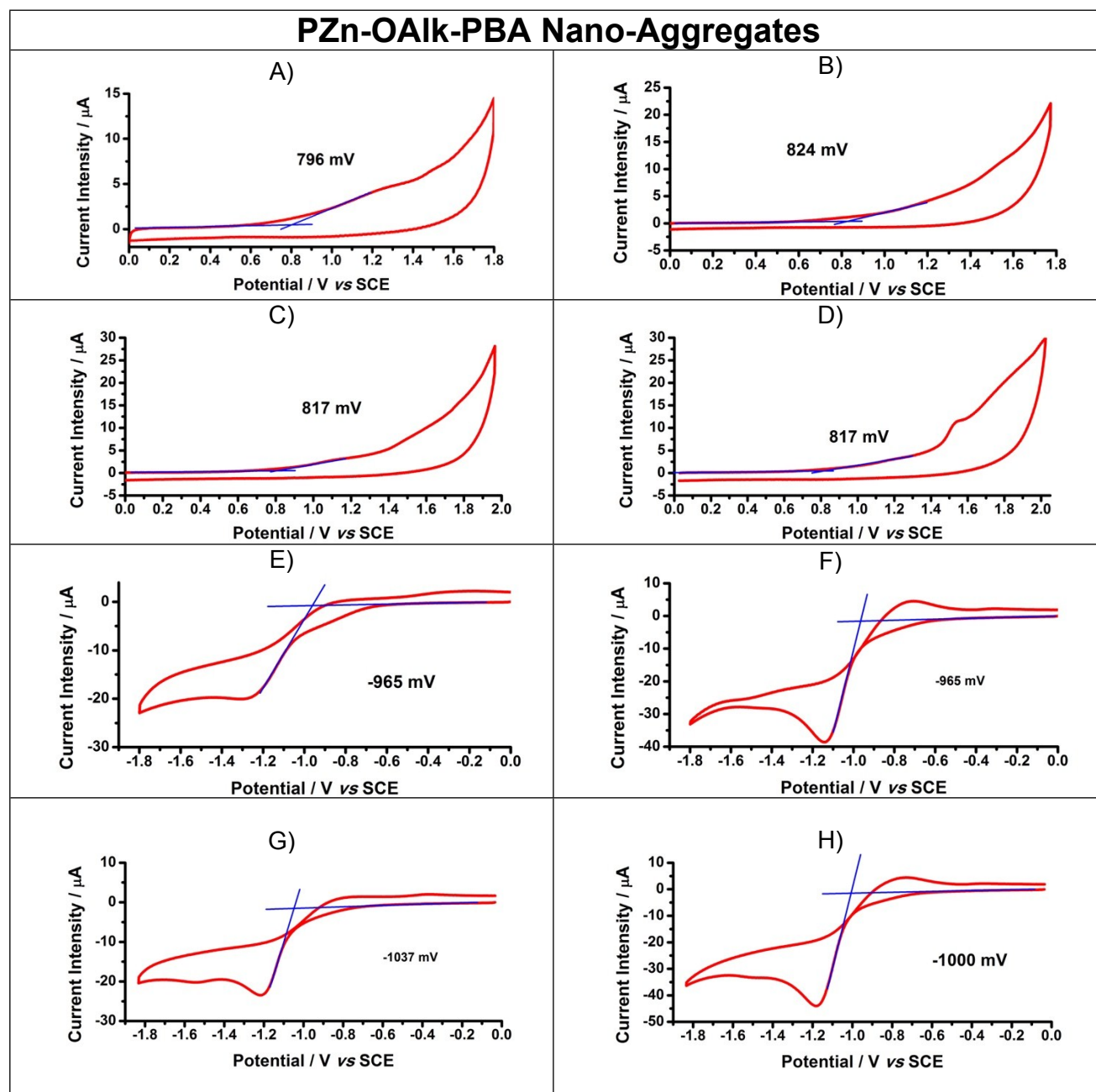


Figure S19: Cyclic voltammetry response of **PZn-OAlk-PBA** aggregates recorded in acetonitrile solvent showing the anodic (A-D) and cathodic (E-H) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40$ V vs SCE in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of individualized **PZn-OAlk-PBA** building blocks drop-casted on the working electrode from a parent DMF solution.

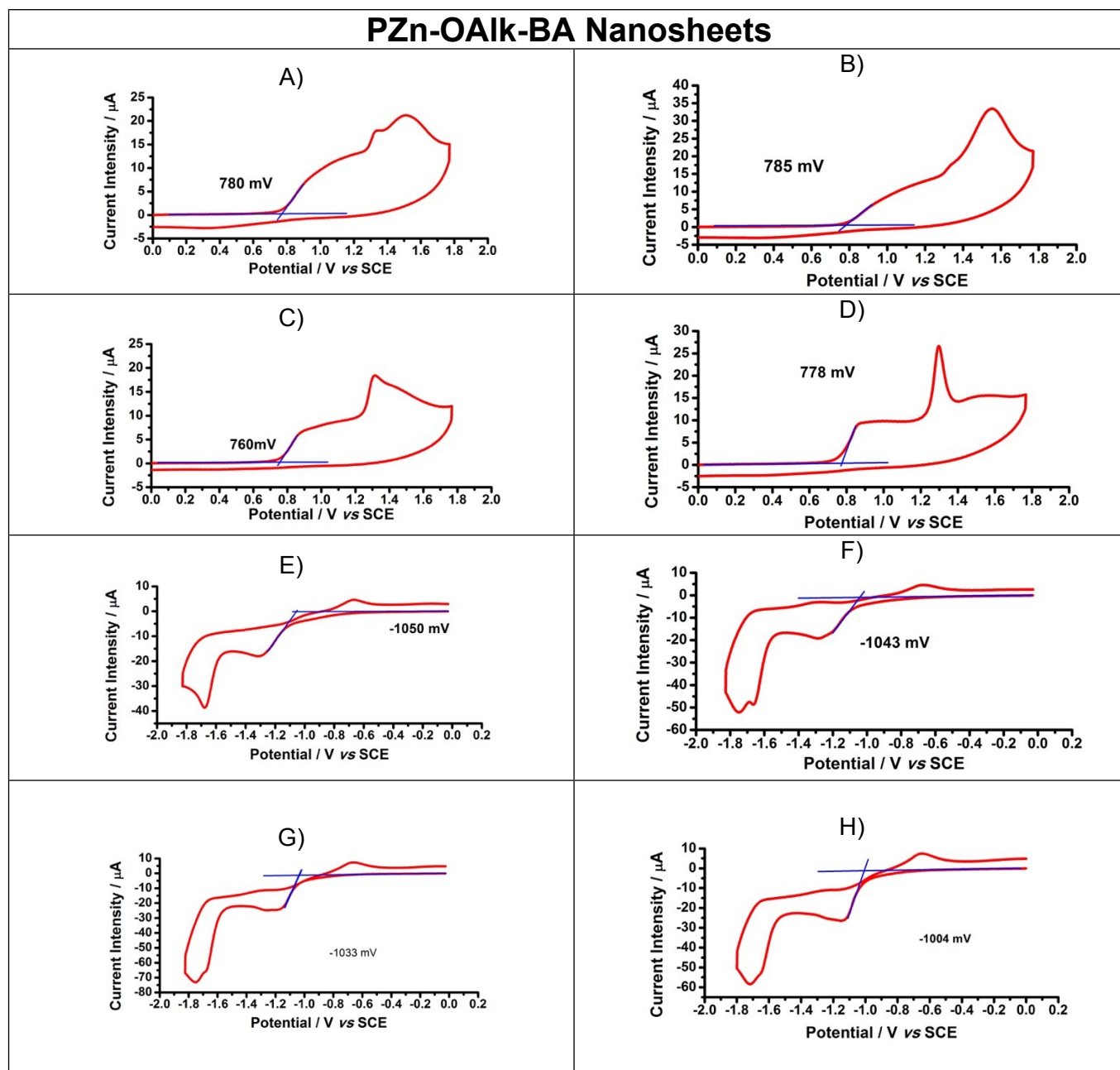


Figure S20: Cyclic voltammetry response of **PZn-OAlk-BA** nanosheets recorded in acetonitrile solvent showing the anodic (A-D) and cathodic (E-H) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40 \text{ V vs SCE}$ in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of supramolecular **PZn-OAlk-BA** polymers drop-casted on the working electrode from parent toluene solution.

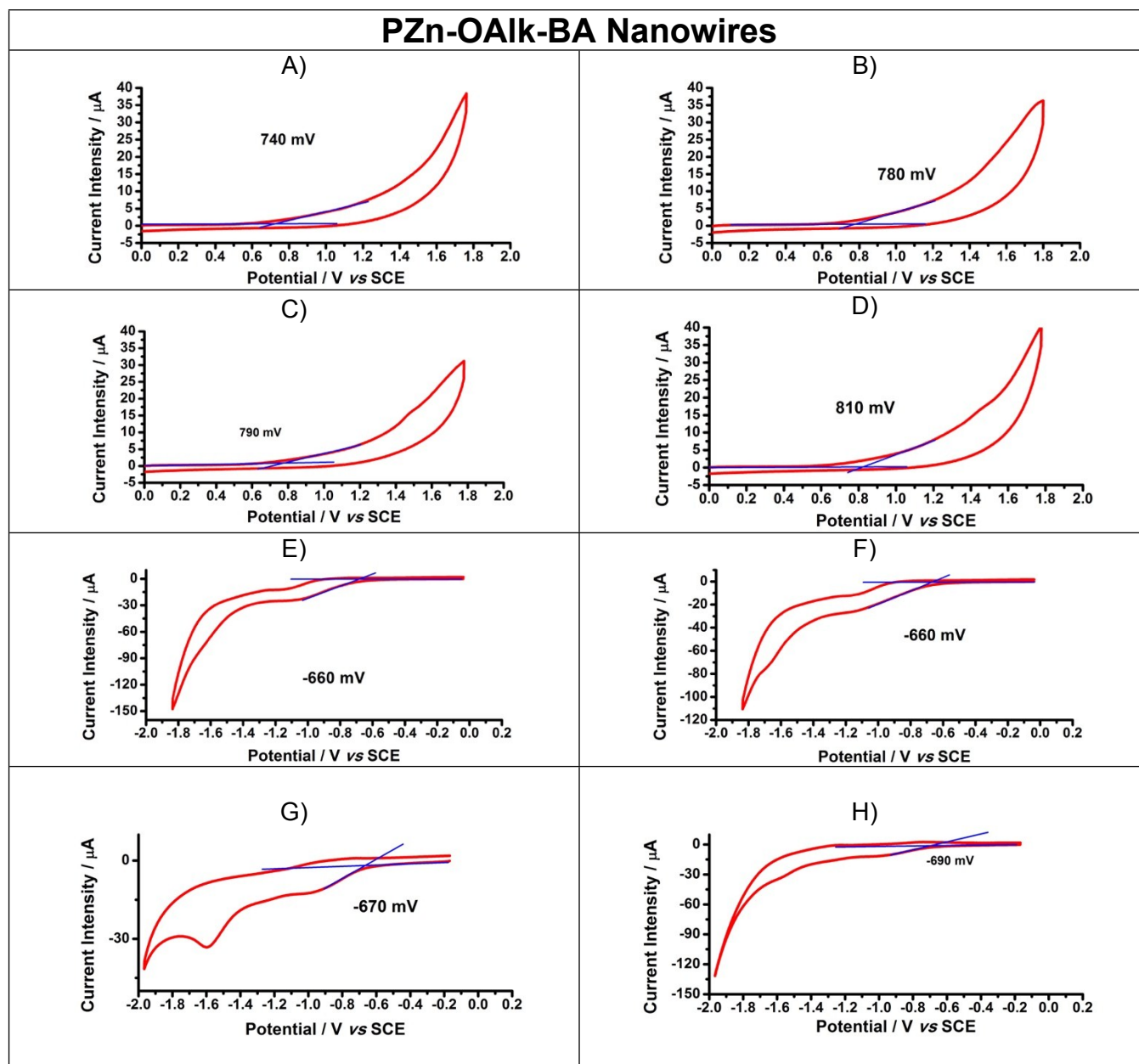


Figure S21: Cyclic voltammetry response of **PZn-OAlk-BA** nanowires recorded in acetonitrile solvent showing the anodic (A-D) and cathodic (E-H) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40 \text{ V vs SCE}$ in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of individualized **PZn-OAlk-BA** building blocks drop-casted on the working electrode from a parent DMF solution.

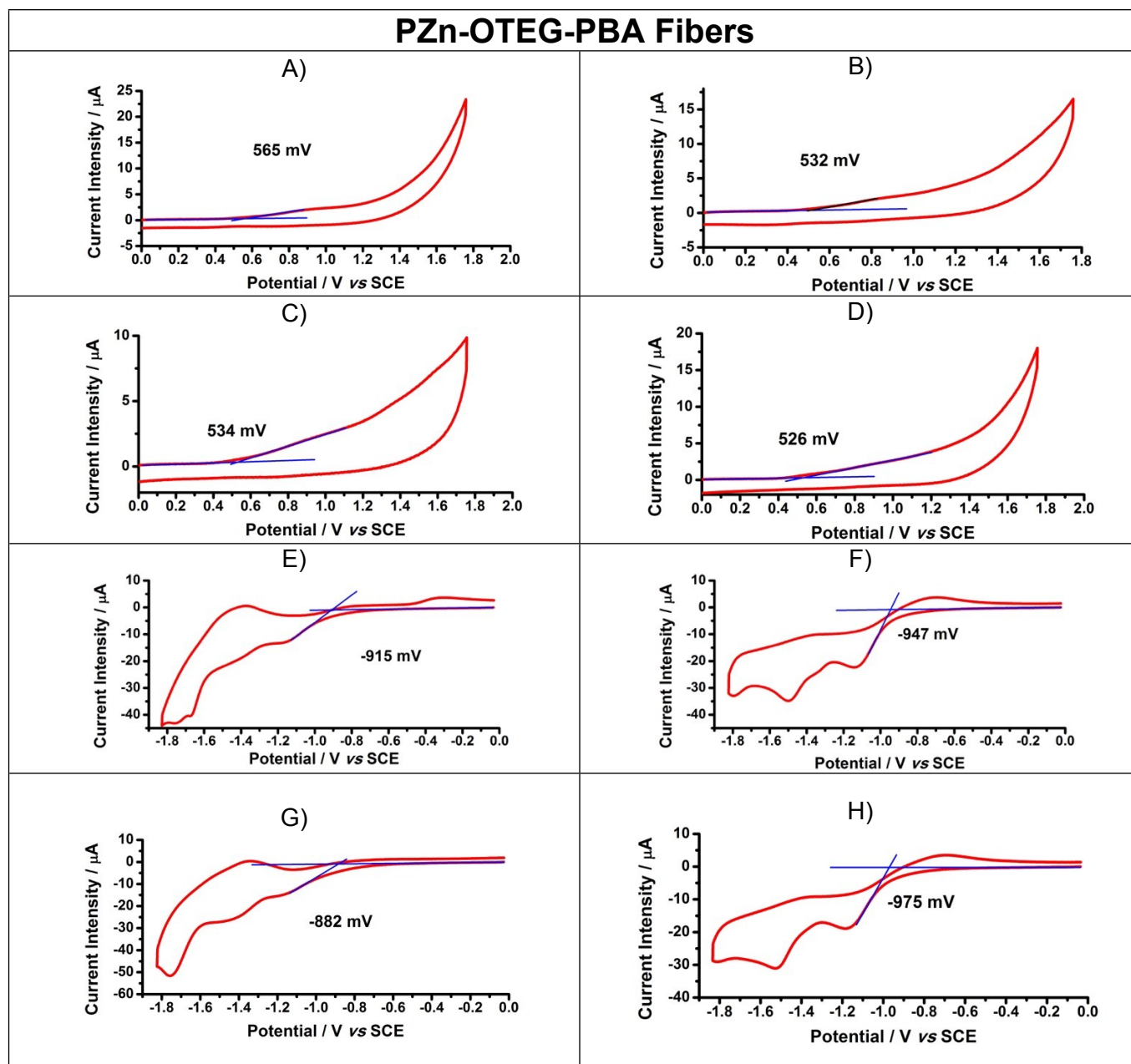


Figure S22: Cyclic voltammetry response of **PZn-OTEG-PBA** fibers recorded in acetonitrile solvent showing the anodic (A-D) and cathodic (E-H) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40 \text{ V vs SCE}$ in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of supramolecular **PZn-OTEG-PBA** polymers drop-casted on the working electrode from parent toluene solution.

