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SUPPORTING INFORMATION

Exceptionally Strong Effect of Small Structural Variations in Functionalized 3,4-Phenylenedioxythiophenes on the Surface Nanostructure and Parahydrophobic Properties of Their Electropolymerized Films

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CONTENTS

Experimental Part

General

^{1}H and ^{13}C NMR spectra were recorded either on a Bruker Avance 400 or Bruker Avance 500 instruments in $CDCl_3$, operating at 400 MHz (^{1}H) / 100 MHz (^{13}C) and 500 MHz (^{1}H) / 125 MHz (^{13}C), respectively. Tetramethylsilane (TMS) (δ_H, δ_C = 0.00 ppm) was used as an internal standard. Electron impact mass spectra (positive mode, EI+) were recorded on a GC-MS system consisting of a HP 5890 gas chromatograph (Hewlett Packard Series II) with a HP 8971 EI-MS detector, operating at 70 keV, or on microTOF LC Bruker Daltonics mass spectrometer. Electrospray (ESI+) mass spectra were recorded on Thermo Finnigan LCQ DECA ion-trap mass spectrometer. MALDI mass-spectra were recorded at the EPSRC National Mass Spectrometer Facility (NMSF), Swansea, UK.

Microwave-assisted reactions were performed on a CEM Discovery SP microwave reactor equipped with an autosampler in temperature-controlled dynamic conditions.

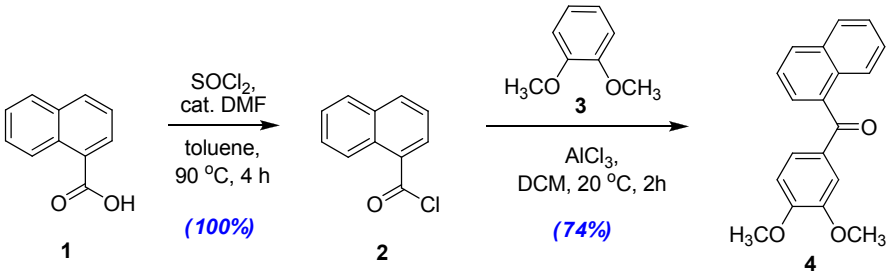
Thin layer chromatography (TLC) was carried out using Merck TLC silica gel 60 UV-254 aluminium sheets. Purification of synthesized compounds by flash chromatography was performed on Teledyn ISCO Combiflash Rf 200 flash chromatograph on silica gel 40–60 μm (40–250 mesh).

DFT calculations

Computational studies were carried out using density functional theory (DFT) with the Gaussian 09 package of programs.[1] The geometries of **1Na-PheDOT**, **2Na-PheDOT** and **9Ant-PheDOT** monomers, and **(2Na-PheDOT)$_2$** dimer were fully optimized for isolated molecules in a gas phase, with no constraints. Becke's three-parameter hybrid exchange functional[2,3] with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP)[4] and Pople's 6-31G split valence basis set supplemented by d-polarization functions for heavy atoms were employed.

Synthesis

(3,4-Dimethoxyphenyl)(naphthalen-1-yl)methanone (4)



Step 1: In 250 mL three-neck round bottom flask, 1-naphtoic acid (**1**) (20.04 g, 116 mmol, 1.0 eq.) was dissolved in toluene (90 mL). To this solution, $SOCl_2$ (13 mL, 180 mmol, 1.5 eq.) and catalytic amount of *N,N*-dimethylformamide (DMF) (3 drops) were added and the mixture was heated with stirring at 90 °C for 4 hours. The mixture was cooled to warm temperature and toluene and an excess of thionyl chloride were distilled off in vacuum (ca. 20 mbar; heating the mixture at the end to ~100 °C to evaporate all volatiles to dryness). The residual 1-naphtoyl chloride (**2**) (22.2 g, 100%; off-white solid) was used in the next step without further purification and characterization.

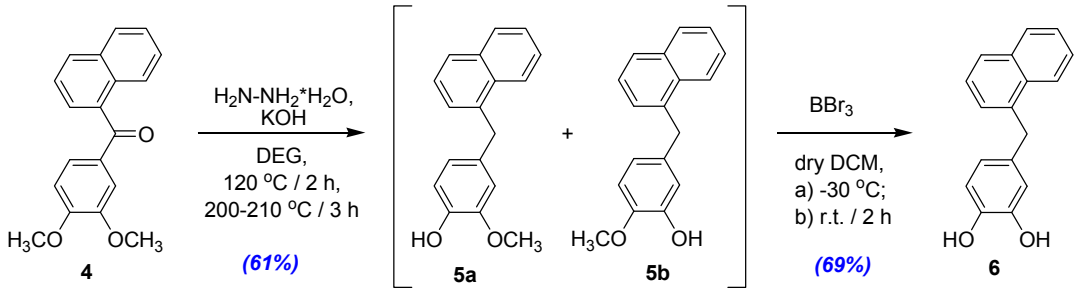
Step 2: In 1 L three-neck round bottom flask under nitrogen atmosphere, the obtained 1-naphthoyl chloride (**2**) was dissolved in anhydrous dichloromethane (DCM) (600 mL) and 1,2-dimethoxybenzene (**3**) (16 mL, 125 mmol, 1.08 eq.) was added. The stirred mixture was cooled to 0 °C and anhydrous $AlCl_3$ (18.8 g, 141 mmol, 1.21 eq.) was added in portions over 5–10 minutes, keeping the temperature between 0 and +10 °C. The mixture was allowed warm slowly to room temperature, stirred at room temperature for 1 hour and then stirred under reflux for 24 hours. After cooling to room temperature, diluted HCl (≈ 1 M concentration; 250 mL) was slowly added to the stirred mixture (*Caution: add HCl slowly in the beginning; the reaction is exothermic, with a gas evolution*), DCM layer was separated and aqueous layer was extracted with DCM (3 × 150 mL). Combined organic layers were washed with saturated Na_2CO_3 (150 mL), dried with $MgSO_4$, filtered, the solvent was evaporated and the residue was dried *in vacuo* (to remove an excess of 1,2-dimethoxybenzene) affording crude product (33.8 g, 99 %) as a viscous orange-brown oil. The crude product was dissolved in DCM and passed through silica gel column (D×H ≈ 4.5 × 9 cm), which was then washed with DCM (800 mL). Solvent evaporation gave crude product (31.6 g, 92.8%) as light-yellow semi-solid. It was recrystallized from a minimum amount of methanol to afford pure compound **4** (25.08 g, 74%) as colorless crystals.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.99 (2H, t, *J* = 7.1 Hz), 7.91 (1H, d, *J* = 7.7 Hz), 7.66 (1H, d, *J* = 1.8 Hz), 7.58–7.45 (4H, m), 7.28 (1H, dd, *J* = 7.3, 1.9 Hz), 6.81 (1H, d, *J* = 8.4 Hz), 3.95 (3H, s, OCH_3), 3.93 (3H, s, OCH_3)

^{13}C-NMR (100 MHz, $CDCl_3$): *δ* [ppm] = 196.76 (C=O), 153.65, 149.14, 136.94, 133.67, 131.19, 130.96, 130.66, 128.34, 127.01, 126.81, 126.42, 126.38, 125.74, 124.38, 111.44, 109.82, 56.11 (OCH_3), 56.07 (OCH_3)

MS (EI$^+$): *m/z* = 292.10 (M^+, 100 %); calcd. for $C_{19}H_{16}O_3$: 292.11.

4-(Naphthalen-1-ylmethyl)benzene-1,2-diol (6)



Step 1: In 500 mL round bottom flask, 1-naphthoyl-3,4-dimethoxybenzene (22.1 g, 76 mmol, 1.00 eq.) was dissolved in diethylene glycol (DEG) (150 mL) with slight heating. To this solution, hydrazine hydrate (60% N_2H_4 in H_2O; 30 mL, 370 mmol, 4.9 eq.) and KOH (19.2 g, 340 mmol, 4.5 eq.) were added and the mixture was stirred with heating at 120 °C for 2 hours. The temperature was raised to 190 °C with distilling off the volatiles (water, an excess of hydrazine and, partially, DEG). The mixture was stirred at 200–210 °C for 3 hours, cooled down to room temperature, diluted with water and extracted with DCM several times. Combined DCM extracts were washed with diluted HCl, then with water, dried over $MgSO_4$, filtered and evaporated to dryness to afford crude product (16.32 g, 77.5%) as a brown oil. The crude product was dissolved in minimum amount of toluene and purified by column chromatography on silica gel eluting the product with toluene to afford (after solvent evaporation) pure compound **5** (12.2 g, 61%) as yellowish solid. According to ^{1}H NMR, it represents a mixture of two demethylated regioisomers **5a** and **5b** (in ~ 1:1 ratio). So, apart of reduction of carbonyl group in Wolff-Kishner reaction, partial demethylation occurred during the heating of an intermediate hydrazone in an alkali conditions at high temperature.

Compounds (5a+5b):

^{1}H-NMR (400 MHz, $CDCl_3$, TMS, 5120 scans): δ [ppm] = 8.05–7.95 (2H, m, naphthalene), 7.88–7.81 (2H, m, naphthalene), 7.78–7.71 (2H, m, naphthalene), 7.50–7.37 (6H, m, naphthalene), 7.32–7.26 (2H, m, naphthalene), 6.84–6.62 (6H, m, benzene), [5.52 + 5.47] (2H, s, 2×OH), [4.37 + 4.35] (4H, s, 2×CH_2), [3.84 + 3.78] (6H, s, 2×OCH_3).

MS (EI^+): *m/z* = 264.15 (M^+, 100 %); calcd. for $C_{18}H_{16}O_2$: 264.12.

Step 2: Under nitrogen atmosphere, in 500 mL three-neck round bottom flask equipped with stirring bar, thermometer, bubbler and dropping funnel, the above product (**5a+5b**) was dissolved in anhydrous DCM (350 mL). The solution was cooled down to –30 °C and, with stirring, a solution of BBr_3 (17.0 mL, 179 mmol, 4.08 eq.) in anhydrous DCM (50 mL) was added dropwise over 20 minutes. The reaction mixture was allowed to warm up to room temperature and stirred for two hours. The mixture was quenched with water (350 mL) (*caution: in the beginning, add water dropwise and slowly, with continuing stirring*) and stirred at room temperature for 2 hours. The mixture was saturated with sodium chloride, DCM layer was separated and the aqueous phase was extracted with DCM (4 × 150 mL). Combined DCM layers were washed with sodium chloride solution (2 × 500 mL), dried over $MgSO_4$, filtered and the solvent was evaporated to yield crude compound **6** (8.60 g, 78 %) as a grey crystalline solid. The crude product was purified by flash chromatography on silica gel (120 g column, UV-detection at λ = 304 and 318 nm) eluting with using DCM:Et_2O = 1:1 v/v to afford pure compound **6** (7.96 g, yield 69% in the step (B), 40 % overall yield in two steps) as a grey crystalline solid.

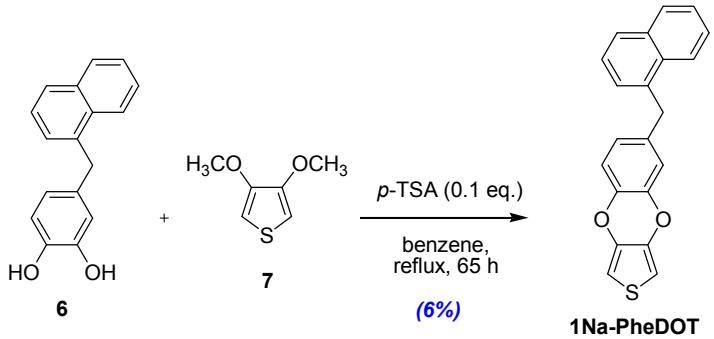
TLC: R_f = 0.88 (Et_2O); 0.80 (EtOAc); 0.20 (DCM).

^{1}H-NMR (400 MHz, $CDCl_3$): *δ* [ppm] = 7.98–7.95 (1H, m, naphthalene H-4/5), 7.86–7.84 (1H, m, naphthalene H-5/4), 7.75 (1H, d, *J* = 8.2 Hz, naphthalene H-8), 7.46–7.39 (3H, m, naphthalene H-3,6,7), 7.29 (1H, d, *J* = 7.0 Hz, naphthalene H-2), 6.77 (1H, d, *J* = 8.0 Hz, benzene H-5), 6.68–6.65 (2H, m, benzene H-3,6), 5.00 (1H, s, OH), 4.99 (2H, s, OH), 4.34 (2H, s, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): *δ* [ppm] = 143.42, 141.69, 136.73, 133.95, 133.88, 132.10, 128.65, 127.27, 127.16, 125.96, 125.56, 125.54, 124.30, 121.25, 115.78, 115.38, 38.36.

MS (EI^+): *m/z* = 250.09 (M^+, 100 %); calcd. for $C_{17}H_{14}O_2$: 250.10.

6-(Naphthalen-1-ylmethyl)benzo[b]thieno[3,4-e]-[1,4]dioxine (1Na-PheDOT)



Under nitrogen atmosphere, 3,4-dimethoxythiophene (**7**) (2.04 g, 13.9 mmol, 1.00 eq.), 4-(naphthalen-1-ylmethyl)benzene-1,2-diol (**6**) (8.00 g, 32.0 mmol, 2.30 eq.), *p*-toluenesulfonic acid monohydrate (270 mg, 1.40 mmol, 0.10 eq.) and benzene (80 mL) were placed into a 250 mL one-neck round bottom flask equipped with a Soxhlett extractor with an extraction thimble, containing molecular sieves (4Å). The reaction mixture was refluxed (oil bath, 100 °C) for 65 hours. After cooling to room temperature,

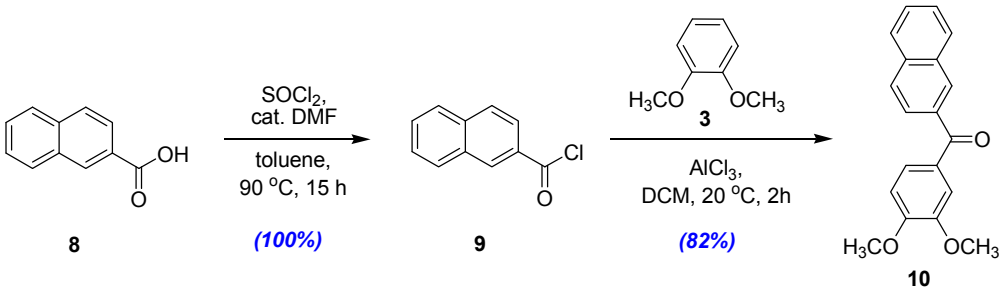
the mixture was filtered through silica gel column (D×H = 4.5 × 8 cm) and eluted with toluene (450 mL). The solvent was evaporated to dryness to yield crude compound (1.36 g, 30%) as a brown oil. The crude product was purified by flash chromatography on silica gel (120 g column, UV-detection at λ = 284, 305 nm) using PE:DCM = 1:0.6 v/v as an eluent to afford pure compound **1Na-PheDOT** (279 mg, 6%**)** as a white crystalline solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.95–7.93 (1H, m, naphthalene H-4/5), 7.87–7.85 (1H, m, naphthalene H-5/4), 7.77 (1H, d, J = 8.2 Hz, naphthalene H-8), 7.47–7.41 (3H, m, naphthalene H-3,6,7), 7.30 (1H, d, J = 6.9 Hz, naphthalene H-2), 6.83–6.76 (2H, m, benzene H-5,6), 6.72 (1H, s, benzene H-3), 6.40 (1H, d, J = 3.6 Hz, thiophene H-2/5), 6.37 (1H, d, J = 3.6 Hz, thiophene H-2/5), 4.35 (2H, s, CH_2).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 140.68, 139.15, 139.11, 136.56, 136.08, 133.99, 131.99, 128.73, 128.73, 127.39, 127.35, 126.07, 125.64, 125.54, 124.13, 123.71, 116.86, 116.61, 100.85, 100.79, 38.27.

MS (EI$^+$): m/z = 330.11 (M^+, 100 %); calcd. for $C_{21}H_{14}O_2S$: 330.07.

(3,4-Dimethoxyphenyl)(naphthalen-2-yl)methanone (10)[5]

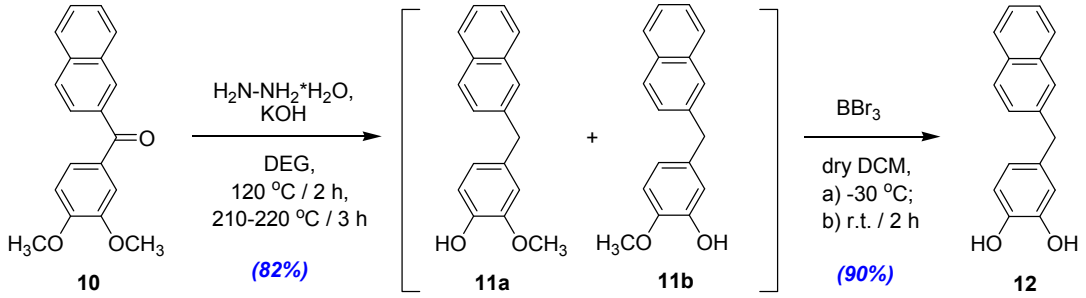


Step 1: In 250 mL three-neck round bottom flask, 2-naphtoic acid (**8**) (20.58 g, 120 mmol, 1.0 eq.) was dissolved in toluene (90 mL). To this solution, $SOCl_2$ (13 mL, 180 mmol, 1.5 eq.) and catalytic amounts of *N,N*-dimethylformamide (DMF) (3 drops) were added and the mixture was heated with stirring at 90 °C overnight. An excess of $SOCl_2$ and toluene were distilled off in vacuum (ca. 20 mbar; heating the mixture at the end to ~100 °C to evaporate all the volatiles to dryness). The residual 2-naphtoyl chloride (**9**) (22.78 g, 100%; off-white solid) was used in the next step without further purification and characterization.

Step 2: In 1 L three-neck round bottom flask under nitrogen atmosphere, the obtained 1-naphthoyl chloride (**9**) was dissolved in anhydrous dichloromethane (DCM) (600 mL) and 1,2-dimethoxybenzene (**3**) (17.8 mL, 140 mmol, 1.16 eq.) was added. The stirred mixture was cooled to 0 °C and anhydrous $AlCl_3$ (18.2 g, 136 mmol, 1.14 eq.) was added in portions over 5–10 minutes, keeping the temperature between 0 and +10 °C. The mixture was allowed warm slowly to room temperature, stirred at room temperature for 1 hour and then stirred under reflux for 24hours. After cooling to room temperature, diluted HCl (~ 1 M concentration; 250 mL) was slowly added to the stirred mixture (*caution: do it slowly in the beginning; the reaction is exothermic, with a gas evolution*), DCM layer was separated and aqueous layer was extracted with DCM (3 × 150 mL). Combined organic layers were washed with saturated Na_2CO_3 (150 mL), dried with $MgSO_4$, filtered and the solvent was evaporated dryness affording crude product (36.7 g, >100 %) as a viscous light-brown semi-solid. The crude product was recrystallized from ethanol to yield pure product **10** (28.73 g, 82%) as light beige solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.23 (1H, s), 7.89 (4H, m), 7.57 (1H, m), 7.52 (2H, m), 7.42 (1H, dd, J = 8.2 Hz), 6.89 (1H, d, J = 8.3 Hz), 3.94 (3H, s, OCH_3), 3.92 (3H, s, OCH_3).

4-(Naphthalen-2-ylmethyl)benzene-1,2-diol (12)[5]



Step 1: In 500 mL round bottom flask, 1-naphthoyl-3,4-dimethoxybenzene (**10**) (18.78 g, 64.2 mmol, 1.00 eq.) was dissolved in diethylene glycol (DEG) (150 mL) with slight heating. To this solution, hydrazine hydrate (60% N_2H_4 in H_2O; 25 mL, 305 mmol, 4.8 eq.) and KOH (19.2 g, 340 mmol, 4.5 eq.) were added and the mixture was stirred with heating at 120–130 °C for 2 hours. The temperature was raised to 170–180 °C with distilling off the volatiles (water, an excess of hydrazine and, partially, DEG). The mixture was then stirred at 210–220 °C for 3 hours, cooled down to room temperature, diluted with water and extracted with DCM several times. Combined DCM extracts were washed with diluted HCl, then with water, dried over $MgSO_4$, filtered and evaporated to dryness to afford crude product (16.85 g) as a brown oil. The crude product was dissolved (suspended) in DCM, loaded on the top of a silicagel column (D×H = 4.5 × 9 cm) and eluted with DCM (700 mL) to afford pure product **11** (12.21 g, 72%) as yellowish solid. According to ^{1}H NMR, it represents a mixture of two demethylated isomers **11a** and **11b** (ca. 2:3 ratio), so apart of reduction of the carbonyl group in Wolff-Kishner reaction, partial demethylation occurred during the heating of an intermediate hydrazone in basic conditions at high temperature.

Compounds (11a+11b):

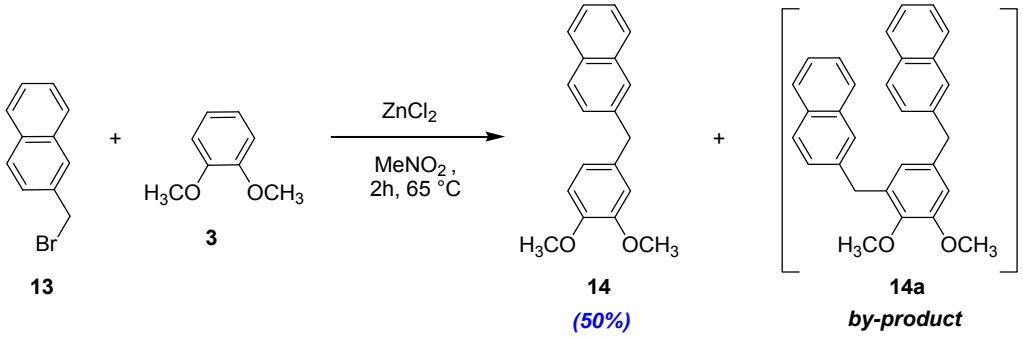
^{1}H-NMR (400 MHz, $CDCl_3$, TMS, 5120 scans): δ [ppm] = 7.85–7.66 (6H, m, naphthalene), 7.60–7.53 (2H, m, naphthalene), 7.49–7.35 (4H, m, naphthalene), 7.35–7.26 (2H, m, naphthalene), 6.80–6.65 (6H, m, benzene), [5.55 + 5.49] (2H, s, 2×OH), [4.06 + 4.03] (4H, s, 2×CH_2), [3.84 + 3.79] (6H, s, 2×OCH_3).

MS (EI$^+$): *m/z* = 264.17 (M^+, 100 %); calcd. for $C_{18}H_{16}O_2$: 264.12.

Step 2: Under nitrogen atmosphere, in 1 L three-neck round bottom flask equipped with stirring bar, thermometer, bubbler and dropping funnel. the above product (**11a+11b**) was dissolved in anhydrous DCM (450 mL). The solution was cooled down to –25 °C and, with stirring, a solution of BBr_3 (16.7 mL, 176 mmol, 4.00 eq.) in anhydrous DCM (100 mL) was added dropwise over 20 minutes. The reaction mixture was allowed to warm up to room temperature and stirred for two hours. The mixture was quenched with water (350 mL) (*caution: in the beginning, add water dropwise and slowly, with continuing stirring*) and stirred at room temperature for 1 hour. The mixture was saturated with sodium chloride, DCM layer was separated and the aqueous phase was extracted with DCM (6 × 100 mL). Combined DCM layers were washed with sodium chloride solution (3 × 100 mL), dried over $MgSO_4$, filtered and the solvent was evaporated to dryness. Crude product was purified by column chromatography on silica gel (eluent: DCM / DCM:Et_2O) to afford pure compound **12** (10.47 g, yield 90% in the step (B), 65 % overall yield in two steps) as a off-white solid.

^{1}H-NMR (400 MHz, $CDCl_3$, TMS, 5120 scans): δ [ppm] = 7.82–7.72 (3H, m, naphthalene), 7.61 (1H, s, naphthalene), 7.48–7.39 (2H, m, naphthalene), 7.30 (1H, dd, *J* = 8.0 Hz, naphthalene), 6.79 (1H, d, *J* = 7.9 Hz, benzene), 6.73–6.65 (2H, m, benzene), 5.06 (1H, s, OH), 5.02 (1H, s, OH), 4.03 (2H, s CH_2).

2-(3,4-Dimethoxybenzyl)naphthalene (14)



1,2-Dimethoxybenzene (**3**) (4.13 g, 29.9 mmol, 2.95 eq.), anhydrous $ZnCl_2$ (1.51 g, 11.1 mmol, 1.09 eq.) and anhydrous nitromethane (100 mL) were placed into a 250 mL two-neck round bottom flask under nitrogen. To this mixture, 2-(bromomethyl)naphthalene (**13**) (2.238 g, 10.1 mmol, 1.00 eq.) was added and the mixture was stirred for two hours at 64°C. Nitromethane was evaporated under reduced pressure, DCM (50 mL) and H_2O (100 mL) were added to the reaction flask and the mixture was left to stir overnight. The DCM layer was separated and the aqueous phase was extracted with DCM (2 × 30 mL). Combined DCM layers were washed with water (3 × 30 mL), dried over Mg_2SO_4, filtered, the solvent was evaporated and the residue was dried *in vacuo* (at 0.02 mbar; to remove an excess 1,2-dimethoxybenzene) to afford crude compound **14** (2.54 g, 90 %) as a brown oil. The crude product was purified by flash chromatography on silica gel (120 g column, UV-detection at λ = 285, 300 nm) using gradient eluent PE:DCM (start with PE, by-products are removed with PE:DCM = 1:1, then target product is eluted with PE:DCM = gradient from 1:1 to 1:2) to yield almost pure compound **14** (1.43 g, 50 %) as a light brownish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.81–7.67 (3H, m, naphthalene H-4,5,8), 7.61 (1H, s, naphthalene H-1), 7.47–7.40 (2H, m, naphthalene H-6,7), 7.31 (1H, d, J = 9.9 Hz, naphthalene H-3), 6.82–6.75 (3H, m, benzene), 4.09 (2H, s, CH_2), 3.86 (3H, s, OCH_3), 3.81 (3H, s, OCH_3).

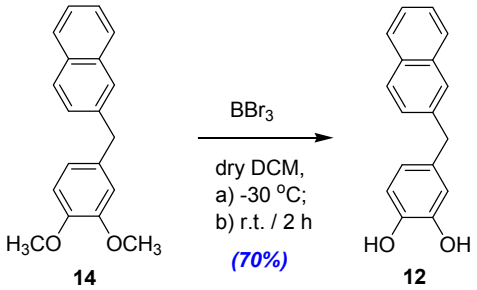
^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 149.00, 147.50, 138.89, 133.62, 133.53, 132.12, 128.06, 127.64, 127.57, 127.54, 126.92, 125.99, 125.35, 121.06, 112.34, 111.25, 55.93, 55.84, 41.68.

MS (EI$^+$): m/z = 278.14 (M^+, 100 %); calcd. for $C_{19}H_{18}O_2$: 278.13.

*It was also found that dialkylation occurs during the reaction to form by-product **14a**, which was identified by MS. With PE:DCM the spots of **14** and **14a** partly overlap, so the target product **14** was partly contaminated with dialkylated product **14a** (~ 7%), but they can be better separated using toluene as an eluent.*

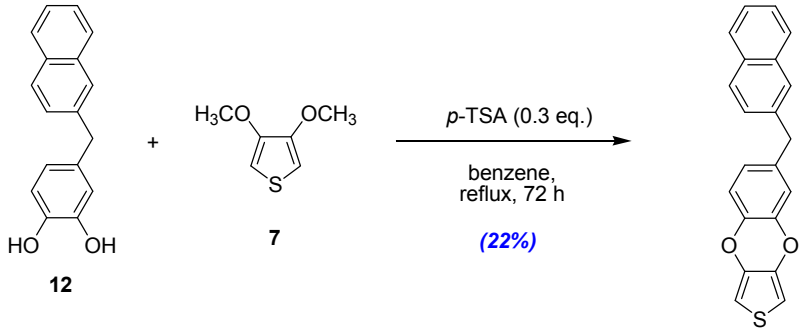
Compound 14a: MS (EI$^+$): m/z = 418.16 (M^+, 100 %); calcd. for $C_{19}H_{18}O_2$: 418.19.

4-(Naphthalen-2-ylmethyl)benzene-1,2-diol (12)



Compound **12** can be obtained by demethylation of dimethoxy-derivative **14** with BBr_3 in similar conditions described above for a mixture of (**11a+11b**) with the yield of 70%.

6-(Naphthalen-2-ylmethyl)benzo[b]thieno[3,4-e]-[1,4]dioxine, (2Na-PheDOT)



This compound was obtained by us previously by the same reaction within the yield of 5 %.[5] *With the below procedure, the yield was increased to 22%.*

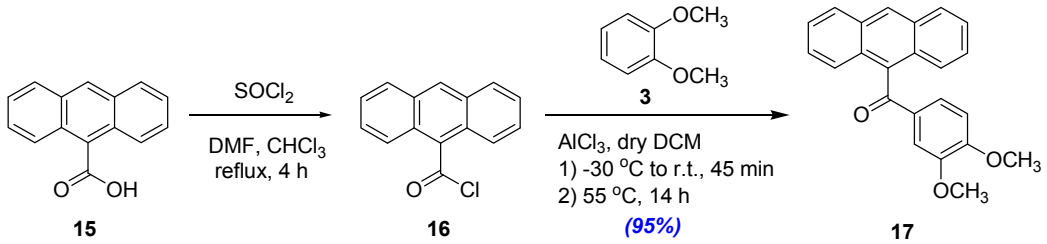
4-(Naphthalen-2-ylmethyl)benzene-1,2-diol (**12**) (10.87g, 43.4 mmol, 3.00 eq.), 3,4-dimethoxythiophene (**7**) (2.10 g, 14.5 mmol, 1.00 eq.), *p*-toluene sulfonic acid monohydrate (832 mg, 4.30 mmol, 0.30 eq.) and benzene (75 mL) were placed into a 250 mL one-neck round bottom flask, under nitrogen. The reaction mixture was stirred under reflux for 3 days (oil bath 100 °C). After cooling to room temperature, the dark brown solution was passed through a silica gel column (4 × 7.5 cm), which was then washed with toluene (~350 mL). The solvent was evaporated to yield crude compound **2Na-PheDOT** (1.52 g, 31.7%) as a brown oil. The crude product was purified by flash chromatography on silica gel (120 g column, UV-detection at λ = 280, 300 nm) using PE:DCM/1:1 v/v as an eluent to afford pure compound **2Na-PheDOT** (1.04 g, 22 %) as a white crystalline solid.

TLC: R_f = 0.65 (DCM:PE/1:1), 0 (PE).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.85–7.72 (3H, m), 7.61 (1H, br.s.), 7.50–7.37 (2H, m), 7.29 (1H, d, *J* = 8.4 Hz), 6.84 (1H, d, *J* = 8.1 Hz), 6.82–6.75 (2H, m), 6.40 (1H, d, *J*=3.6 Hz, thiophene H-2/5), 6.38 (1H, d, *J* = 3.6 Hz, thiophenes H-5/2), 4.04 (2H, s, CH_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.82–7.72 (3H, m), 7.61 (1H, br.s.), 7.48–7.38 (2H, m), 7.29 (1H, dd, *J*=8.4 = 1.6 Hz), 6.84 (1H, d, *J* = 8.2 Hz), 6.82–6.73 (2H, m), 6.40 (1H, d, *J*=3.6 Hz, thiophenes H-2/5), 6.38 (1H, d, *J* = 3.6 Hz, thiophenes H-5/2), 4.04 (2H, s, CH_2).

Anthracene-9-yl(3,4-dimethoxyphenyl)methanone (17)



Step 1: Under nitrogen, 9-anthracenecarboxylic acid (**15**) (10.3 g, 46.3 mmol, 1.00 eq.), SO_2Cl_2 (20.0 mL, 276 mmol, 6.0 eq.), DMF (four drops; as catalyst) and chloroform (100 mL) were placed into a 500 mL three-neck round bottom flask equipped with a reflux condenser, thermometer and an oil bubbler. The reaction mixture stirred under reflux for 4 hours (oil bath, 95 °C). Afterwards, chloroform and $SOCl_2$ were distilled off (oil bath, 120 °C) and the residual $SOCl_2$ was removed in vacuum (20 mbar, oil bath, 120 °C). The obtained yellow solid of anthracene-9-carbonyl chloride (**16**) (11.2 g, 100%) was used in the next step without purification.

Step 2: Under nitrogen, to the flask with obtained anthracene-9-carbonyl chloride (**16**) (11.2 g, 46.4 mmol, 1.00 eq.), 1,2-dimethoxybenzene (**3**) (6.42 g, 46.6 mmol, 1.00 eq.) and anhydrous DCM (250 mL) were added. The solution was cooled down to –30 °C and anhydrous $AlCl_3$ (6.47 g, 48.5 mmol, 1.05 eq.) was added in one portion. The reaction mixture was brought to room temperature, stirred for 45 minutes and then refluxed for 14 hours. The mixture was cooled down to room temperature, diluted with 5% aqueous HCl (170 mL), stirred for one hour, the DCM layer was separated and the aqueous phase was extracted with DCM (2 × 100 mL). The combined DCM layers were washed with saturated Na_2CO_3 (250 mL), H_2O (250 mL), dried over Mg_2SO_4, filtered and the solvent was evaporated to yield pure compound **17** (15.1 g, 95 %) as a yellow solid.

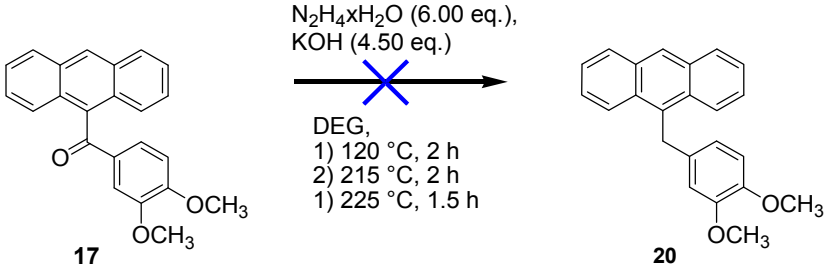
R_f value: 0.43 (DCM); 0 (PE).

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ [ppm] = 8.55 (1H, s, anthracene H-10), 8.06 (2H, d, J = 8.5 Hz, anthracene H-4,5), 7.81 (1H, s, benzene H-3), 7.75 (2H, d, J = 8.7 Hz, anthracene H-1,8), 7.47 (2H, t, J = 7.4 Hz, anthracene H-3,6), 7.39 (3H, t, J = 7.6 Hz, anthracene H-2,7), 7.01 (1H, d (br.), J = 7.9 Hz, benzene H-6), 6.67 (1H, d, J = 8.3 Hz, benzene H-5), 3.97 (3H, s, OCH_3), 3.88 (3H, s, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 198.71, 154.12, 149.42, 134.33, 131.59, 131.06, 128.71, 128.59, 128.14, 126.90, 126.42, 125.48, 110.31, 110.17, 56.10.

MS (EI$^+$): m/z = 342.08 (M^+, 100 %); calcd. for $C_{23}H_{18}O_3$: 342.13.

Unsuccessful reduction of anthracene-9-yl(3,4-dimethoxyphenyl)methanone (17) to 9-(3,4-dimethoxybenzyl)anthracene (20) by Wolff-Kishner reaction

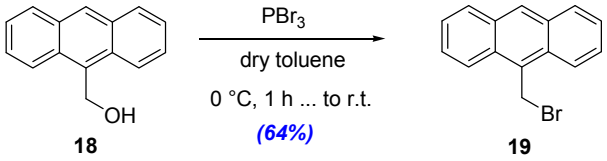


17 **20**

*While Wolff-Kishner reduction of carbonyl group by hydrazine in the presence of KOH works well and we successfully used it for reduction of naphthalene derivatives (see above), an attempt to apply this reaction to anthracene derivative **17** was unsuccessful giving a complex mixture of inseparable products. One side process in this case was an elimination of anthracene, which was isolated in 26% yield.*

Anthracene-9-yl(3,4-dimethoxyphenyl)methanone (**17**) (14.90 g, 43.5 mmol, 1.00 eq.) and hydrazine hydrate (13. 0 g, 260 mmol, 6 eq.) were stirred in diethylene glycol (DGE) (150 mL) for 1 h until full dissolution. KOH (11.0 g, 196 mmol, 4.5 eq.) was added and the mixture was stirred at 120 °C for 2 h. The temperature was increased to ca. 200 °C and an excess of hydrazine and water were distilled off. The mixture was then stirred at 215 °C for 2 h, and then at 225 °C for additional 1.5 h. The mixture was cooled to room temperature, diluted with water (400 mL) and acidified with concentrated HCl (~22 mL) to pH ~2. Toluene (200 mL) was added and the mixture was stirred for 15 min. Toluene layer was separated and aqueous phase was extracted with Et_2O (4 × 150 mL). Organic layers were combined, washed with water (3 × 100 mL), dried over $MgSO_4$ and filtered. Diethyl ether was evaporated and the residual toluene solution was passed through silicagel column, which was then washed with toluene to afford crude mixture of products (8.2 g). The crude product was chromatographed on a silica gel column (H×D = 25×5 cm) using toluene as an eluent. First isolated fraction was identified as pure anthracene (2.01g, 26%). Following fractions represented a complex mixture, which was difficult to separate.