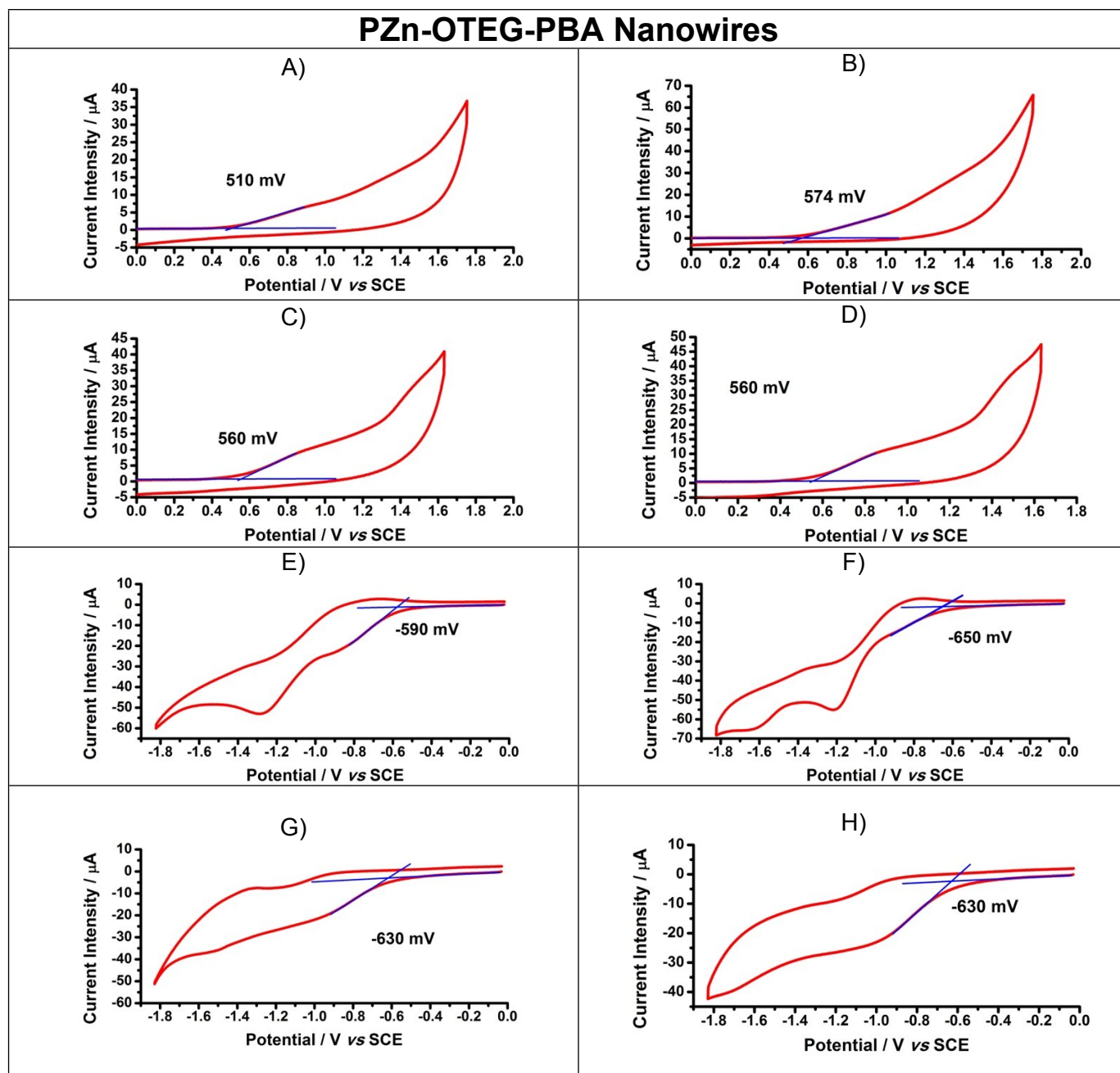


Figure S23: Cyclic voltammetry response of **PZn-OTEG-PBA** nanowires recorded in acetonitrile solvent showing the anodic (A-D) and cathodic (E-H) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40 \text{ V vs SCE}$ in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of individualized **PZn-OTEG-PBA** building blocks drop-casted on the working electrode from a parent DMF solution.

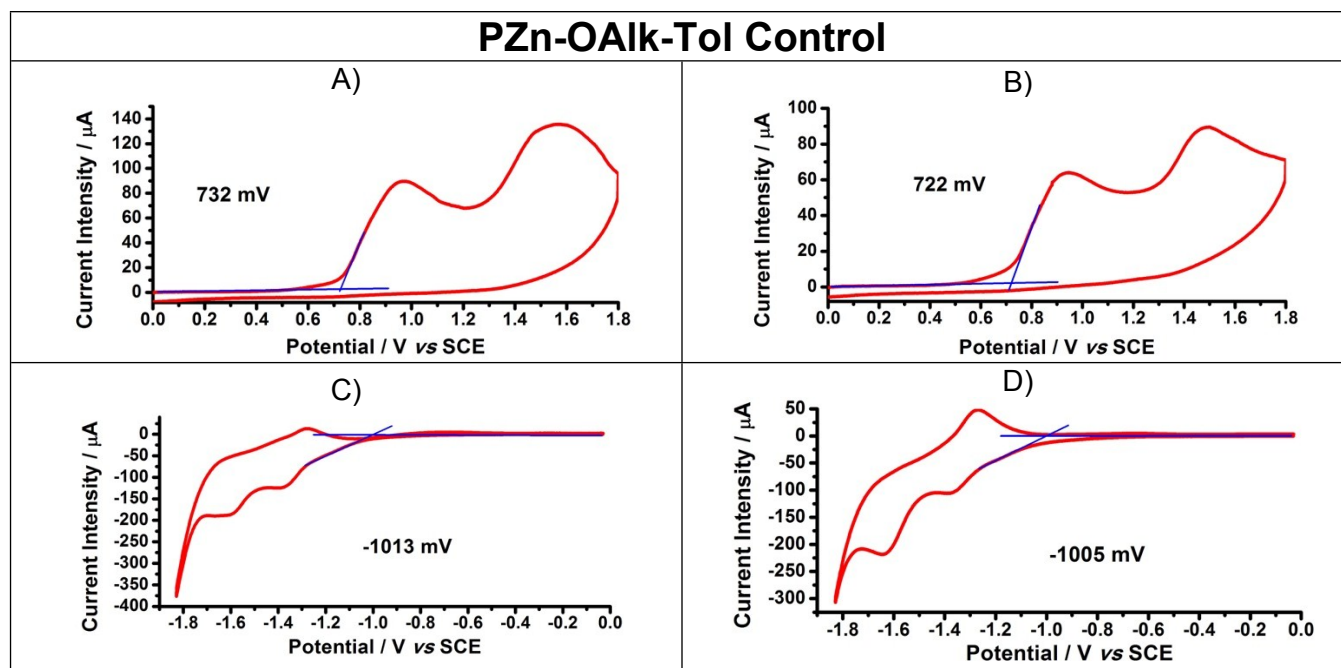


Figure S24: Cyclic voltammetry response of **PZn-OAlk-Tol** aggregates recorded in acetonitrile solvent showing the anodic (A-B) and cathodic (C-D) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40 \text{ V vs SCE}$ in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of individualized **PZn-OAlk-Tol** building blocks drop-casted on the working electrode from a parent DMF solution.

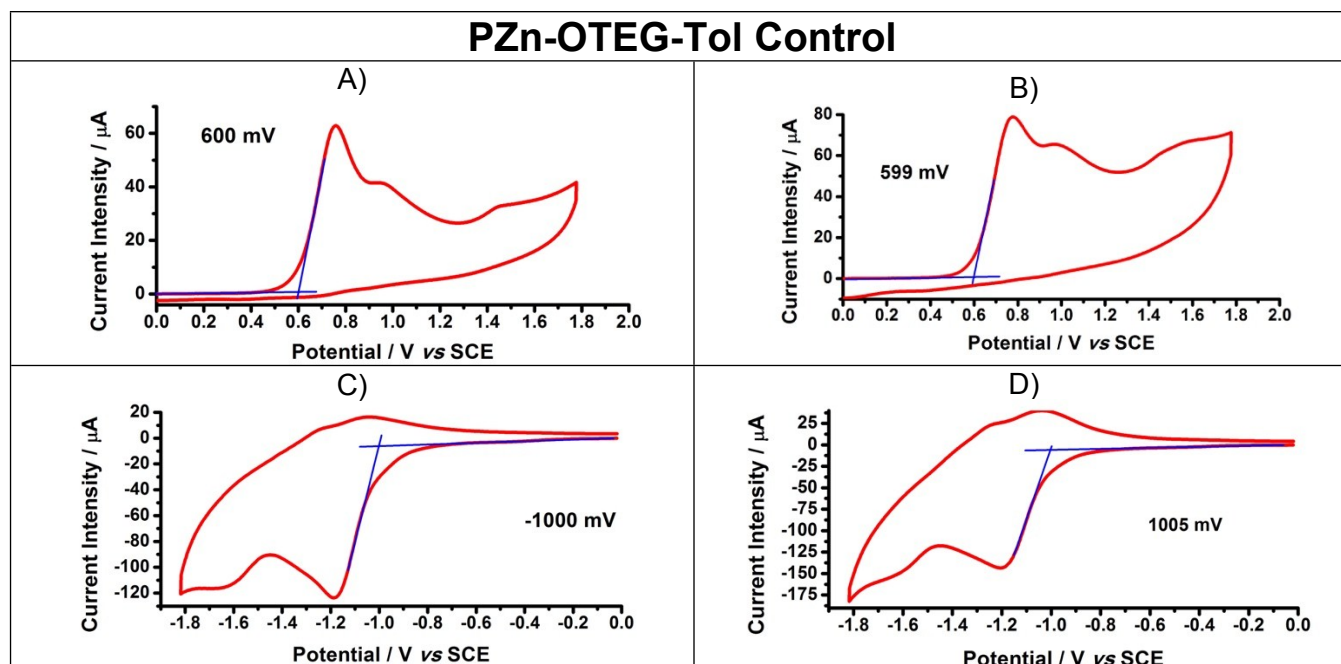


Figure S25: Cyclic voltammetry response of **PZn-OTEG-Tol** aggregates recorded in acetonitrile solvent showing the anodic (A-B) and cathodic (C-D) redox processes. The blue lines correspond to the tangents used to measure the onset potentials. All measurements have been calibrated to SCE standard electrode using Fc/Fc^+ as an internal potentiometric standard $\text{Fc}/\text{Fc}^+ = 0.40 \text{ V vs SCE}$ in acetonitrile. Experimental conditions: 0.1 M TBAP, scan rate = 100 mV s^{-1} , glassy carbon electrode, Ag/AgCl reference electrode. To ensure reproducibility, all the presented measurements have been recorded from different batches of individualized **PZn-OTEG-Tol** building blocks drop-casted on the working electrode from a parent DMF solution.

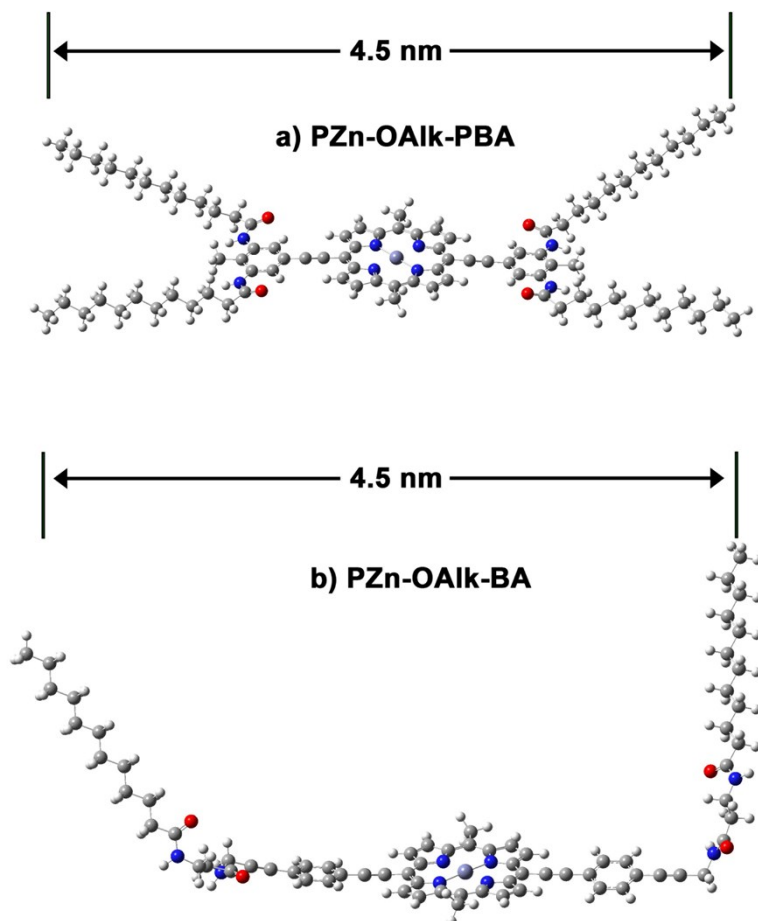


Figure S26: Geometry-optimized **PZn-OAlk-PBA** (A) and **PZn-OAlk-BA** (B) building blocks using density functional theory at the CAM-B3LYP level of theory using cc-pvdz basis set.

6. NMR and MS Spectra

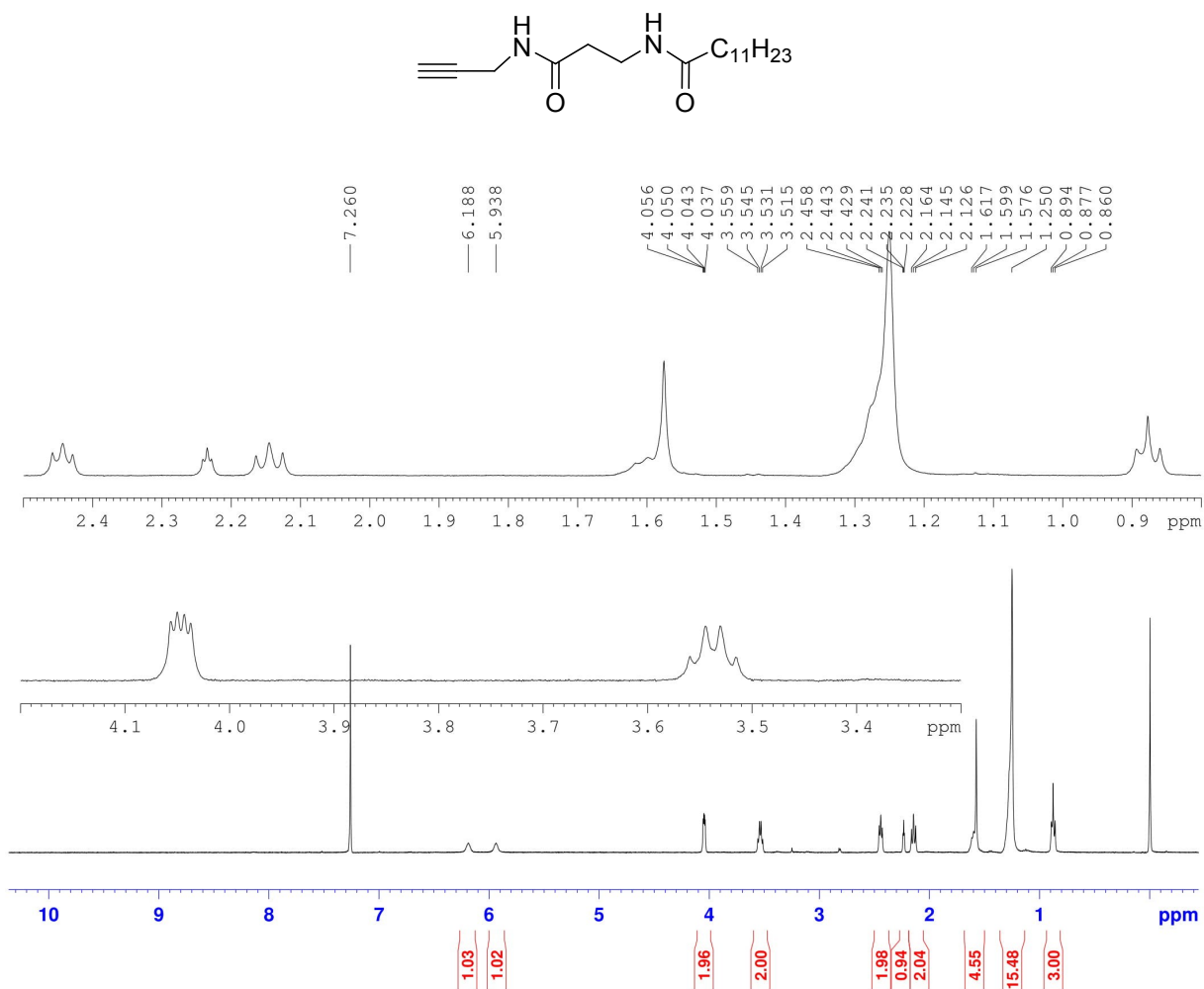


Figure 27: ^1H NMR spectrum (400 MHz, CDCl_3) of Compound 4.

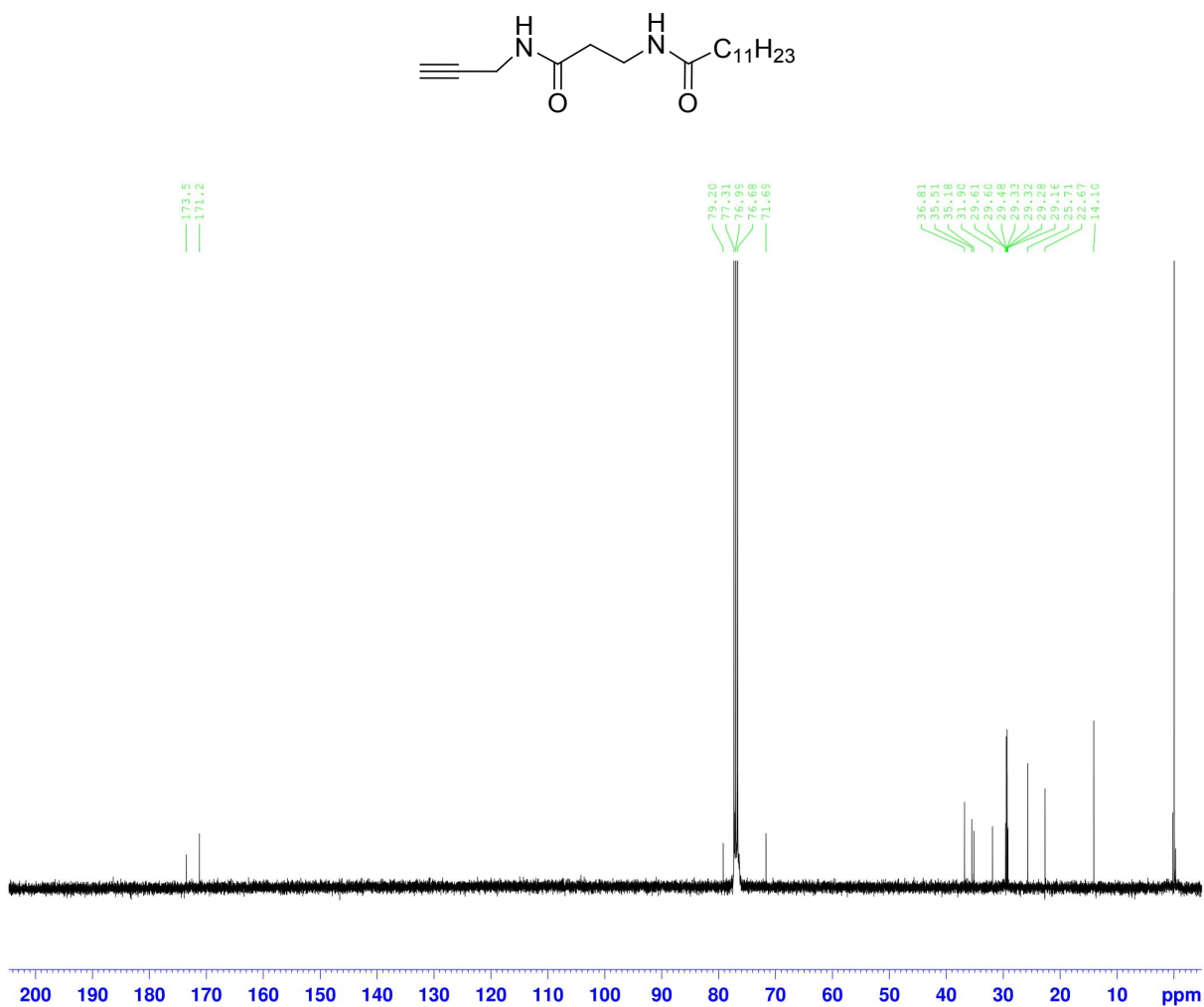


Figure S28: ¹³C NMR spectrum (101 MHz, CDCl₃) of Compound 4.

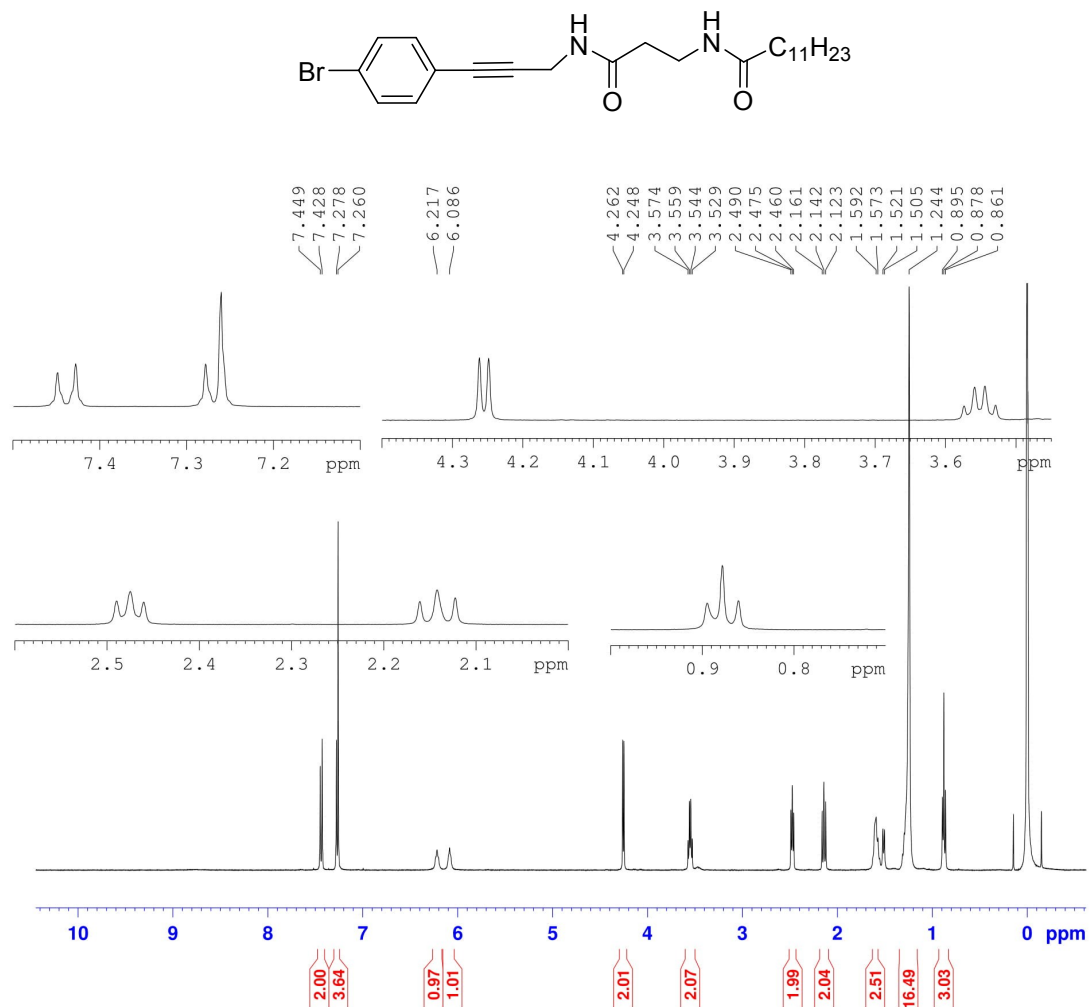


Figure S29: ¹H NMR spectrum (400 MHz, CDCl₃) of Compound 5.

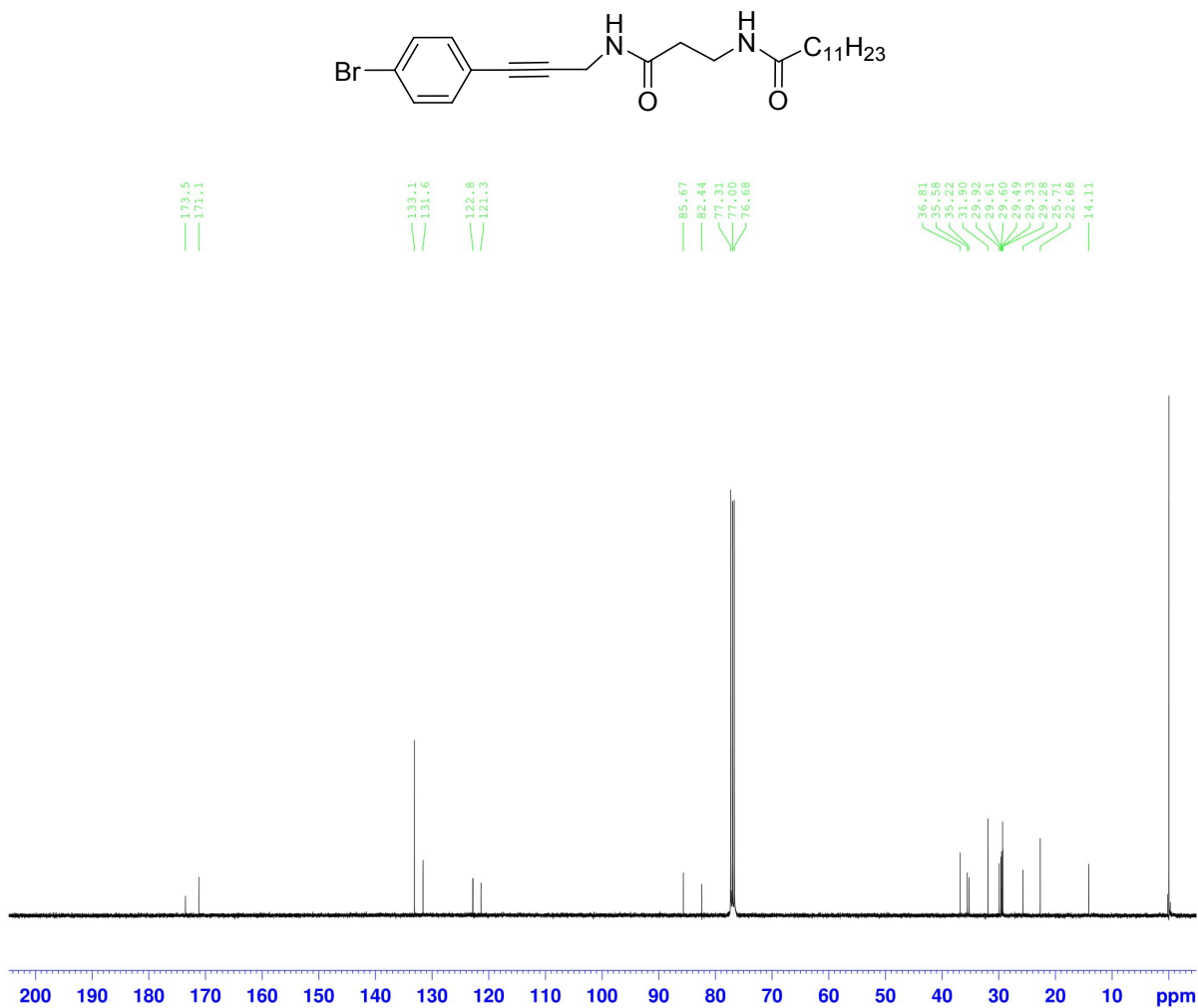


Figure S30: ¹³C NMR spectrum (101 MHz, CDCl₃) of Compound 5.

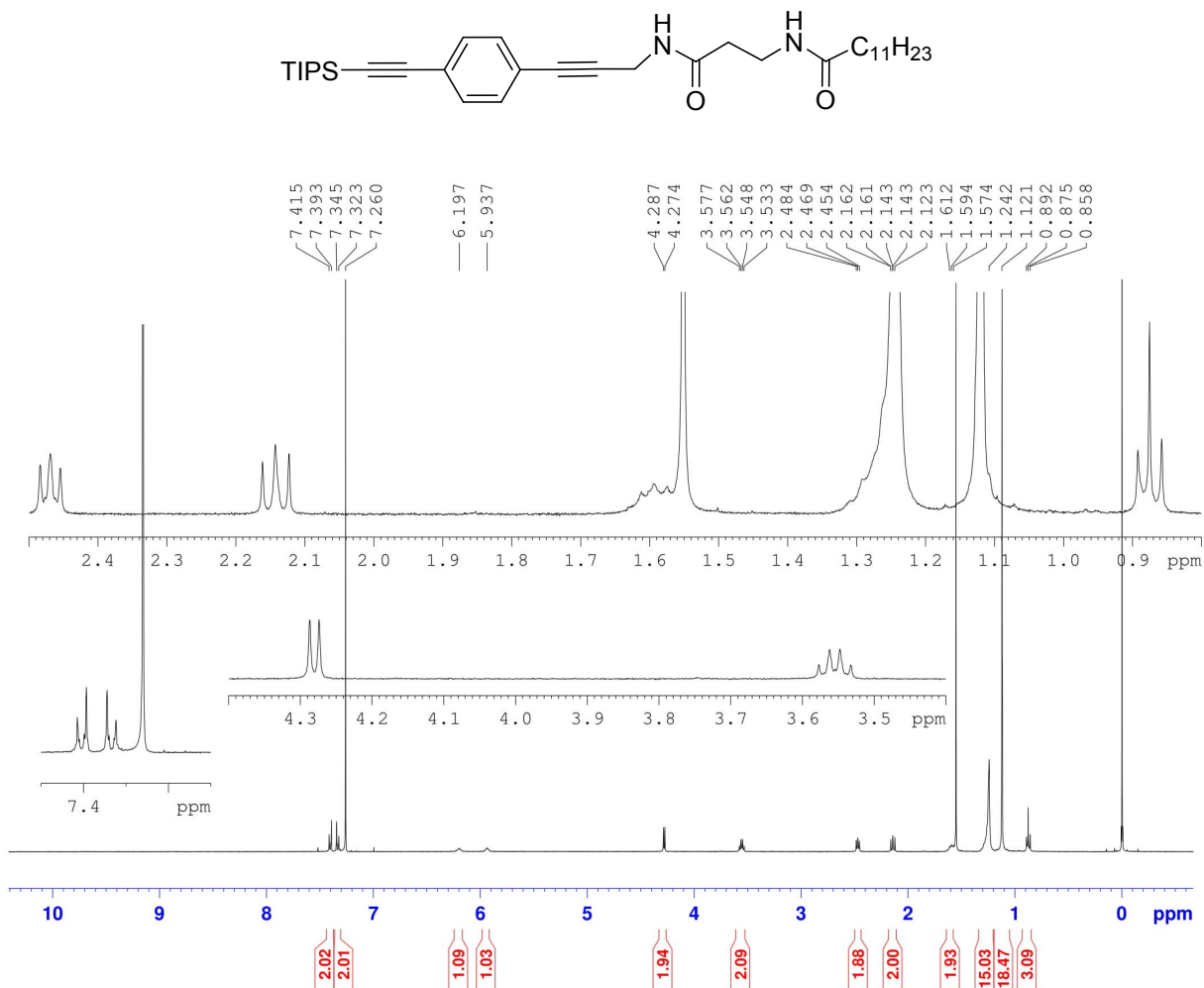


Figure S31: ^1H NMR spectrum (400 MHz, CDCl_3) of Compound **6**.