9-(Bromomethyl)anthracene (19)[6]

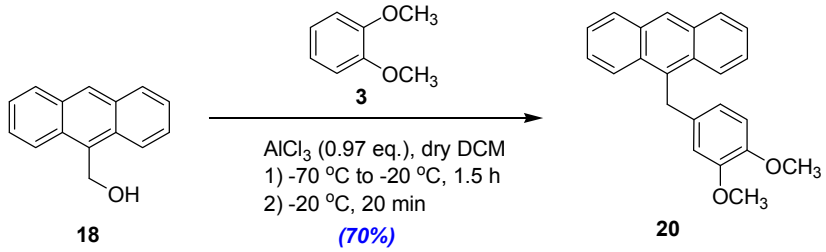


Under nitrogen, into a 1 L three-neck round bottom flask, anthracene-9-ylmethanol **(18)** (15.04 g, 72.2 mmol, 1.00 eq.) was dissolved in toluene (400 mL) and the solution was cooled to 0 °C. To this solution, PBr_3 (9.0 mL, 95 mmol, 1.3 eq.) was added dropwise over 20 minutes and the mixture was stirred at 0 °C for one hour. The mixture was brought to room temperature and diluted with saturated Na_2CO_3 (170 mL). The toluene layer was separated and the aqueous phase was extracted with toluene (2 × 50 mL). Combined toluene layers were washed with water (2 × 100 mL) and then with brine (100 mL), dried over Mg_2SO_4, filtered, concentrated (by distilling off of some toluene) to a volume of ~150 mL, and left to crystallize overnight in a fridge at ca. +5 °C. The precipitate was collected by filtration, washed with cold toluene (50 mL) and dried to afford of pure 9-(bromomethyl)anthracene (**19**) (12.5 g, 64 %) as a yellow crystalline solid.

R_f value: 0.83 (toluene).

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ [ppm] = 8.50 (1H, s, H-10), 8.31 (2H, d, J = 8.9 Hz, H-1,8), 8.04 (2H, d, J = 8.5 Hz, H-4,5), 7.66–7.62 (2H, m, H-2,7), 7.50 (2H, t, J = 7.5 Hz, H-3,6), 5.55 (2H, s, CH_2).

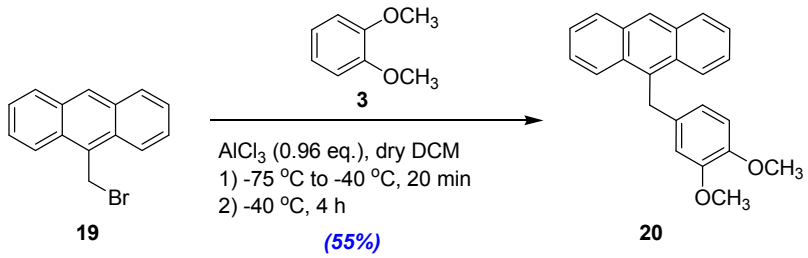
9-(3,4-Dimethoxybenzyl)anthracene (20)



Method A.

Under nitrogen, anthracene-9-ylmethanol (**18**) (510 mg, 2.50 mmol, 1.00 eq.), 1,2-dimethoxybenzene (**3**) (402 mg, 2.90 mmol, 1.19 eq.) and anhydrous DCM (45 mL) were placed into a three-neck round bottom flask. The mixture was cooled to –70 °C and anhydrous $AlCl_3$ (318 mg, 2.40 mmol, 0.97 eq.) was added in one portion. The reaction mixture was allowed to warm slowly to –45 °C (30 min), –30 °C (30 min), and –20 °C (30 min). It was stirred at –20 °C for 20 minutes, diluted slowly with 5% aqueous HCl (40 mL) and stirred for 15 minutes. The DCM layer was separated and the aqueous phase was extracted with DCM (2 × 20 mL). The combined DCM layers were washed with water (3 × 40 mL), dried over Mg_2SO_4, filtered and the solvent was evaporated to dryness to afford crude product (830 mg, >100%) as a yellow solid. The crude product was purified by flash chromatography on silica gel (80 g column, UV-detection at λ = 285, 380 nm) using toluene as an eluent to yield pure compound **20** (550 mg, 70 %) as a yellow solid.

Its NMR spectra and coincide with the product **20** obtained from 9-(bromomethyl)anthracene (**19**) (see below).



19 20

Method B.

Under nitrogen, 9-(bromomethyl)anthracene (**19**) (500 mg, 1.80 mmol, 1.00 eq.), 1,2-dimethoxybenzene (**3**) (263 mg, 1.90 mmol, 1.03 eq.) and anhydrous DCM (45 mL) were placed into a 100 mL three-neck round bottom flask equipped with a thermometer, stirring bar, oil bubbler and a stopper. The mixture was cooled down to –75 °C and anhydrous $AlCl_3$ (236 mg, 1.80 mmol, 0.96 eq.) was added in one portion. The reaction mixture was allowed to warm up slowly to –40 °C for 20 min, stirred at –40 °C for 4 h and diluted slowly with 5% aqueous HCl (40 mL). The DCM layer was separated and the aqueous phase was extracted with DCM (2 × 20 mL). The combined DCM layers were washed with water (3 × 40 mL), dried over Na_2SO_4, filtered and the solvent was evaporated to dryness to afford crude product (705 mg, >100%) as a yellow semi-solid. The crude product was purified by flash chromatography on silica gel (12 g column, UV-detection at λ = 285, 380 nm) using toluene as an eluent to yield pure compound **20** (333 mg, 55 %) as a yellow crystalline solid.

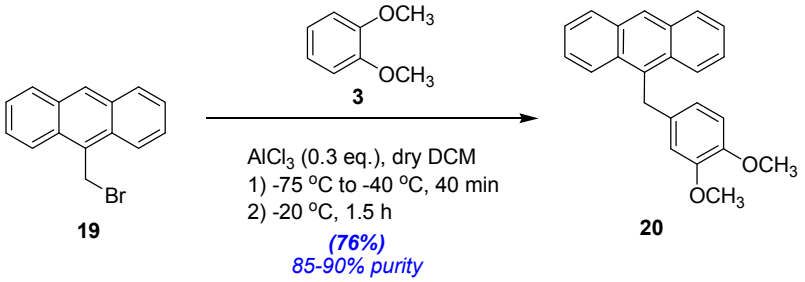
R_f value: 0.7 (DCM); 0.65 (Et_2O); 0.3 (toluene).

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ [ppm] = 8.44 (1H, s, anthracene H-10), 8.24–8.22 (2H, m, anthracene H-4,5), 8.05–8.03 (2H, m, anthracene H-1,8), 7.48–7.45 (4H, m, anthracene H-2,3,6,7), 6.79 (1H, s, benzene H-3), 6.66 (1H, d, J = 8.2 Hz, benzene H-5), 6.51 (1H, d, J = 8.2 Hz, benzene H-6), 4.96 (2H, s, CH_2), 3.78 (3H, s, OCH_3), 3.73 (3H, s, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 148.94, 147.29, 133.46, 131.99, 131.68, 130.55, 129.12, 126.53, 125.86, 124.93, 124.80, 120.02, 111.56, 111.25, 55.85, 55.80, 33.10.

MS (EI$^+$): m/z = 328.09 (M^+, 100 %); calcd. for $C_{23}H_{20}O_2$: 328.15.

***Method C.* Scaled-up synthesis.**



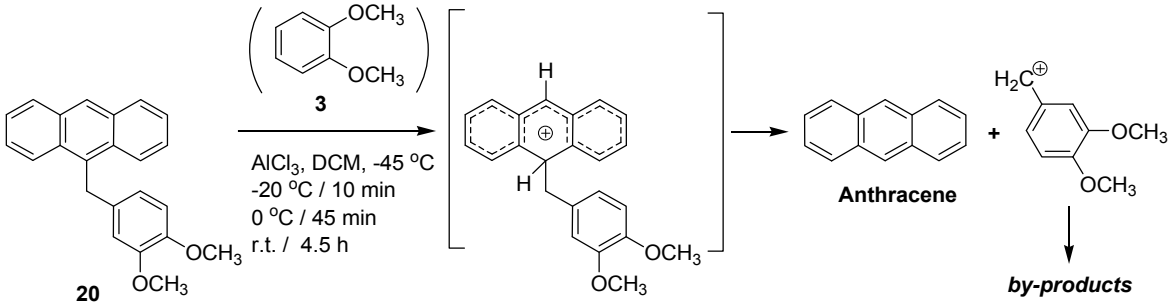
19 20

Under nitrogen, 9-(bromomethyl)anthracene (**19**) (10.91 g, 40.2 mmol, 1.00 eq.), 1,2-dimethoxybenzene (**3**) (6.11 g, 44.2 mmol, 1.1 eq.) and anhydrous DCM (500 mL) were placed into 1 L three-neck round bottom flask. The mixture was cooled down to –75 °C and anhydrous $AlCl_3$ (1.61 g, 12.0 mmol, 0.3 eq.) was added in one portion. The reaction mixture was brought to –20 °C for 40 min, stirred at –20 °C for 1.5 h, diluted slowly with 5% aqueous HCl (500 mL) and stirred for 1 h. The DCM layer was separated and the aqueous phase was extracted with DCM (3 × 100 mL). The combined DCM layers were washed with water (3 × 80 mL), dried over Mg_2SO_4, filtered and the solvent was evaporated to dryness to afford crude product (14.2 g, >100%) as yellow-brown oil. The crude product was purified by flash chromatography on silica gel (120 g column, UV-detection at λ = 285, 380 nm) using toluene, eluting first anthracene (567 mg, 6.53%), following by partly purified (still crude) product (12.35 g, 93%). This crude product was additionally purified by flash chromatography

on silica gel (360 g column, UV-detection at λ = 285, 380 nm; eluent – toluene) to afford compound **20** (10.1 g, 76%) as yellow solid.

According to ^{1}H NMR spectrum, the purity of the sample is ca. 85–90% and it can be used in further synthesis of catechol **21** without further purification.

Testing the stability of compound 20 in acidic conditions.



*When synthesis of compound **20** was performed with warming up the reaction mixture at the end of the reaction to room temperature (before the quenching the mixture with water), the yield of the product was substantially lower. It was also found that some amount of anthracene was formed in the reaction (as monitored by TLC of the reaction mixture or by TLC analysis of the crude product). This assumes low stability of compound **22** in acidic conditions (in presence of $AlCl_3$ as a Lewis acid). To check this supposition, we performed the experiment monitoring the transformations of the mixture of pure compound **20** with $AlCl_3$ in dry DCM under nitrogen.*

Under nitrogen, 9-(3,4-dimethoxybenzyl)anthracene (**20**) (20 mg, 0.061 mmol) and 1,2-dimethoxybenzene (**3**) (17.3 mg, 0.125 mmol) were dissolved in dry DCM (2 mL) and the mixture was cooled down to –45 °C. Dry $AlCl_3$ (8.2 mg, 0.061 mmol) was added in one portion and the mixture was stirred with stepwise increase of the temperature and monitoring the reaction by taking the probes for TLC analysis:

–45 °C (light yellowish solution) // –45 °C to –20 °C. / 10 min (light brownish solution),

–20 °C to 0 °C, 10 min (light brown solution) // 0 °C, 45 min (brown solution),

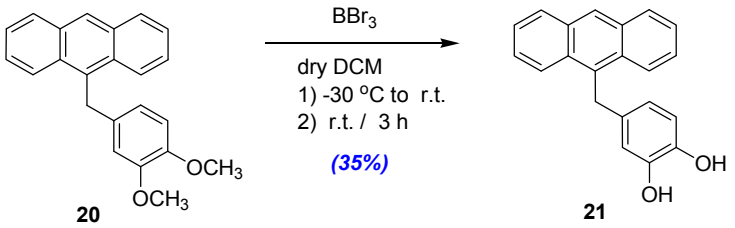
0 °C to +20 °C, 10 min (brown solution) // +20 °C, 4.5 h.

Some amount of anthracene was detected by TLC after stirring the reaction mixture at 0 °C for 30 min. The relative intensity of the anthracene spot was increased when the mixture was stirred at room temperature, with substantial amount of anthracene to be formed after 1.5-3 h.

This confirms that the target product **20**, obtained by Friedel-Crafts alkylation of 1,2-dimethoxybenzene (**3**) by 9-bromomethylanthracene (**19**) is unstable in acidic conditions at room temperature. Therefore, the reaction temperature during alkylation should not exceed –20–40 °C (we failed the alkylation reaction when it was performed with heating and substantial amount of anthracene was detected by TLC in the crude product). This instability is more likely a Brønsted acid-catalyzed reaction: it starts as protonation of C-1 atom of anthracene to form carbocation, following by elimination of 3,4-dimethoxybenzyl cation and re-aromatization of the anthracene ring (other pathways with Lewis acid catalysis are also possible).

This also can (at least partly) explain the low yields of catechol **21** in the demethylation reaction of compound **20** with weaker Lewis acid BBr_3.

9-(3,4-dihydroxybenzyl)anthracene (21)



20 21

Under nitrogen, 9-(3,4-dimethoxybenzyl)anthracene (**20**) (7.74 g, 23.6 mmol, 1.00 eq.) and anhydrous DCM (240 mL) were placed into a 500 mL three-neck round bottom flask equipped with stirring bar, thermometer and an oil bubbler. The mixture was cooled to –30 °C and a solution of BBr_3 (9.0 mL, 95 mmol, 4.0 eq.) in anhydrous DCM (22 mL) was added dropwise over 20 minutes via syringe to the reaction flask. The mixture was allowed to warm up to room temperature and stirred for three hours. The reaction mixture was diluted slowly with H_2O (300 mL) and stirred under nitrogen for 45 minutes. The DCM layer was separated and the aqueous phase was extracted with DCM (3 × 100 mL). The combined DCM layers were washed with water (4 × 200 mL), dried over $MgSO_4$, filtered and the solvent was evaporated to yield crude compound **21** (6.60 g, 93 %) as a grey-brown solid. The crude product was purified by flash chromatography on silica gel (220 g column, UV-detection at λ = 285, 390 nm) using DCM as an eluent* to afford pure catechol **21** (2.48 g, 35 %) as a off-white (light brownish) crystalline solid.

* *Repeated syntheses/purification showed that flash chromatography purification of this compound works better in a gradient eluent from toluene to toluene:Et_2O = 4:1 that gives analytically pure compound **21** as colorless crystalline solid..*

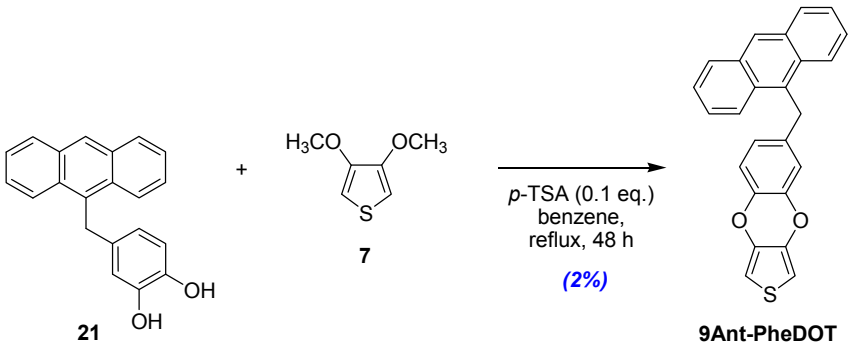
R_f value: 0.68 (Et_2O), 0.58 (Et_2O:toluene = 1:1), 0.51 (Et_2O:toluene = 1:2), 0.24 (Et_2O:toluene = 1:4), 0.12 (DCM); 0.07 (toluene); 0.04 (Et_2O:PE = 4:1); 0 (PE);

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ [ppm] = 8.42 (1H, s, anthracene H-10), 8.22–8.17 (2H, m, anthracene H-4,5), 8.04–7.99 (2H, m, anthracene H-1,8), 7.47–7.42 (4H, m, anthracene H-2,3,6,7), 6.71 (1H, d, J = 8.2 Hz, benzene H-6), 6.64 (1H, dd, J = 8.0, 1.8 Hz, benzene H-5), 6.50 (1H, d, dd, J = 1.7 Hz, benzene H-3), 4.91 (1H, s, OH), 4.88 (2H, s, CH_2), 4.84 (1H, s, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 143.37, 141.61, 133.98, 132.00, 131.65, 130.46, 129.10, 126.50, 125.89, 124.92, 124.77, 120.69, 115.37, 115.20, 32.72.

MS (EI$^+$): m/z = 300.27 (M^+, 100 %); calcd. for $C_{21}H_{16}O_2$: 300.12.

6-(Anthracen-9-ylmethyl)benzo[b]thieno[3,4-e][1,4]dioxine



21 7 9Ant-PheDOT

Under nitrogen atmosphere, 9-(3,4-dihydroxybenzyl)anthracene (**21**) (2.228 g, 7.42 mmol, 1.00 eq.), 3,4-dimethoxythiophene (**7**) (1.338 g, 9.28 mmol, 1,25 eq.) and *p*-toluenesulfonic acid monohydrate

(0.142 g, 0.742 mmol, 0.10 eq.) in benzene (18 mL) were heated under reflux for 48 hours (*initial yellow suspension was dissolved when heated to reflux and the mixture changed the color to dark brown during the reaction*). The solvent was removed under vacuum, the residue was transferred onto the column with silica gel (3 × 10 cm) and eluted with PE:toluene, 2:1 to afford crude product (857 mg, ~30 %) as yellow powder.

The crude product was purified by flash chromatography on silica gel (120 g column; UV-detection at λ = 285, 380 nm). First fraction eluted with PE represents anthracene (598 mg, 45%). Further elution with gradient from PE to PE:toluene, 2:1 gave crude compound **9Ant-PheDOT** (123 mg, 4.4%) as yellow powder (~80% purity, according to ^{1}H NMR). This product was purified again by flash chromatography ({80 g + 40 g} RediSep™ Gold columns 20–40 μm spherical silica gel; UV-detection at λ = 285, 380 nm; PE:toluene, 7:3) to afford pure compound **9Ant-PheDOT** (48 mg, 1.7 %) as light yellowish powder.

At the final step, compound **9Ant-PheDOT** can also be purified by recrystallization from refluxed DCM (cooling to 0 ^{o}C) to give analytically pure sample.

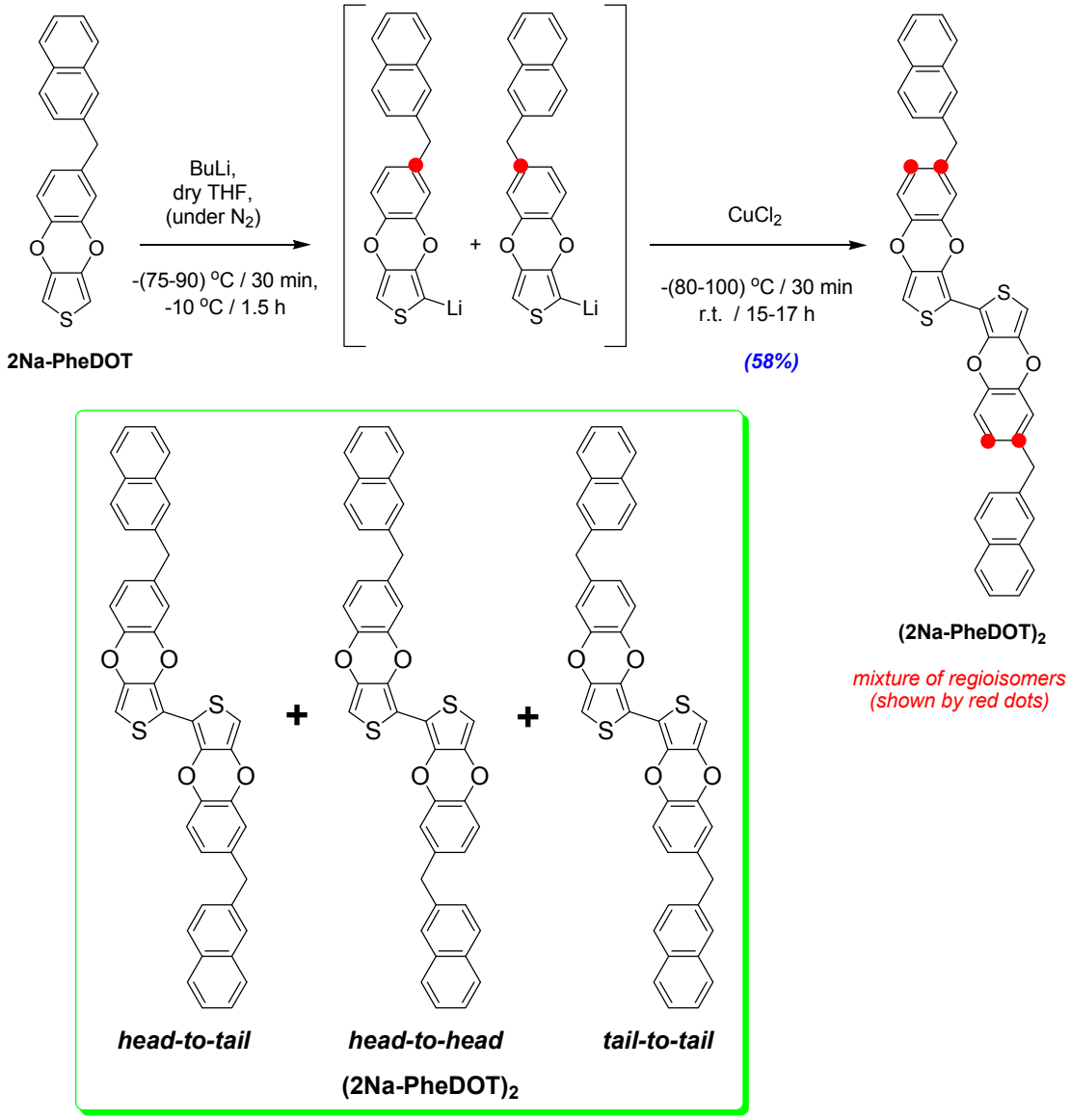
R_f value: 0.46 (PE:toluene = 2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.44 (1H, s, anthracene H-10), 8.24–8.11 (2H, m, anthracene H-4,5), 8.07–8.0 (2H, m, anthracene H-1,8), 7.54–7.41 (4H, m, anthracene H-2,3,6,7), 6.80–6.70 (2H, m, benzene H-5,6), 6.60 (1H, s, benzene H-3), 6.36 (1H, d, *J* = 3.6 Hz, thiophene), 6.30 (1H, d, *J*=3.56 Hz, thiophene), 4.91 (2H, s, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.71, 139.11, 139.04, 138.97, 136.76, 131.69, 131.28, 130.47, 129.22, 126.82, 126.08, 124.98, 124.55, 123.23, 116.65, 116.37, 100.80, 100.77, 32.64 (CH_2).

MS (EI^+): *m/z* = 380.09 (M^+, 100 %); calcd. for $C_{25}H_{16}O_2S$: 380.10.

2Na-PheDOT dimer, $(2Na\text{-}PheDOT)_2$



Synthesis 1: Under nitrogen, **2Na-PheDOT** (160 mg, 0.484 mmol, 1.00 eq.) and anhydrous THF (10 mL) were placed into a dry two-neck round bottom flask. The solution was stirred and cooled down to –(80 – 90) °C, and n-BuLi (1.6 M in hexane, 0.34 mL, 0.544 mmol, 1.12 eq.) was added dropwise over 10 minutes to the reaction flask keeping the temperature in the range of –(75 – 80) °C. The reaction mixture was allowed to warm slowly to +10 °C and stirred at this temperature for an additional 1 h. The mixture was cooled again to –(80 – 90) °C, anhydrous (oven dried at ~170 °C) $CuCl_2$ (70 mg, 0.521 mmol, 1.08 eq.) was quickly added in one portion, the mixture was allowed to warm slowly to room temperature and stirred at this temperature for 17 hours.

Tetrahydrofuran was removed by flushing nitrogen through the mixture, warm toluene (10 mL) was added to the residue and the mixture was filtered through short silica gel plug (3 cm height column) eluting the product with warm toluene (5 × 10 mL). The solvent was evaporated to yield crude product (100 mg, 62.9%) as a yellow powder. The crude product was purified by flash chromatography on silica gel (40 g silica gel column, eluents: PE (to remove by-products), then toluene, UV-detection at 295, 320 nm) to afford pure dimer **$(2Na\text{-}PheDOT)_2$** (60 mg, 38%) as a yellowish powder.

The solubility of the dimer ***(2Na-PheDOT)$_2$*** *is low, so column purification of a large quantity (while efficient) is problematic. The product can be more efficiently purified by recrystallization from benzene or toluene (after initial pre-purification on the short column), - depicted in Synthesis 2..*

Synthesis 2: Under nitrogen, **2Na-PheDOT** (502 mg, 1.50 mmol, 1.00 eq.) and anhydrous THF (25 mL) were placed into a three-neck round bottom flask. The stirred solution was cooled to –90 °C and nBuLi (1.6 M in hexane, 1.00 mL, 1.60 mmol, 1.05 eq.) was added dropwise over 10 minutes to the reaction flask keeping the temperature of the reaction mixture at –(80 – 90) °C. The mixture was stirred at –(70 – 80) °C for 15 min, then allowed to warm slowly to –10 ^{o}C (ca. 1.5 h) and stirred at this temperature for 30 min. The mixture was again cooled to –100 ^{o}C and anhydrous (oven dried at ~170 ^{o}C) $CuCl_2$ (220 mg, 1.60 mmol, 1.08 eq.) was added in one portion. The mixture was allowed to warm slowly to room temperature and stirred for 15 hours (under nitrogen). Tetrahydrofuran was evaporated to dryness, water (25 mL) was added to the residue, the mixture was stirred for 30 min and the solid was filtered off, washed with hexane and dried *in vacuo* to yield crude product (567 mg) as a grey (light bluish) solid (the color is from traces of Cu salt).

The crude product was suspended in hot toluene, transferred onto a glass column with silica gel (D×H ~ 2×8 cm) and eluted with hot toluene (~500 mL). Toluene solution was concentrated to the volume of ca. 20 mL and left to crystallize. The precipitate was filtered off, washed with cold toluene (0.5 mL) and dried *in vacuo* to afford pure dimer **(2Na-PheDOT)$_2$** (290 mg, 58%) as a white crystalline solid.

TLC: R_f = 0.75 (toluene); 0.23 (PE).

^{1}H NMR* (400 MHz, $CDCl_3$): δ (ppm) 7.85–7.72 (6H, m, naphthalene H-4,4',5,5',8,8'), 7.61 (2H, br.s., naphthalene H-1,1'), 7.50–7.38 (4H, m, naphthalene H-6,6',7,7'), 7.29 (2H, m, naphthalene H-3,3'), 6.97–6.70 (6H, m, benzene), [6.40 + 6.38 + 6.35] (2H in total, three singlets from the regioisomers, thiophene H-5,5'), [4.05 + 4.04] (4H in total, two singlets from the regioisomers, CH_2).

^{13}C NMR* (100 MHz, $CDCl_3$): δ (ppm) *140.56*, 140.54, 140.50, 139.11, 139.05, 139.03, 138.67, 138.61, 138.55, 138.11, 138.05, 137.17, 137.15, 136.90, 136.87, 134.95, 134.81, 133.58, 132.15, 128.23, 127.64, 127.58, 127.56, 127.41, 127.40, *127.38*, 127.08, 127.05, 126.08, 125.48, *125.47*, 124.45, 124.12, 124.11, 117.52, 117.22, 117.20, 116.96, 116.93, 116.66, 109.89, 109.79, 109.72, 99.48, 99.40, [41.25 + 41.22] (CH_2).

MS (EI+): *m/z* 658.18 (M^+, 100%); calcd for $C_{42}H_{26}O_4S_2$: 658.13.

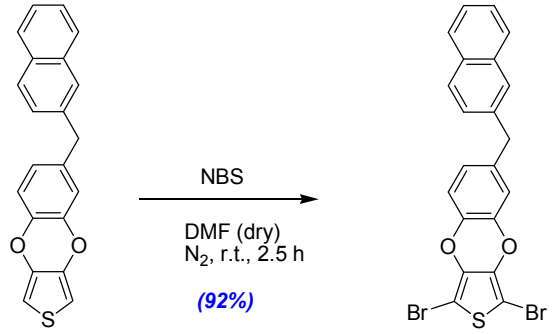
MS (ESI+): *m/z* 659.3 (MH^+, 100%); calcd for $C_{42}H_{26}O_4S_2$: 658.13.

Comments:

** in ^{1}H NMR spectra, three thiophene peaks at [6.40 + 6.38 + 6.35] are of similar intensities. After recrystallization from benzene, the sample showed decreased intensities of the peaks at 6.40 and 6.35 ppm with respect to the intensity of the middle signal at 6.38, indicating that one of the regioisomer is of lower solubility and is crystallized first. The total integral of these three peaks are not changed on recrystallization and remains as 2H.*

*** As the product is a mixture of regioisomers, the total numbers of carbon signals don't coincide with a single isomer structure.*

1,3-Dibromo-6-(naphthalen-1-ylmethyl)benzo[b]thieno[3,4-e][1,4]dioxine (22)



2Na-PheDOT **22**

*Bromination of **2Na-PheDOT** was performed by N-bromosuccinimide (NBS) in DMF, similar to bromination of unsubstituted **PheDOT**.*[7]

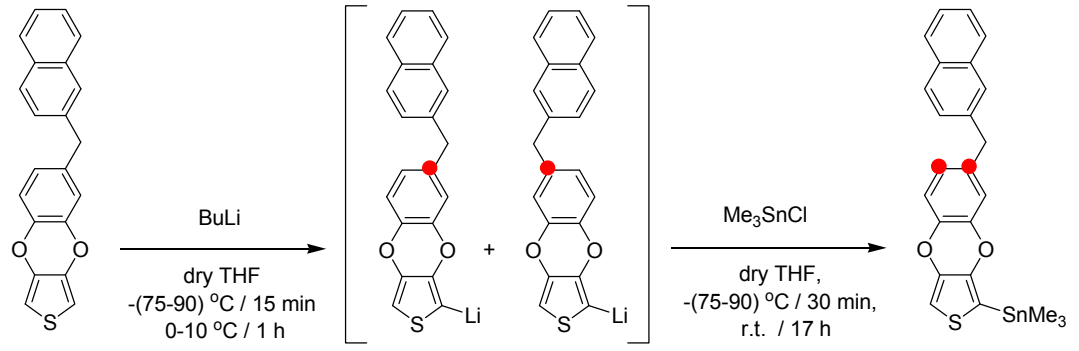
Under nitrogen, **2Na-PheDOT** (100.0 mg, 0.303 mmol, 1.00 eq.) was dissolved in dry DMF (1 mL) and *N*-bromosuccinimide (NBS) (115.3 mg, 0.648 mmol, 2.14 eq.) was added to the reaction mixture in one portion and stirred at room temperature 2.5 hours protecting from the light. The reaction progress was monitored by TLC on silica gel [eluent: PE:DCM = 2:1 v/v]. The resulting white precipitate was collected by filtration, washed with warm water (7 × 6 mL) and dried *in vacuo* to afford pure compound **22** (134.5 mg, 92%) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85–7.75 (3H, m), 7.62 (1H, br.s.), 7.50–7.40 (2H, m), 7.28 (1H, d, J = 8.4 Hz), 6.95 (1H, d, J = 8.1 Hz), 6.88 (1H, s), 6.86 (1H, d, J = 9.4 Hz), 4.06 (2H, s, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.71, 138.24, 137.78, 137.74, 137.45, 137.35, 133.58, 132.17, 128.30, 127.65, 127.55, 127.37, 127.16, 126.14, 125.56, 124.75, 117.36, 116.85, 86.94, 86.84, 41.22 (CH_2).

MS (EI+): *m/z* 487.95 (M^+, 100%, ^{79}Br/^{79}Br), 489.92 (58.1%, ^{79}Br/^{78}Br), 486.02 (48.5%, ^{81}Br/^{81}Br); calcd for $C_{21}H_{12}Br_2O_2S$: 487.89 (100%, ^{79}Br/^{79}Br), 485.89 (51.4%, ^{79}Br/^{78}Br), 489.89 (48.6%, ^{81}Br/^{81}Br).

Trimethyl(7-(naphthalen-1-ylmethyl)benzo[b]thieno[3,4-e][1,4]dioxin-1-yl)stannane (23)



2Na-PheDOT

(96%)
(85% purity)

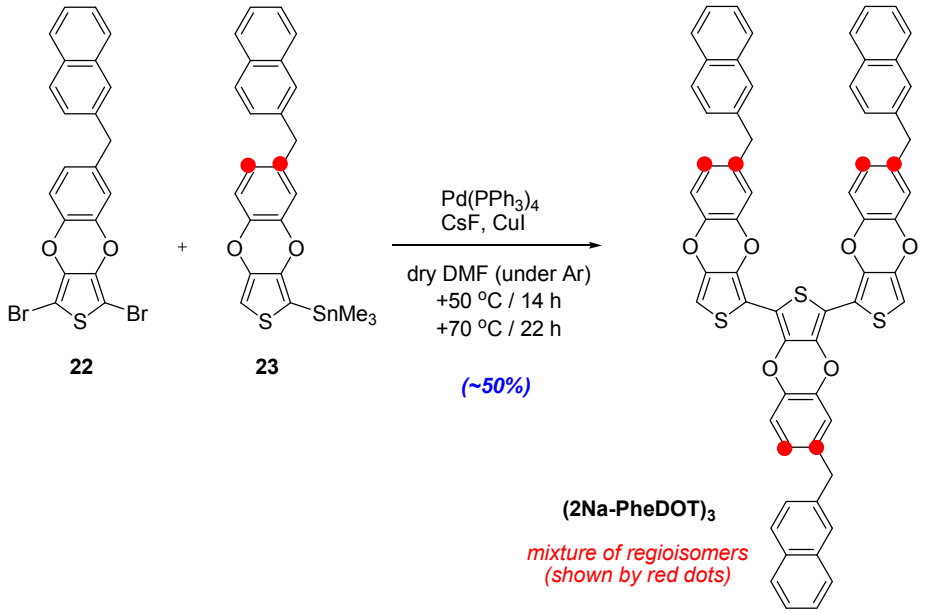
23
mixture of regioisomers (shown by red dots)

Under nitrogen, in a three-neck flask, **2Na-PheDOT** (243 mg, 0.735 mmol, 1.00 eq.) was dissolved in dry THF (10 mL) and the mixture was cooled –(80 – 90) °C. n-BuLi (1.6 M in hexane, 0.51 mL, 0.816 mmol, 1.11 eq.) was added dropwise to this solution over a period of 10 min keeping the temperature in the range of –(75 – 80) °C. The mixture was allowed to warm slowly to +10 °C for ca 30 min and stirred at this temperature for an additional 1 h. The solution was then cooled again to –(80 – 90) °C

and a solution of Me_3SnCl (1.0 M in THF, 0.83 mmol, 1.13 eq.) was added dropwise over 10 min with vigorous stirring. This solution was allowed to warm to room temperature and stirred for 17 h. The solvent was evaporated by flushing nitrogen through the flask and the residue was diluted with 5 % aqueous NH_4Cl (20 mL) and hexane (20 mL). Organic layer was separated and the aqueous layer was extracted with hexane (2 × 8 mL). Combined organic layers were washed with water (15 mL), filtered through 0.5 µm membrane filter, hexane was evaporated and the residue was dried *in vacuo* (0.03 mbar) to afford stannic compound **23** (349 mg, 96%) as yellowish oil. According to ^{1}H NMR, the purity of the sample is ~85%. It was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.72 (3H, m), 7.62 (1H, br.s.), 7.34–7.28 (2H, m), 7.33–7.26 (1H, m), 6.85–6.72 (3H, m), [1H in total, two regioisomers: (6.64, t, $J_{H\text{-}Sn}$ = 6.6 Hz) + (6.62, t, $J_{H\text{-}Sn}$ = 6.8 Hz), thiophene H-2/5], 4.04 (2H, s, CH_2), [9H in total, two regioisomers: (0.39, t, $J_{H\text{-}Sn}$ = 28.8 Hz) + (0.38, t, $J_{H\text{-}Sn}$ = 29.2 Hz), $(CH_3)_3Sn$)].

2Na-PheDOT trimer, $(2Na\text{-}PheDOT)_3$



Under argon, stannic derivative **23** from the above synthesis (340 mg / 85% purity, 0.586 mmol, 2.42 eq.), dibromide **22** (118 mg, 0.242 mmol, 1.00 eq), Pd $(PPh_3)_4$ (28 mg, 0.024 mmol, 0.1 eq.), dry CuI (9.1 mg, 0.048 mmol, 0.2 eq.) and dry CsF (147 mg, 0.968 mmol, 4.0 eq.) were charged to the flask with stirring bar and dried *in vacuo* (<0.05 mbar) for 1 hour. The flask was purged with argon, dry DMF (4 mL) was added and the mixture was stirred + 50 °C for 14 hours and then + 70 ° C for additional 22 hours, during which period the color of the mixture (suspension) is changed from light-brown to darker brownish-orange color. The reaction progress was monitored by TLC of the reaction mixture probes.

After completion of the reaction, the solvent was evaporated to dryness, 10% HCl (20 mL) was added to the residue and the mixture was stirred for 10 min. The precipitate was filtered off, washed with warm water (10 × 10 mL) and dried *in vacuo* to afford crude material (391 mg, > 100%) as a brown solid. The crude product was transferred into Soxhlet apparatus with a short silica gel column (D×H = 2 × 4 cm) and washed with hot PE (4 × 300 mL). After evaporation of PE, starting monomer **2Na-PheDOT** (94 mg) as a white solid was regenerated. The residual product on the silica gel column in the Soxhlet apparatus was then extracted by hot toluene for 2 days to yield (after solvent evaporation) crude trimer **$(2Na\text{-}PheDOT)_3$** (99.6 mg, 41.7%) as a light brown solid.

Further extraction of the residue in the Soxhlet apparatus with hot toluene for 1 day gave an additional portion of somewhat less pure trimer **(2Na-PheDOT)$_3$** (19.7 mg, 8.2%) as a light brown solid.