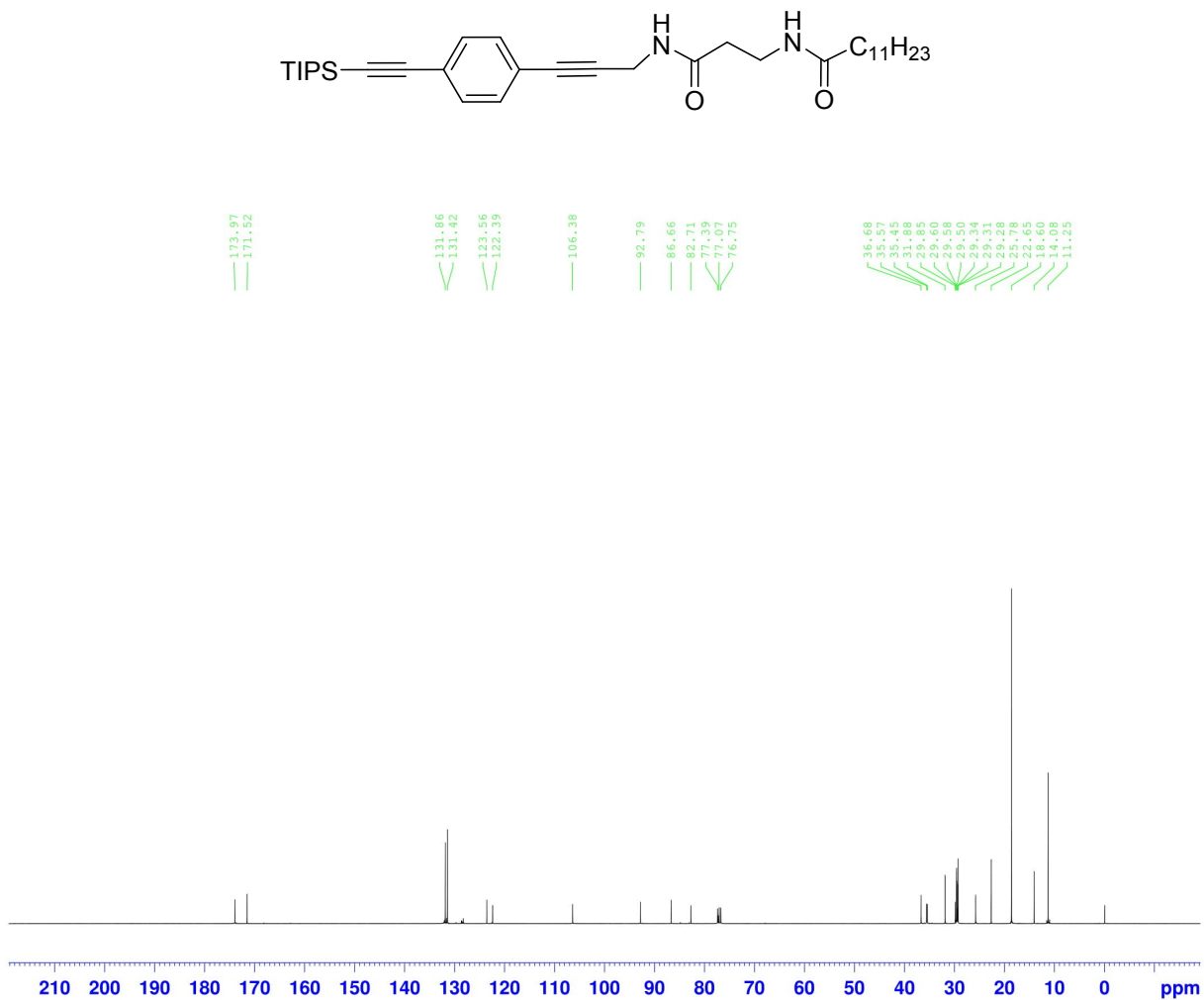


Figure S32: ¹³C NMR spectrum (101 MHz, CDCl₃) of Compound 6.

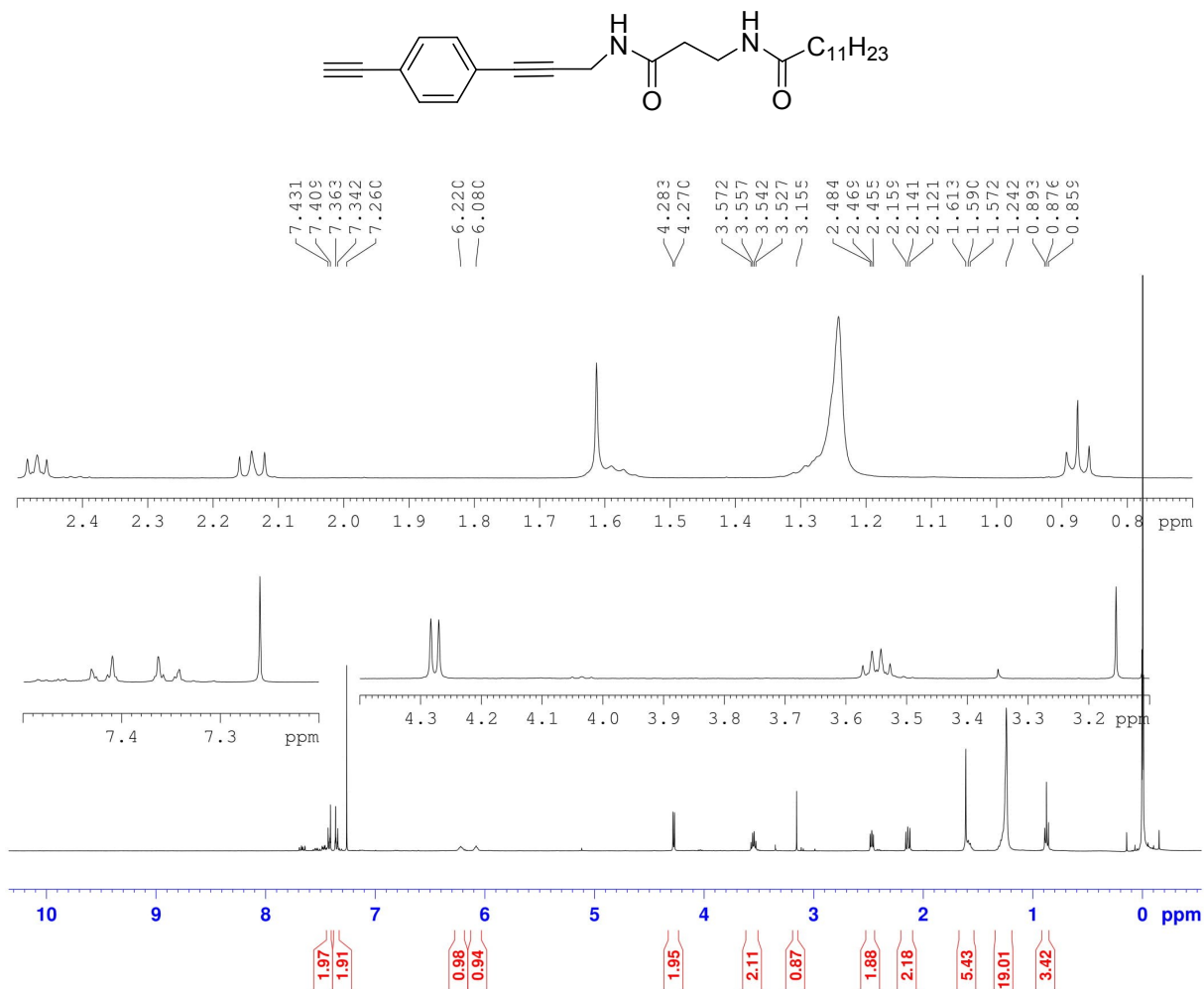


Figure S33: ¹H NMR spectrum (400 MHz, CDCl₃) of Compound 7.

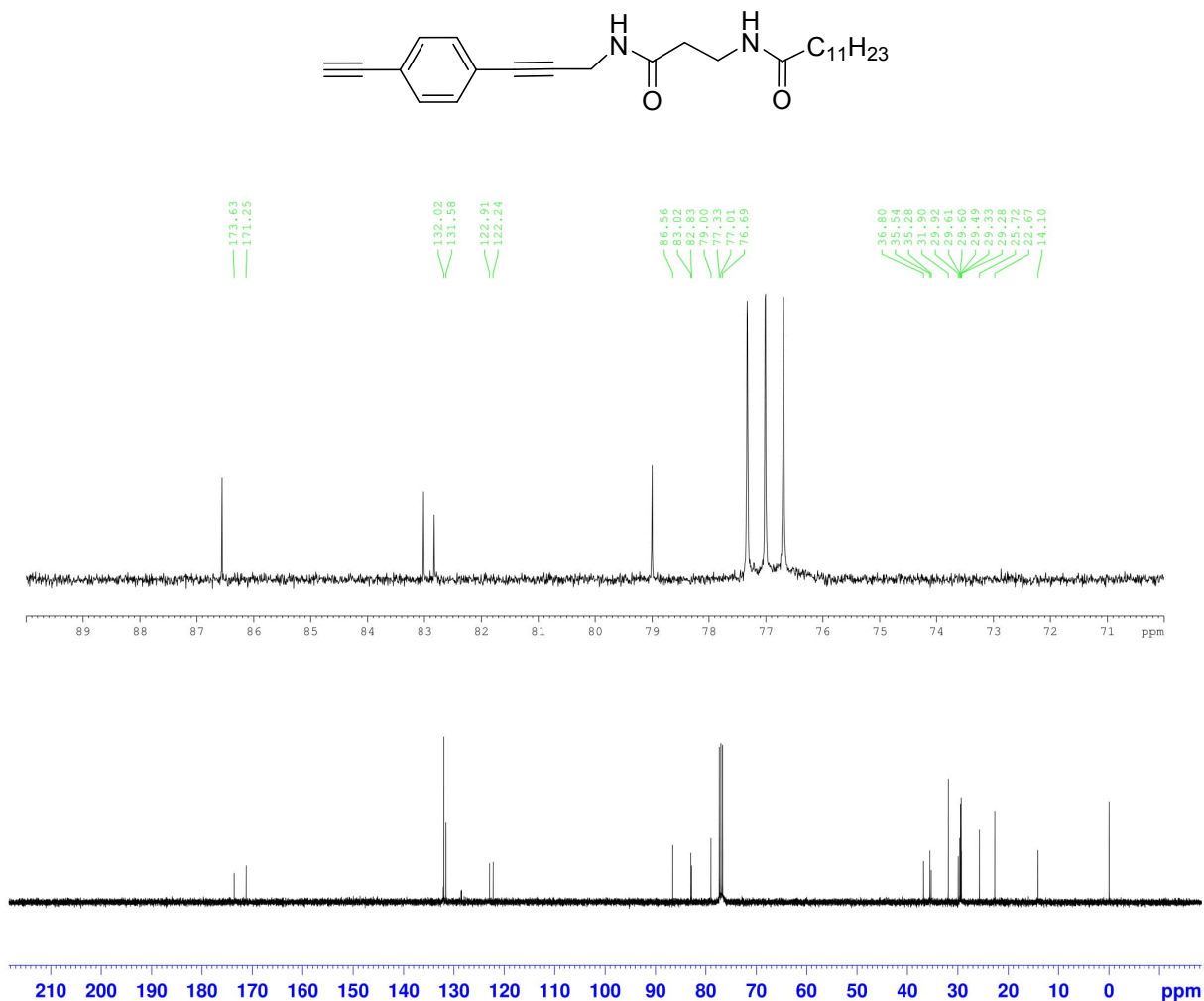


Figure S34: ¹³C NMR spectrum (101 MHz, CDCl₃) of Compound 7.

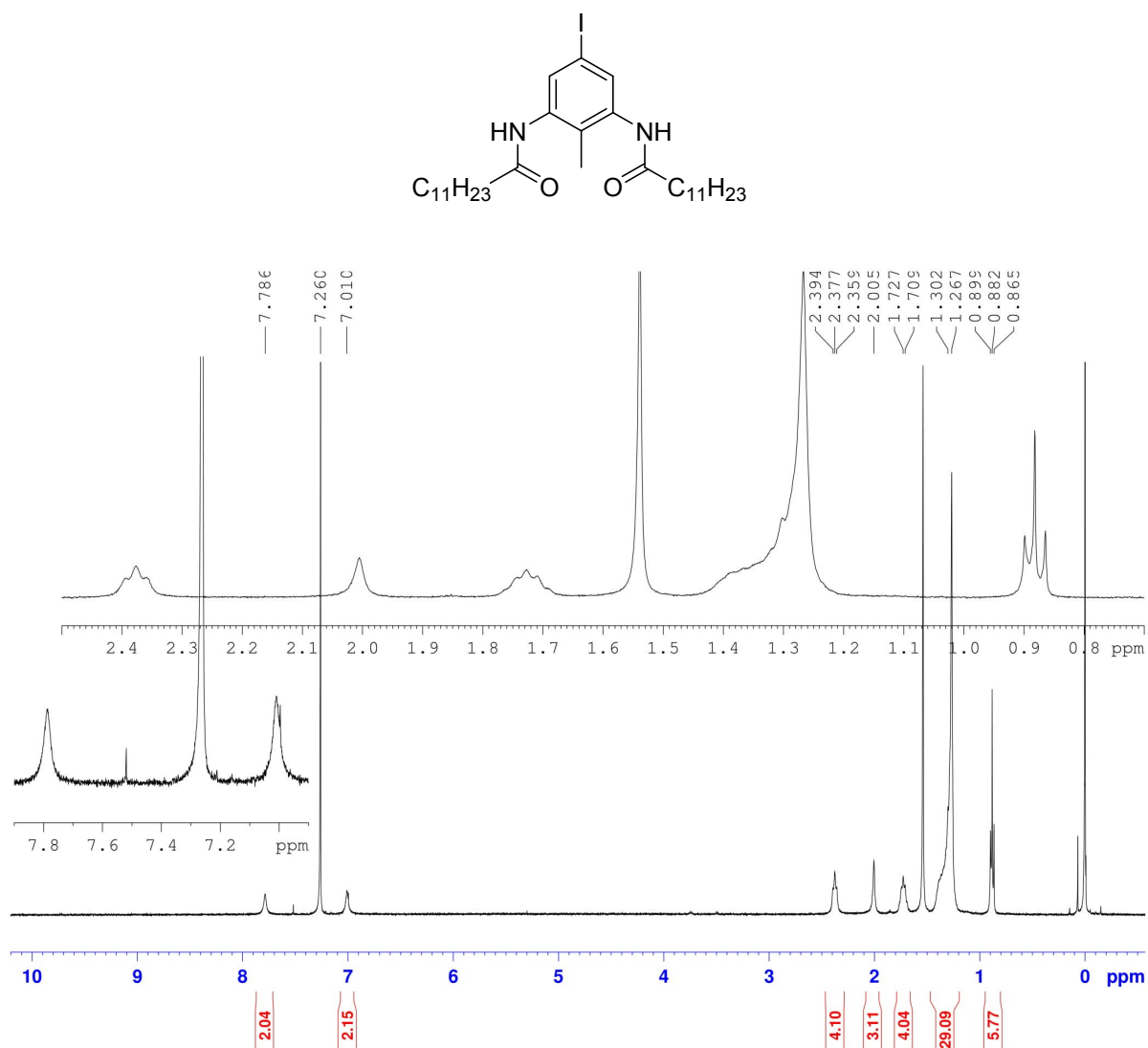


Figure S35: ¹H NMR spectrum (400 MHz, CDCl₃, 333 K) of Compound **10**.