The trimer (**2Na-PheDOT)$_3$** is very insoluble material, so we were unable to record a good quality ^{1}H NMR spectrum for it to identify and properly integrate all the signals. It was characterized by MALDI MS showing good coincidence of experimental and theoretical mass spectra (including isotope mass distribution of the molecular ion; see a copy of its MS in ESI).

MS (MALDI): *m/z*: 986.1841; calcd for $C_{63}H_{38}O_6S_3$: 986.1831.

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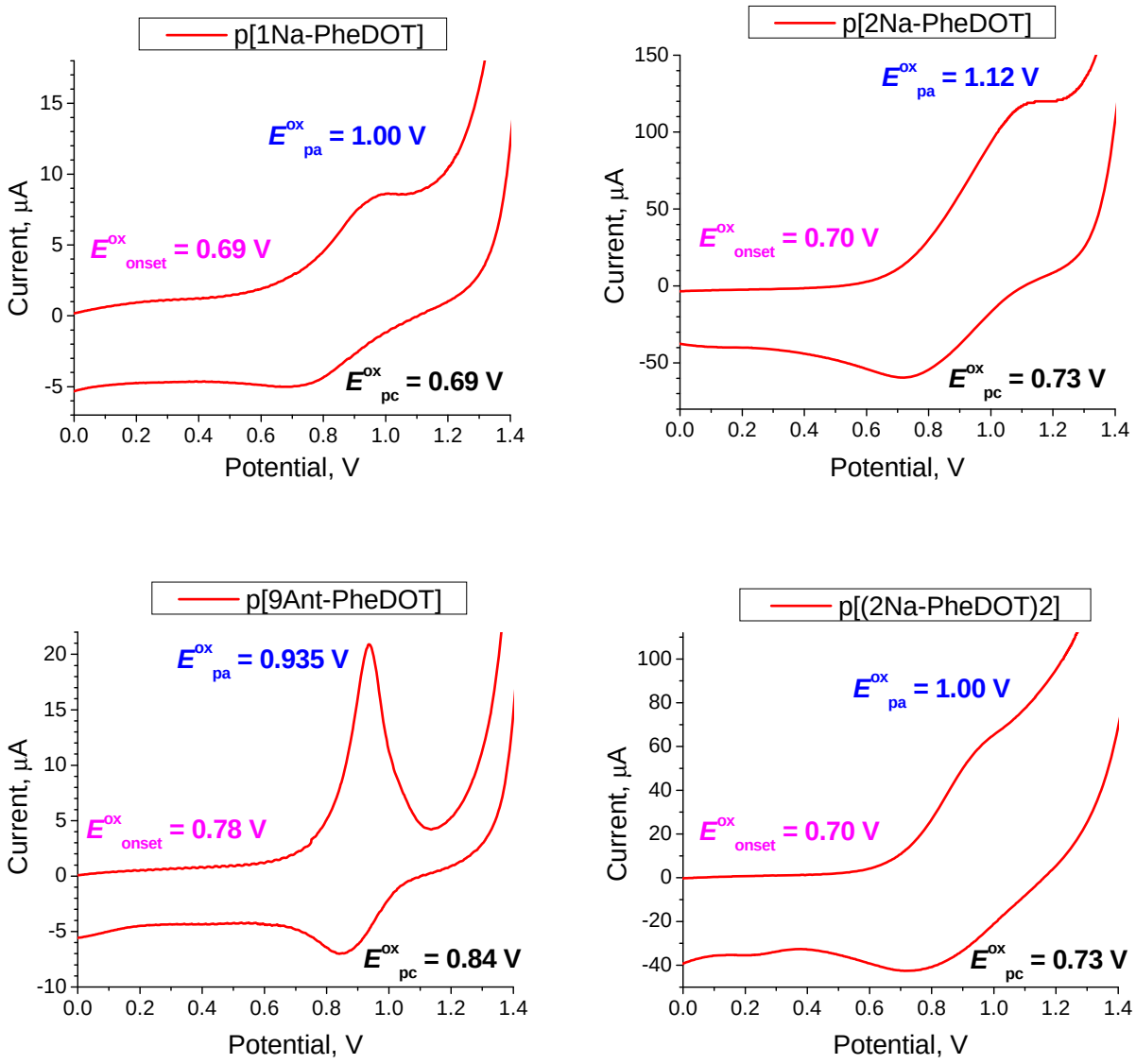
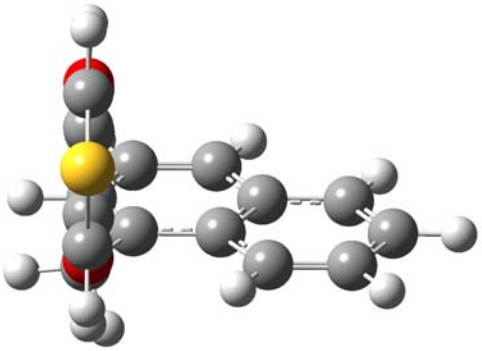
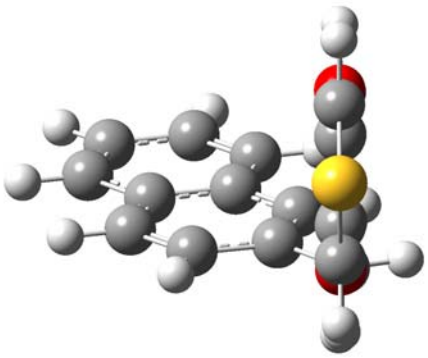


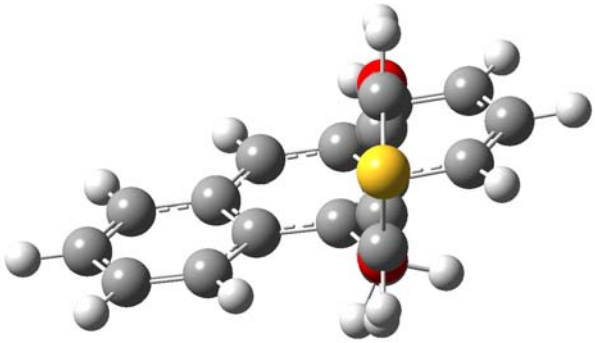
Figure S1. Cyclic voltammograms of electrodeposited films of **p[1Na-PheDOT]**, **p[2Na-PheDOT]**, **p[9Ant-PheDOT]**, and **p[(2Na-PheDOT)$_2$]** polymers in 0.1 M **Bu_4NClO_4** / DCM, scan rate 20 mV/s. Working electrode: gold plate (2 cm^2). Potentials are versus SCE reference electrode.



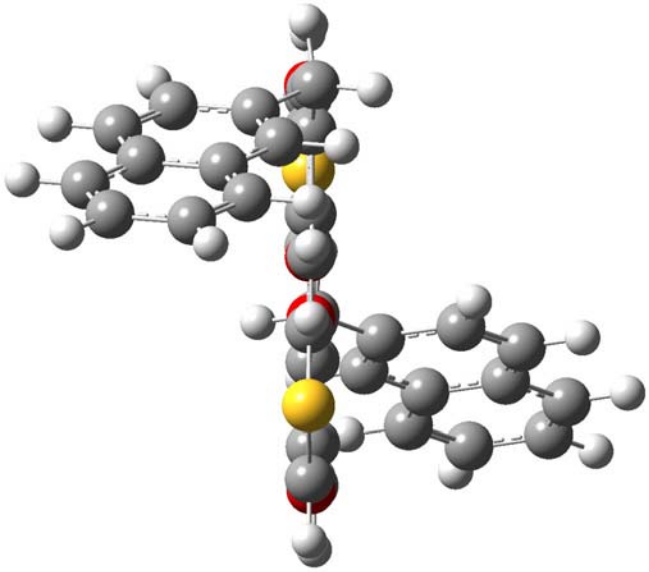
1Na-PheDOT
E_{total} =- –1357.2819824 Hartree
LUMO = –1.041 eV
HOMO = –5.427 eV
E_g = 4.386 eV



2Na-PheDOT
E_{total} = –1357.28452 Hartree
LUMO = –1.001 eV
HOMO = –5.435 eV
E_g = 4.434 eV



9Ant-PheDOT
E_{total} =- –1510.914667 Hartree
LUMO = –1.735 eV
HOMO = –5.230 eV
E_g = 3.495 eV



(2Na-PheDOT)$_2$
E_{total} = –2713.3813966 Hartree
LUMO = –1.186 eV
HOMO = –5.261 eV
E_g = 4.075 eV

Figure S2. B3LYP/6-31G(d) optimized geometries (in a gas phase) for **1Na-PheDOT**, **2Na-PheDOT** **9Ant-PheDOT**, and **(2Na-PheDOT)$_2$** showing the orientation of naphthalene and anthracene groups out-of-plane of the PheDOT moiety and their HOMO/LUMO energies and the energy gaps (E_g). For clarity, the projections of the structures are shown with an orientation of PheDOT moiety to be perpendicular to the plane of the sheet.

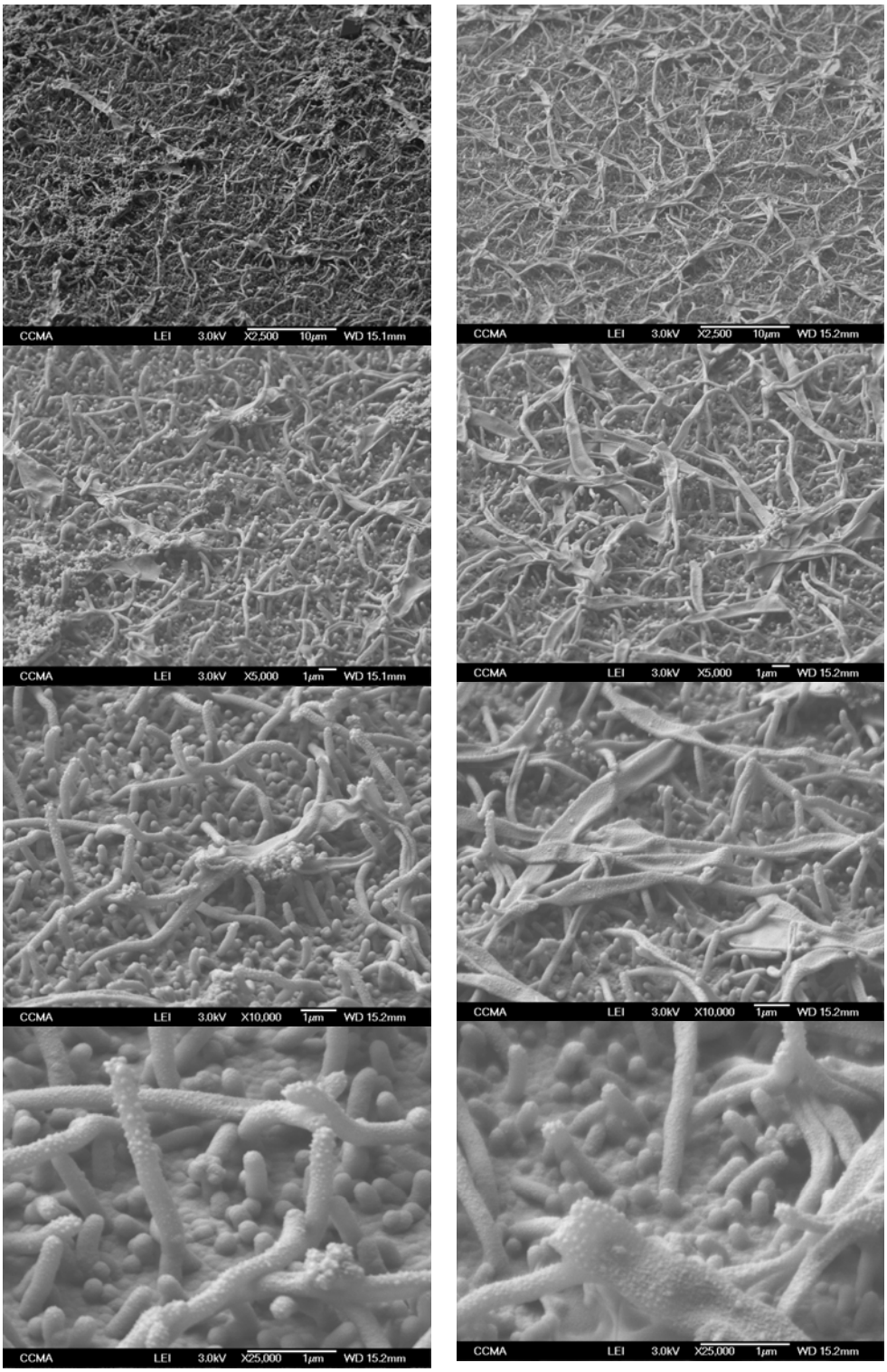


Figure S3. SEM images of the **p[1Na-PheDOT]** polymer surfaces obtained by electropolymerization of **1Na-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charge of Q_s = **100 mC cm^{-2}**, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×2,500, ×5,000, ×10,000, ×25,000.
The images in two columns correspond to the different places of the sample.

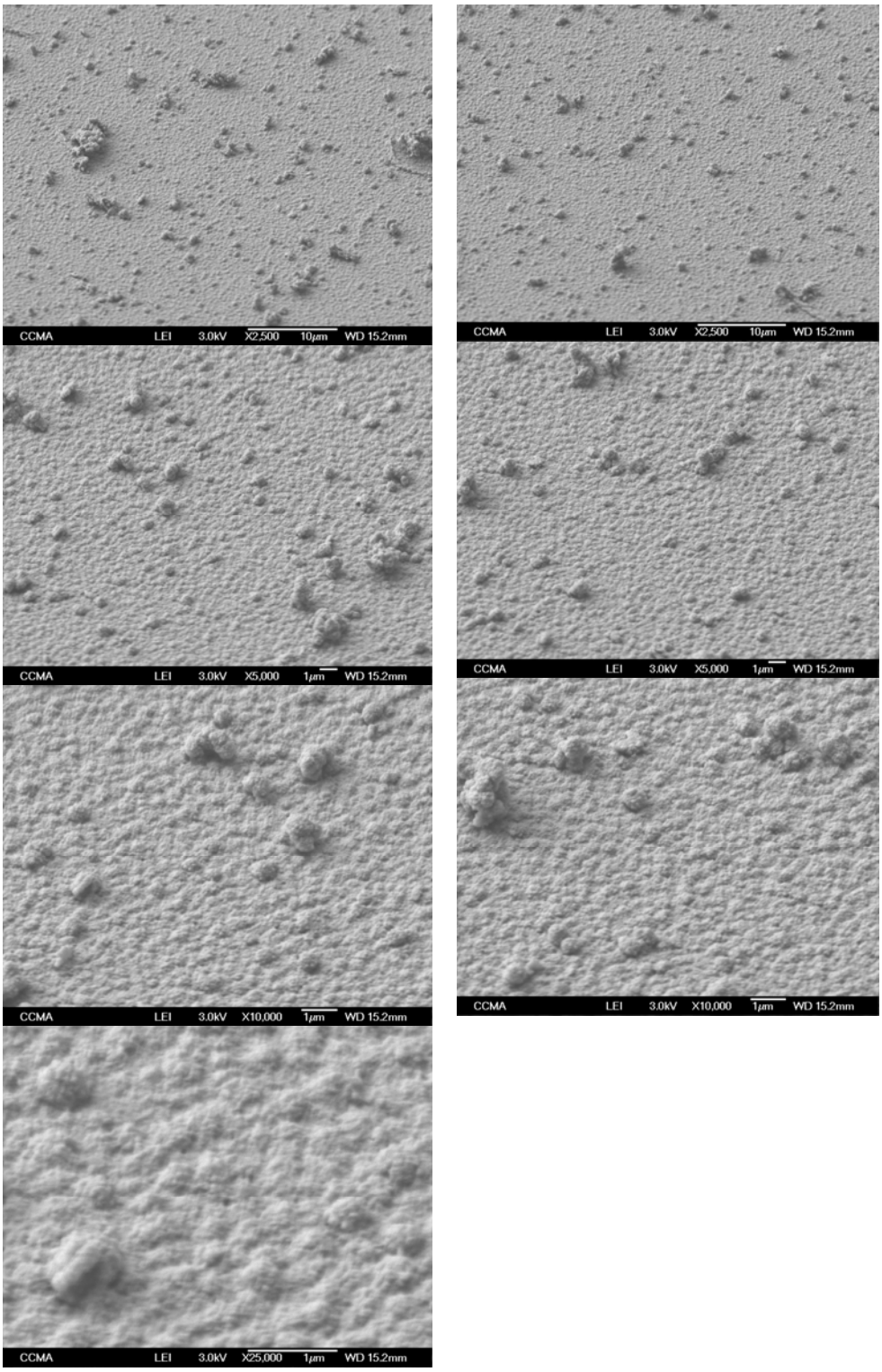


Figure S4. SEM images of the **p[2Na-PheDOT]** polymer surfaces obtained by electropolymerization of the dimer **(2Na-PheDOT)$_2$** (0.5 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 – 1.80$ V *vs.* SCE and the deposition charge of Q_s = **100 mC cm^{-2}**, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×2,500, ×5,000, ×10,000, ×25,000.
The images in two columns correspond to the different places of the sample.

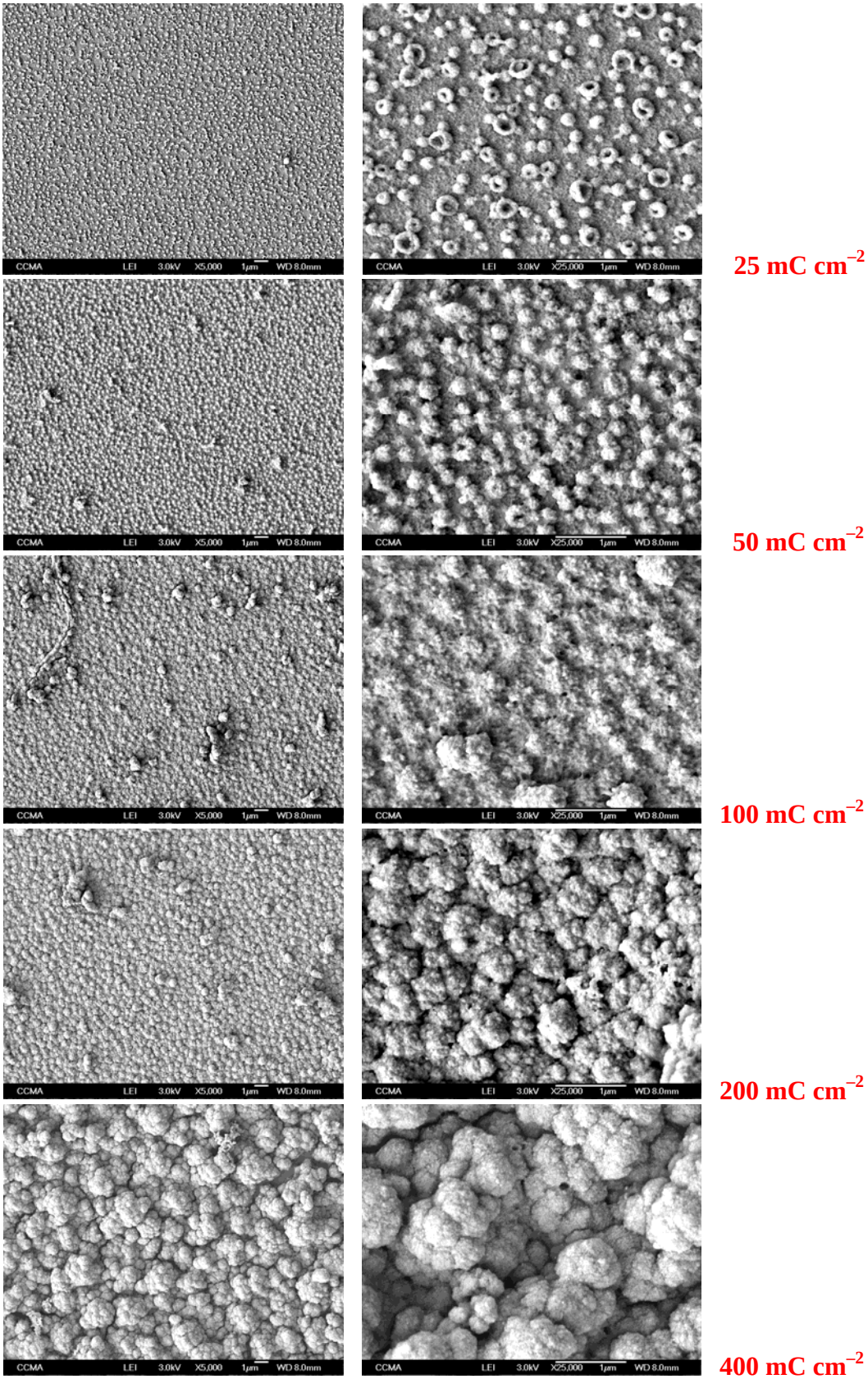


Figure S5. SEM images of the **p[2Na-PheDOT]** polymer surfaces obtained by electropolymerization of the dimer **(2Na-PheDOT)$_2$** (0.5 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of Q_s = 25, 50, 100, 200 and 400 mC cm^{-2}. Magnification: ×5,000 (left column), ×25,000 (right column).

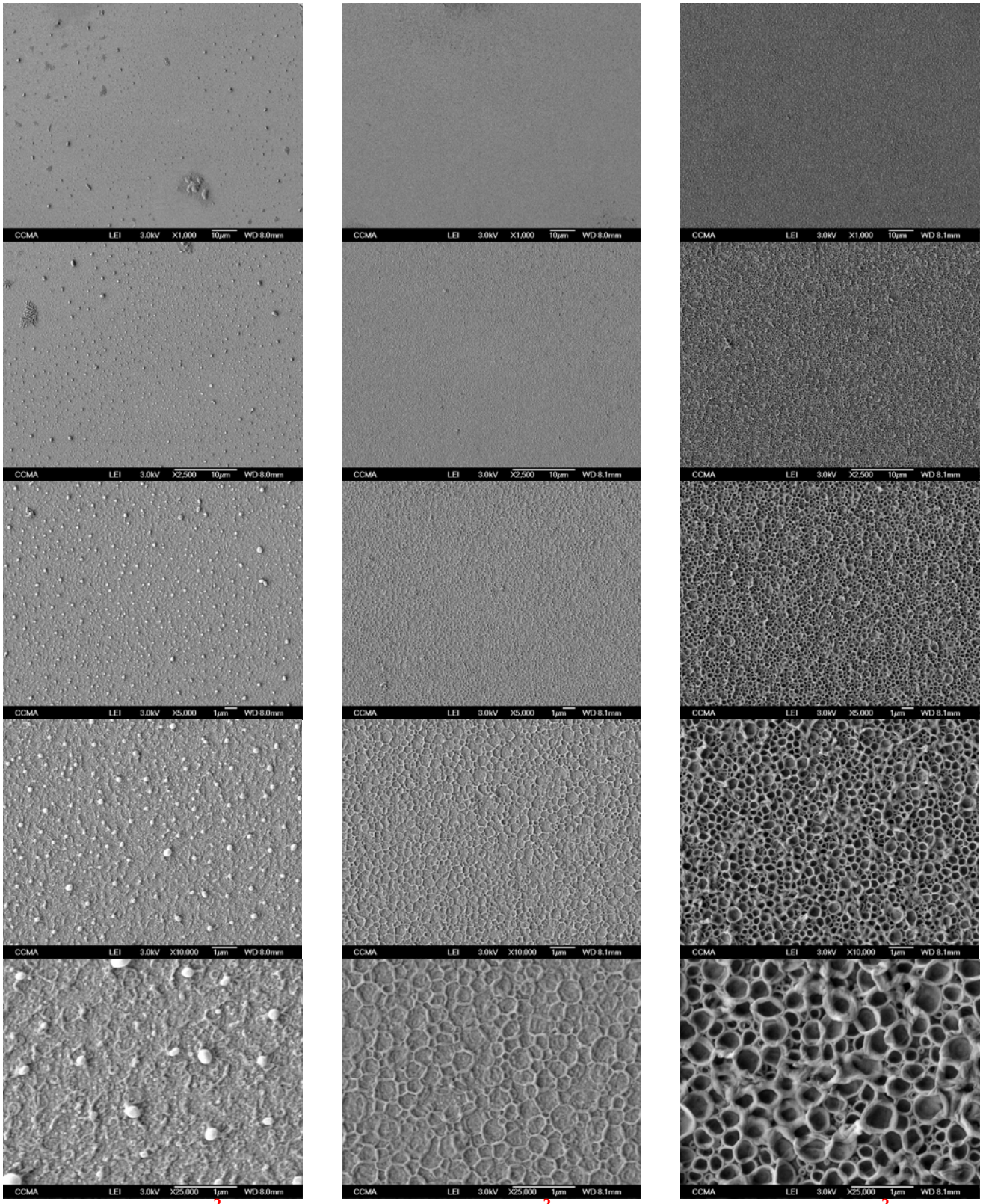


Figure S6. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M Bu_4NClO_4 / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of Q_s = 12.5, 25, and 50 mC cm^{-2}. Magnification from the top to the bottom: ×1,000, ×2,500, ×5,000, ×10,000, ×25,000.

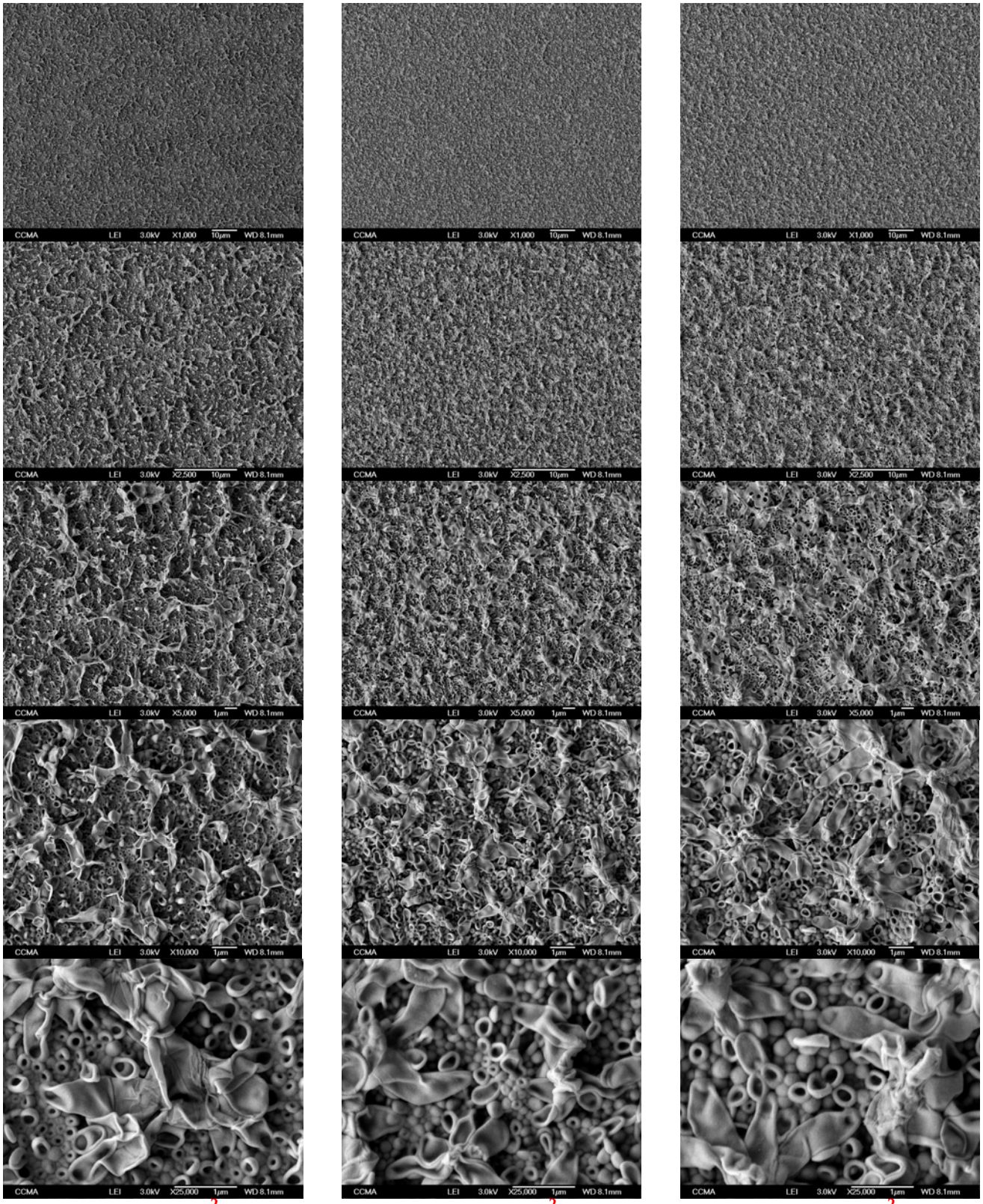


Figure S7. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M Bu_4NClO_4 / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70$–1.80 V *vs.* SCE and the deposition charges of Q_s = 100, 200, and 400 mC cm^{-2}. Magnification from the top to the bottom: ×1,000, ×2,500, ×5,000, ×10,000, ×25,000.

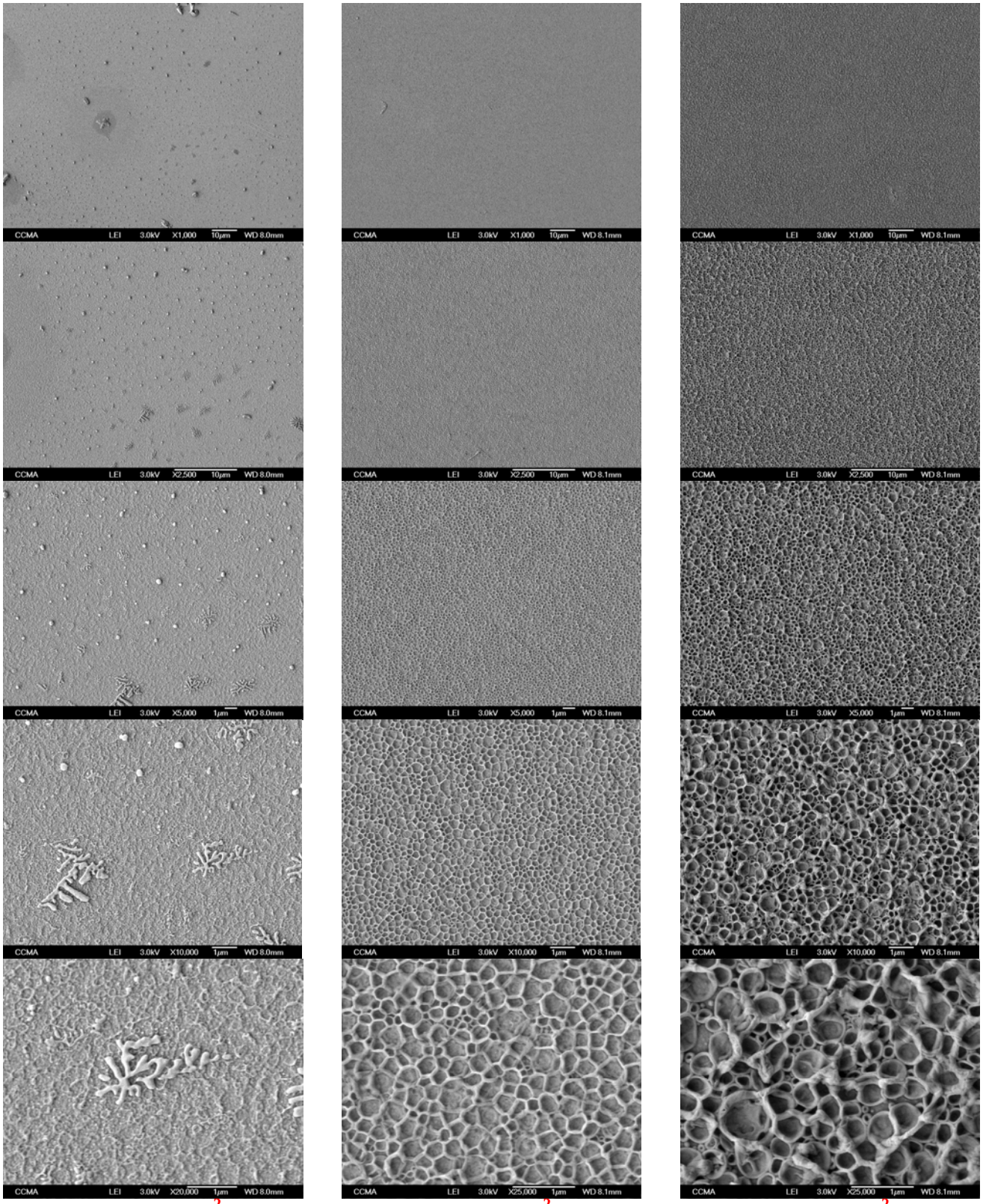


Figure S8. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M Bu_4NClO_4 / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of Q_s = 12.5, 25, and 50 mC cm^{-2}. Magnification from the top to the bottom: ×1,000, ×2,500, ×5,000, ×10,000, ×25,000.
Different areas of the sample (as of Figures S4) are shown.

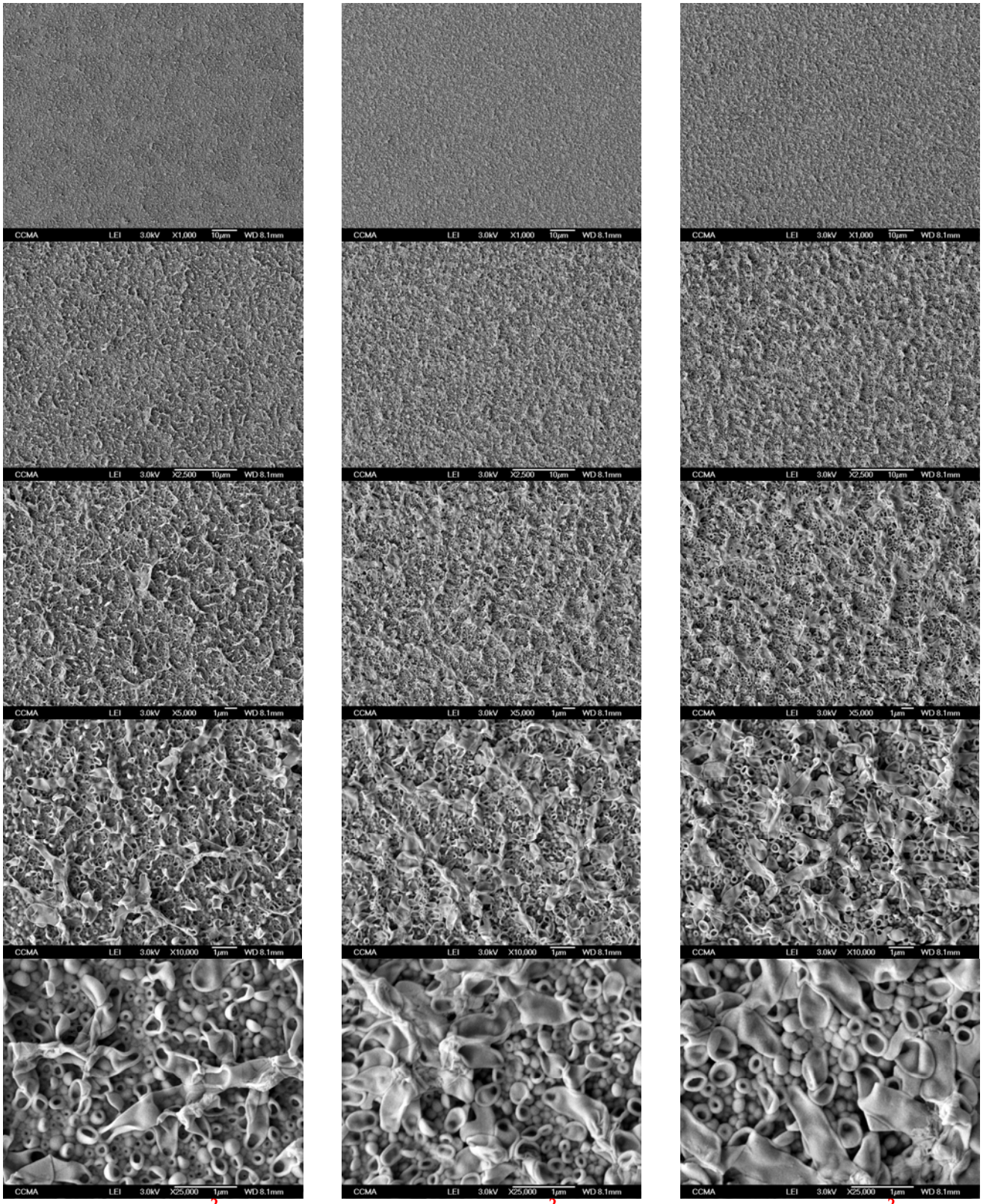


Figure S9. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M Bu_4NClO_4 / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70–1.80$ V *vs.* SCE and the deposition charges of Q_s = 100, 200, and 400 mC cm^{-2}. Magnification from the top to the bottom: ×1,000, ×2,500, ×5,000, ×10,000, ×25,000.
Different areas of the sample (as of Figures S5) are shown.

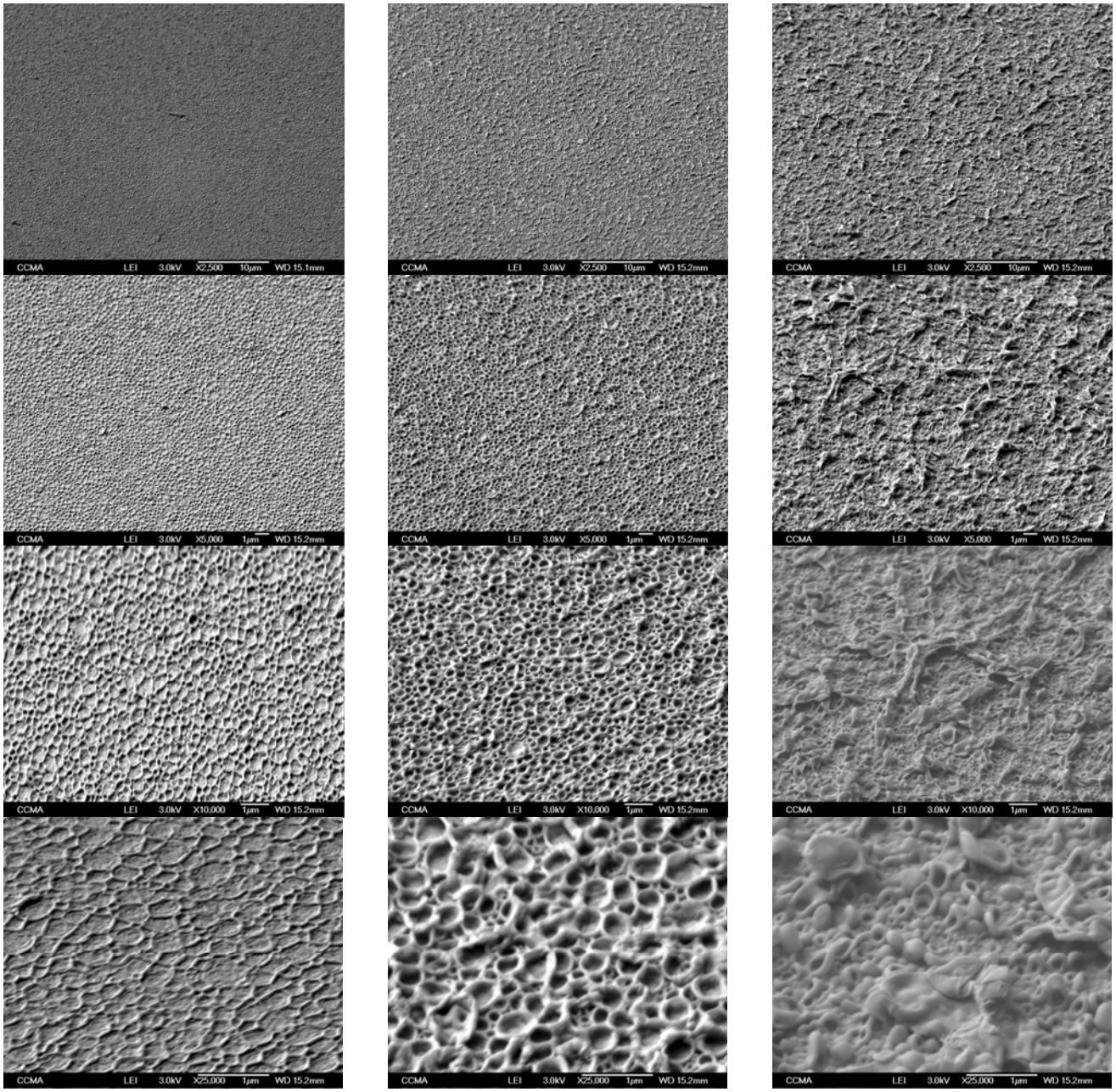
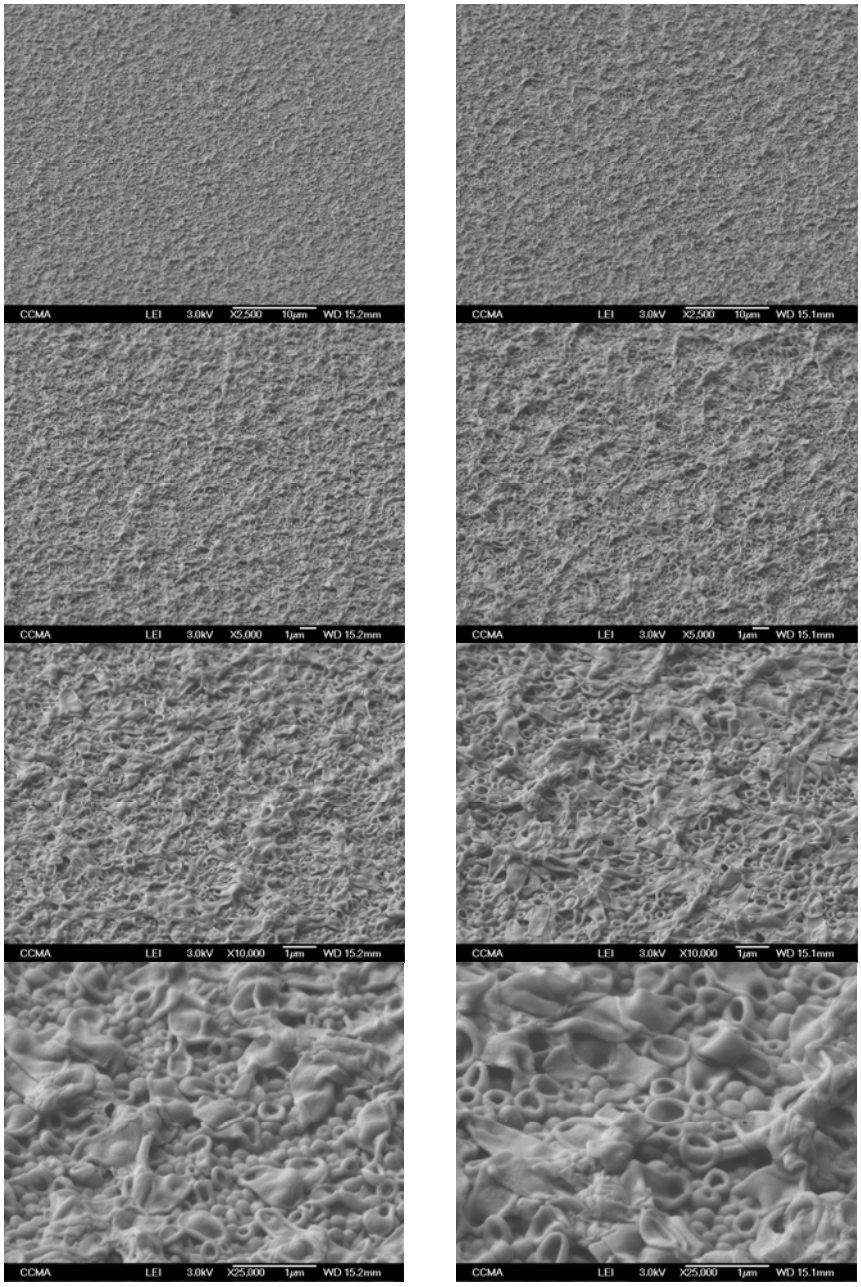


Figure S10. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of $Q_s = 25$, 50, and 100 mC cm^{-2}, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×2,500, ×5,000, ×10,000, ×25,000.



200 mC cm^{-2} **400 mC cm^{-2}**

Figure S11. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of $Q_s = 200$ and 400 mC cm^{-2}, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×2,500, ×5,000, ×10,000, ×25,000.

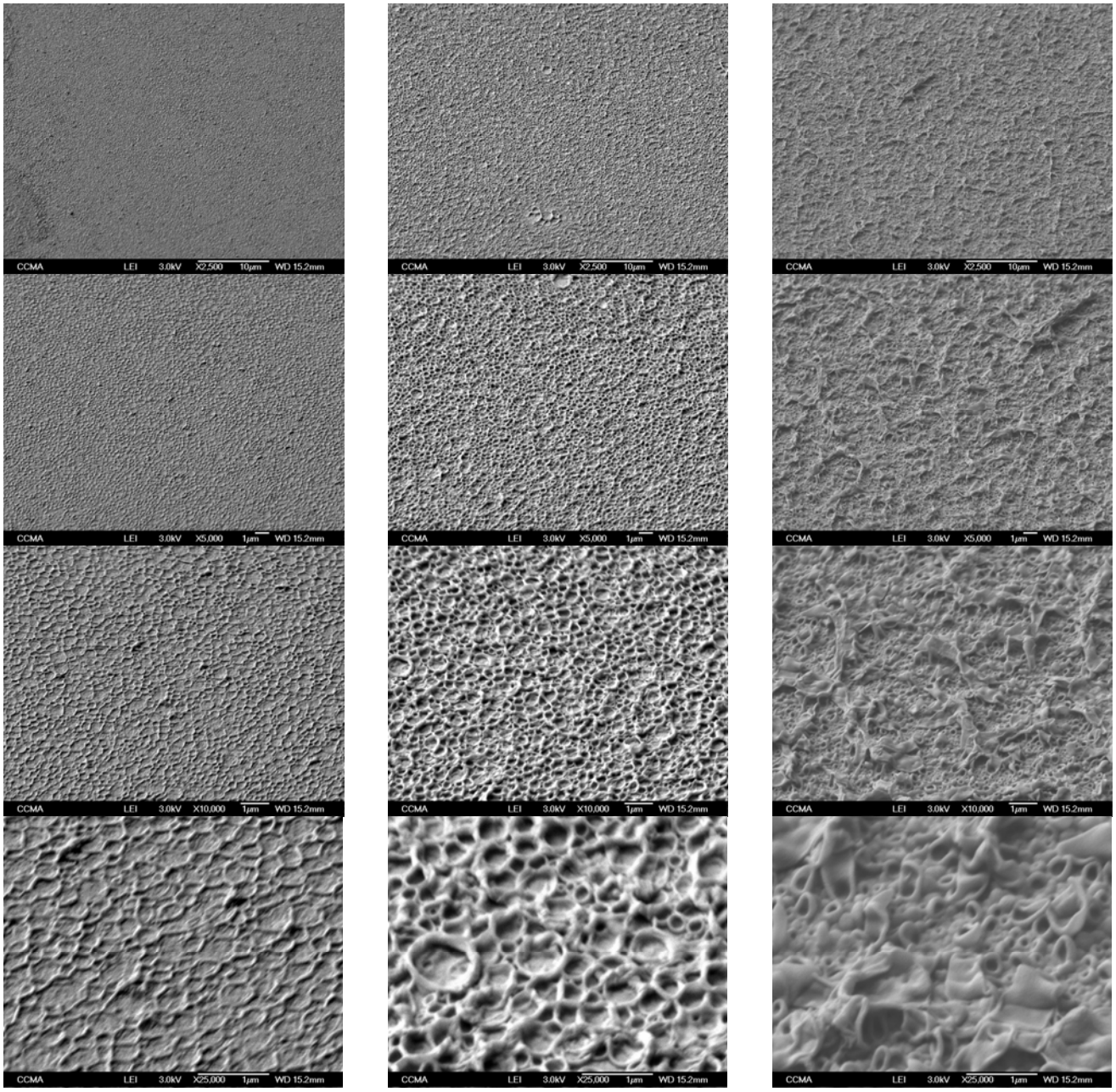


Figure S12. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of $Q_s = 25$, 50, and 100 mC cm^{-2}, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×2,500, ×5,000, ×10,000, ×25,000.
Different areas of the sample (as of Figures S8) are shown.

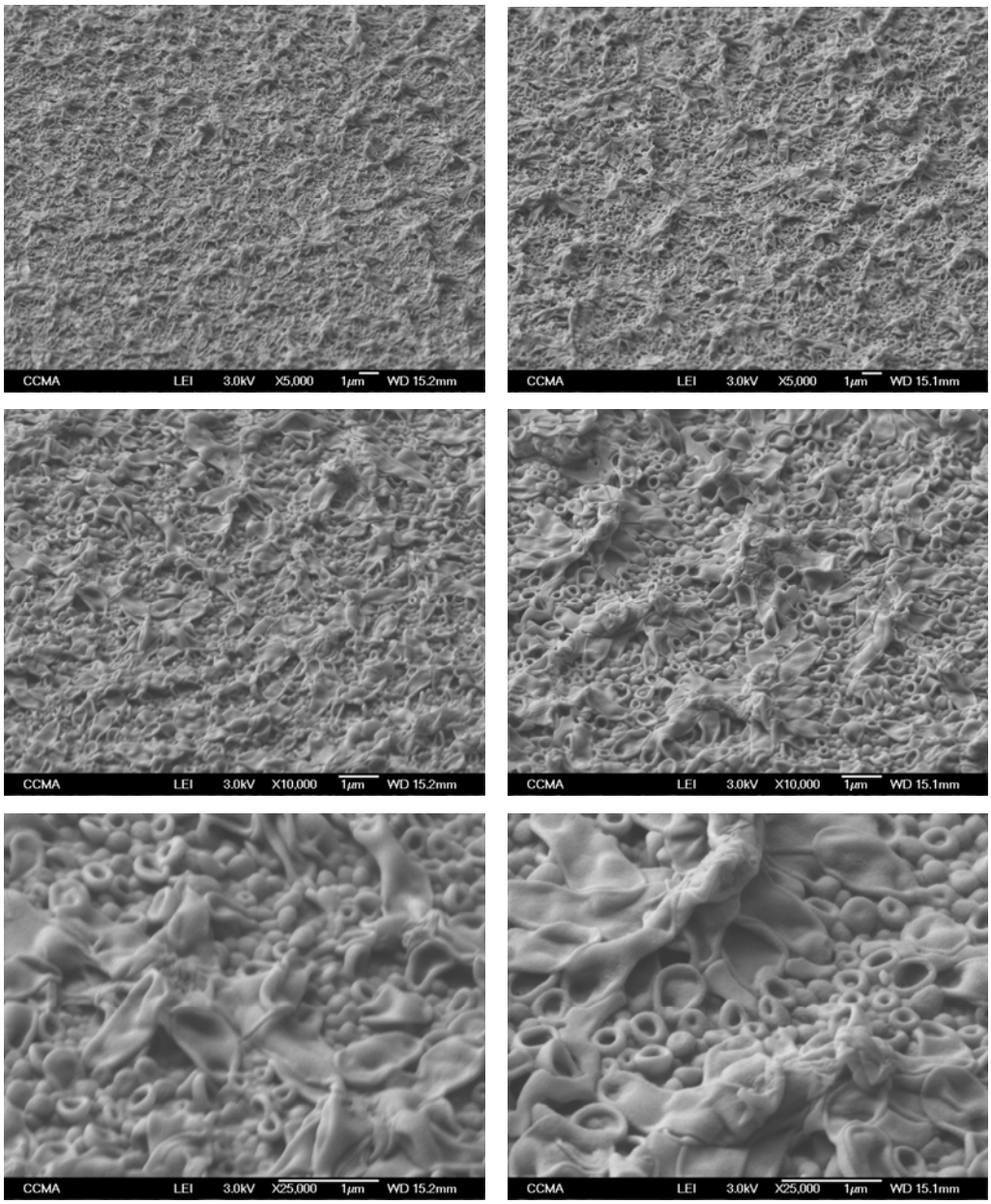


Figure S13. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of $Q_s = 200$ and 400 mC cm^{-2}, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×5,000, ×10,000, ×25,000.
Different areas of the sample (as of Figures S9) are shown.

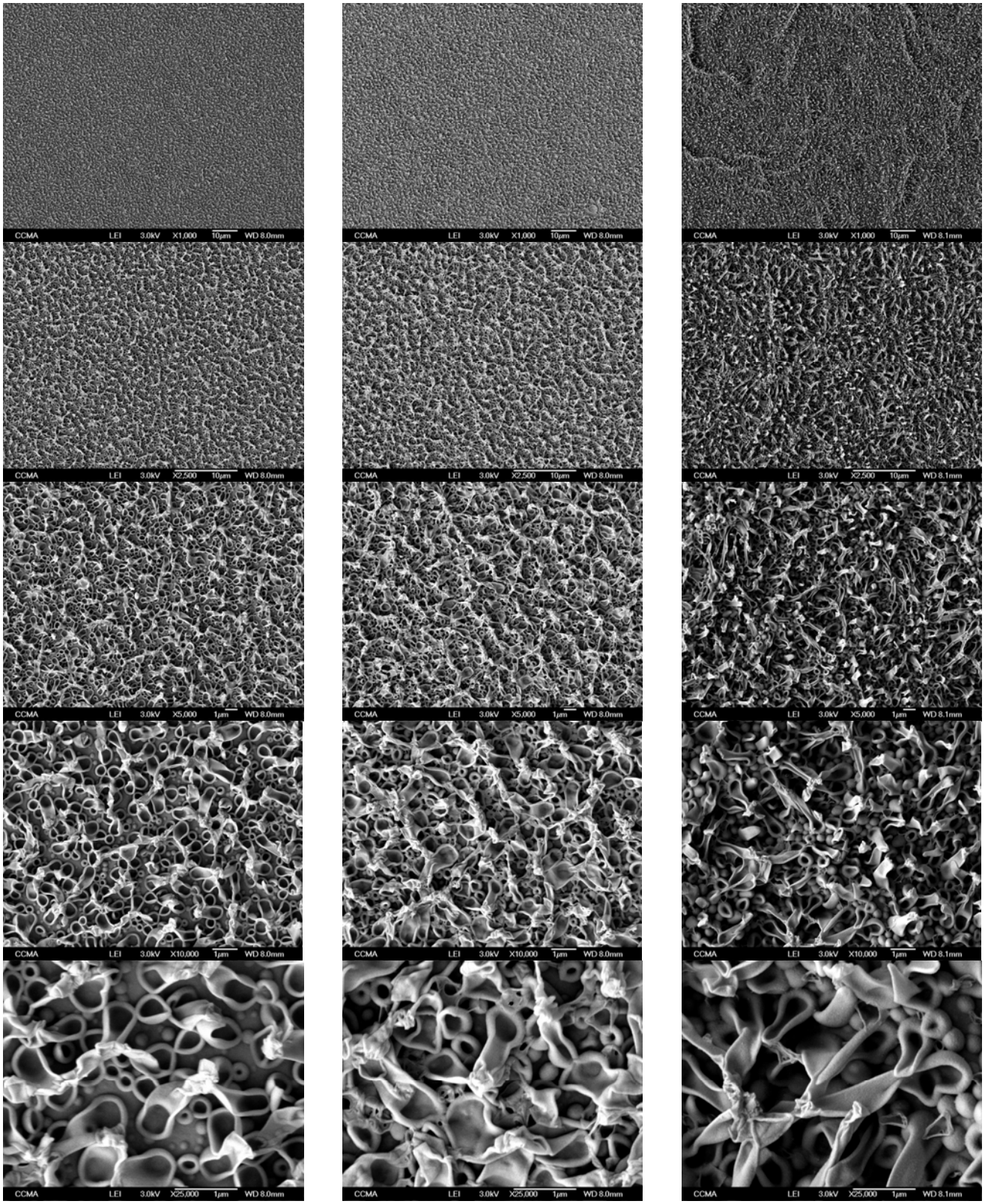


Figure S14. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M Bu_4NClO_4 / DCM in potentiodynamic conditions by cyclic voltammetry (E = –1 / +1.7–1.8 V) after 1, 3 and 5 scans of depositions. Magnification from the top to the bottom: ×1,000, ×2,500, ×5,000, ×10,000, ×25,000.

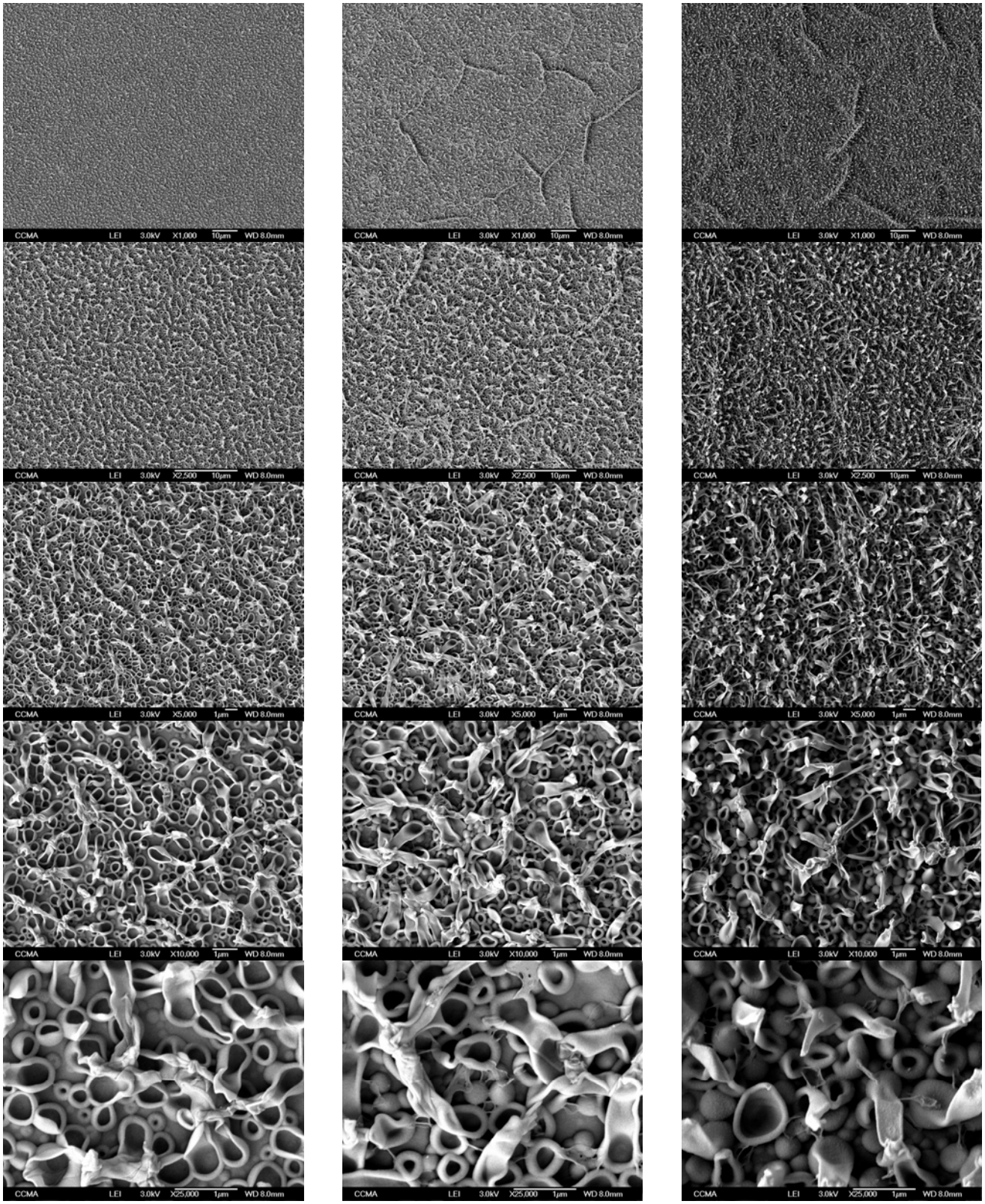


Figure S15. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiodynamic conditions by cyclic voltammetry (E = –1 / +1.7–1.8 V) after 1, 3 and 5 scans of depositions. Magnification from the top to the bottom: ×1,000, ×2,500, ×5,000, ×10,000, ×25,000. Different areas of the sample (as of Figures S12) are shown.

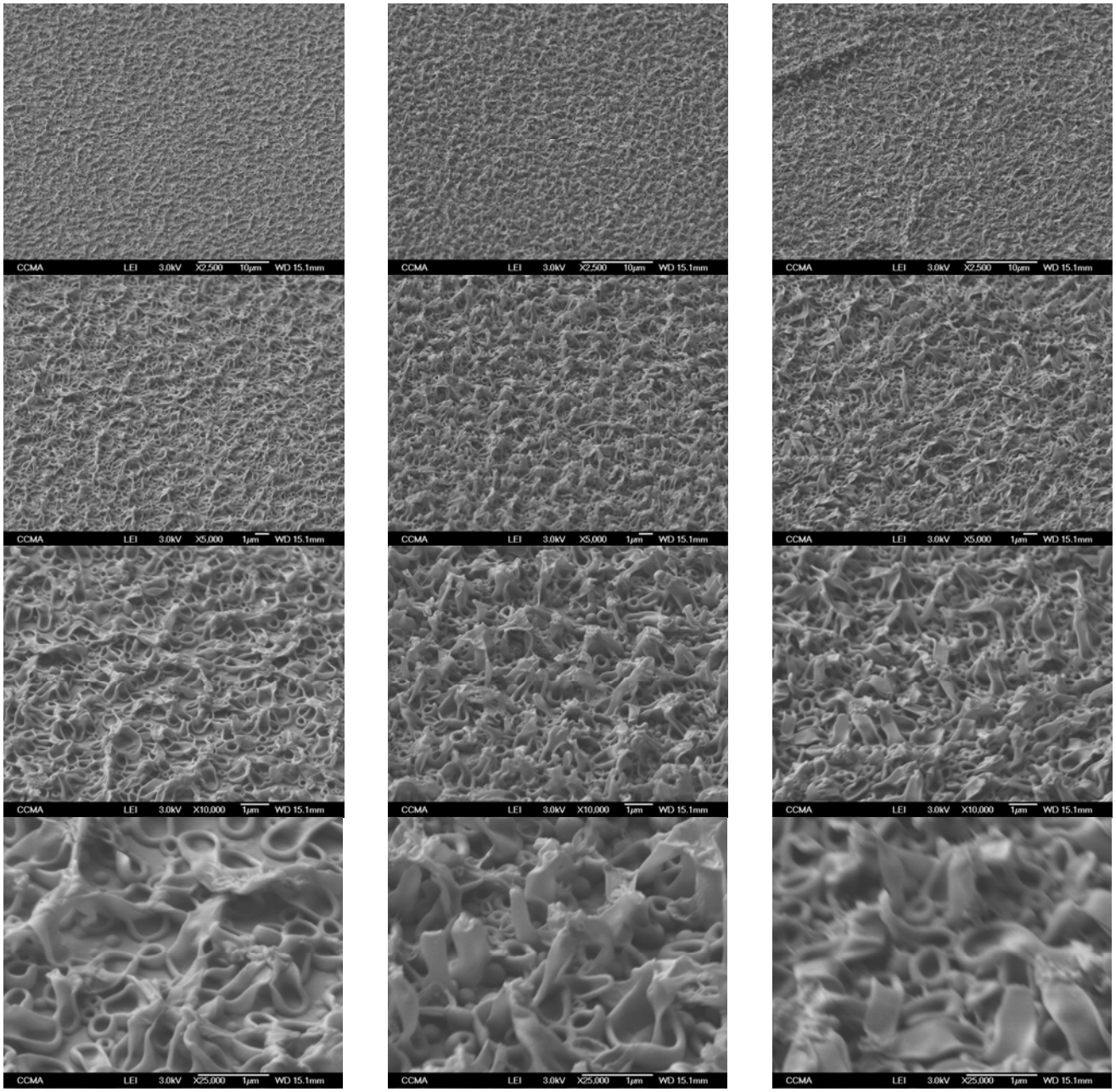


Figure S16. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiodynamic conditions by cyclic voltammetry (E = –1 / +1.7–1.8 V) after 1, 3 and 5 scans of depositions, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×2,500, ×5,000, ×10,000, ×25,000.

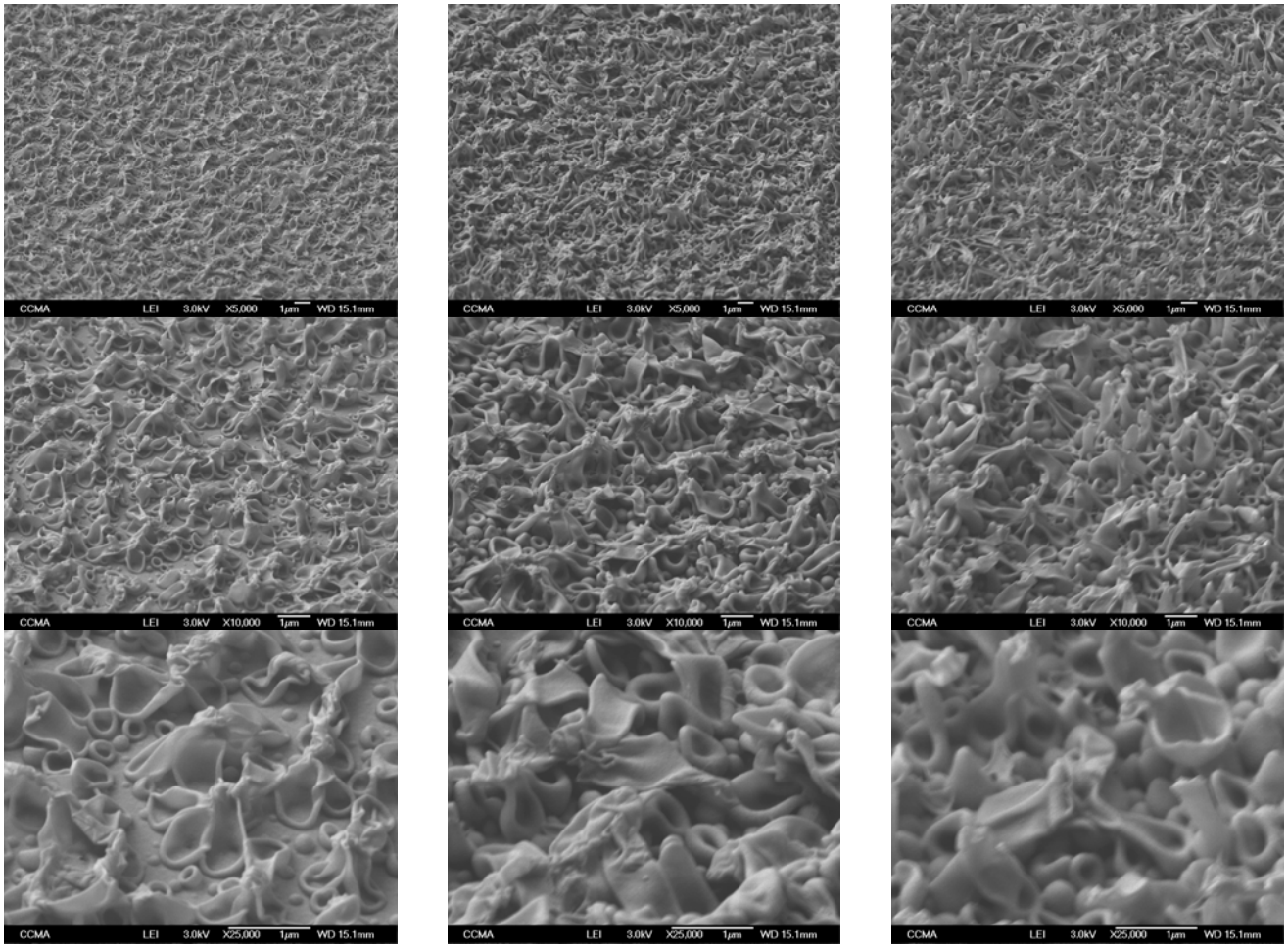


Figure S17. SEM images of the **p[9Ant-PheDOT]** polymer surfaces obtained by electropolymerization of **9Ant-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / DCM in potentiodynamic conditions by cyclic voltammetry (E = –1 / +1.7–1.8 V) after 1, 3 and 5 scans of depositions, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×5,000, ×10,000, ×25,000.
Different areas of the sample (as of Figures S14) are shown.

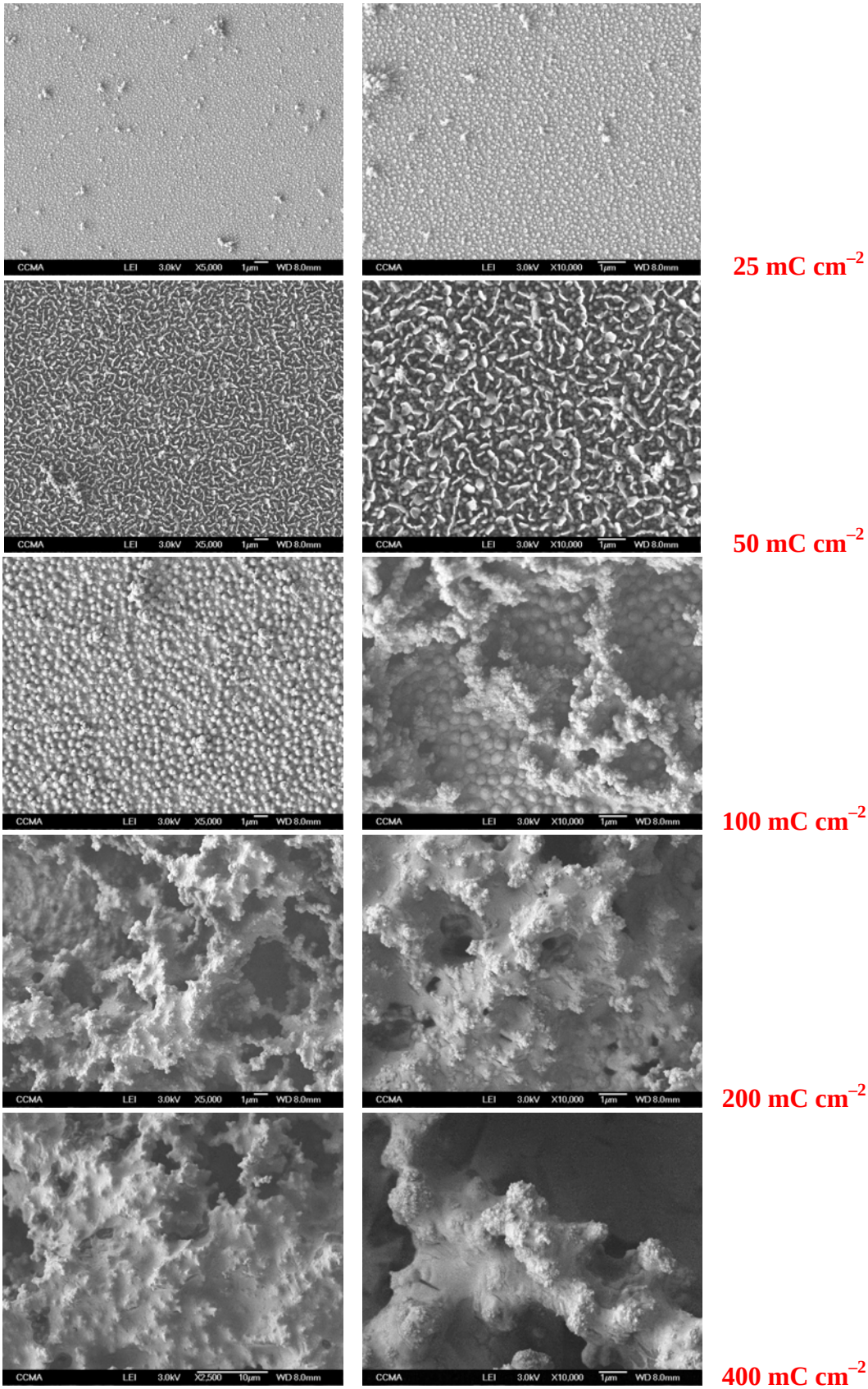


Figure S18. SEM images of the **p[1Na-PheDOT]** polymer surfaces obtained by electropolymerization of **1Na-PheDOT** (10 mM) in 0.1 M Bu_4NPF_6 / DCM in potentiostatic conditions at constant potential of $E^{ox} \approx 1.70 - 1.80$ V *vs.* SCE and the deposition charges of $Q_s = 25$, 50, 100, 200 and 400 mC cm^{-2}. Magnification: ×5,000 (left column), ×10,000 (right column).

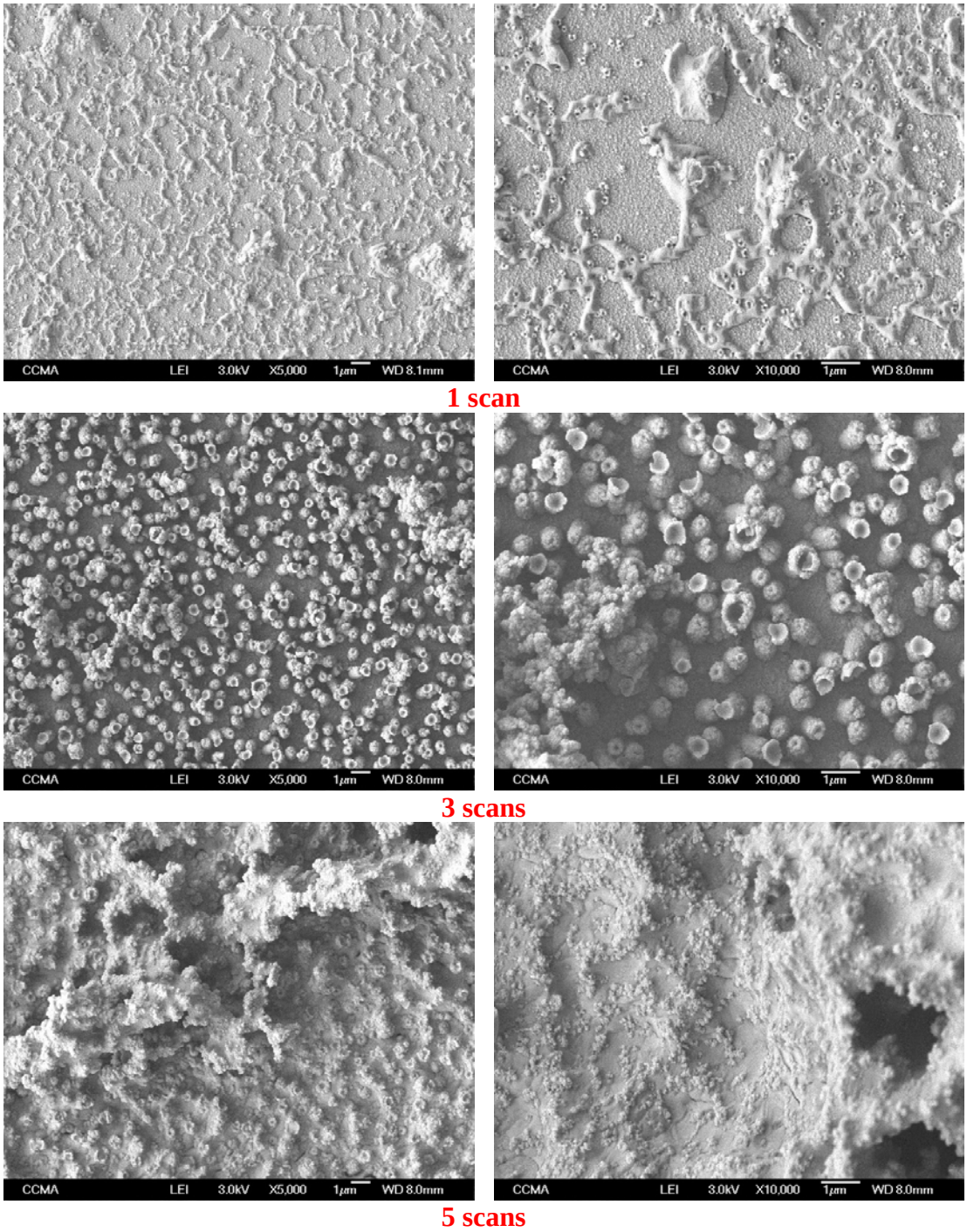


Figure S19. SEM images of the **p[1Na-PheDOT]** polymer surfaces obtained by electropolymerization of **1Na-PheDOT** (10mM) in 0.1 M Bu_4NPF_6 / DCM in potentiodynamic conditions by cyclic voltammetry (E = –1 / + 1.70–1.80 V *vs.* SCE) after 1, 3 and 5 scans. Magnification: ×5,000 (left column), ×10,000 (right column)..