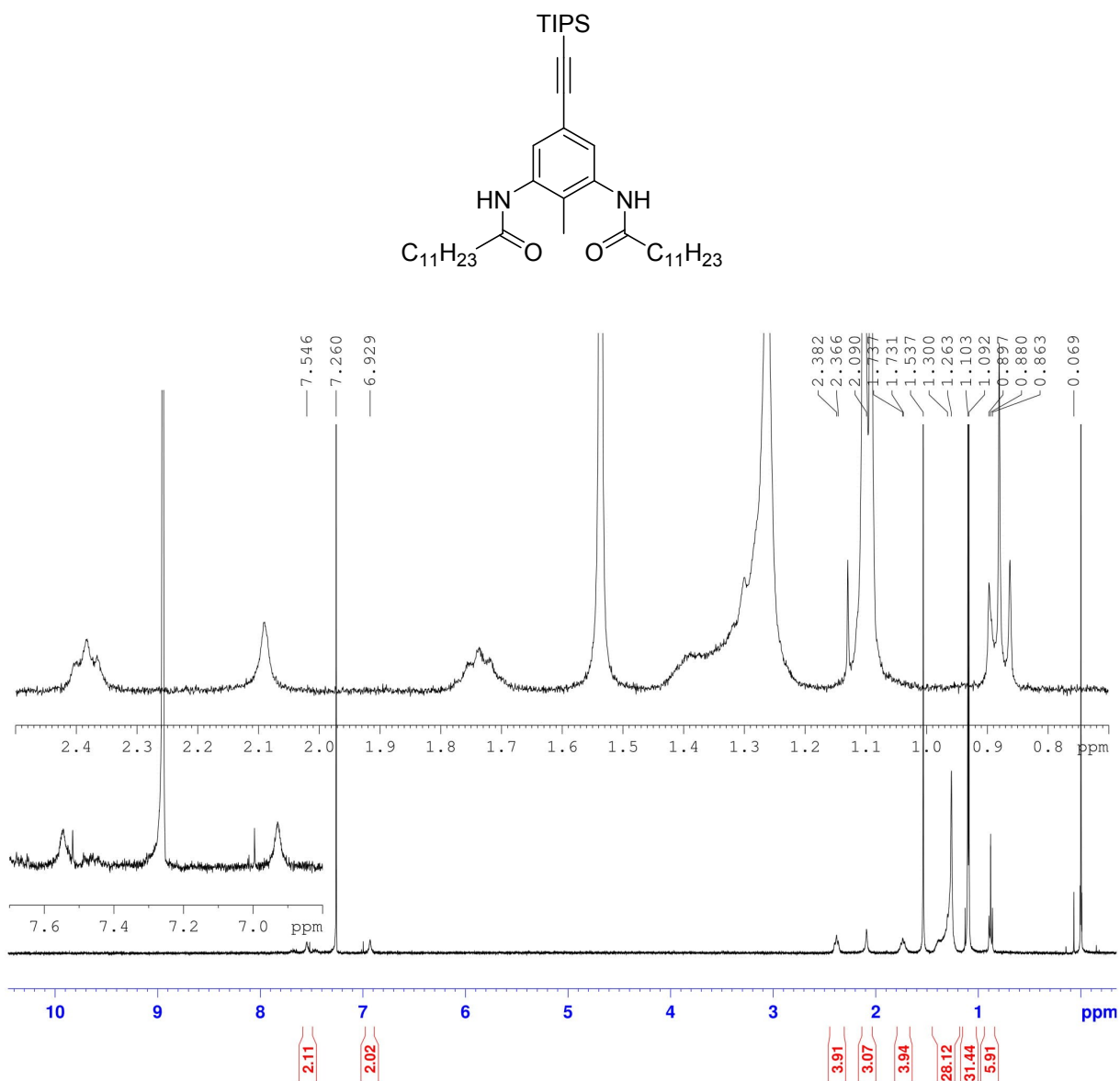


Figure S36: ^1H NMR spectrum (400 MHz, CDCl_3) of Compound **10**.

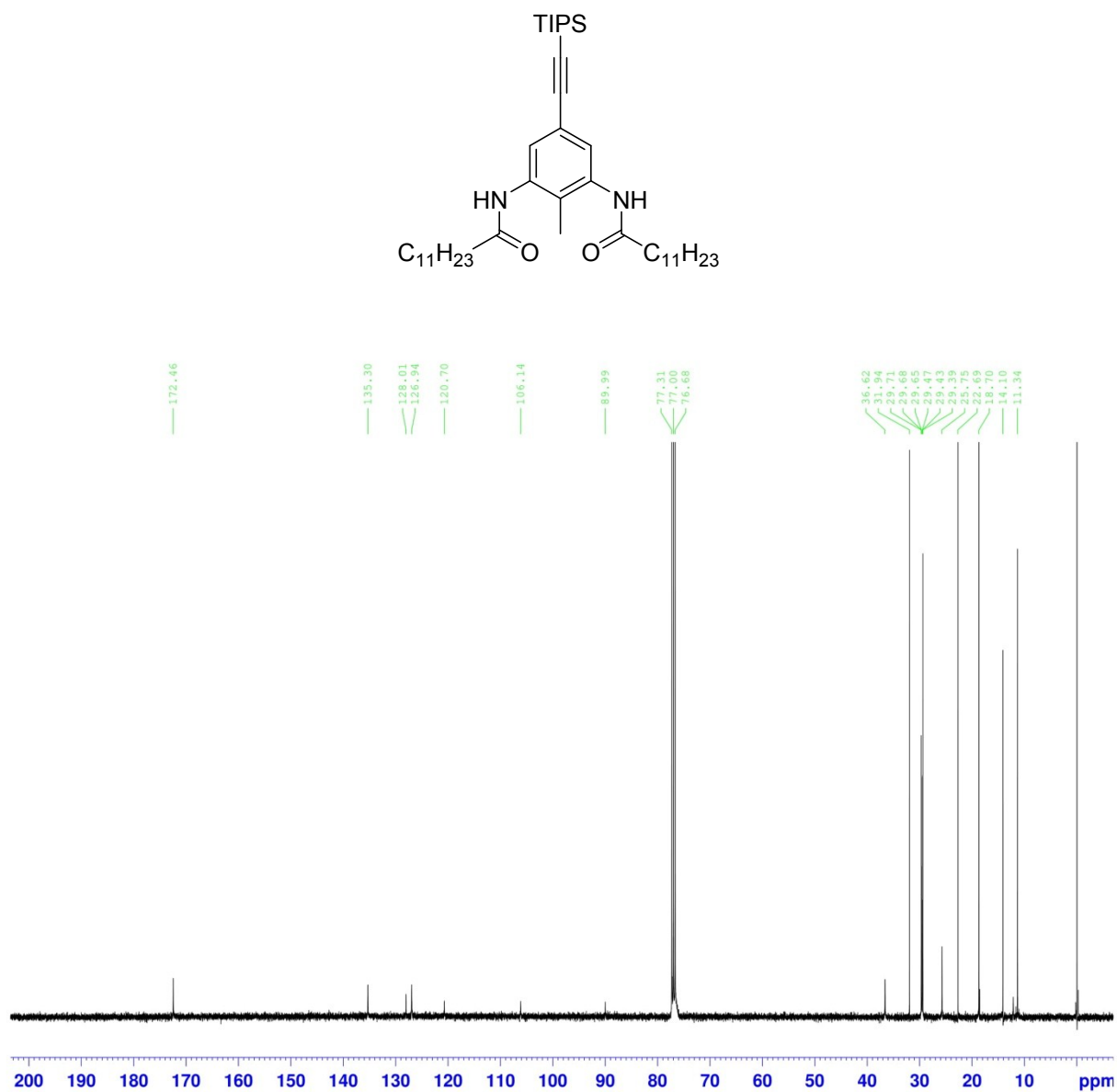


Figure S37: ¹³C NMR spectrum (101 MHz, CDCl₃) of Compound 11.

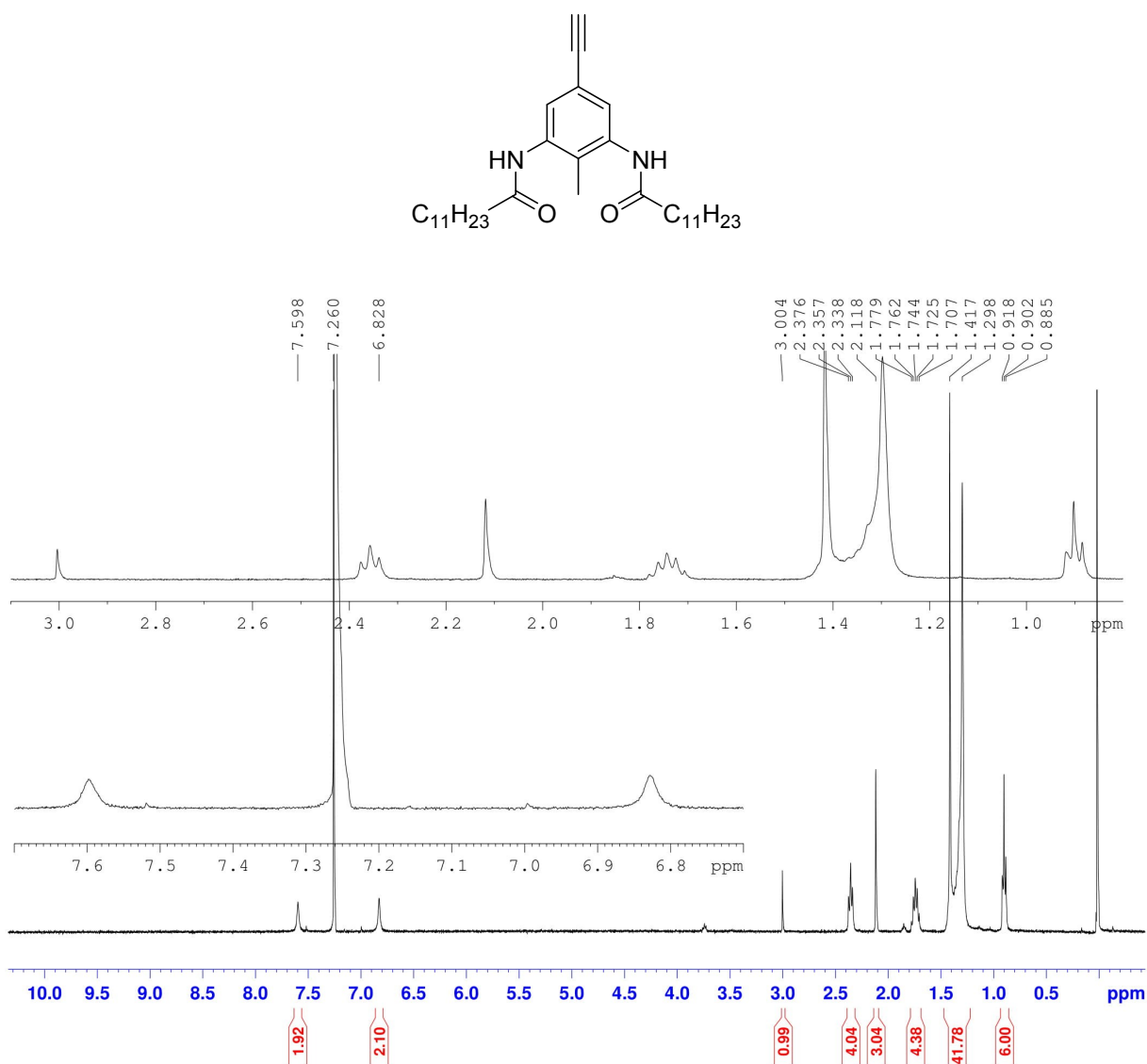


Figure S38: ¹H NMR spectrum (400 MHz, CDCl₃, 333 K) of Compound 12.

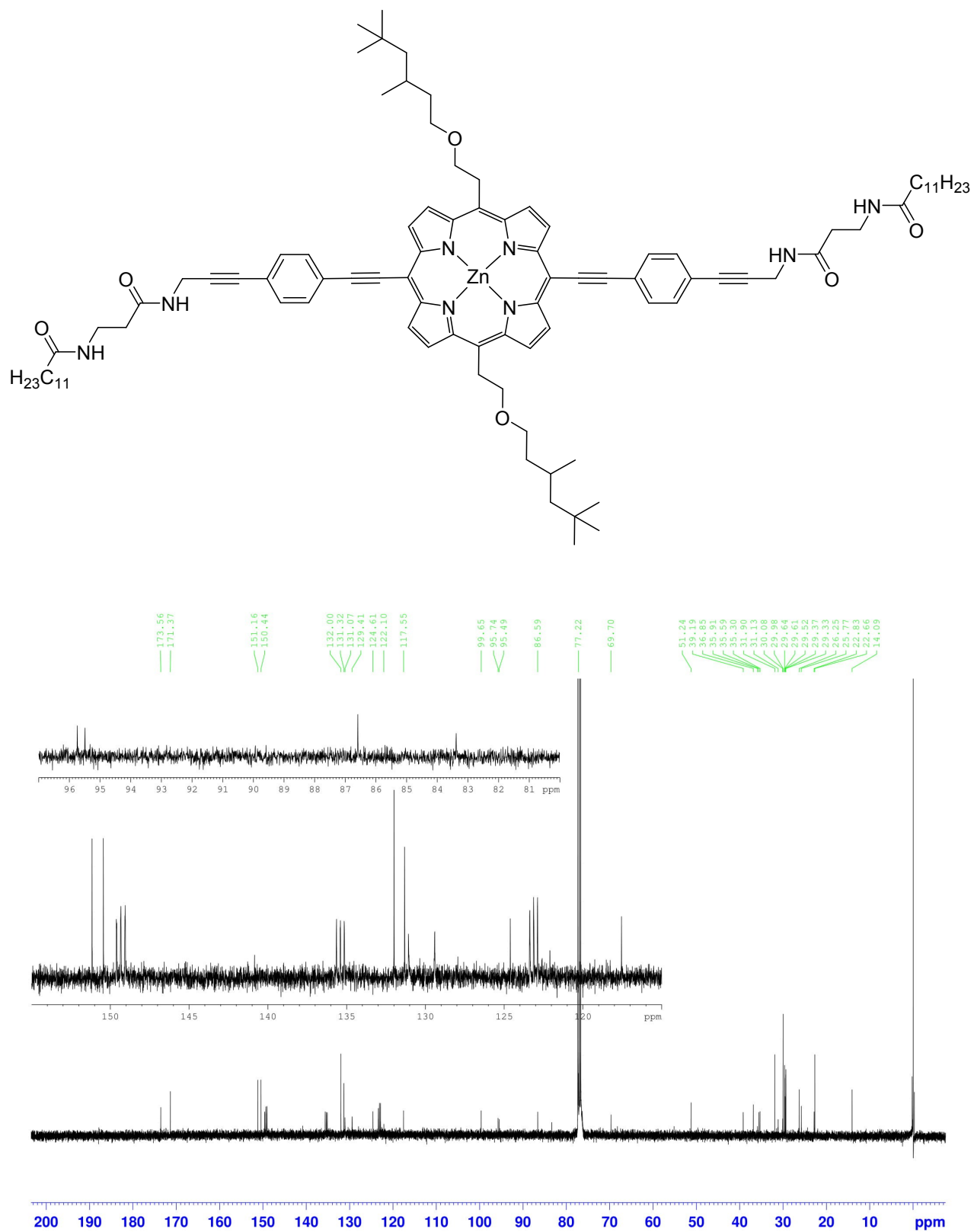


Figure S40: ^{13}C NMR spectrum (101 MHz, CDCl_3) of PZn-OAlk-BA.