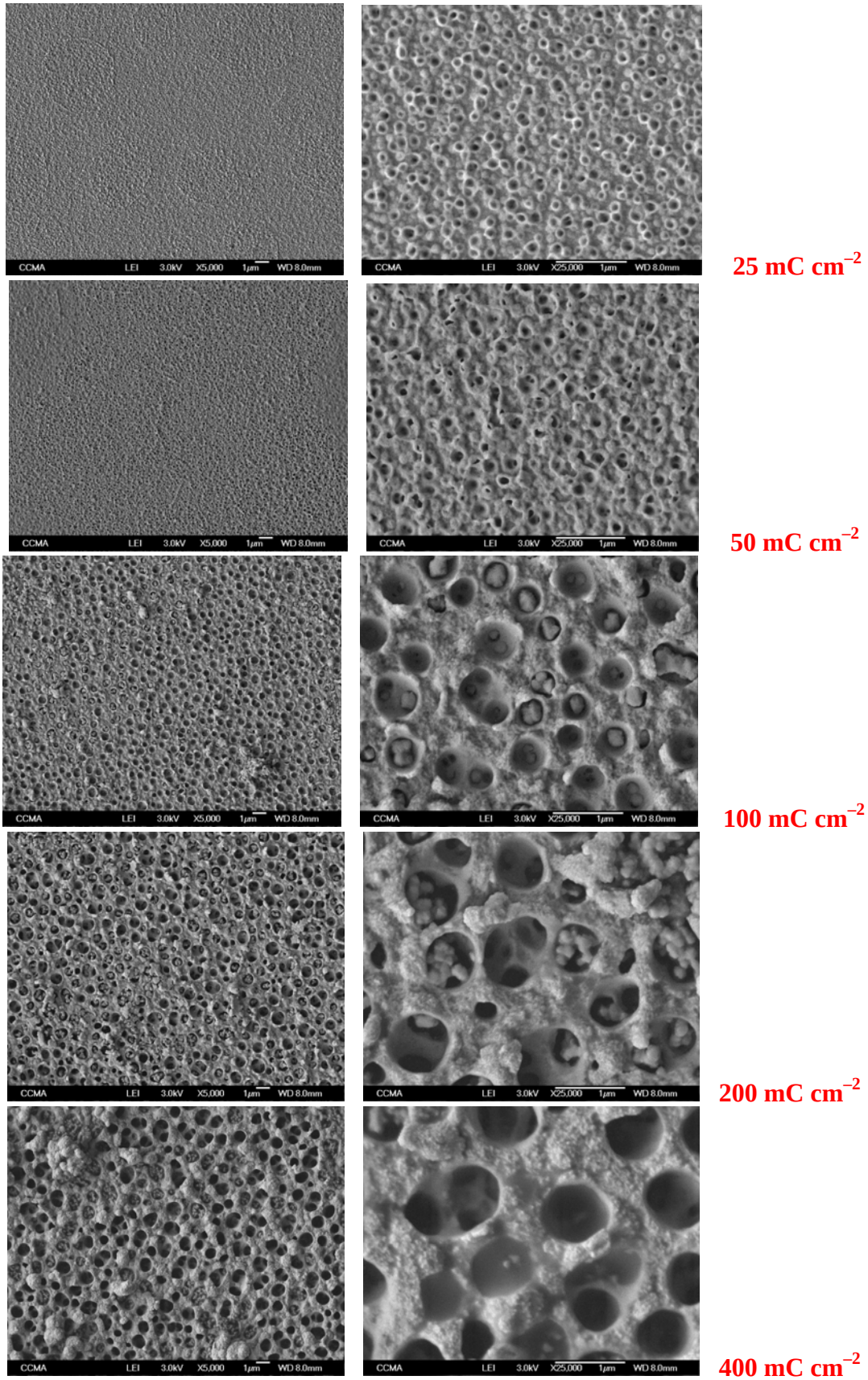
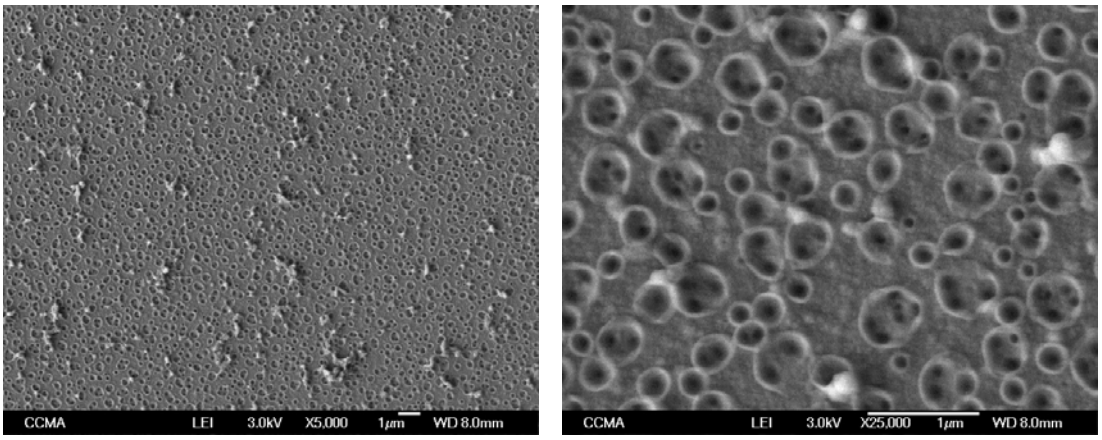
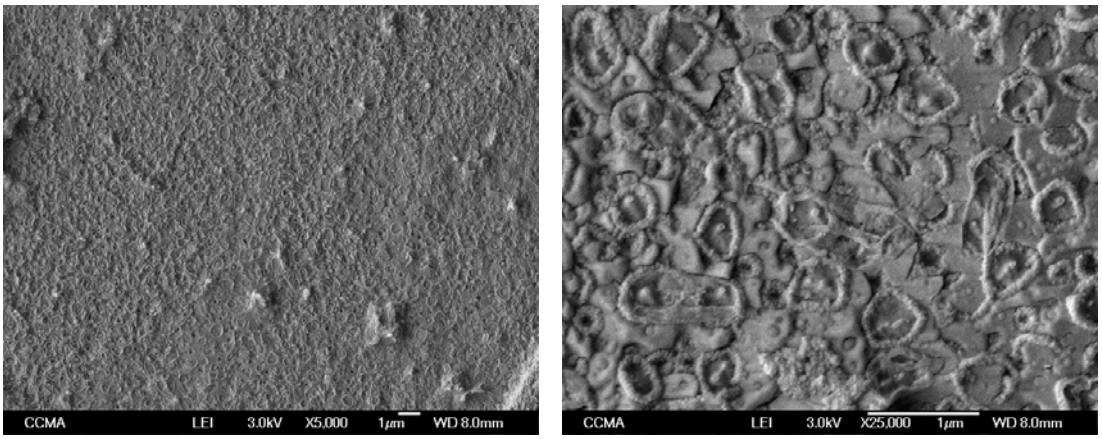


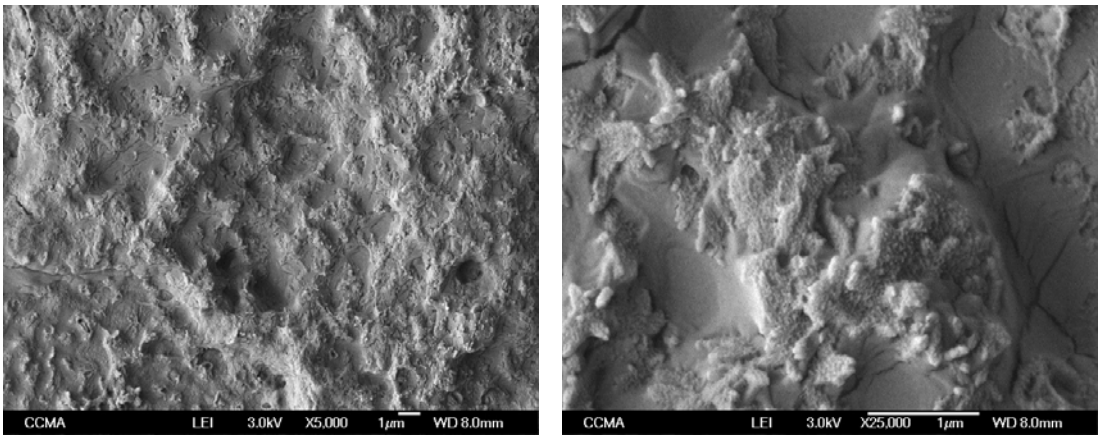
Figure S20. SEM images of the **p[2Na-PheDOT]** polymer surfaces obtained by electropolymerization of the dimer **(2Na-PheDOT)$_2$** (0.5 mM) in 0.1 M Bu_4NPF_6 / DCM in potentiostatic conditions at constant potential of E^{ox} = 1.67 V *vs.* SCE and the deposition charges of Q_s = 25, 50, 100, 200 and 400 mC cm^{-2}. Magnification: ×5,000 (left column), ×25,000 (right column).



1 scan



3 scans



5 scans

Figure S21. SEM images of the **p[2Na-PheDOT]** polymer surfaces obtained by electropolymerization of the dimer **(2Na-PheDOT)$_2$** (0.5 mM) in 0.1 M Bu_4NPF_6 / DCM in potentiodynamic conditions by cyclic voltammetry (E = –1 / + 1.67 V *vs.* SCE) after 1, 3 and 5 scans. Magnification: ×5,000 (left column), ×25,000 (right column).

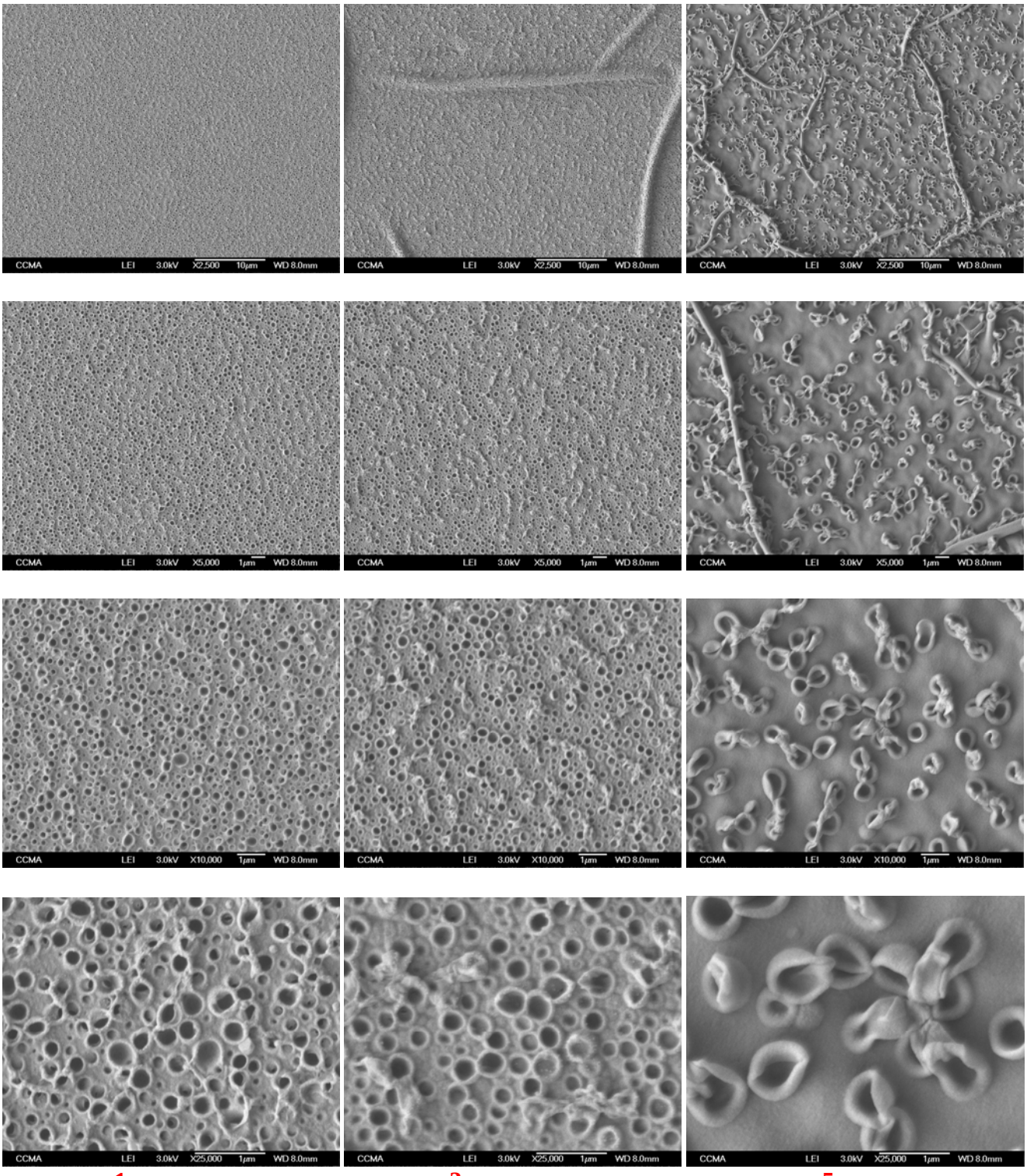


Figure S22. SEM images of the **p[2Na-PheDOT]** polymer surfaces obtained by electropolymerization of **2Na-PheDOT** (10 mM) in 0.1 M Bu_4NClO_4 / (DCM + H_2O) in potentiodynamic conditions by cyclic voltammetry (E = –1 / +1.8 V) after 1, 3 and 5 scans of depositions.
Magnification from the top to the bottom: ×2,500, ×5,000, ×10,000, ×25,000.

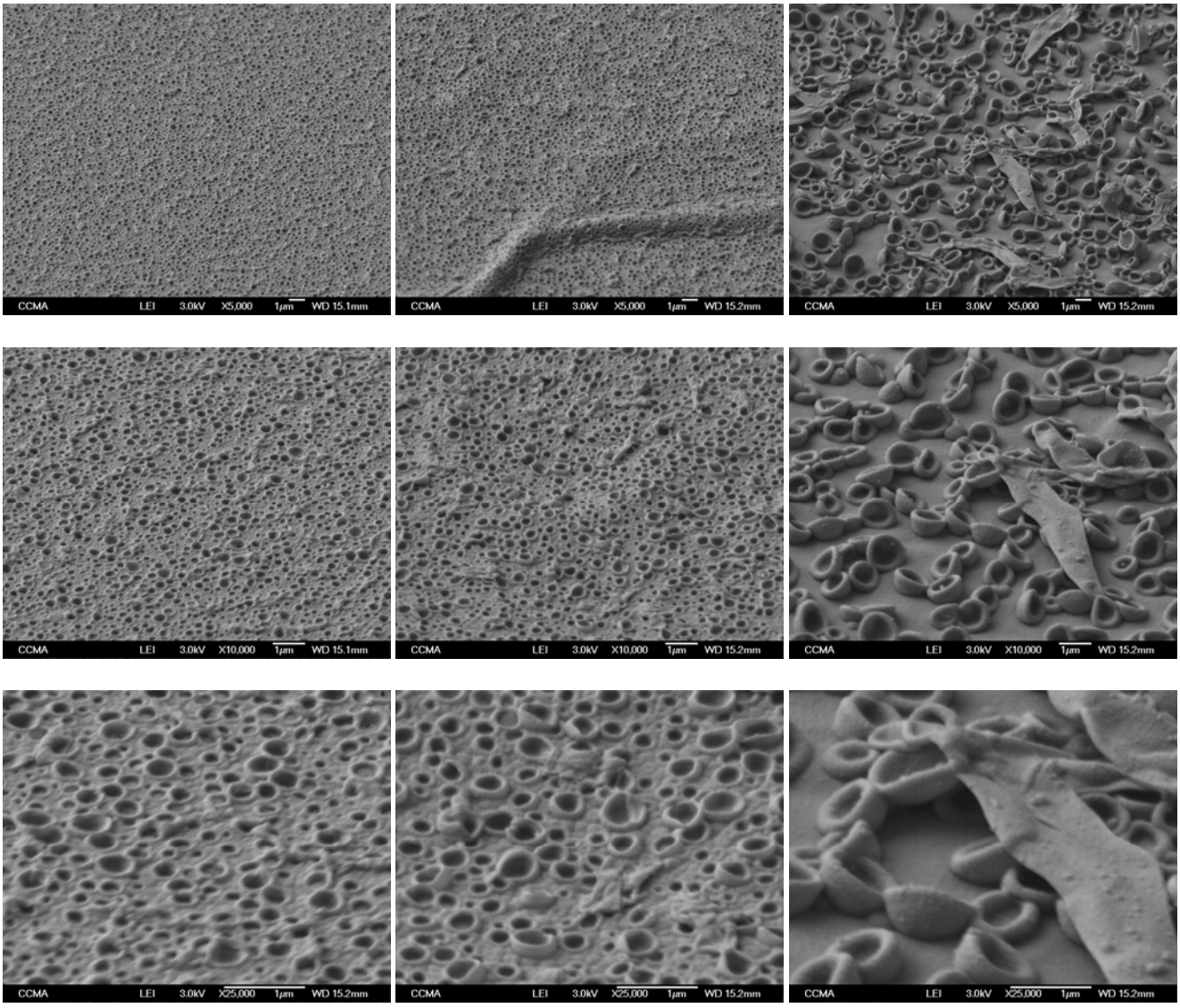
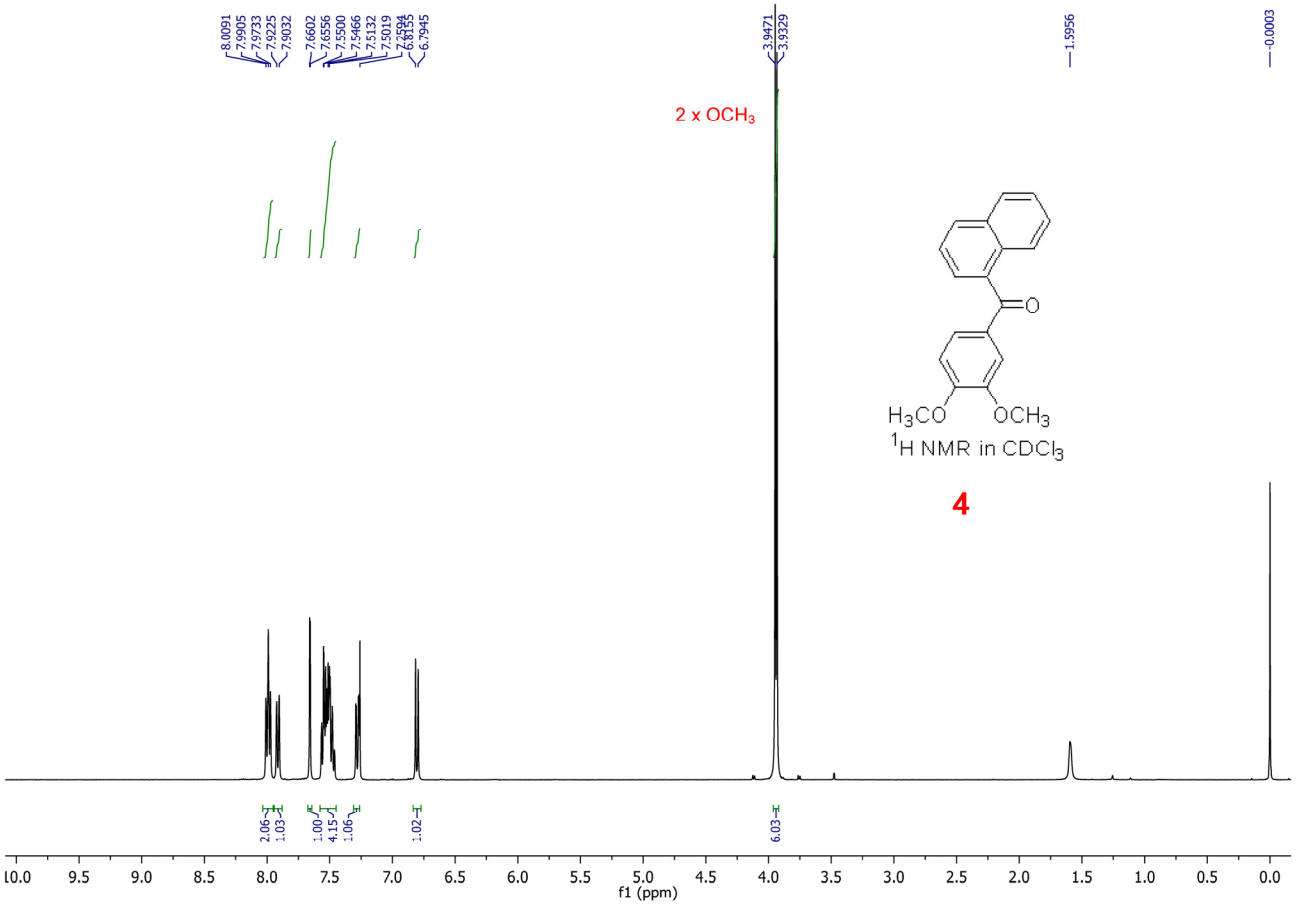
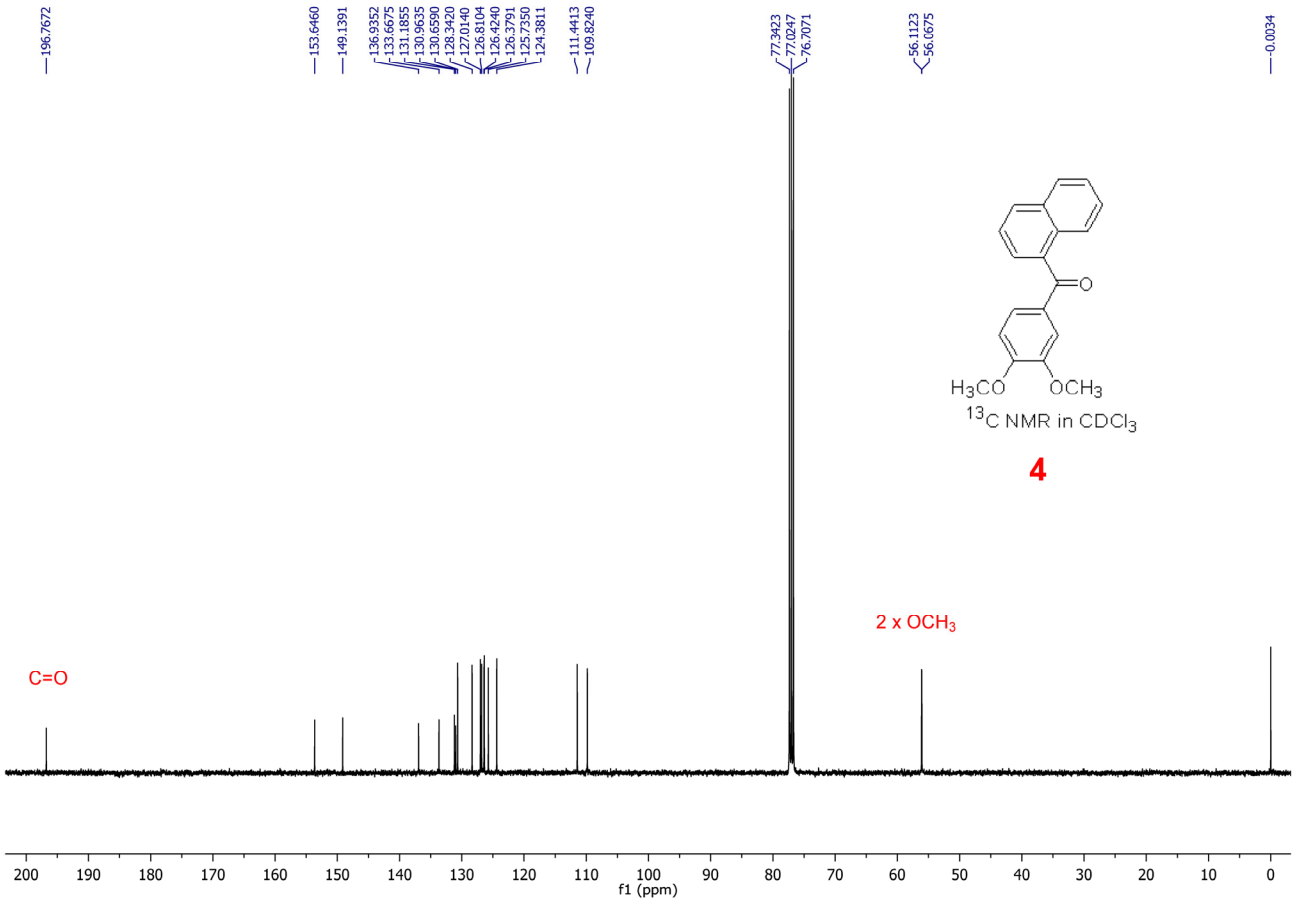
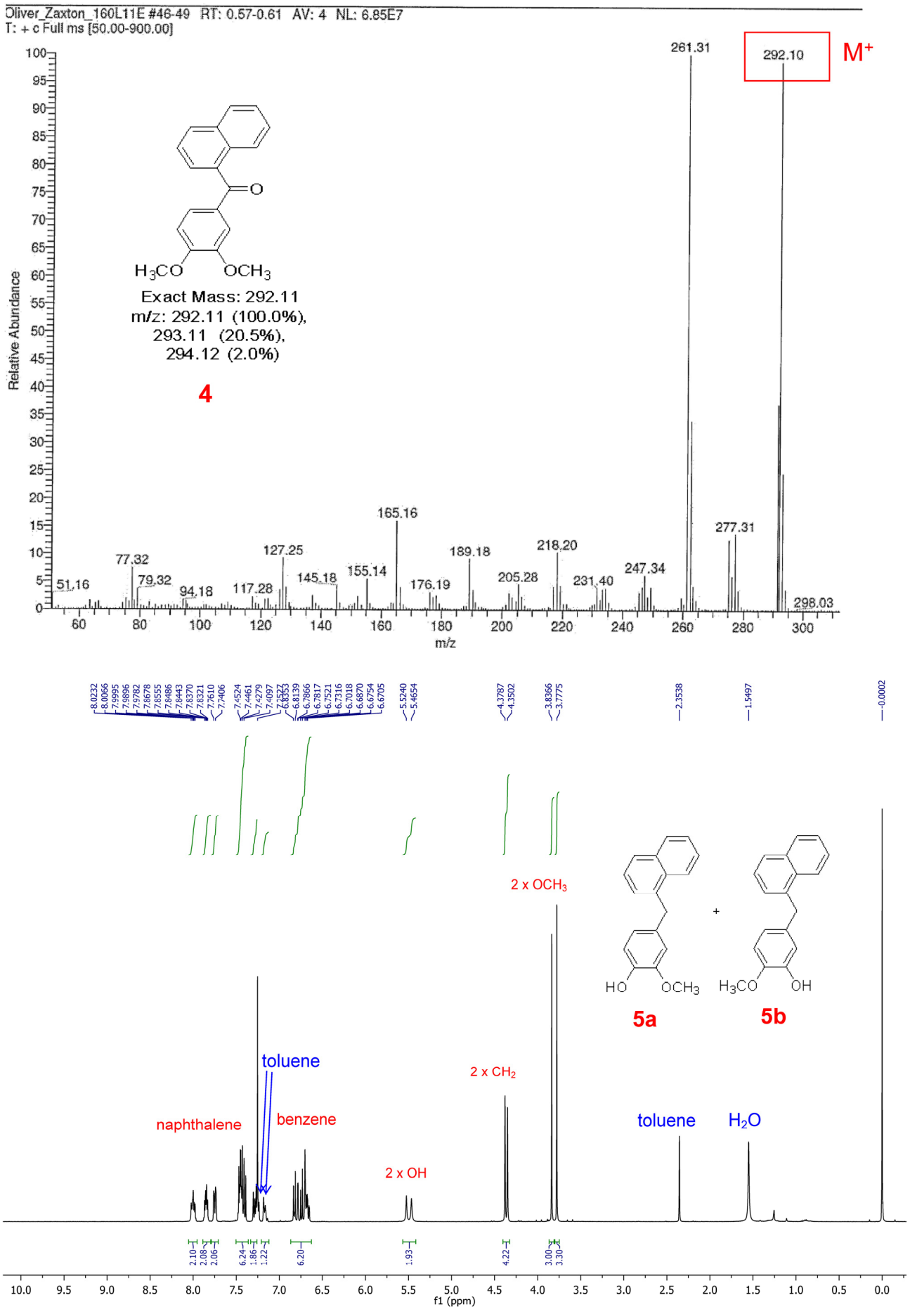
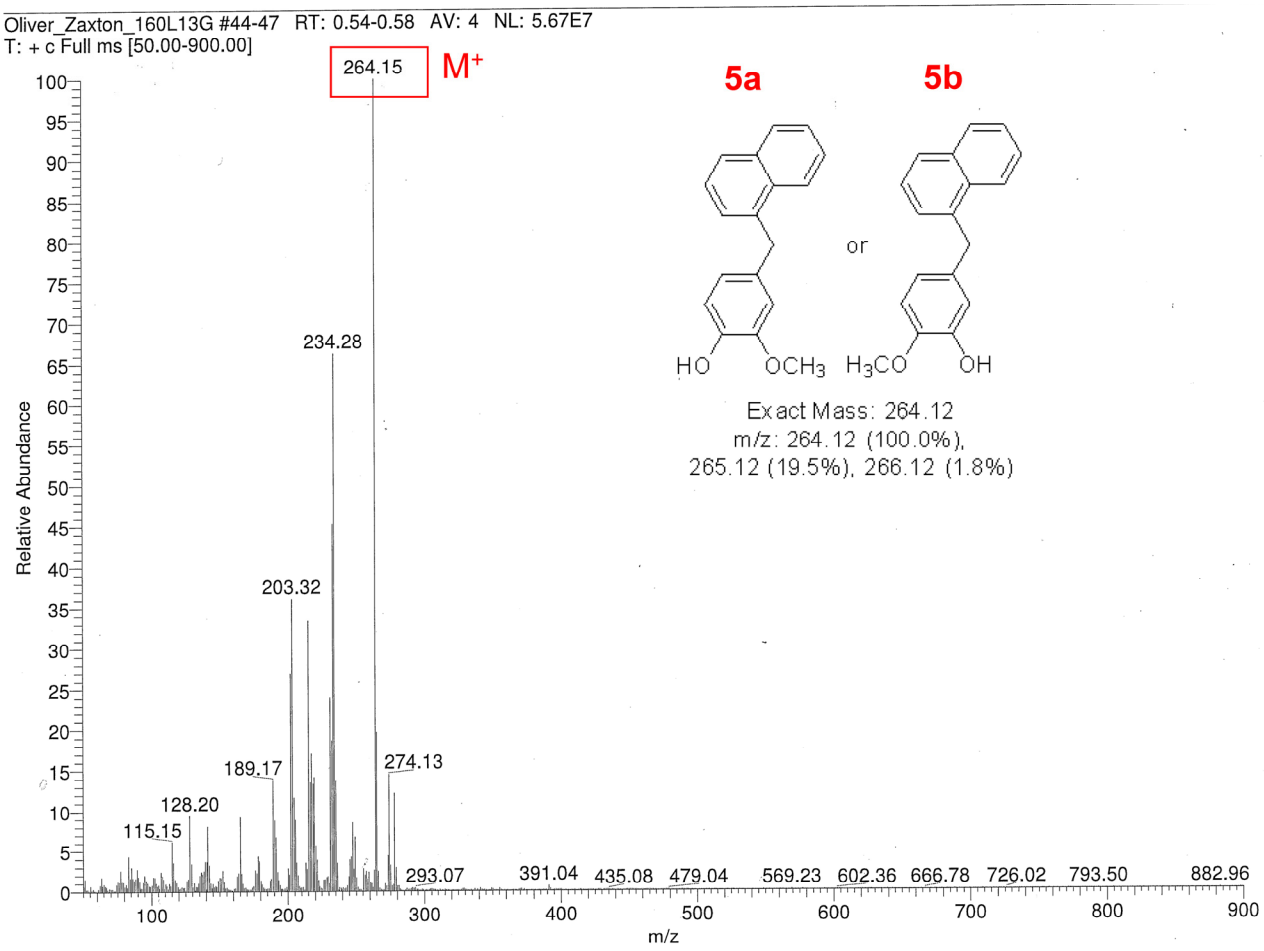


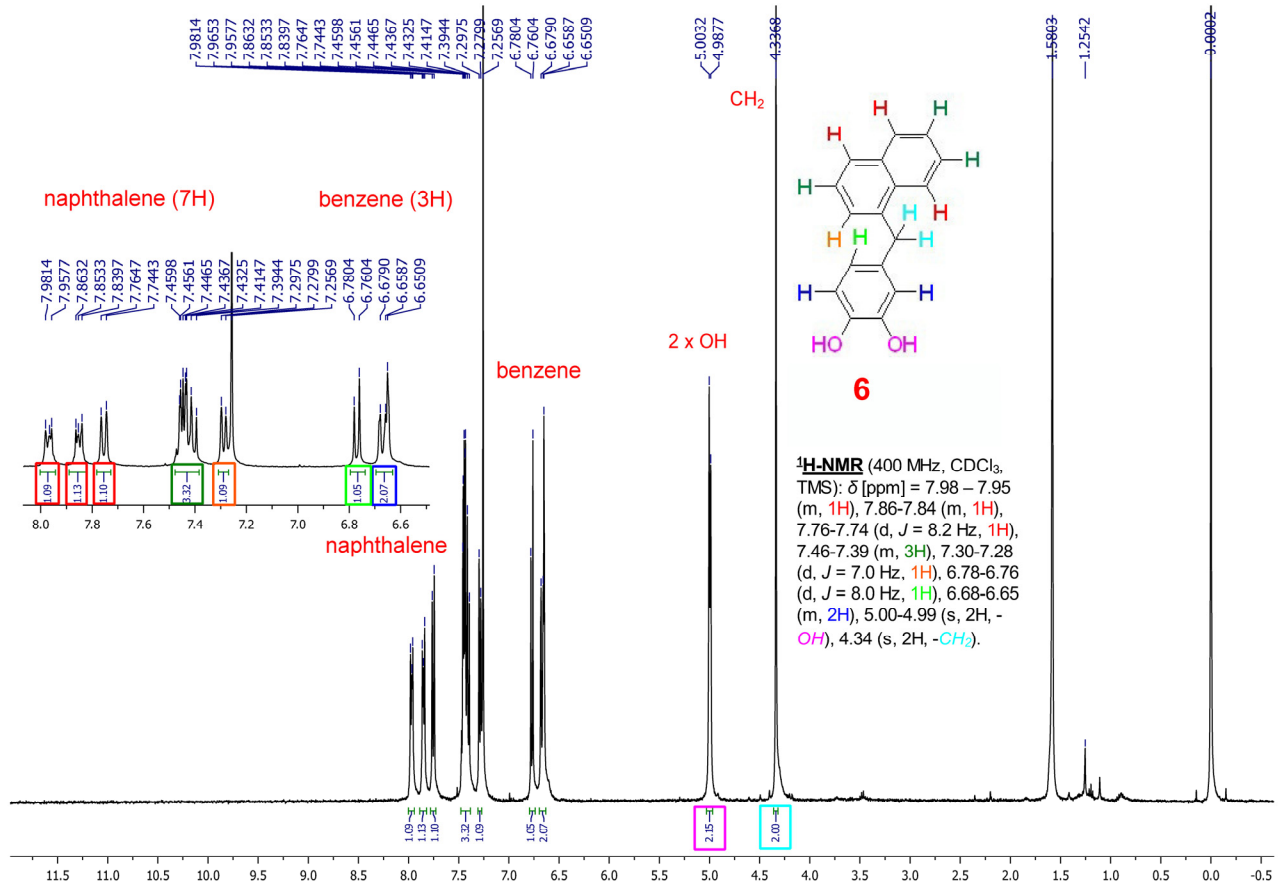
Figure S23. SEM images of the **p[2Na-PheDOT]** polymer surfaces obtained by electropolymerization of **2Na-PheDOT** (10 mM) in 0.1 M **Bu_4NClO_4** / (DCM + H_2O) in potentiodynamic conditions by cyclic voltammetry (E = –1 / +1.8 V) after 1, 3 and 5 scans of depositions, with a substrate inclination of 45 °.
Magnification from the top to the bottom: ×5,000, ×10,000, ×25,000.

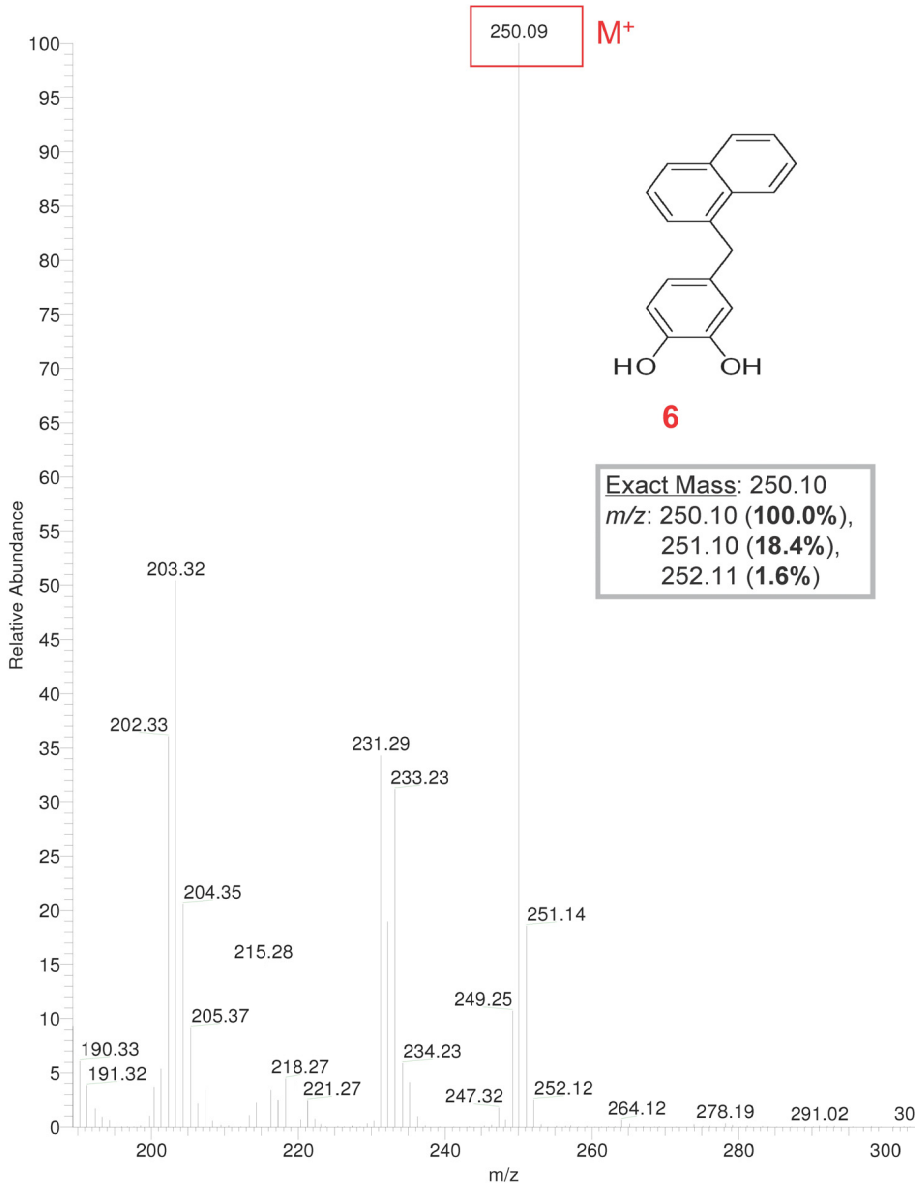

8.0091
7.9905
7.9733
7.9225
7.9032
7.6602
7.6556
7.5500
7.5466
7.5132
7.5019
7.2594
6.8155
6.7945
3.9471
3.9329
1.5956
-0.0003
2 x OCH3
O
H3CO
OCH3
1H NMR in CDCl3
4
2.06
1.03
1.00
4.15
1.06
1.02
6.03
f1 (ppm)

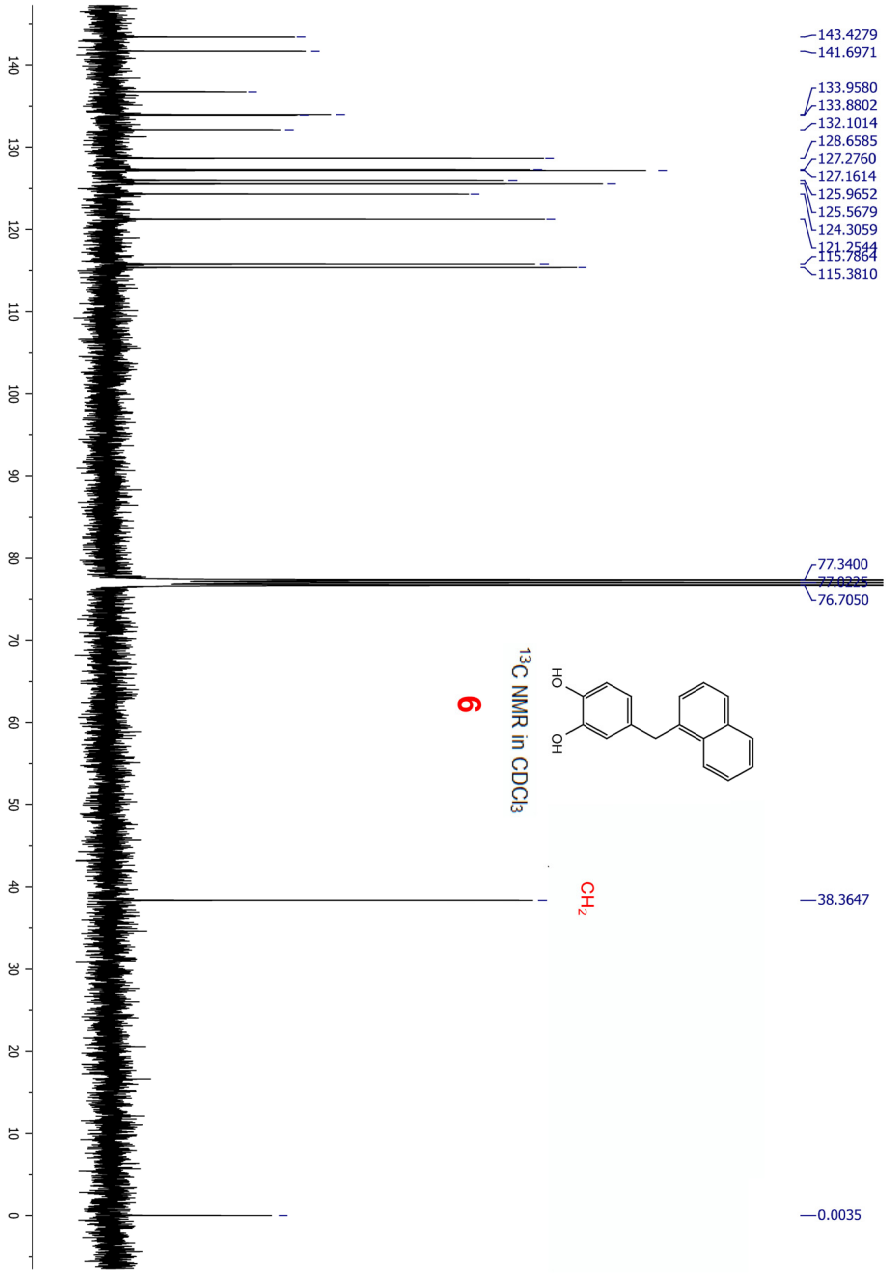

196.7672
153.6460
149.1391
136.9352
133.6675
131.1855
130.9635
130.6590
128.3420
127.0140
126.8104
126.4240
126.3791
125.7350
124.3811
111.4413
109.8240
77.3423
77.0247
76.7071
56.1123
56.0675
-0.0034
O
H3CO
OCH3
13C NMR in CDCl3
4
2 x OCH3
C=O
f1 (ppm)

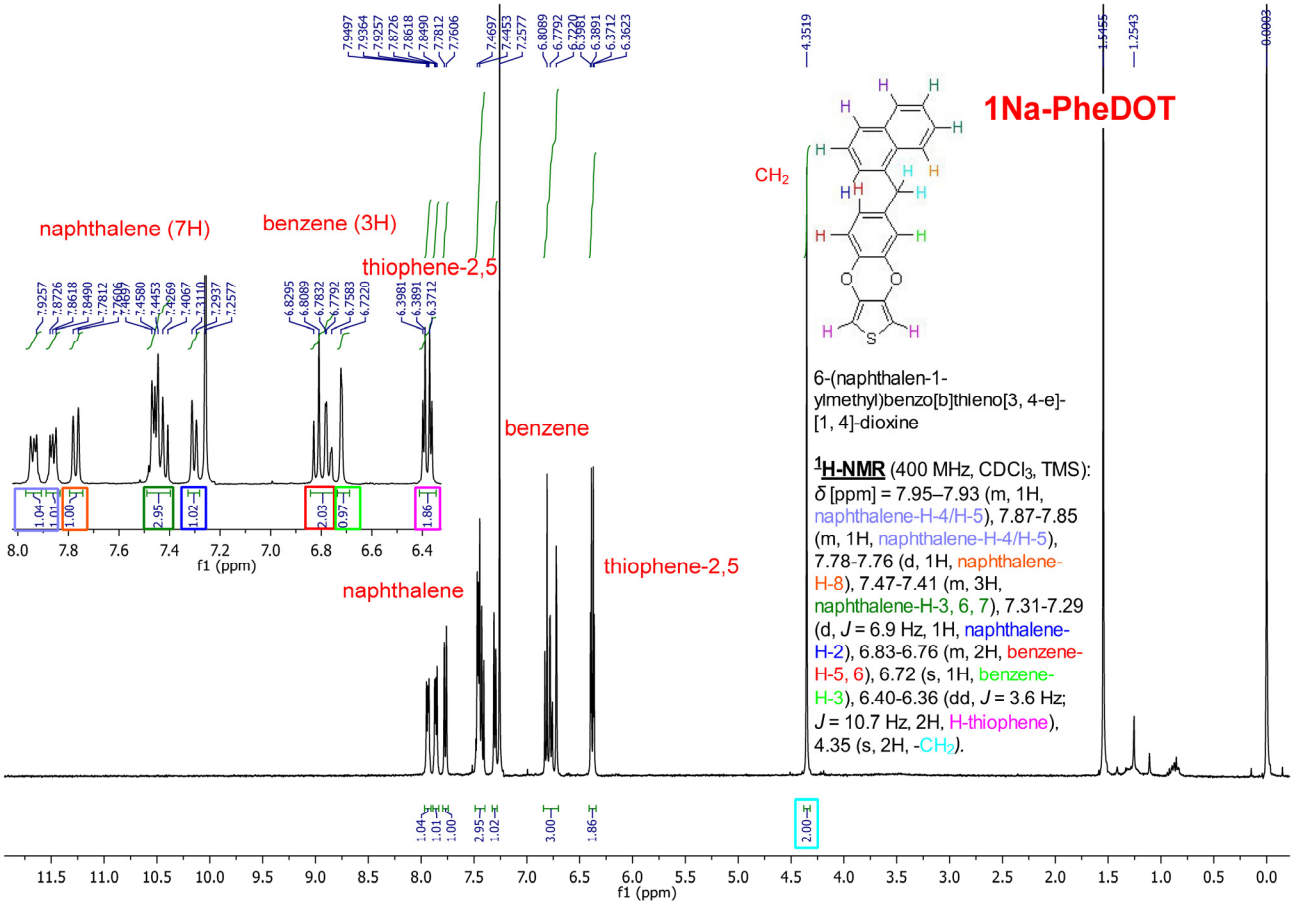

Oliver_Zaxton_160L11E #46-49 RT: 0.57-0.61 AV: 4 NL: 6.85E7
T: + c Full ms [50.00-900.00]
Relative Abundance
m/z
261.31
292.10
M+
277.31
298.03
165.16
127.25
189.18
218.20
247.34
205.28
231.40
155.14
145.18
176.19
117.28
94.18
77.32
79.32
51.16
Exact Mass: 292.11
m/z: 292.11 (100.0%),
293.11 (20.5%),
294.12 (2.0%)
4
2 x OCH3
5a
5b
toluene
naphthalene
benzene
2 x CH2
2 x OH
toluene
H2O
f1 (ppm)

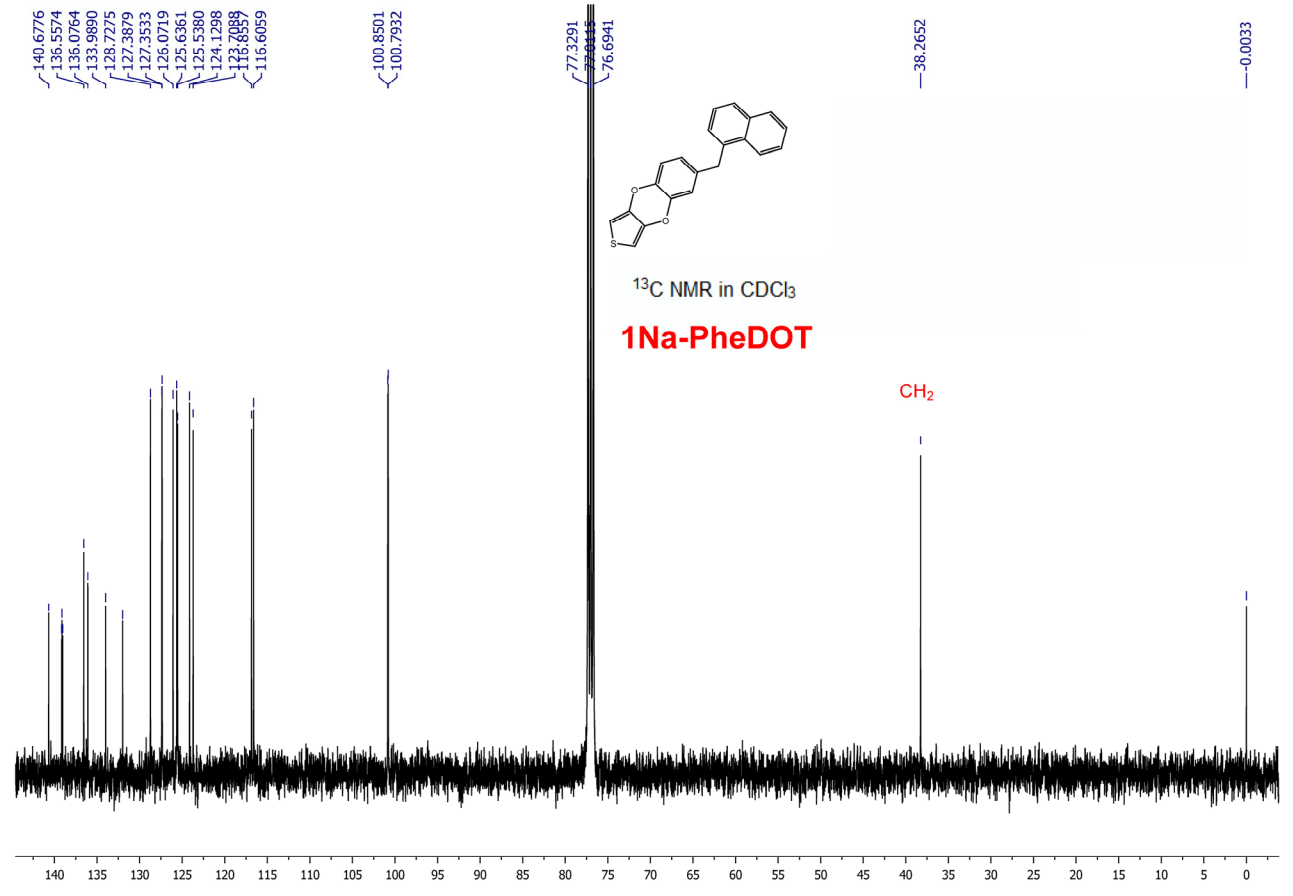

Oliver_Zaxton_160L13G #44-47 RT: 0.54-0.58 AV: 4 NL: 5.67E7
T: + c Full ms [50.00-900.00]
264.15
M+
234.28
203.32
189.17
274.13
128.20
115.15
293.07
391.04
435.08
479.04
569.23
602.36
666.78
726.02
793.50
882.96
Relative Abundance
m/z
5a
5b
or
HO
OCH3
H3CO
OH
Exact Mass: 264.12
m/z: 264.12 (100.0%),
265.12 (19.5%), 266.12 (1.8%)

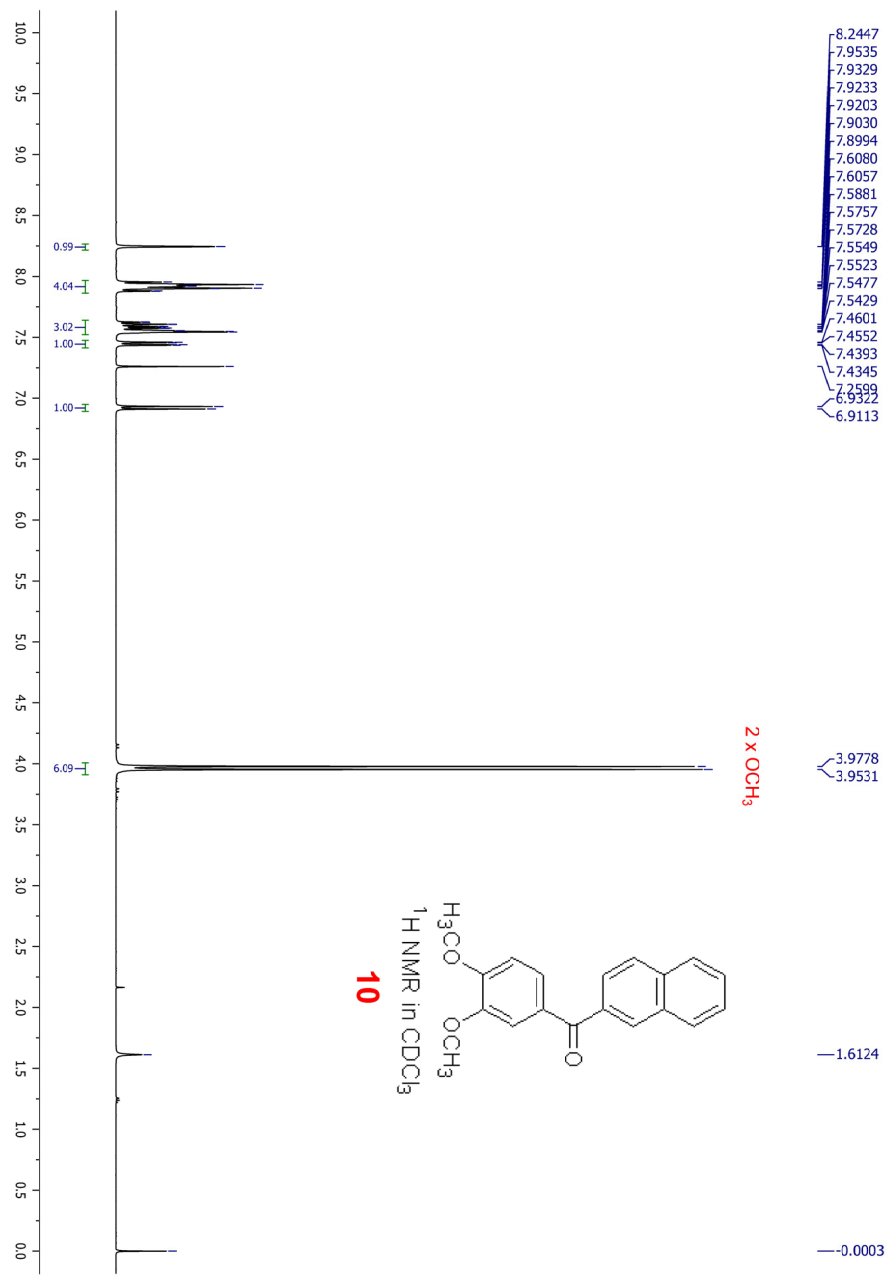

naphthalene (7H)
benzene (3H)
benzene
naphthalene
CH2
2 x OH
6
1H-NMR (400 MHz, CDCl3, TMS): δ [ppm] = 7.98 – 7.95 (m, 1H), 7.86-7.84 (m, 1H), 7.76-7.74 (d, J = 8.2 Hz, 1H), 7.46-7.39 (m, 3H), 7.30-7.28 (d, J = 7.0 Hz, 1H), 6.78-6.76 (d, J = 8.0 Hz, 1H), 6.68-6.65 (m, 2H), 5.00-4.99 (s, 2H, -OH), 4.34 (s, 2H, -CH2).

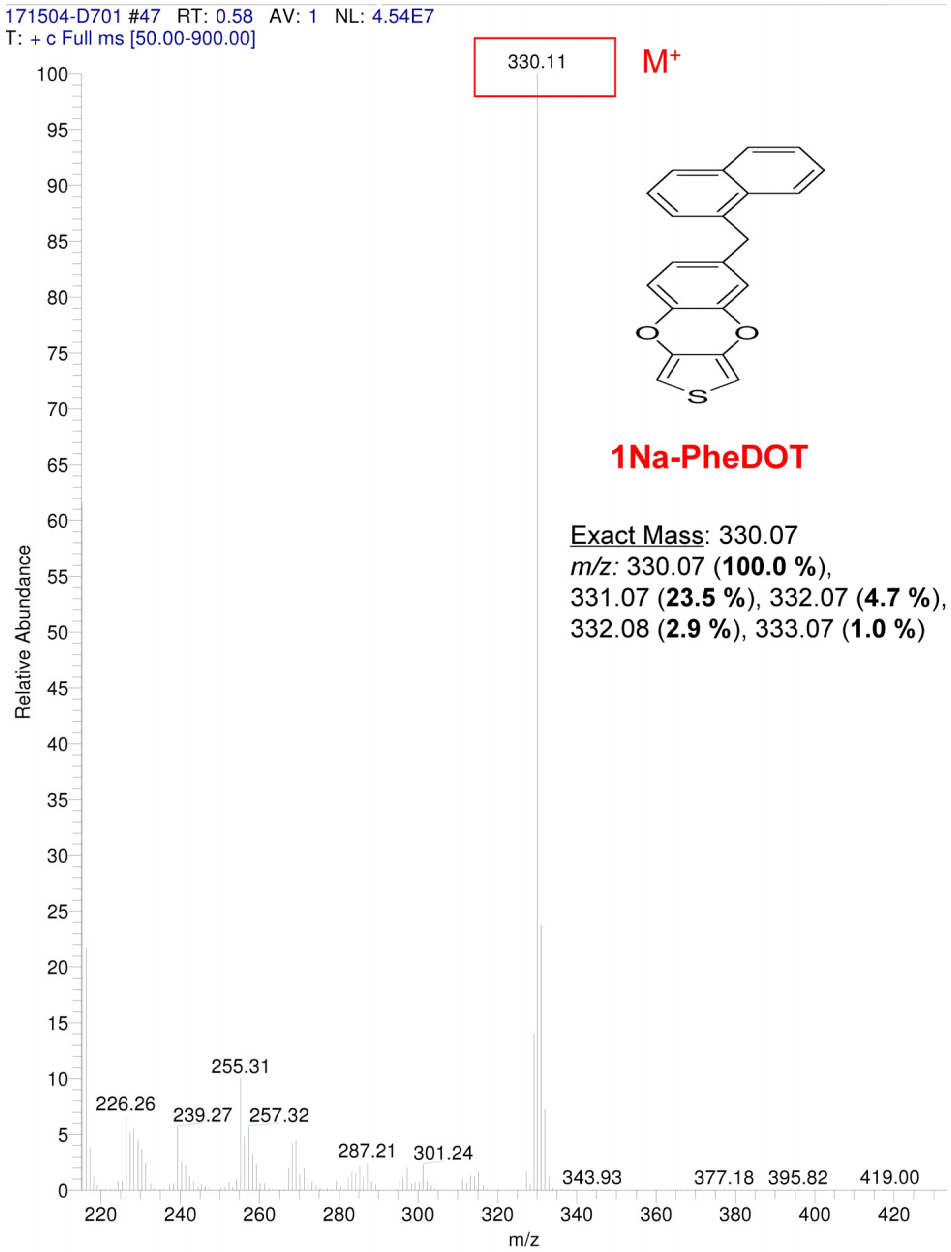

250.09
M+
HO
OH
6
Exact Mass: 250.10
m/z: 250.10 (100.0%),
251.10 (18.4%),
252.11 (1.6%)
Relative Abundance
m/z
203.32
202.33
231.29
233.23
204.35
251.14
215.28
249.25
205.37
190.33
191.32
218.27
221.27
234.23
247.32
252.12
264.12
278.19
291.02


143.4279
141.6971
133.9580
133.8802
132.1014
128.6585
127.2760
127.1614
125.9652
125.5679
124.3059
121.2544
115.7864
115.3810
77.3400
77.0325
76.7050
38.3647
0.0035
13C NMR in CDCl3
6
HO
OH
CH2


1Na-PheDOT
naphthalene (7H)
benzene (3H)
thiophene-2,5
benzene
thiophene-2,5
naphthalene
CH2
6-(naphthalen-1-ylmethyl)benzo[b]thieno[3, 4-e]-[1, 4]-dioxine
1H-NMR (400 MHz, CDCl3, TMS):
δ [ppm] = 7.95–7.93 (m, 1H, naphthalene-H-4/H-5), 7.87-7.85 (m, 1H, naphthalene-H-4/H-5), 7.78-7.76 (d, 1H, naphthalene-H-8), 7.47-7.41 (m, 3H, naphthalene-H-3, 6, 7), 7.31-7.29 (d, J = 6.9 Hz, 1H, naphthalene-H-2), 6.83-6.76 (m, 2H, benzene-H-5, 6), 6.72 (s, 1H, benzene-H-3), 6.40-6.36 (dd, J = 3.6 Hz; J = 10.7 Hz, 2H, H-thiophene), 4.35 (s, 2H, -CH2).
f1 (ppm)

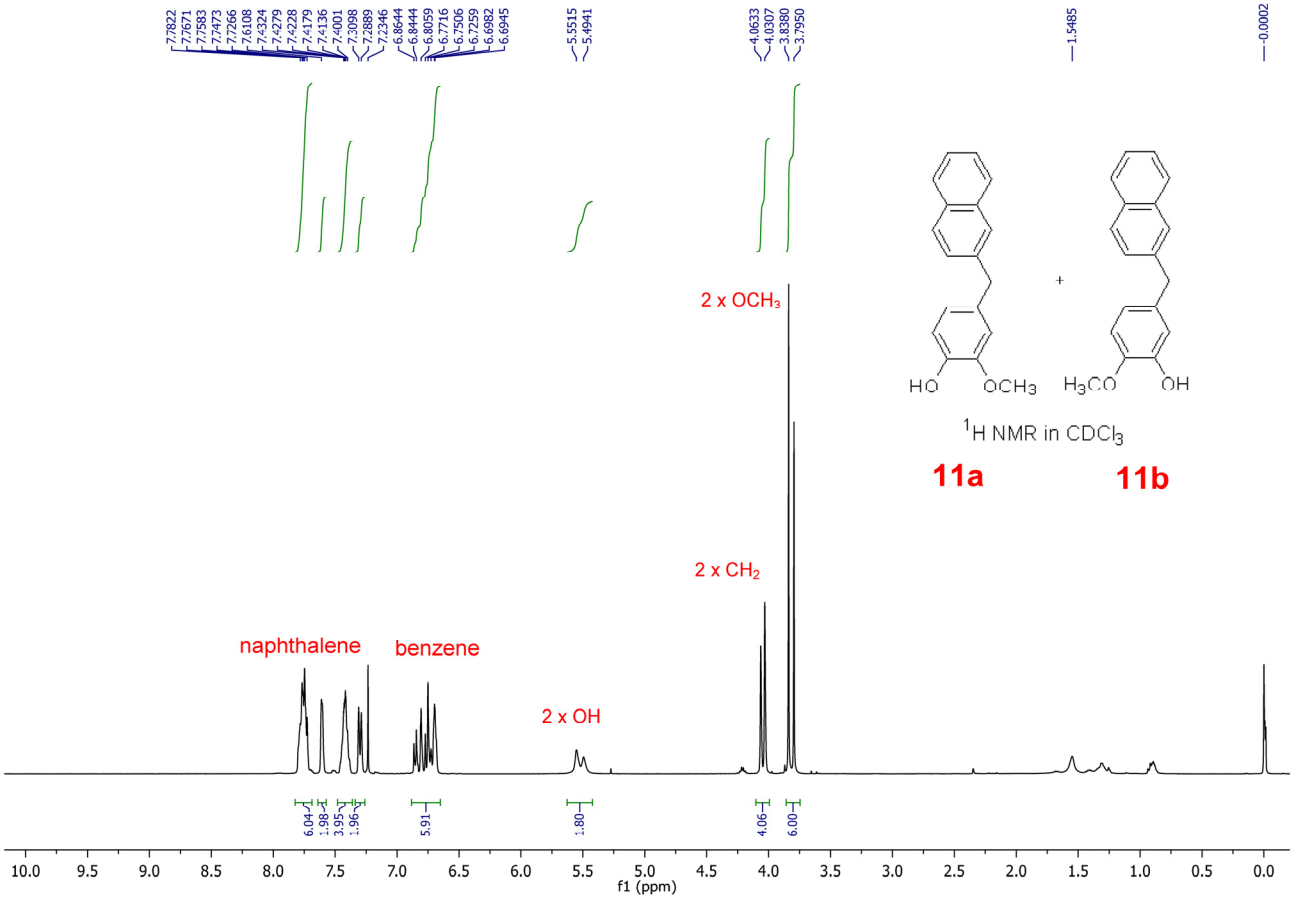

13C NMR in CDCl3
1Na-PheDOT
CH2
f1 (ppm)