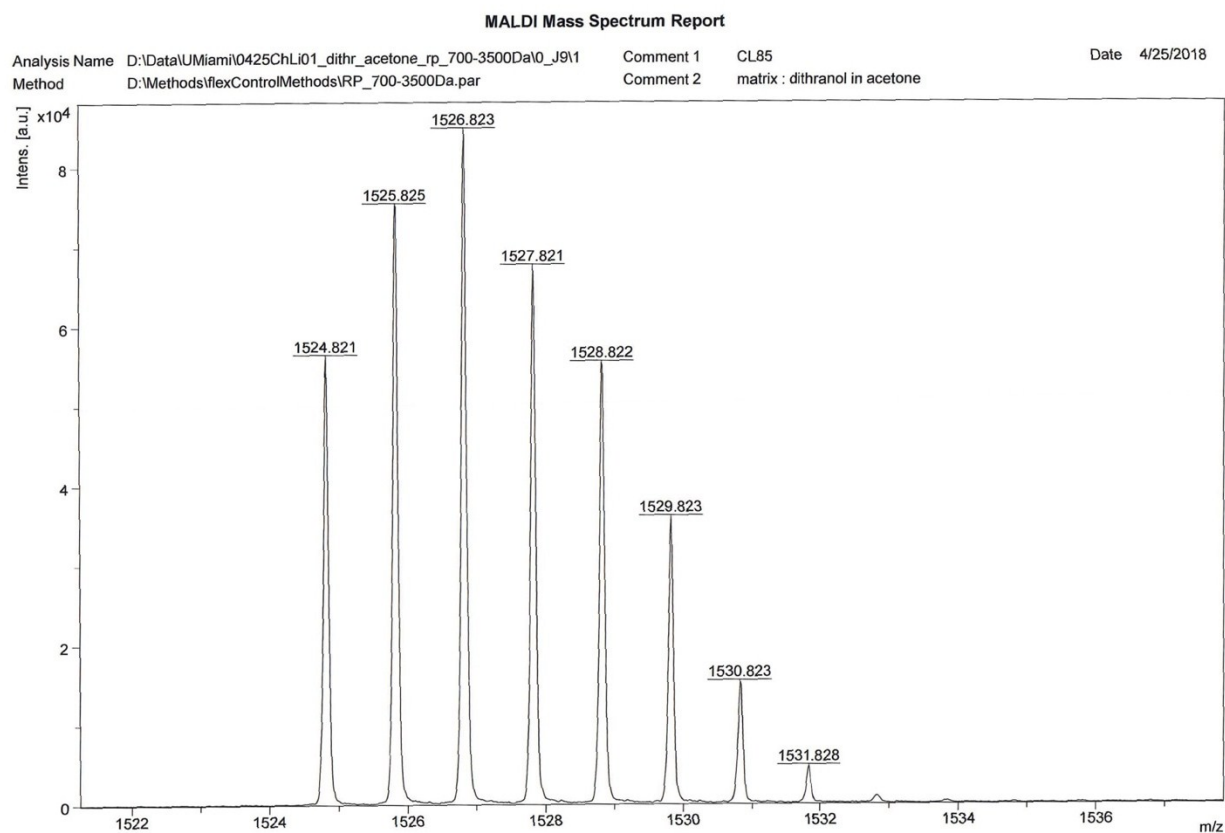


Figure S41: High-resolution mass spectrum (MALDI) of **PZn-OAlk-BA**.

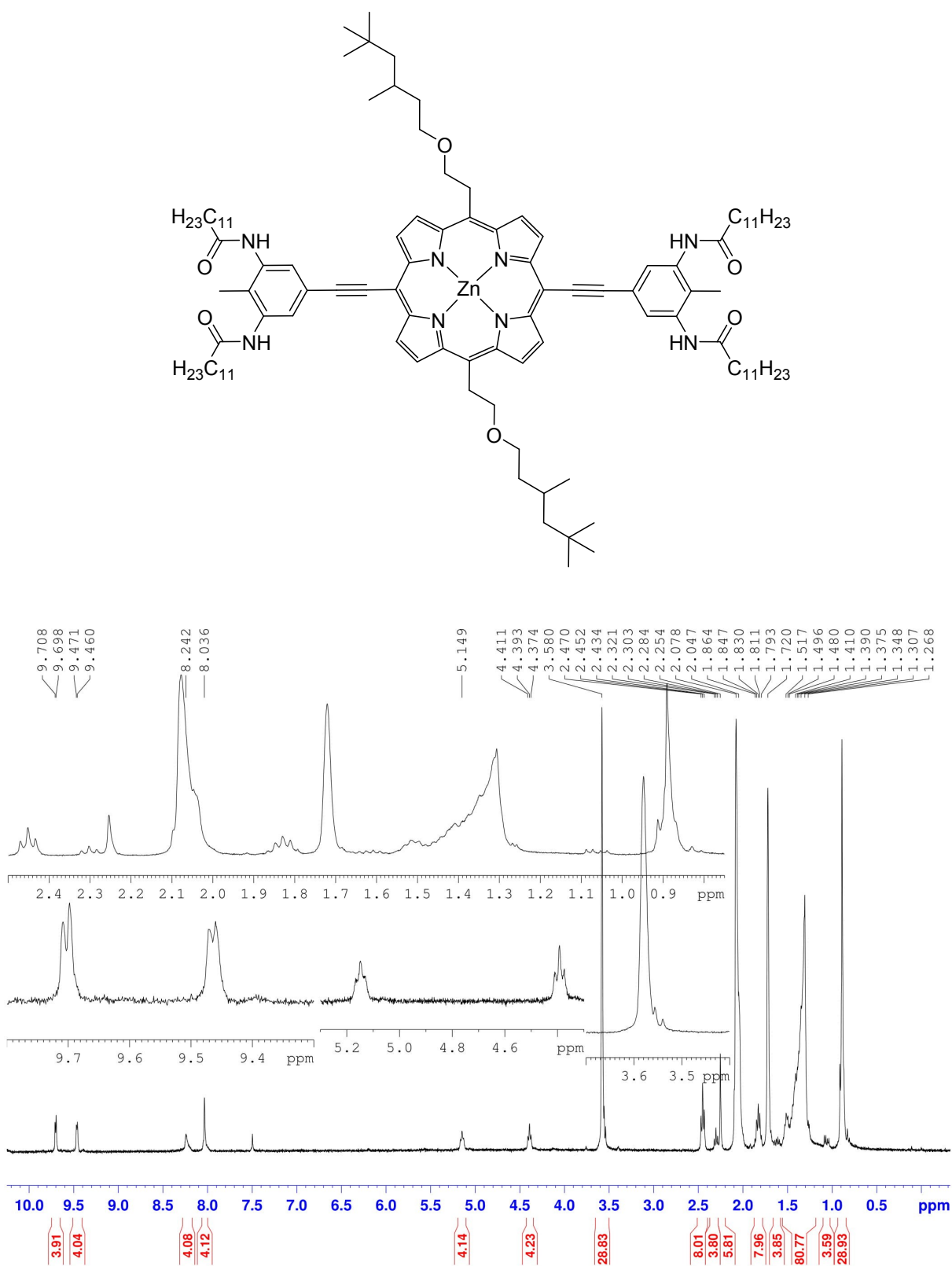


Figure S42: ^1H NMR spectrum (400 MHz, THF-D8, 333 K) of PZn-OAlk-PBA.

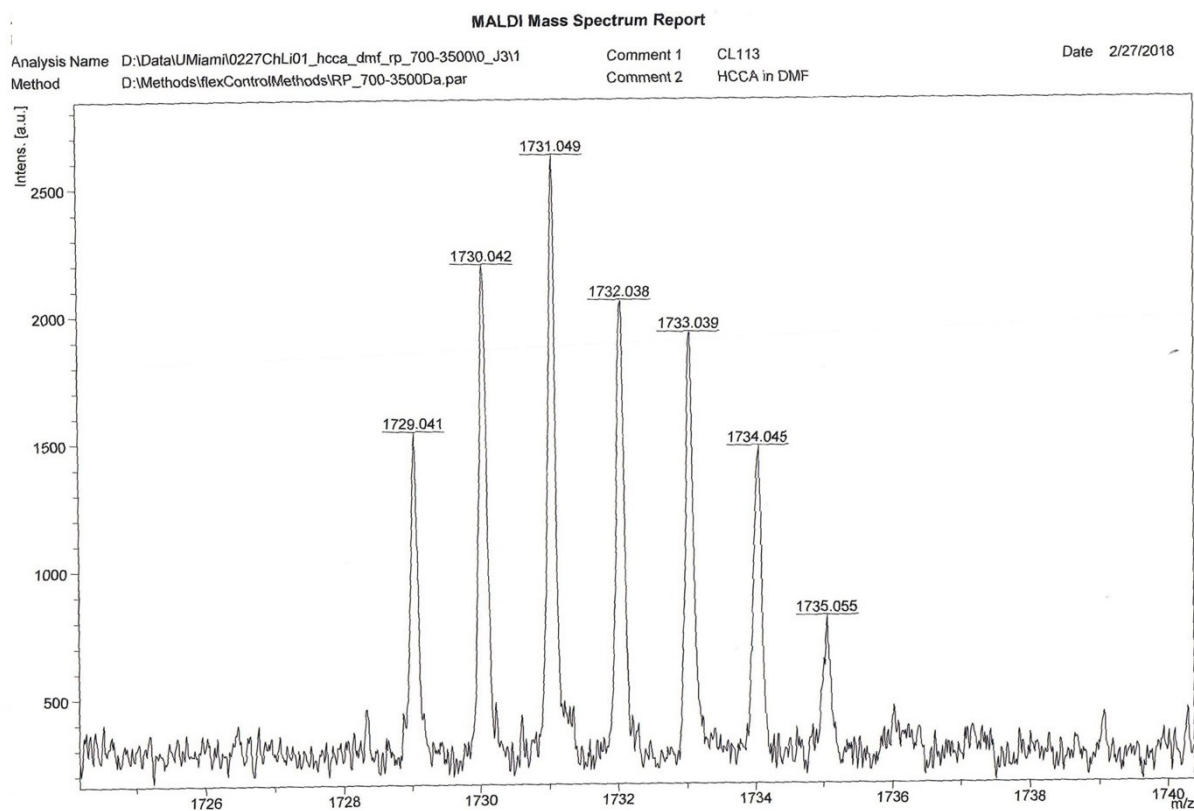


Figure S43: High-resolution mass spectrum (MALDI) of **PZn-OAlk-PBA**.

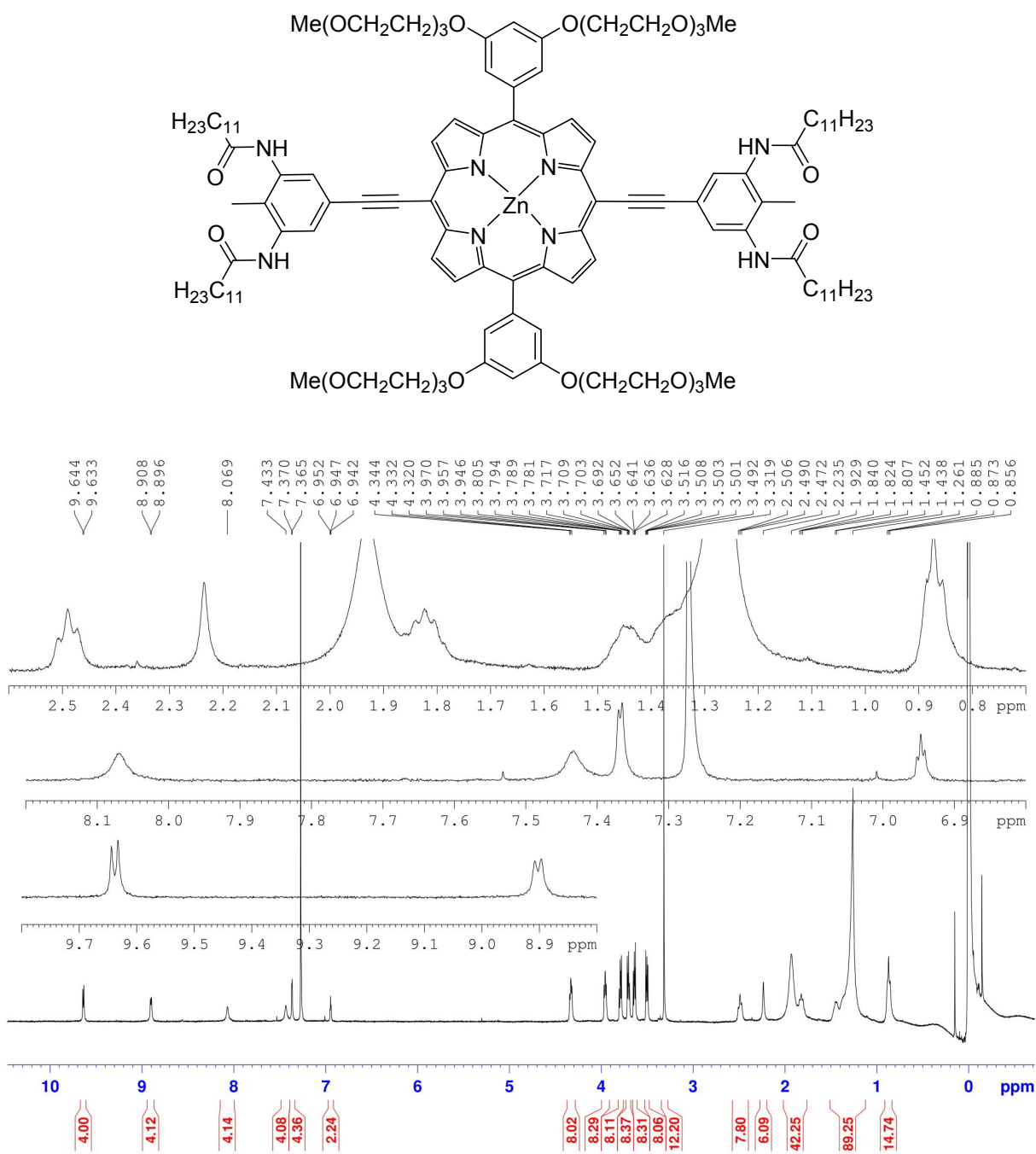


Figure S44: ^1H NMR spectrum (400 MHz, CDCl_3) of **PZn-OTEG-PBA**.