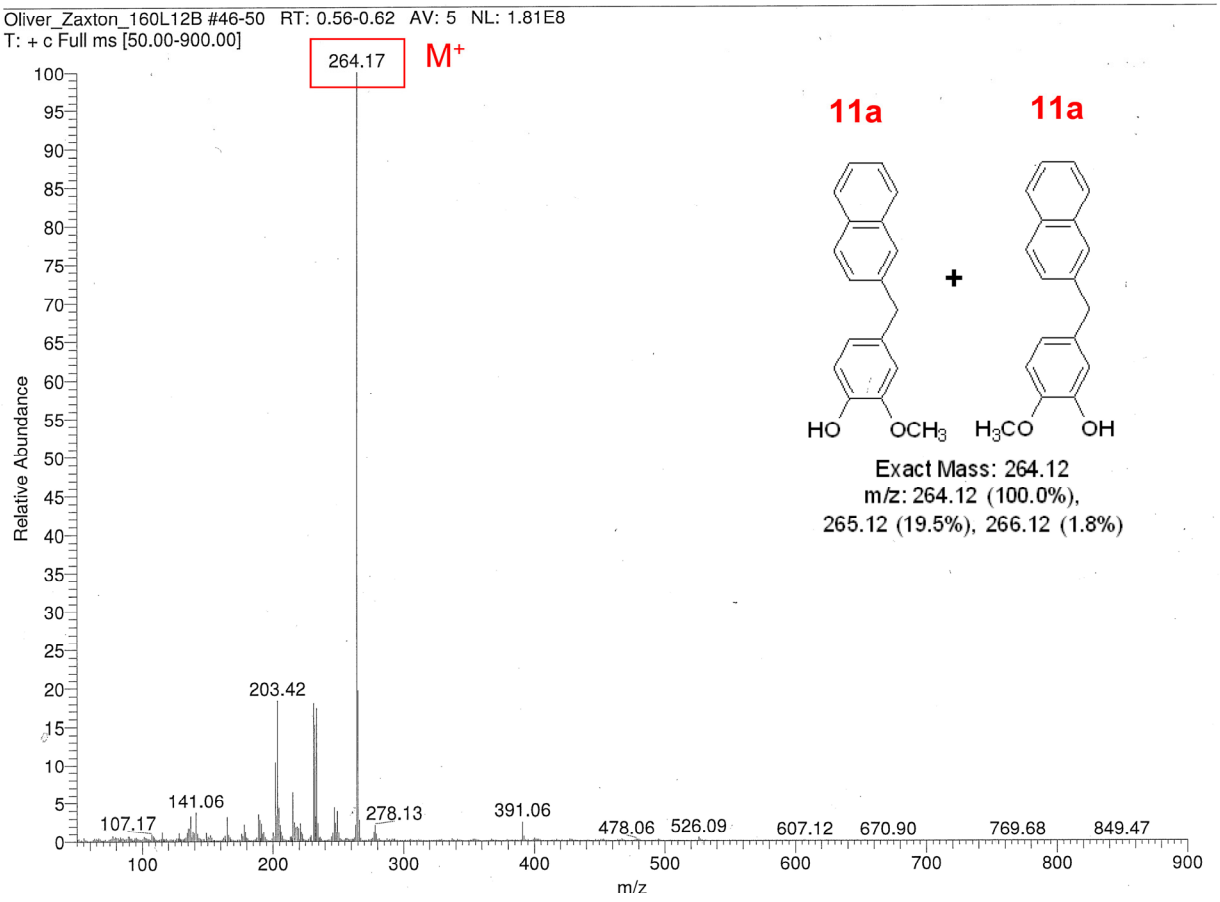


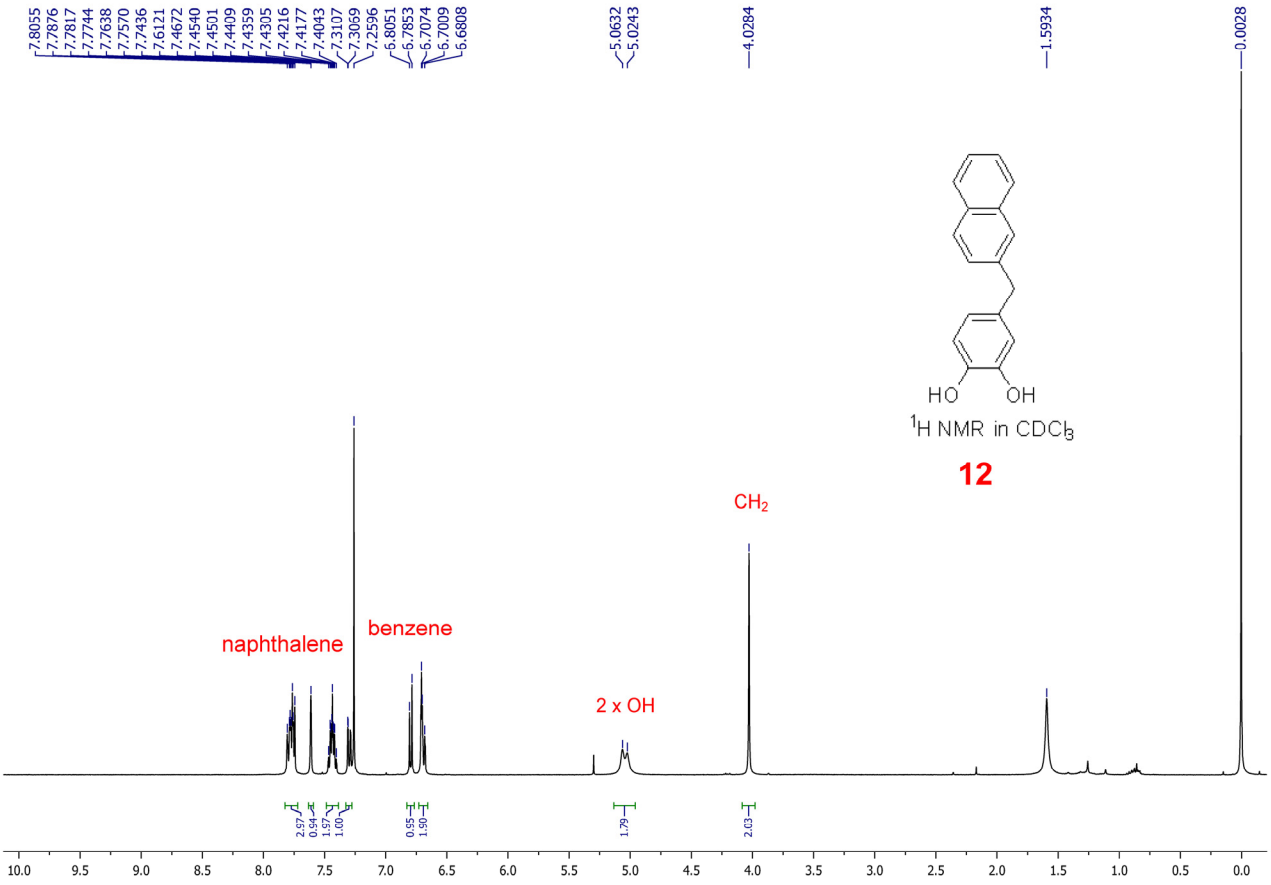


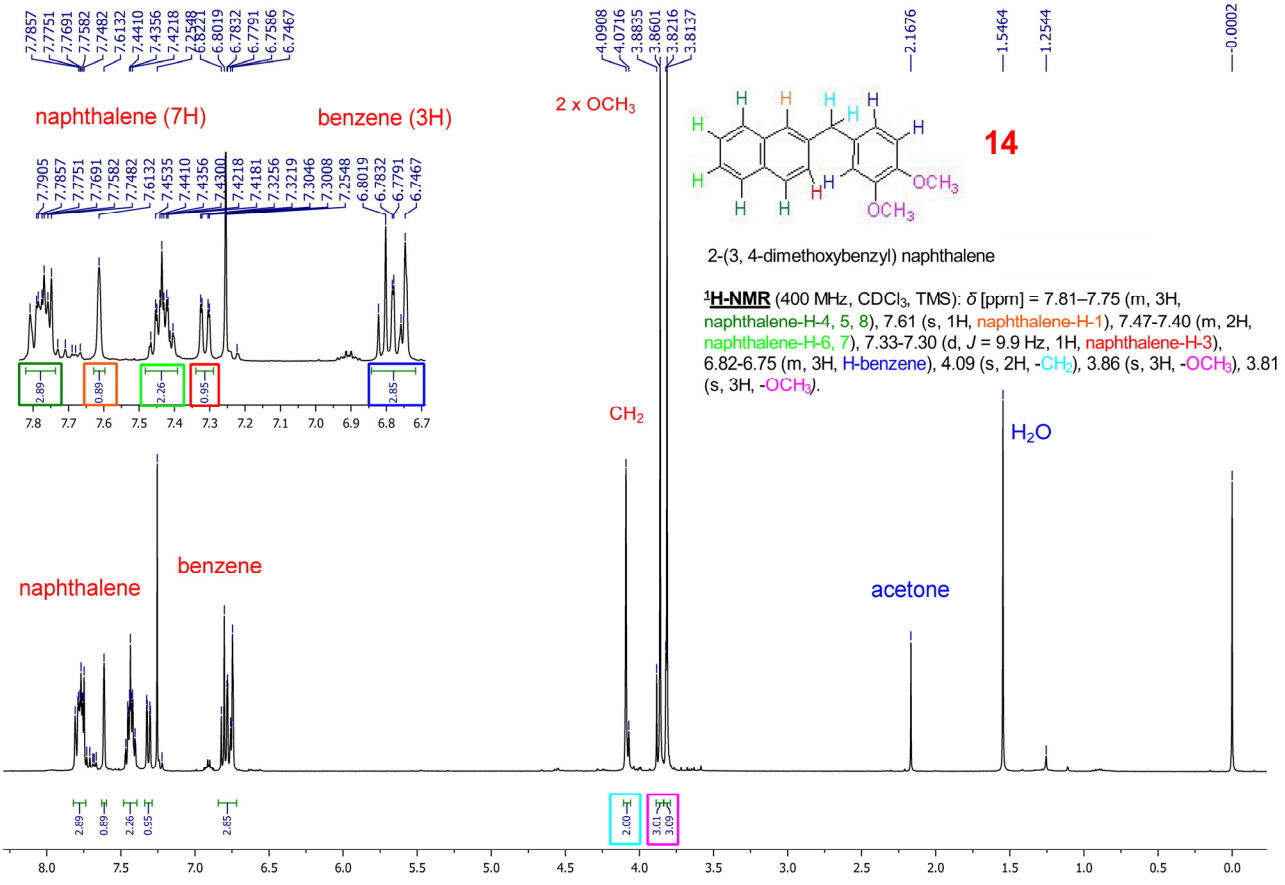
1Na-PheDOT

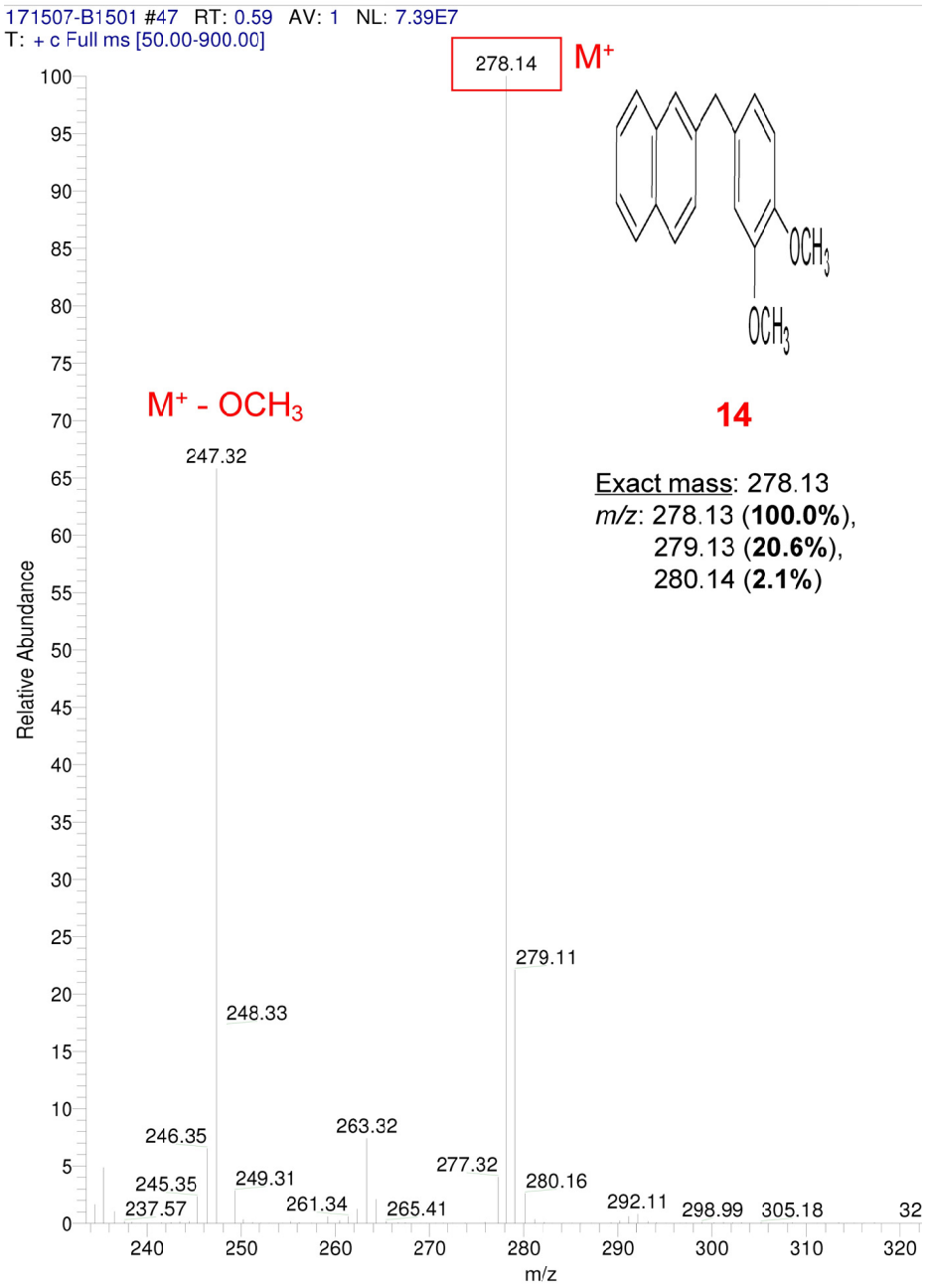
Exact Mass: 330.07
m/z: 330.07 (**100.0 %**), 331.07 (**23.5 %**), 332.07 (**4.7 %**), 332.08 (**2.9 %**), 333.07 (**1.0 %**)

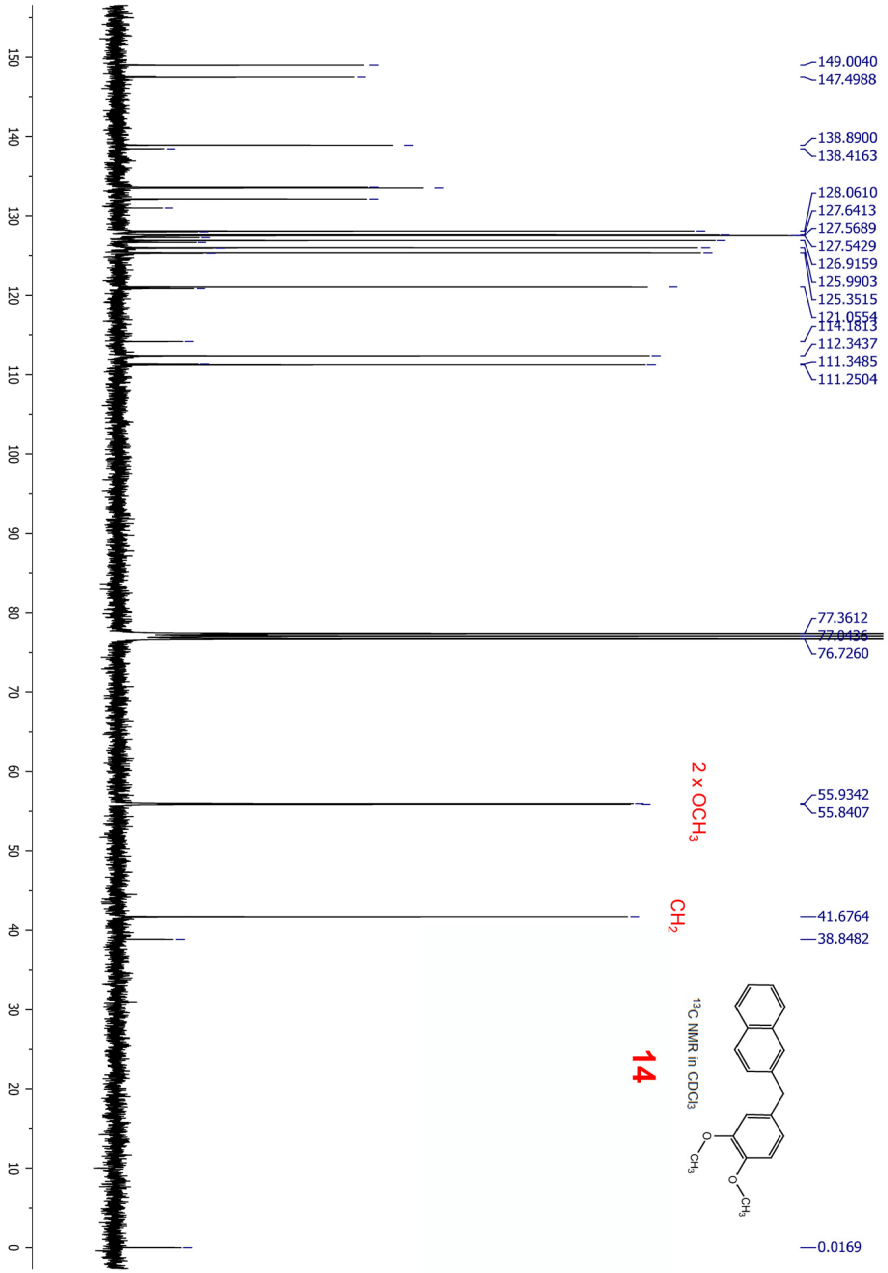

2 x OCH3
2 x CH2
naphthalene
benzene
2 x OH
HO
OCH3
H3CO
OH
1H NMR in CDCl3
11a
11b
f1 (ppm)

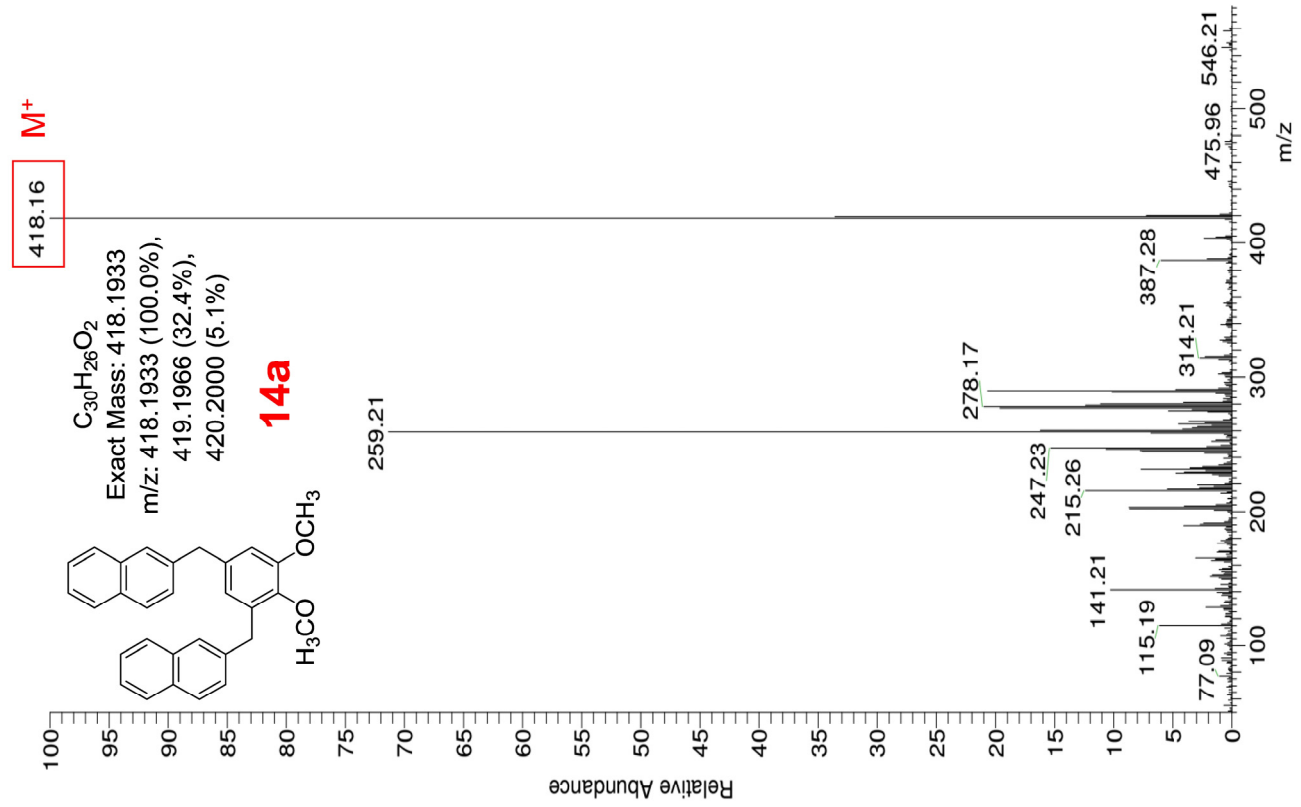

Oliver_Zaxton_160L12B #46-50 RT: 0.56-0.62 AV: 5 NL: 1.81E8
T: + c Full ms [50.00-900.00]
264.17
M+
11a
11a
HO
OCH3
H3CO
OH
Exact Mass: 264.12
m/z: 264.12 (100.0%),
265.12 (19.5%), 266.12 (1.8%)
Relative Abundance
m/z

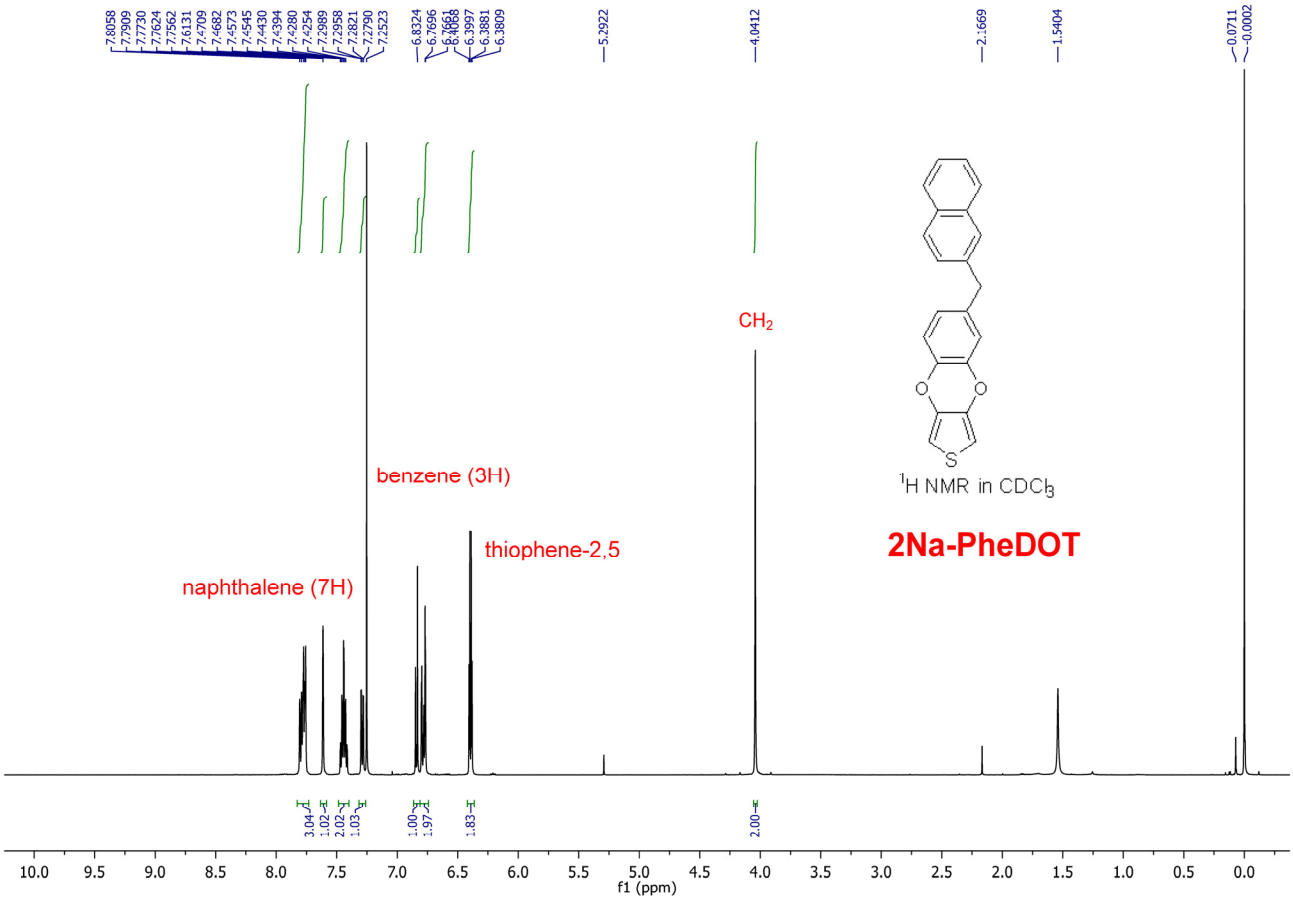

HO
OH
^{1}H NMR in CDCl$_3$
12
CH$_2$
naphthalene
benzene
2 x OH

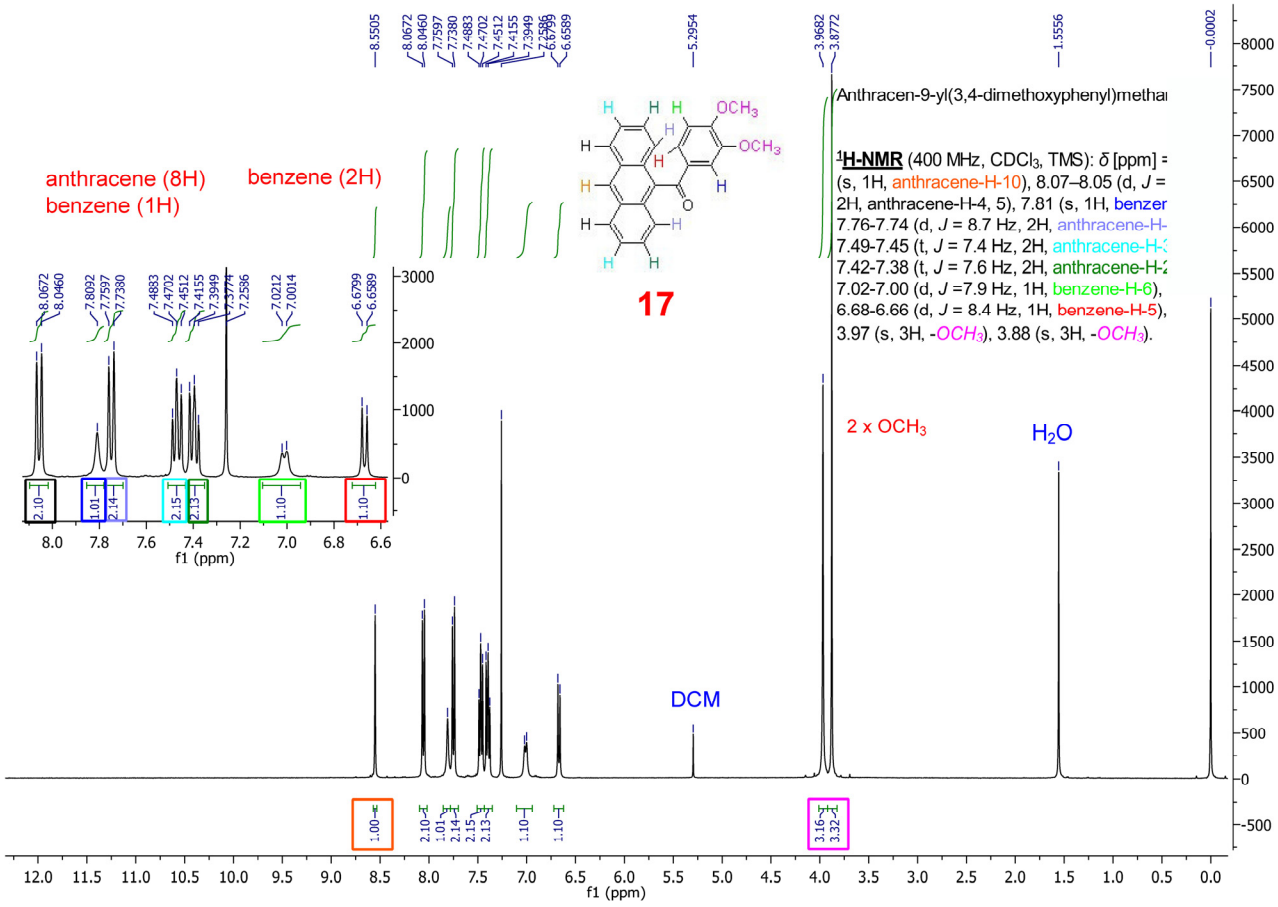

naphthalene (7H)
benzene (3H)
2 x OCH$_3$
14
2-(3, 4-dimethoxybenzyl) naphthalene
^{1}H-NMR (400 MHz, CDCl$_3$, TMS): δ [ppm] = 7.81–7.75 (m, 3H, naphthalene-H-4, 5, 8), 7.61 (s, 1H, naphthalene-H-1), 7.47-7.40 (m, 2H, naphthalene-H-6, 7), 7.33-7.30 (d, J = 9.9 Hz, 1H, naphthalene-H-3), 6.82-6.75 (m, 3H, H-benzene), 4.09 (s, 2H, -CH$_2$), 3.86 (s, 3H, -OCH$_3$), 3.81 (s, 3H, -OCH$_3$).
CH$_2$
H$_2$O
acetone
naphthalene
benzene

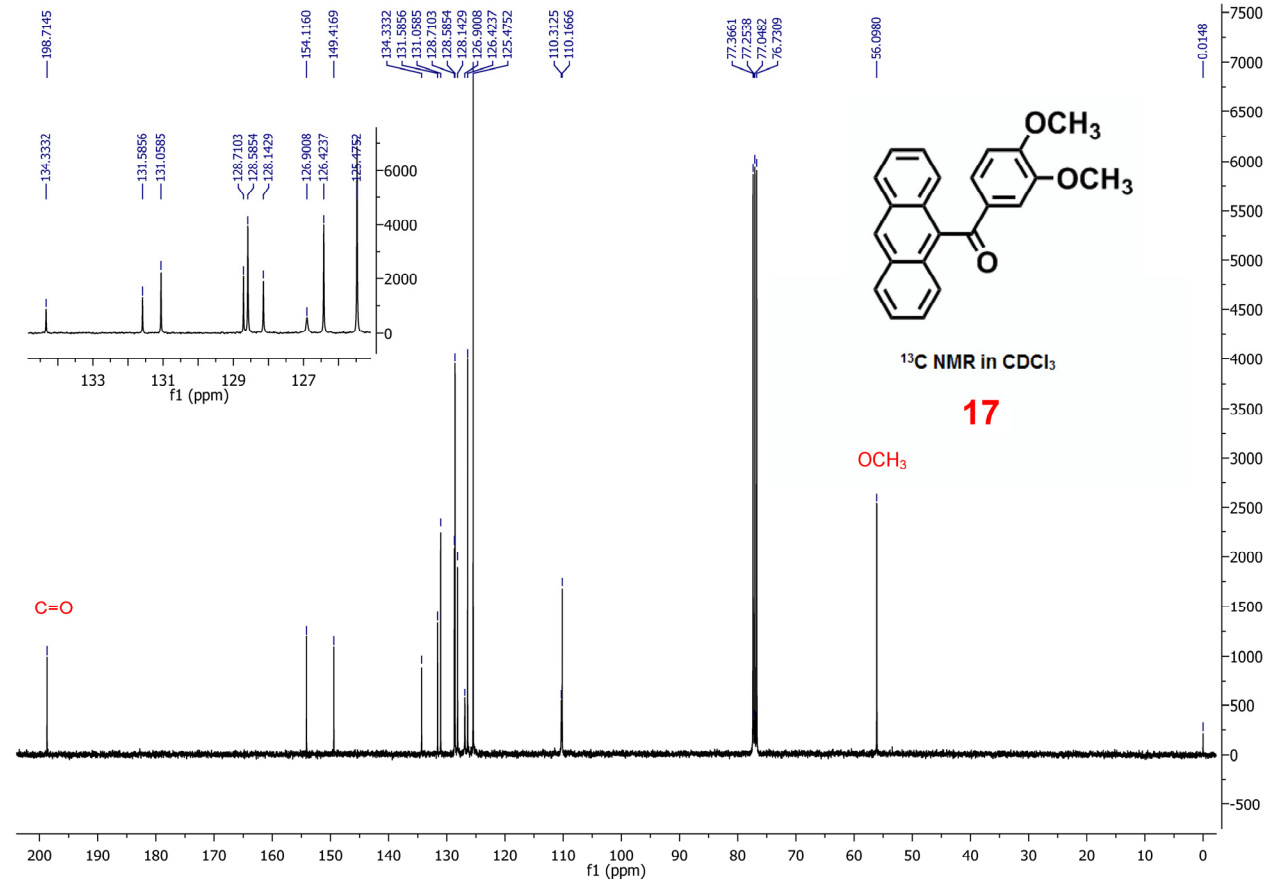

171507-B1501 #47 RT: 0.59 AV: 1 NL: 7.39E7
T: + c Full ms [50.00-900.00]
278.14
M+
OCH3
OCH3
M+ - OCH3
14
Exact mass: 278.13
m/z: 278.13 (100.0%),
279.13 (20.6%),
280.14 (2.1%)
247.32
279.11
248.33
246.35
263.32
277.32
280.16
245.35
249.31
237.57
261.34
265.41
292.11
298.99
305.18
Relative Abundance
m/z

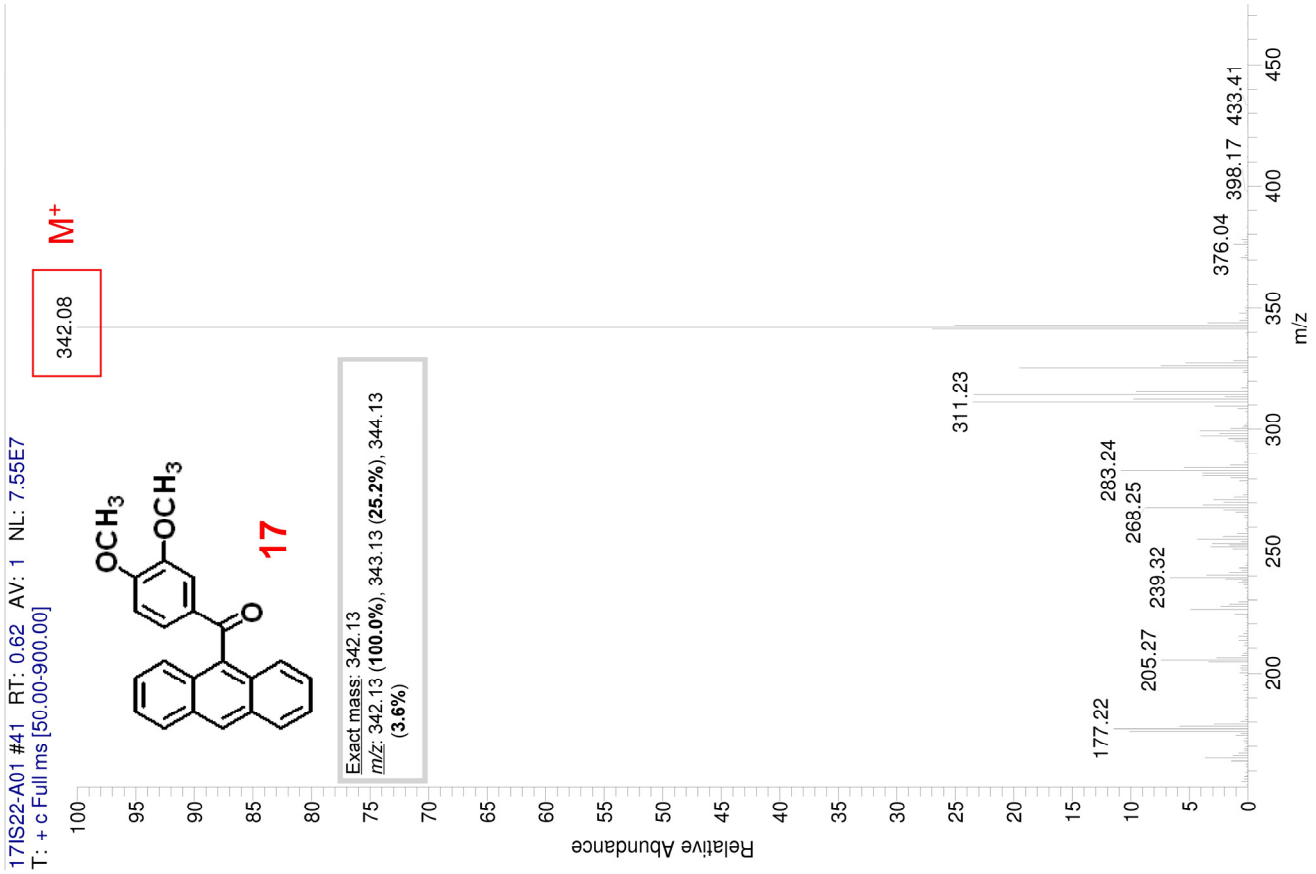

149.0040
147.4988
138.8900
138.4163
128.0610
127.6413
127.5689
127.5429
126.9159
125.9903
125.3515
121.0554
114.1813
112.3437
111.3485
111.2504
77.3612
77.0436
76.7260
55.9342
55.8407
41.6764
38.8482
0.0169
2 x OCH3
CH2
13C NMR in CDCl3
14

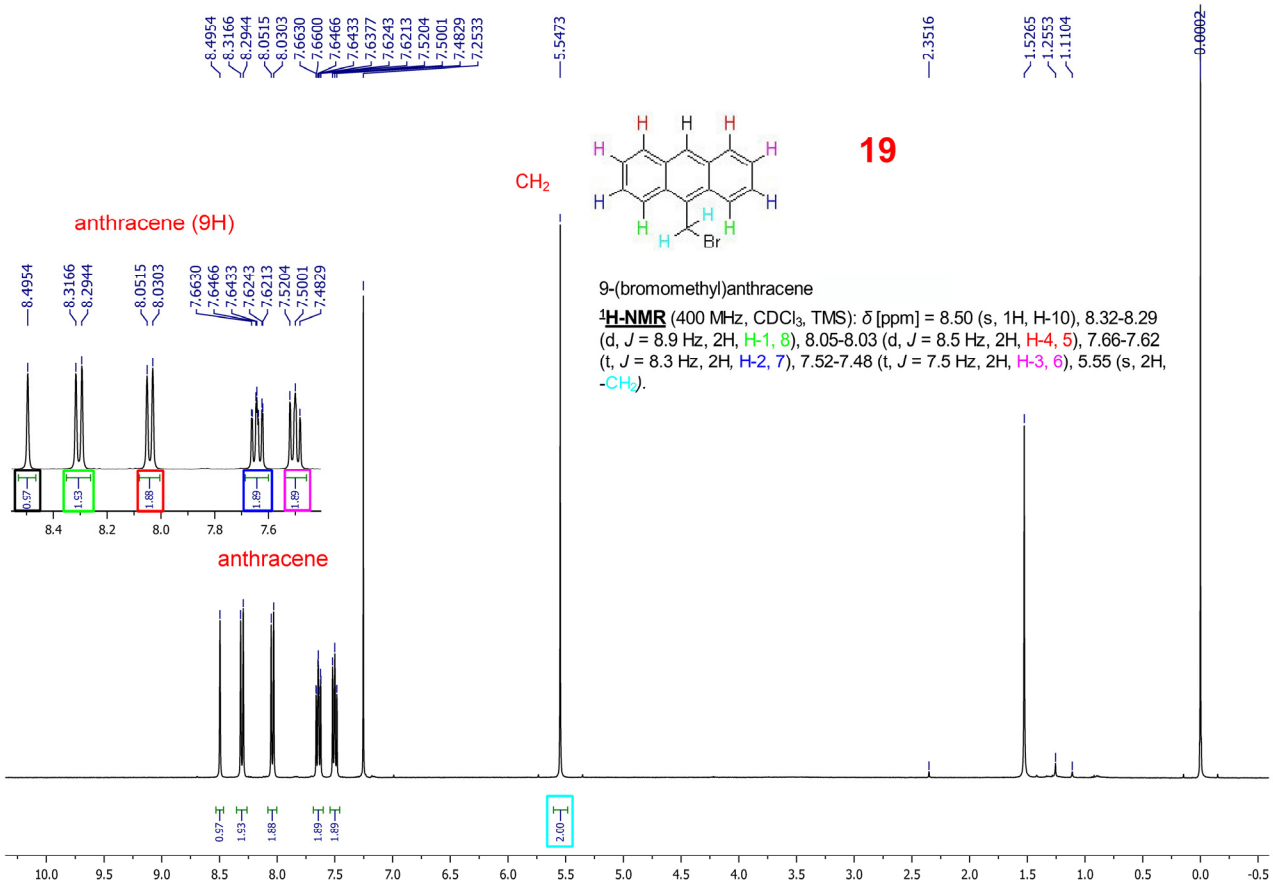

M+
418.16
$C_{30}H_{26}O_2$
Exact Mass: 418.1933
m/z: 418.1933 (100.0%),
419.1966 (32.4%),
420.2000 (5.1%)
14a
H_3CO
OCH_3
259.21
278.17
247.23
215.26
387.28
314.21
141.21
115.19
77.09
475.96
546.21
Relative Abundance
m/z

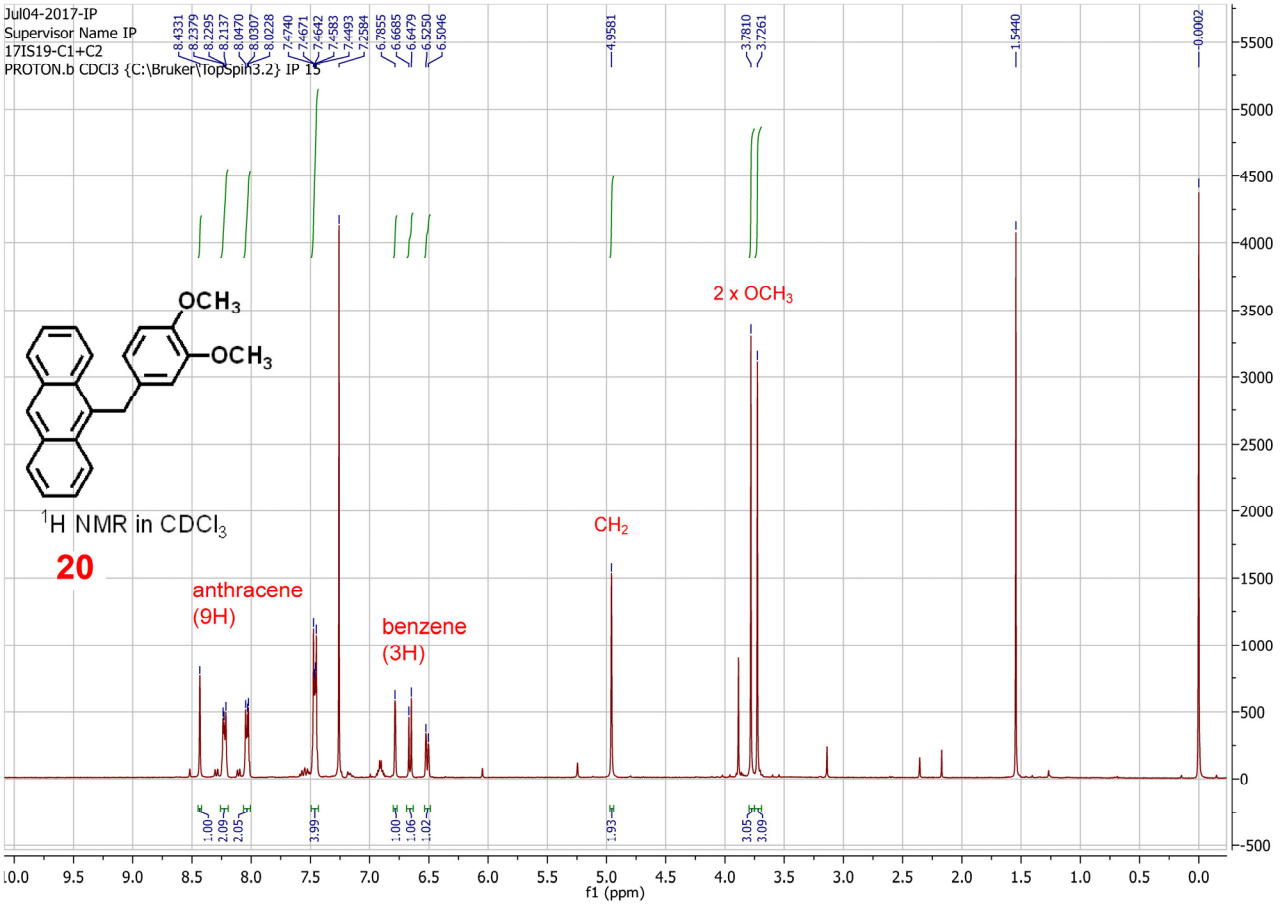

naphthalene (7H)
benzene (3H)
thiophene-2,5
CH_2
^{1}H NMR in $CDCl_3$
2Na-PheDOT
f1 (ppm)