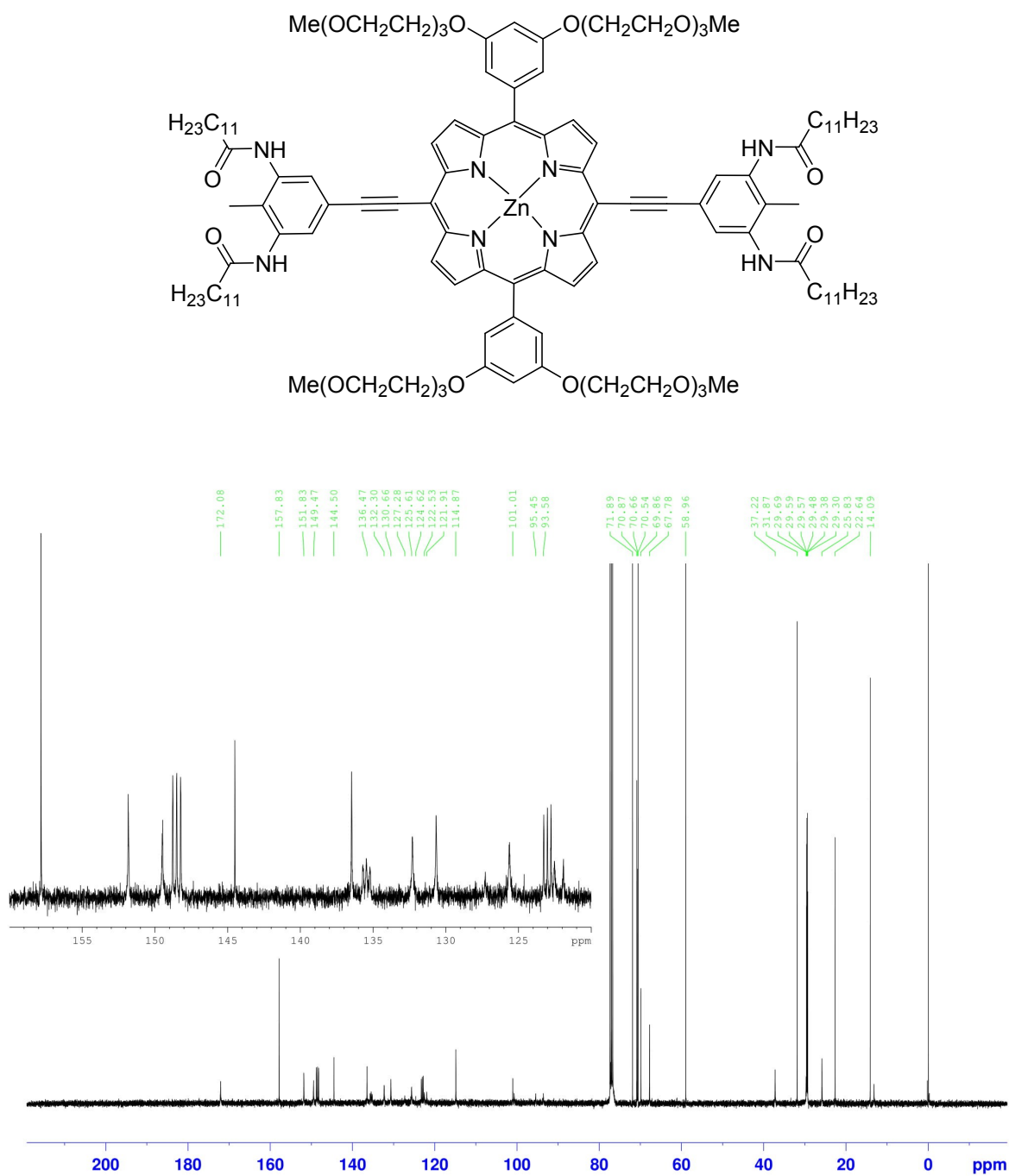


Figure S45: ^{13}C NMR spectrum (101 MHz, CDCl_3) of PZn-OTEG-PBA.

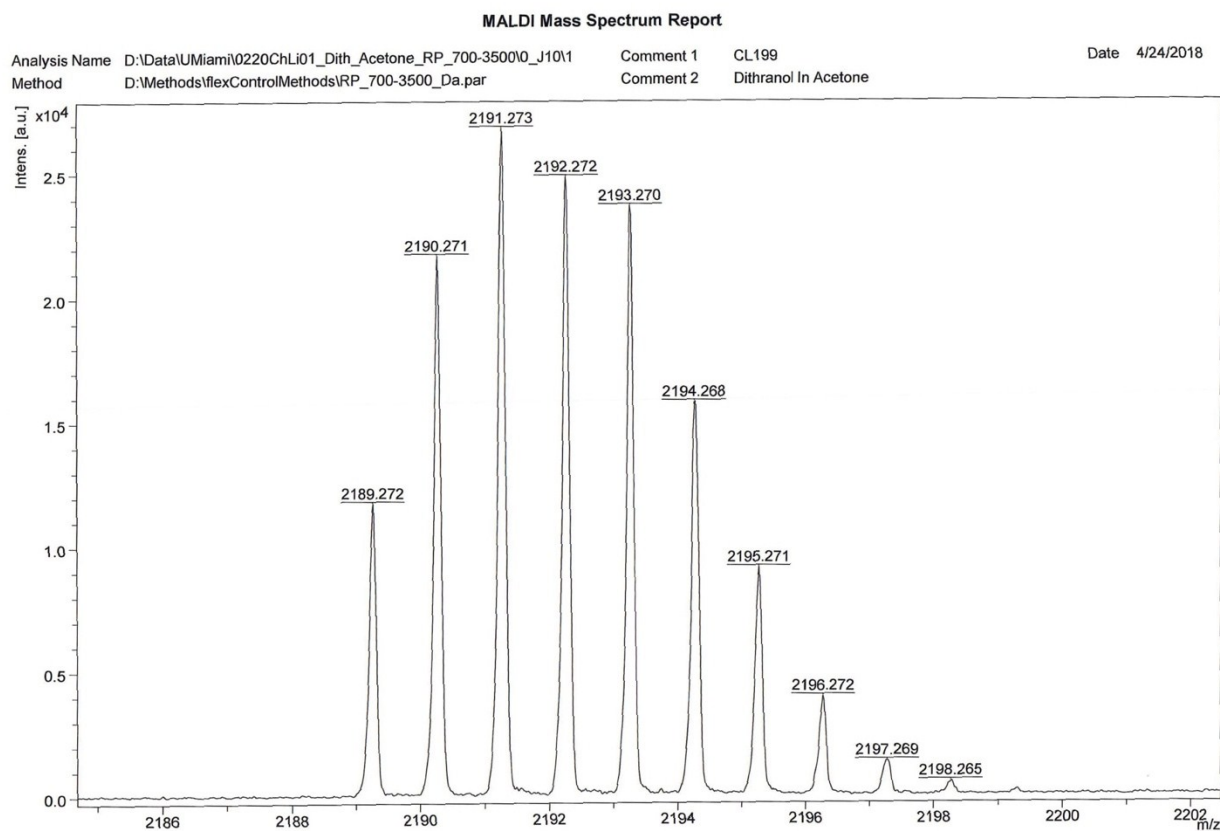


Figure S46: High-resolution mass spectrum (MALDI) of **PZn-OTEG-PBA**.

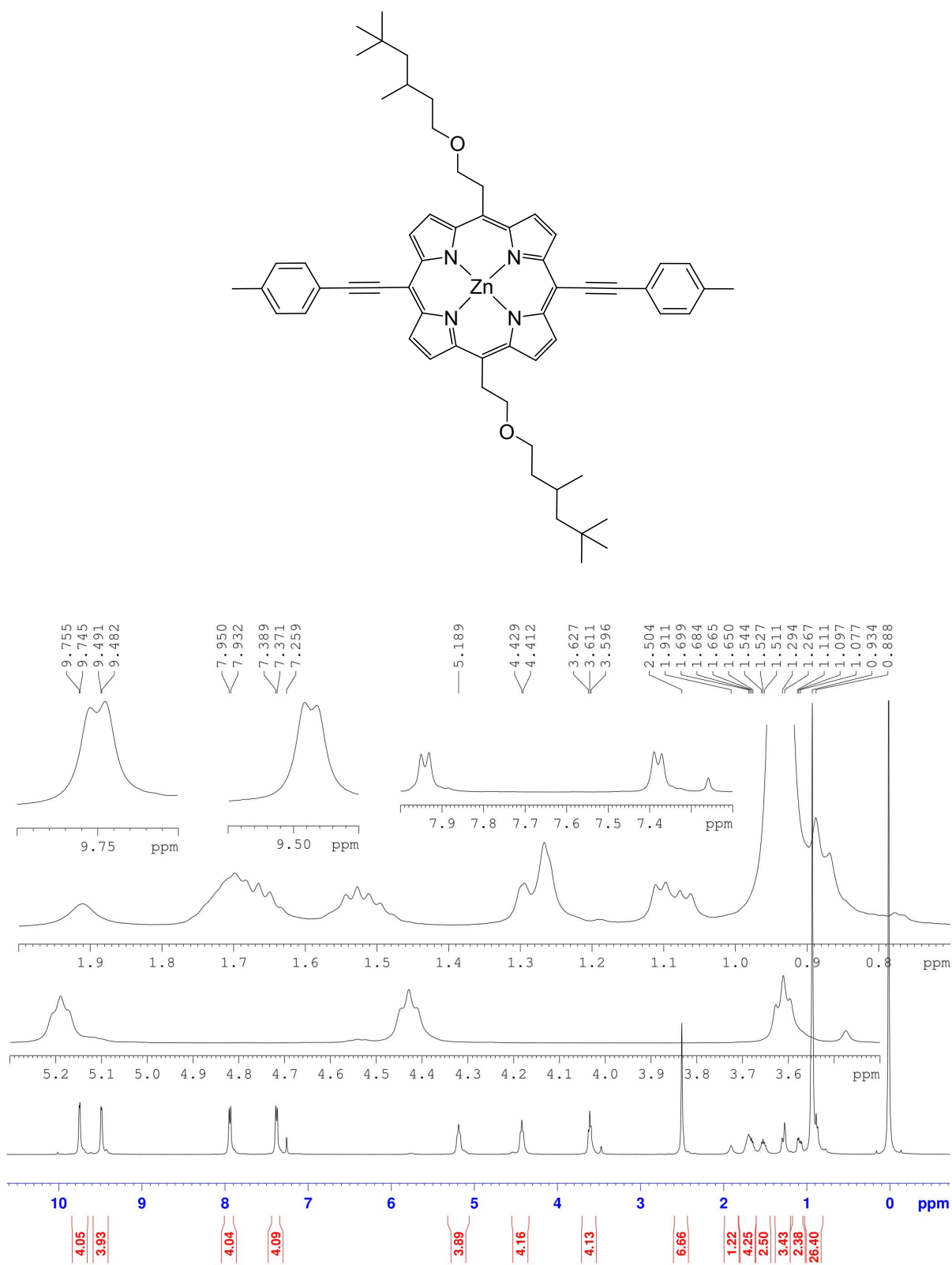


Figure S47: ^1H NMR spectrum (400 MHz, CDCl_3) of **PZn-OAlk-Tol**.

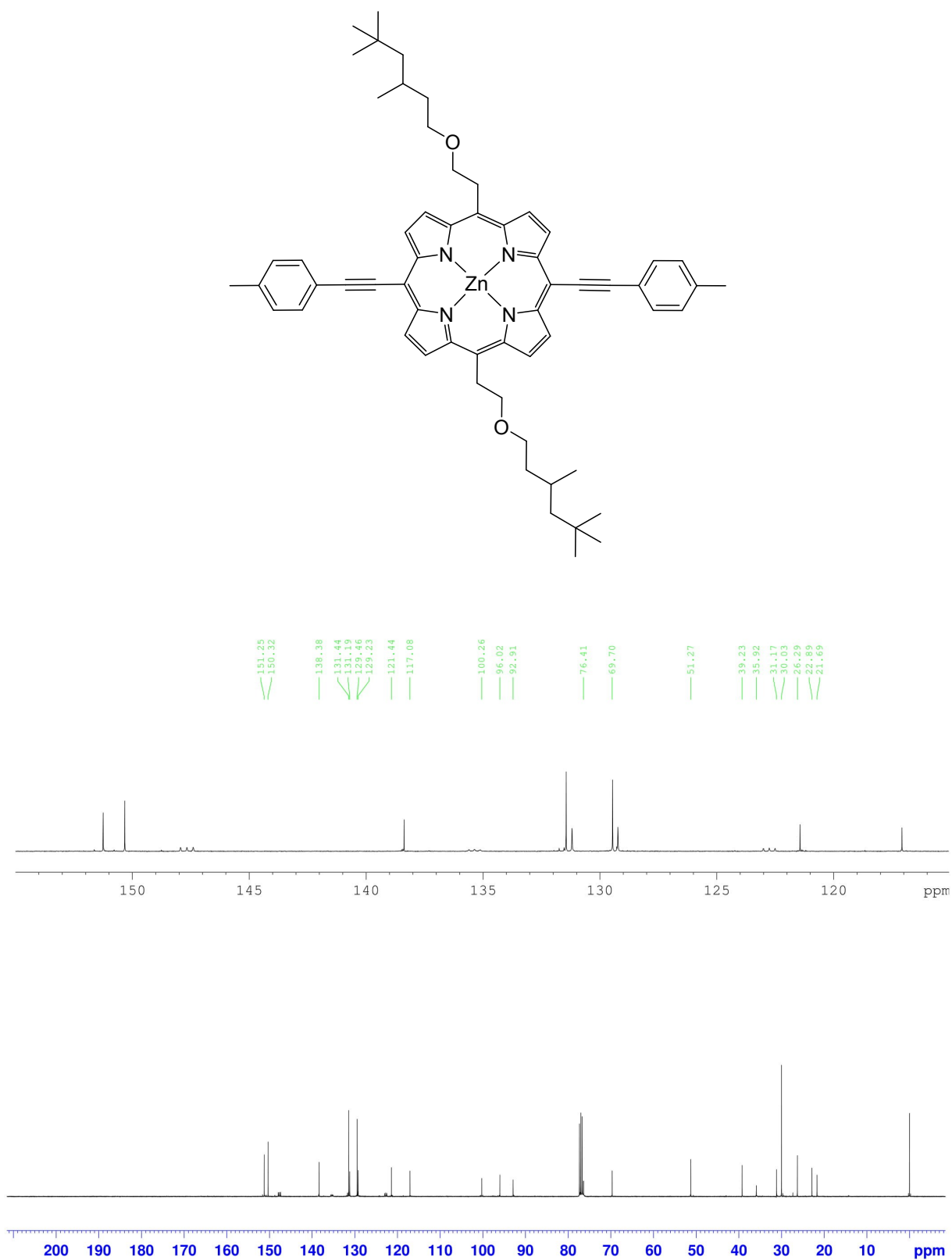


Figure S48: ^{13}C NMR spectrum (101 MHz, CDCl_3) of PZn-OAlk-Tol.

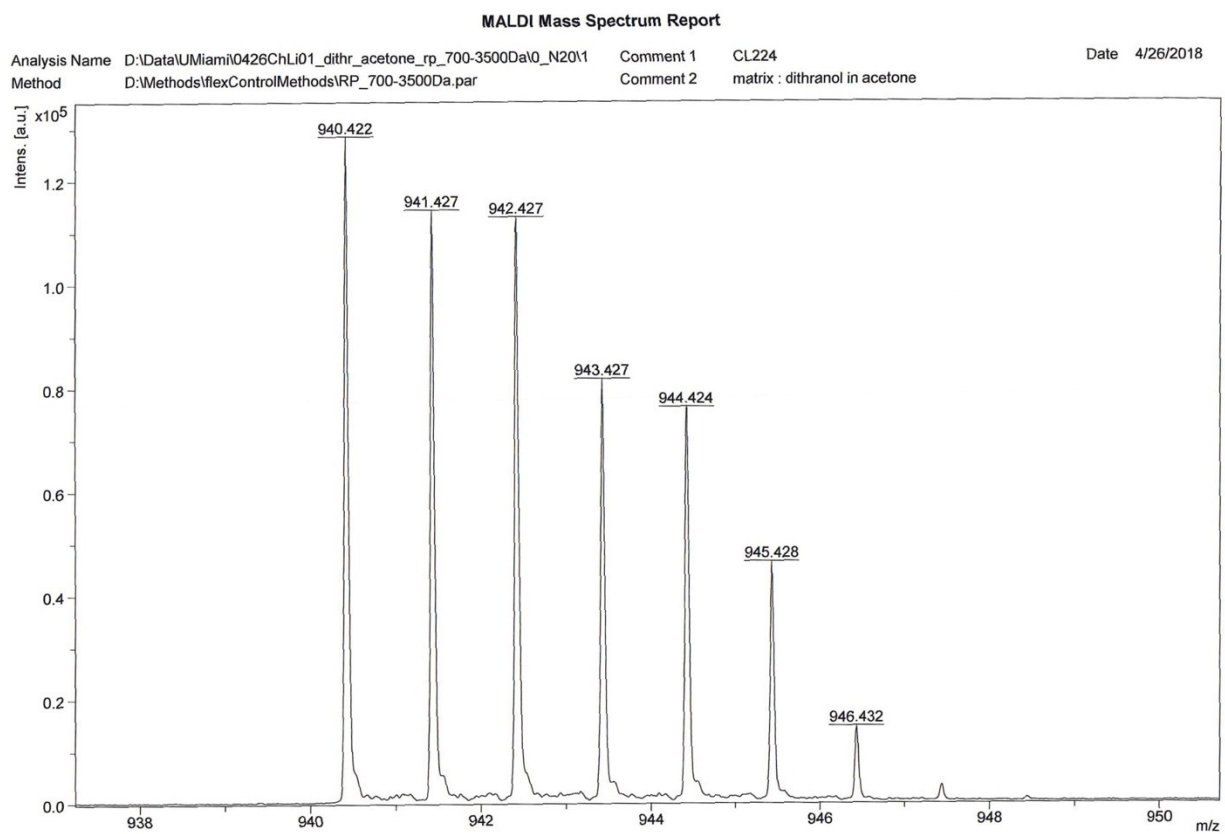


Figure S49: High-resolution mass spectrum (MALDI) of **PZn-OAlk-Tol**.

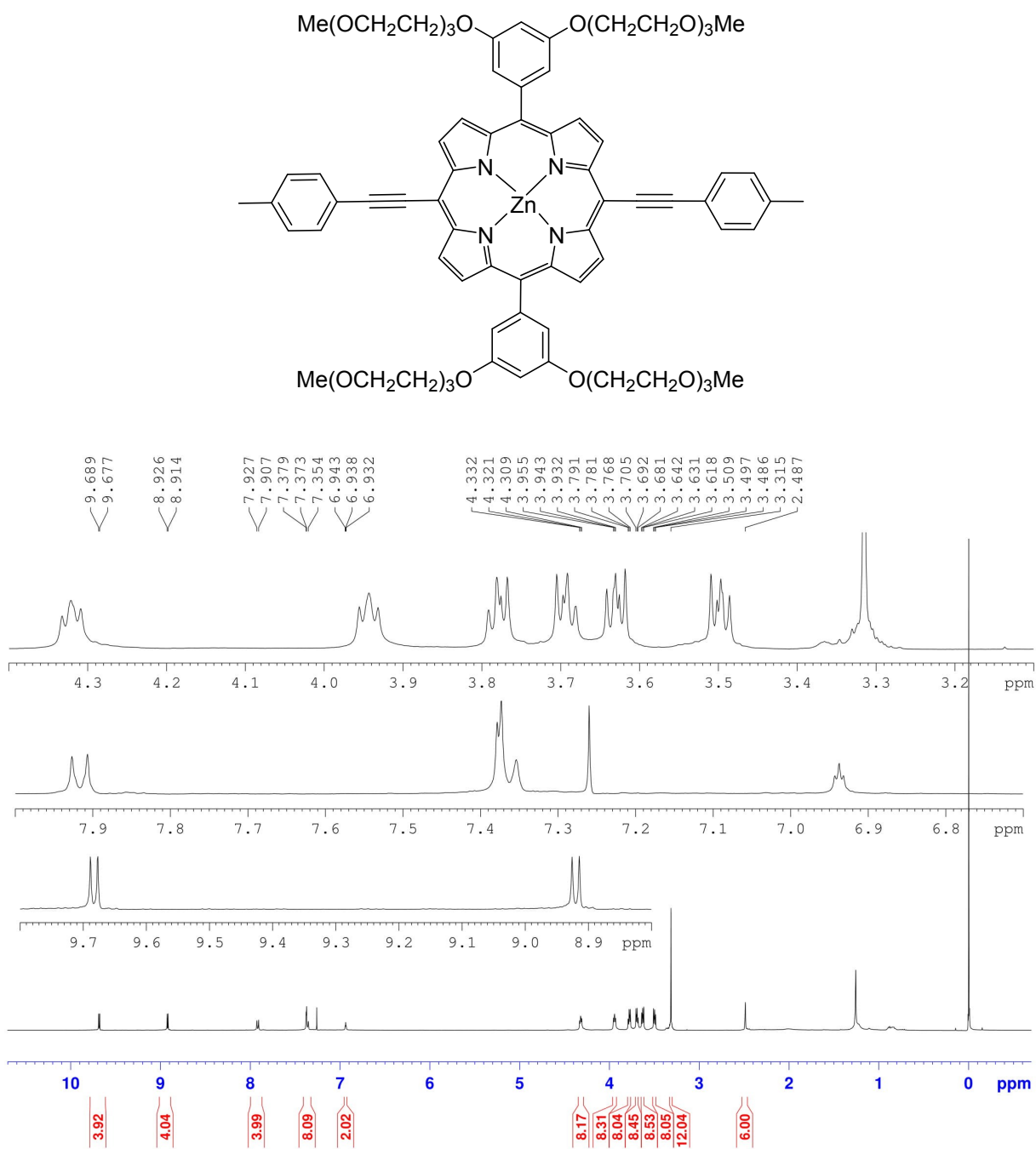


Figure S50: ^1H NMR spectrum (400 MHz, CDCl_3) of **PZn-OTEG-Tol**.

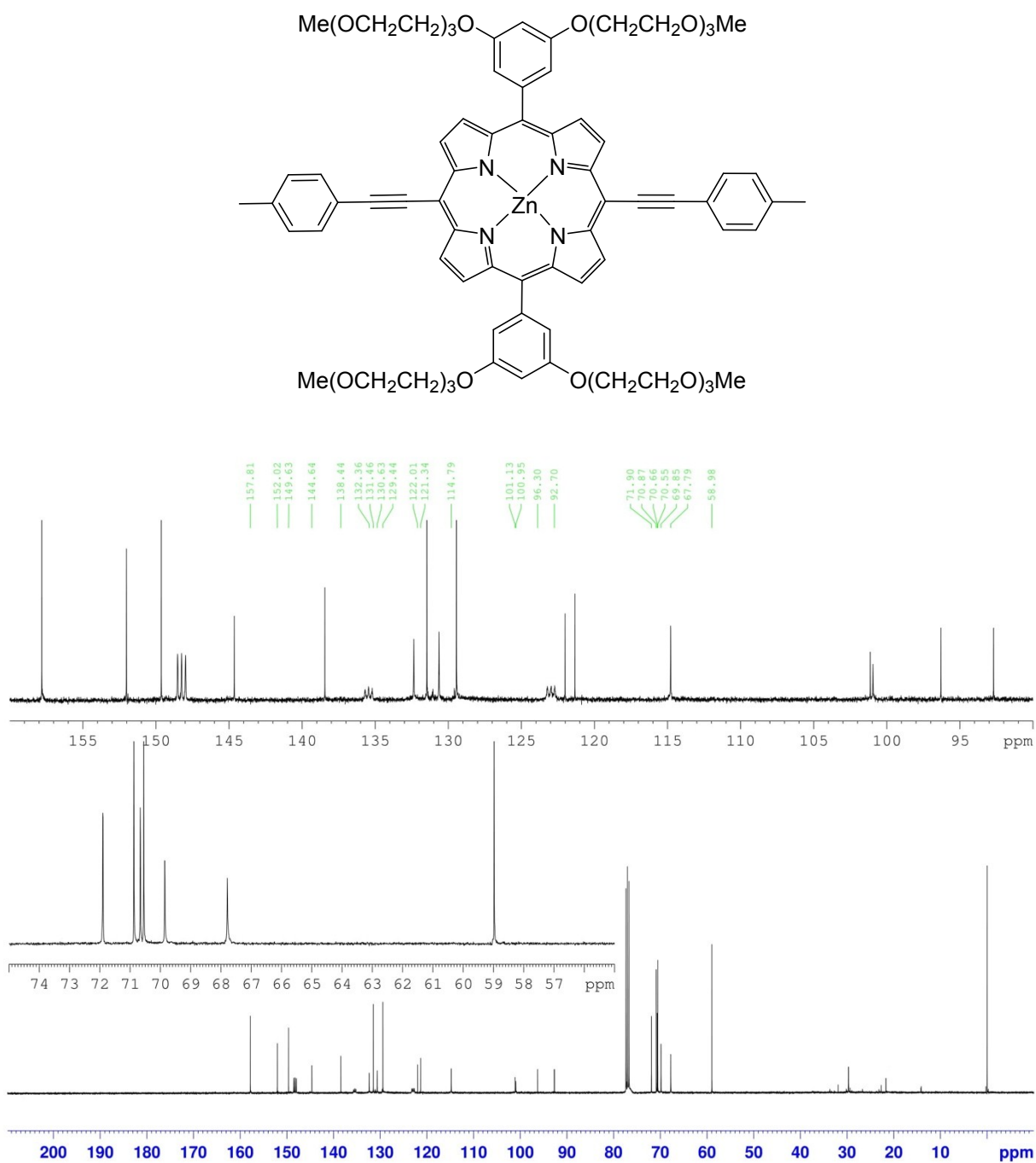


Figure S51: ^{13}C NMR spectrum (101 MHz, CDCl₃) of **PZn-OTEG-Tol**.

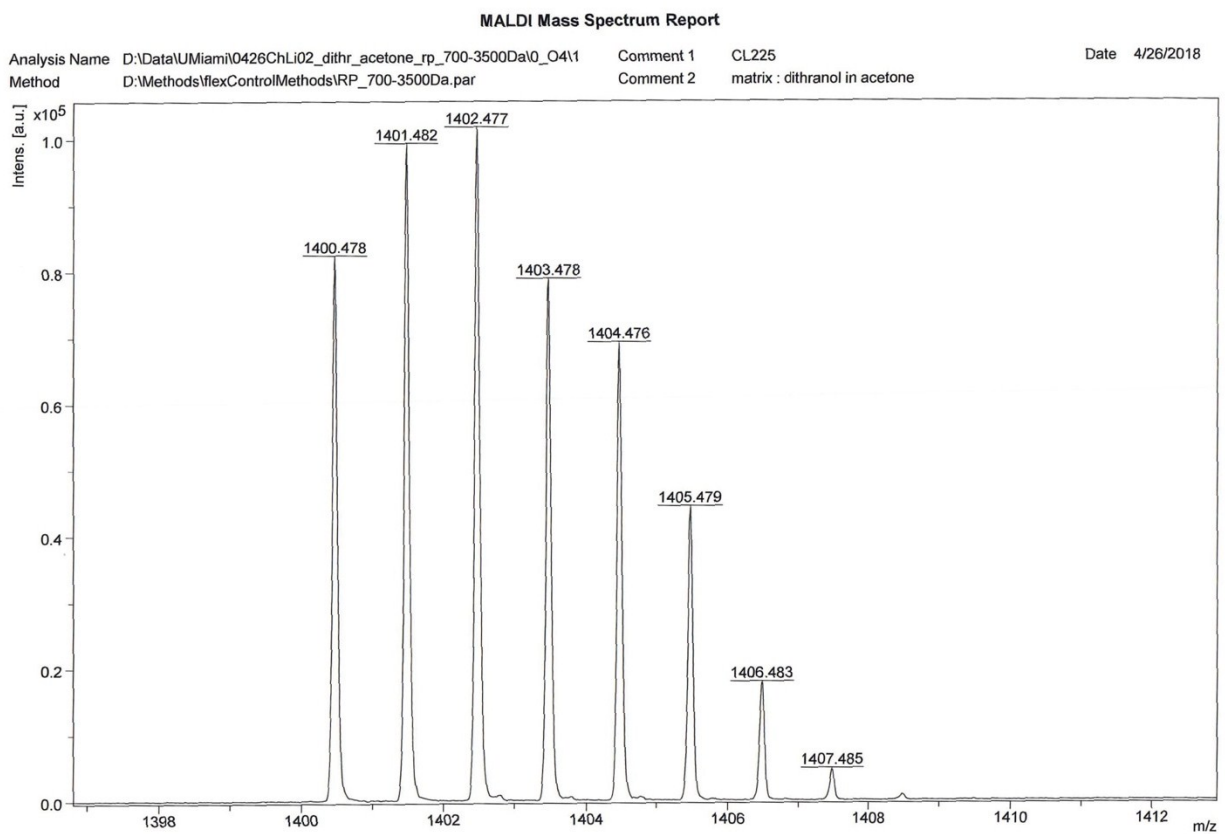


Figure S52: High-resolution mass spectrum (MALDI) of **PZn-OTEG-Tol**.

7. Tables S1 and S2

Table S1: Transition in cm^{-1} and associated oscillator strength of PZn-derived building blocks calculated from the associated ground state absorption spectra.

Individualized building blocks	Transition in cm^{-1} (Associated Oscillator Strength) 20°C
PZn-OAlk-PBA	From Figure S1: 22041 (0.469) 22491 (0.330)
PZn-OAlk-BA	From Figure S2: 22044 (0.458) 22754 (0.325)
PZn-OTEG-BA	From Figure S3: 21905 (0.295) 22681 (0.457)

Table S2: Transition in cm^{-1} and associated oscillator strength of PZn-based supramolecular polymer calculated from the associated ground state absorption spectra.

Supramolecular Polymer	Transition in cm^{-1} (Associated Oscillator Strength) 100°C	Transition in cm^{-1} (Associated Oscillator Strength) 0°C
PZn-OAlk-PBA	From Figure S4: 22041 (0.367) 22658 (0.271)	From Figure S7: 22187 (0.167) 23298 (0.166) 24454 (0.134)
PZn-OAlk-BA	From Figure S5: 22089 (0.504) 22754 (0.326)	From Figure S8: 24011 (0.132) 23053 (0.179) 21945 (0.515)
PZn-OTEG-BA	From Figure S6: 22137 (0.448) 22840 (0.223)	From Figure S9: 23617 (0.175) 23135 (0.157) 22052 (0.025)

8. References

- 1.Çolak, N.; Yıldırım, Y.; Kavutcu, M.; Nurlu, N. The Synthesis of Novel Methotrexate-like Compounds. *Monatshefte für Chemie - Chemical Monthly* **2007**, *138*, 1283-1287.
- 2.Jursic, B. S.; Neumann, D. Preparation of N-acyl derivatives of amino acids from acyl chlorides and amino acids in the presence of cationic surfactant. A variation of the Schotten-Baumann Method of Benzoylation of amino acids. *Synt. Commun.* **2001**, *31*, 555-564.
- 3.Sivaramakrishna, D.; Swamy, M. J. Structure, supramolecular organization and phase behavior of N-acyl-β-alanines: Structural homologues of mammalian brain constituents N-acylglycine and N-acyl-GABA. *Chem. Phys. Lip.* **2016**, *201*, 1-10.
- 4.Arotsky, J.; Butler, R.; Darby, A. C. Iodination and iodo-compounds. Part III. Iodination of some aromatic nitro-compounds with iodine in 20% oleum. *J. Chem. Soc. C: Organic* **1970**, 1480-1485.
- 5.Camerel, F.; Ulrich, G.; Ziessel, R. New Platforms Integrating Ethynyl-Grafted Modules for Organogels and Mesomorphic Superstructures. *Org. Lett.* **2004**, *6*, 4171-4174.
- 6.Frail, P. R.; Susumu, K.; Huynh, M.; Fong, J.; Kikkawa, J. M.; Therien, M. J. Modulation of Dark Conductivity over a 1×10^{-12} to 1×10^{-5} S/cm Range Through Ancillary Group Modification in Amorphous Solids of Ethyne-Bridged (Porphinato)zinc(II) Oligomers. *Chem. Mater.* **2007**, *19*, 6062-6064.
- 7.Ogi, S.; Sugiyasu, K.; Manna, S.; Samitsu, S.; Takeuchi, M. Living supramolecular polymerization realized through a biomimetic approach. *Nat. Chem.* **2014**, *6*, 188-195.
- 8.Smolders, M. M. J.; Nieuwenhuizen, M. M. L.; de Greef, T. F. A.; van der Schoot, P.; Schenning, A. P. H. J.; Meijer, E. W. How to Distinguish Isodesmic from Cooperative Supramolecular Polymerisation. *Chem. Eur. J.* **2010**, *16*, 362-367.
- 9.*Supramolecular Polymers, Second Edition*. Taylor & Francis: Durham, NC, 2005.
- 10.Smolders Maarten, M. J.; Nieuwenhuizen Marko, M. L.; de Greef Tom, F. A.; van der Schoot, P.; Schenning Albertus, P. H. J.; Meijer, E. W. How to Distinguish Isodesmic from Cooperative Supramolecular Polymerisation. *Chem. Eur. J.* **2009**, *16*, 362-367.
- 11.De Greef, T. F. A.; Smolders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. Supramolecular Polymerization. *Chem. Rev.* **2009**, *109*, 5687-5754.