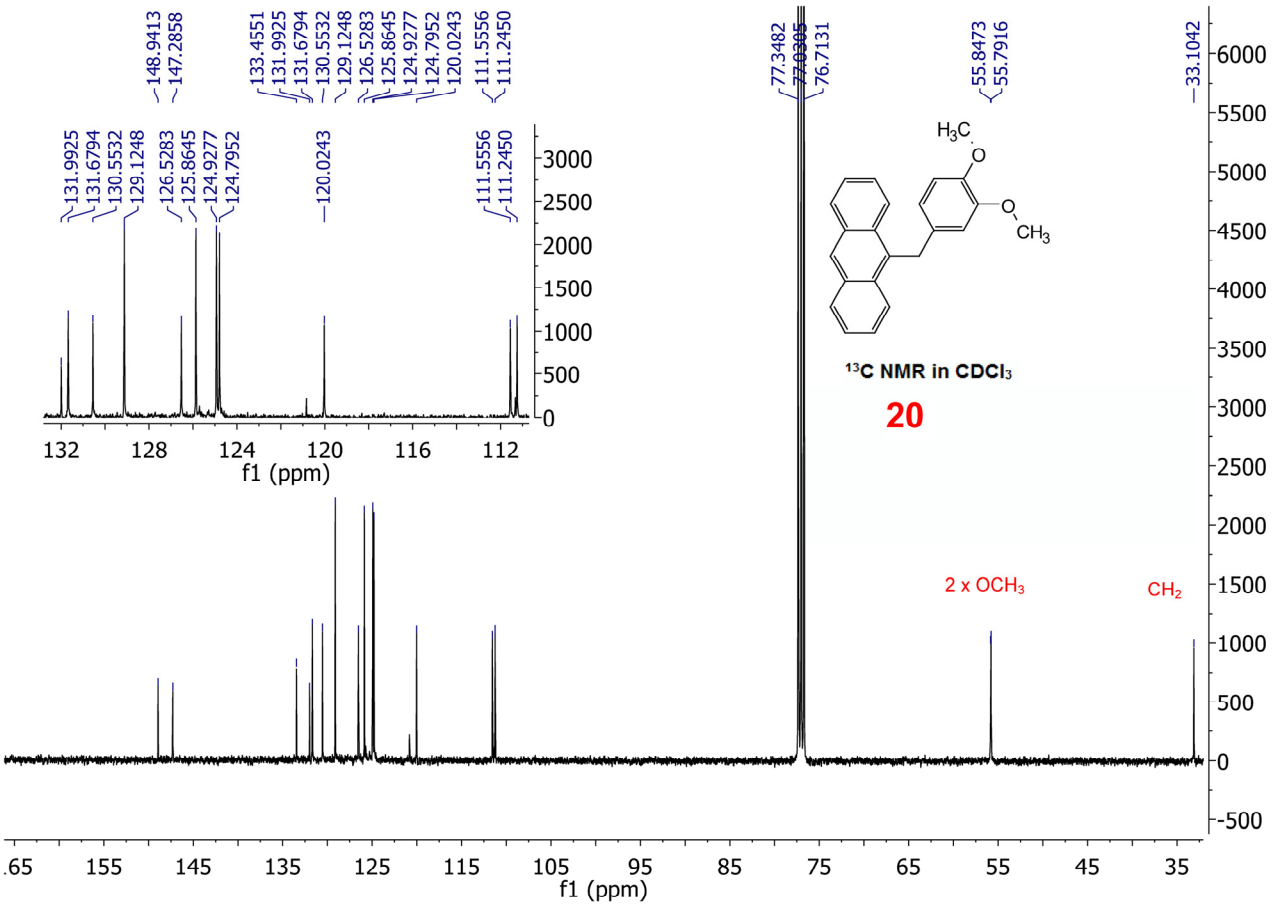

anthracene (8H)
benzene (1H)
benzene (2H)
17
Anthracen-9-yl(3,4-dimethoxyphenyl)methan
¹H-NMR (400 MHz, CDCl3, TMS): δ [ppm] =
(s, 1H, anthracene-H-10), 8.07–8.05 (d, J =
2H, anthracene-H-4, 5), 7.81 (s, 1H, benzer
7.76-7.74 (d, J = 8.7 Hz, 2H, anthracene-H-
7.49-7.45 (t, J = 7.4 Hz, 2H, anthracene-H-
7.42-7.38 (t, J = 7.6 Hz, 2H, anthracene-H-
7.02-7.00 (d, J =7.9 Hz, 1H, benzene-H-6),
6.68-6.66 (d, J = 8.4 Hz, 1H, benzene-H-5),
3.97 (s, 3H, -OCH3), 3.88 (s, 3H, -OCH3).
2 x OCH3
H2O
DCM
f1 (ppm)

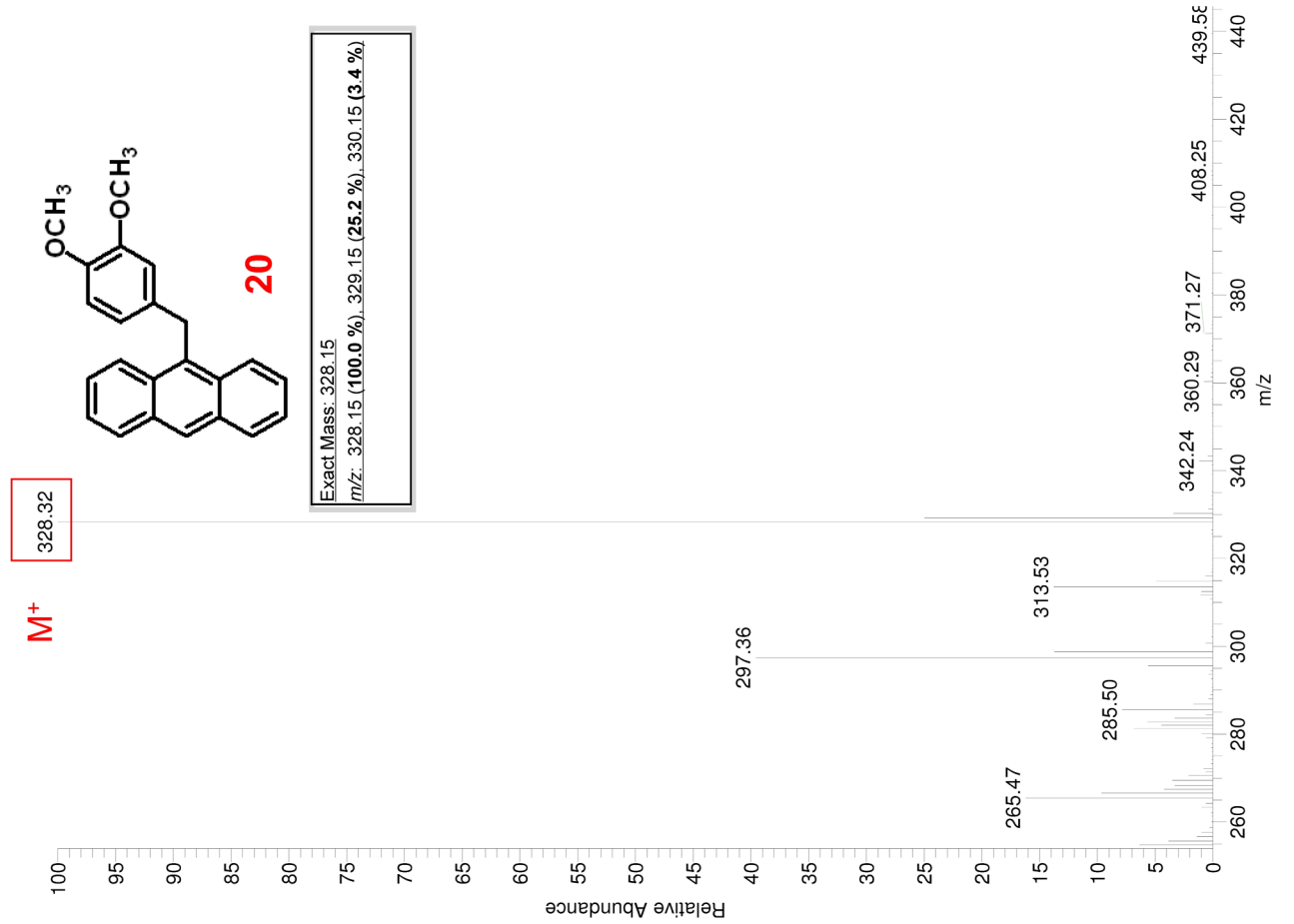

C=O
OCH3
OCH3
OCH3
13C NMR in CDCl3
17
f1 (ppm)

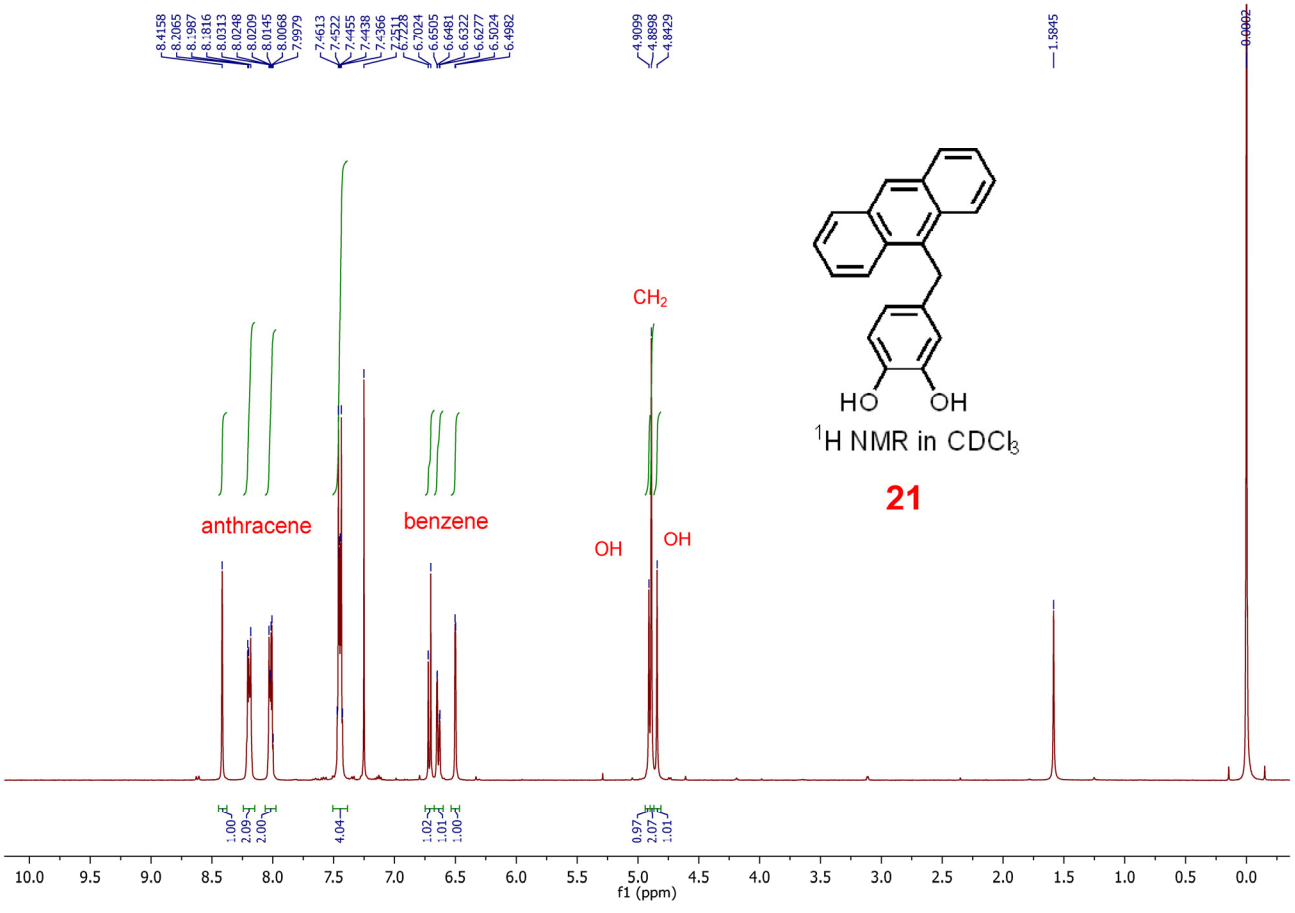

17IS22-A01 #41 RT: 0.62 AV: 1 NL: 7.55E7
T: + c Full ms [50.00-900.00]
M+
342.08
17
Exact mass: 342.13
m/z: 342.13 (100.0%), 343.13 (25.2%), 344.13 (3.6%)
311.23
283.24
268.25
239.32
205.27
177.22
376.04
398.17
433.41
Relative Abundance
m/z

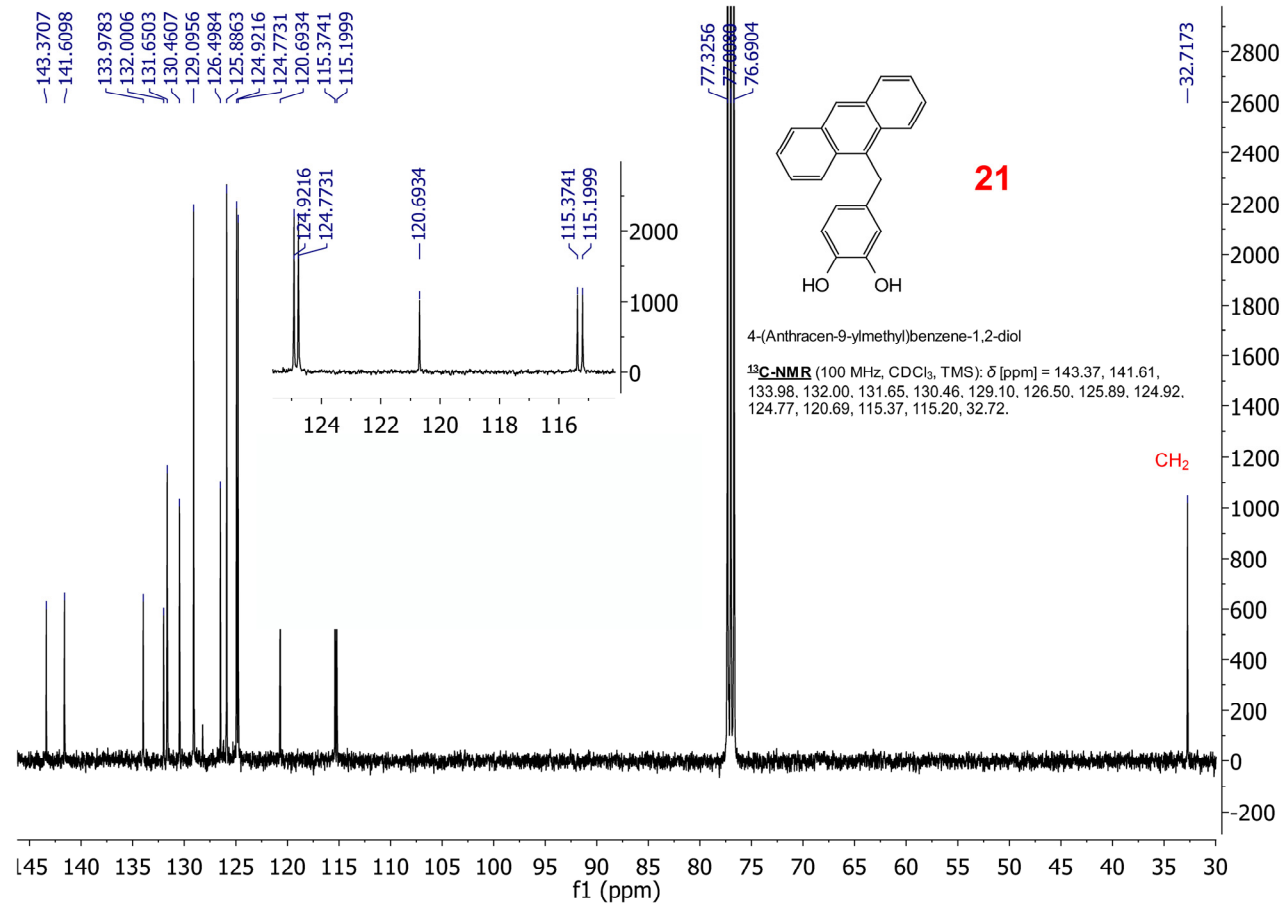

8.4954
8.3166
8.2944
8.0515
8.0303
7.6630
7.6600
7.6466
7.6433
7.6377
7.6243
7.6213
7.5204
7.5001
7.4829
7.2533
5.5473
2.3516
1.5265
1.2553
1.1104
0.0002
CH2
19
anthracene (9H)
anthracene
9-(bromomethyl)anthracene
1H-NMR (400 MHz, CDCl3, TMS): δ [ppm] = 8.50 (s, 1H, H-10), 8.32-8.29 (d, J = 8.9 Hz, 2H, H-1, 8), 8.05-8.03 (d, J = 8.5 Hz, 2H, H-4, 5), 7.66-7.62 (t, J = 8.3 Hz, 2H, H-2, 7), 7.52-7.48 (t, J = 7.5 Hz, 2H, H-3, 6), 5.55 (s, 2H, -CH2).

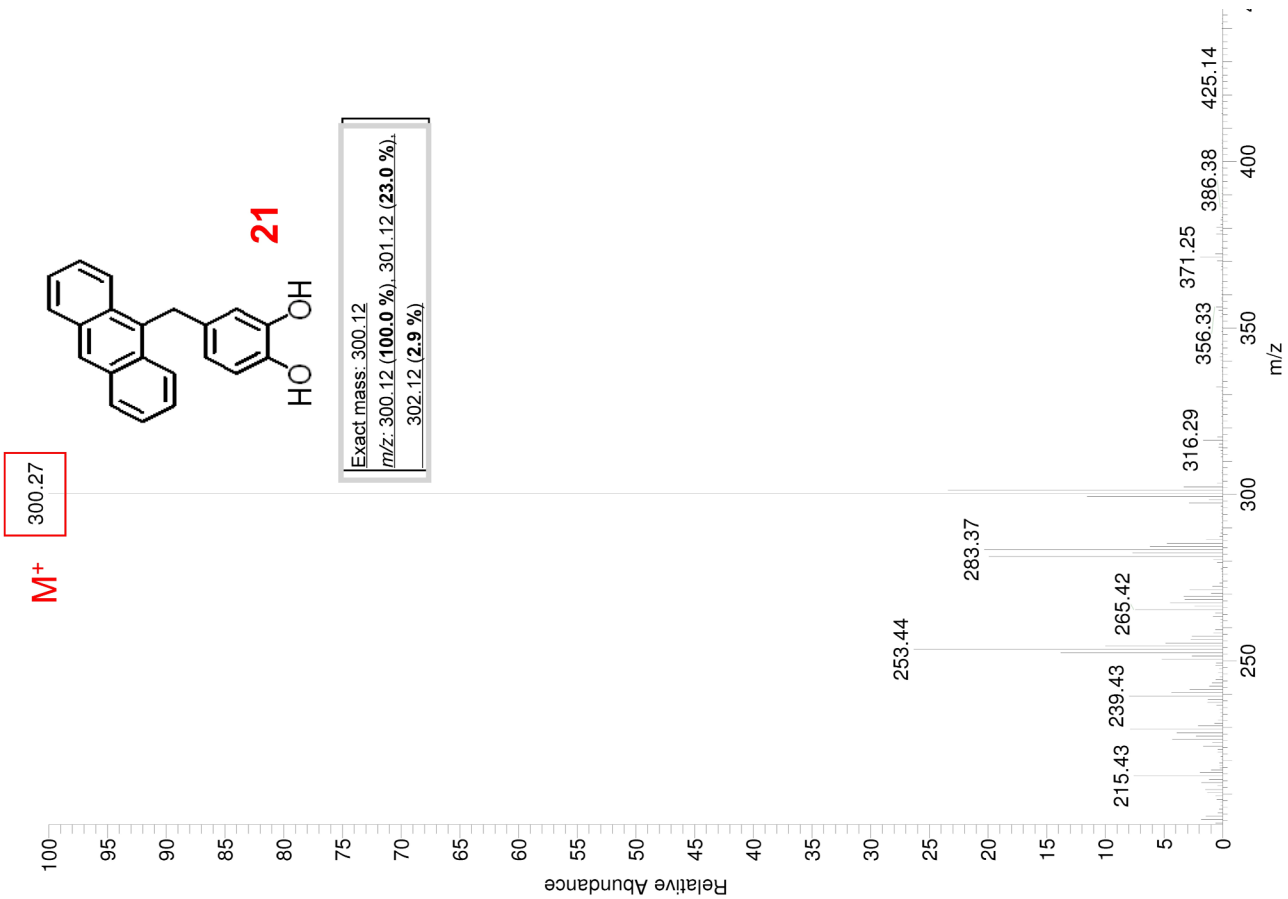

Jul04-2017-IP
Supervisor Name IP
17IS19-C1+C2
PROTON.b CDCl3 {C:\Bruker\TopSpin3.2} IP 15
OCH3
OCH3
1H NMR in CDCl3
20
anthracene
(9H)
benzene
(3H)
CH2
2 x OCH3
f1 (ppm)

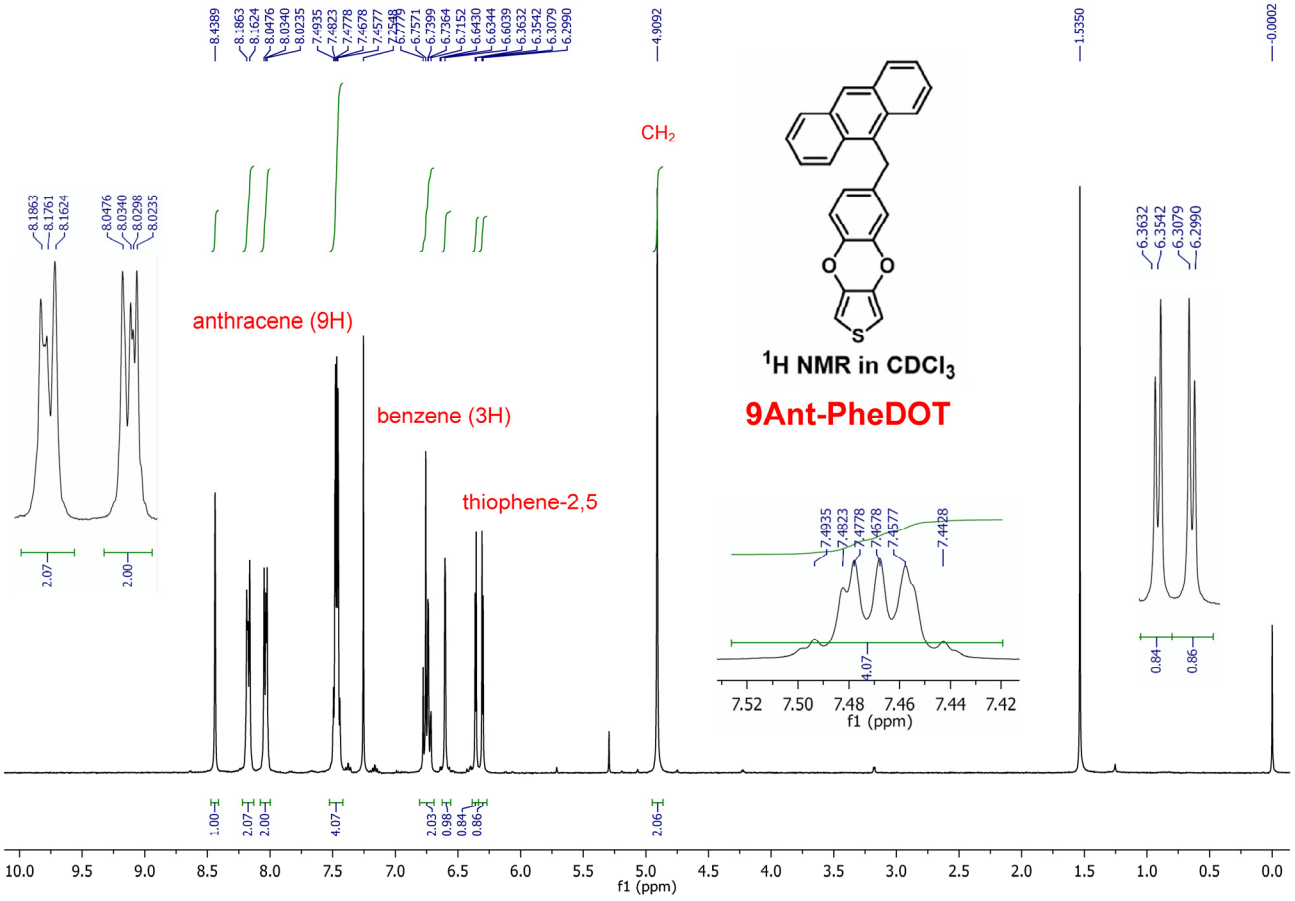

H3C
O
O
CH3
13C NMR in CDCl3
20
2 x OCH3
CH2
f1 (ppm)

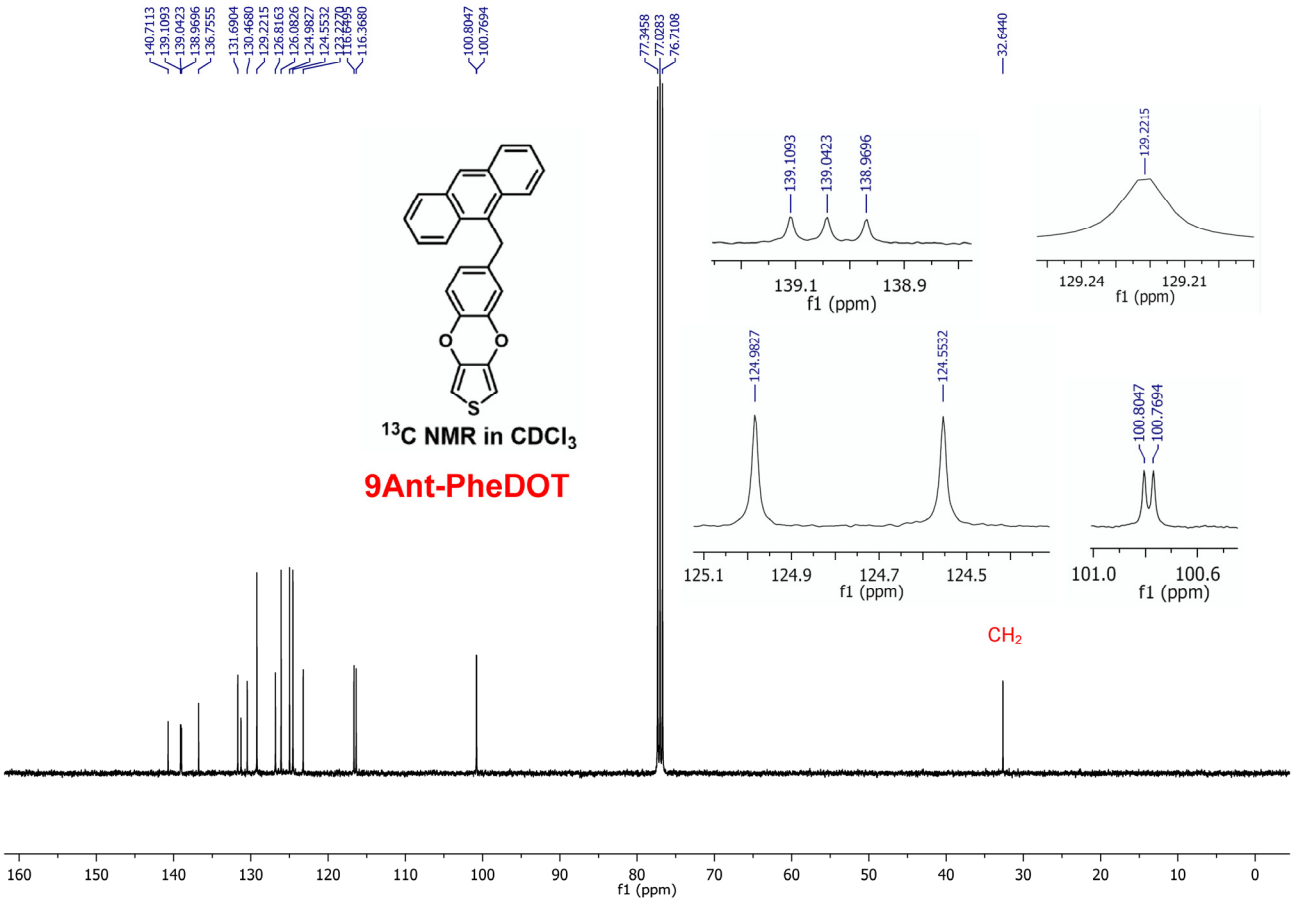

OCH3
OCH3
20
Exact Mass: 328.15
m/z: 328.15 (100.0 %), 329.15 (25.2 %), 330.15 (3.4 %)
M+
328.32
297.36
313.53
285.50
265.47
342.24
360.29
371.27
408.25
439.58
Relative Abundance
m/z

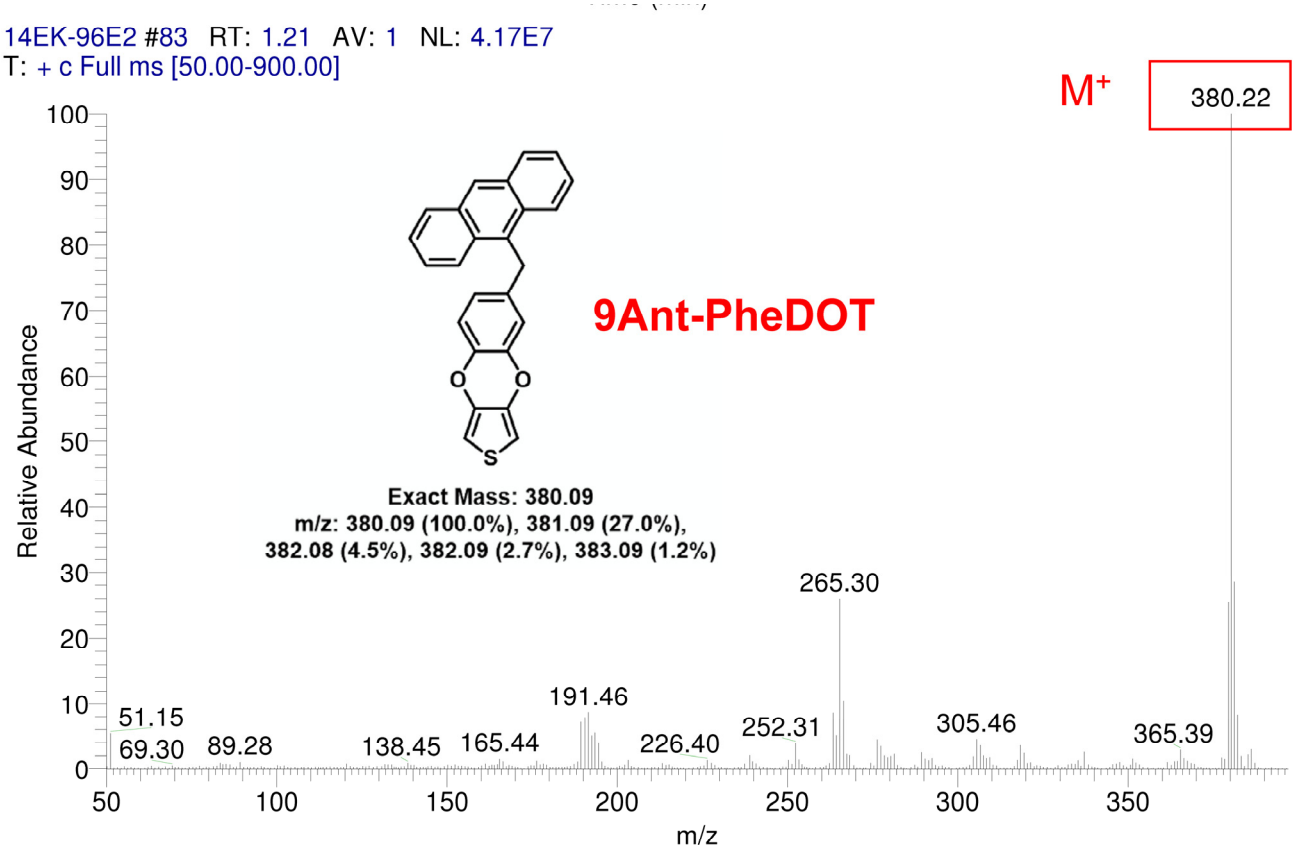

anthracene
benzene
CH2
OH
OH
HO
OH
1H NMR in CDCl3
21
f1 (ppm)

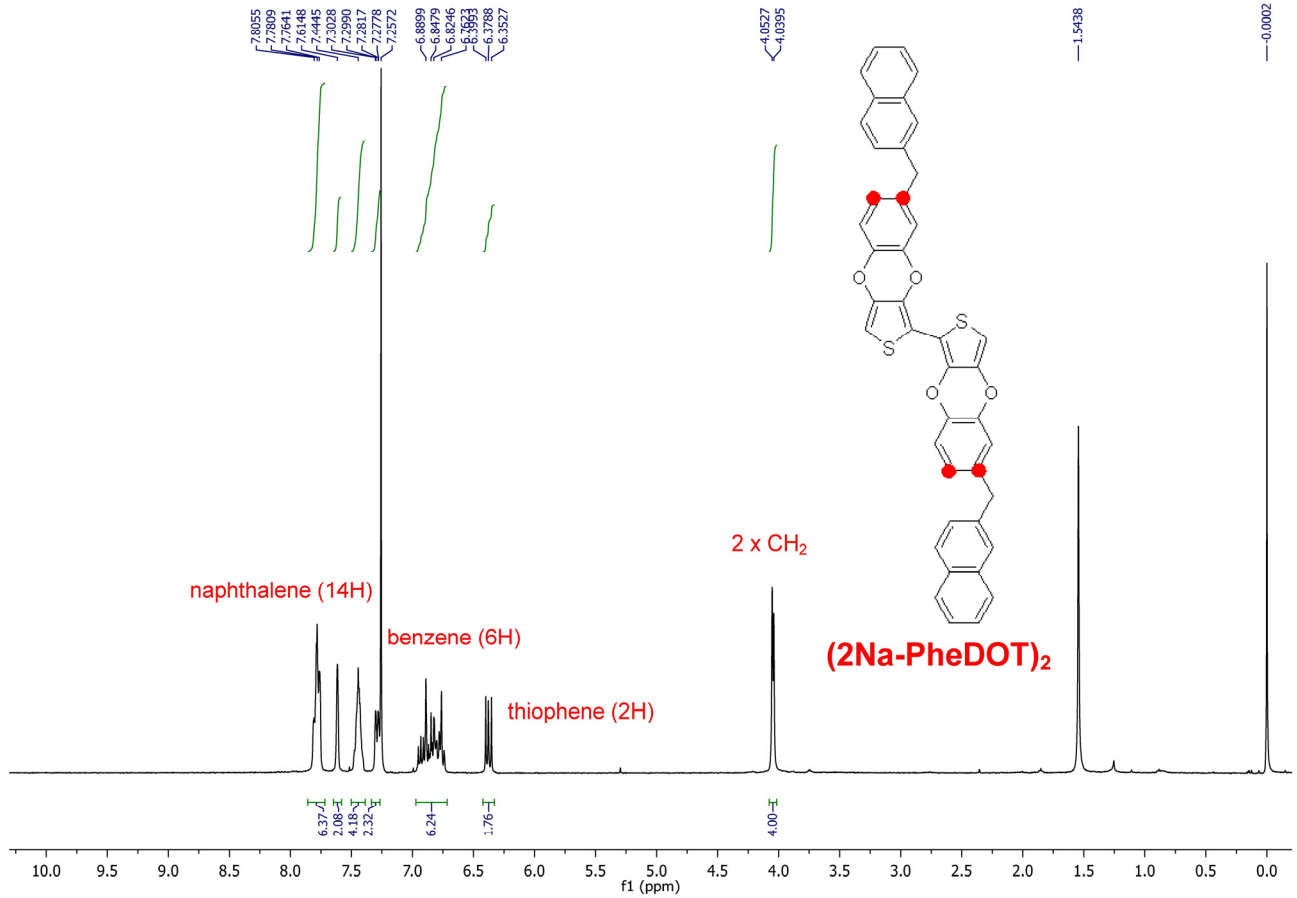

143.3707
141.6098
133.9783
132.0006
131.6503
130.4607
129.0956
126.4984
125.8863
124.9216
124.7731
120.6934
115.3741
115.1999
77.3256
77.0000
76.6904
32.7173
21
HO
OH
4-(Anthracen-9-ylmethyl)benzene-1,2-diol
13C-NMR (100 MHz, CDCl3, TMS): δ [ppm] = 143.37, 141.61, 133.98, 132.00, 131.65, 130.46, 129.10, 126.50, 125.89, 124.92, 124.77, 120.69, 115.37, 115.20, 32.72.
CH2
f1 (ppm)

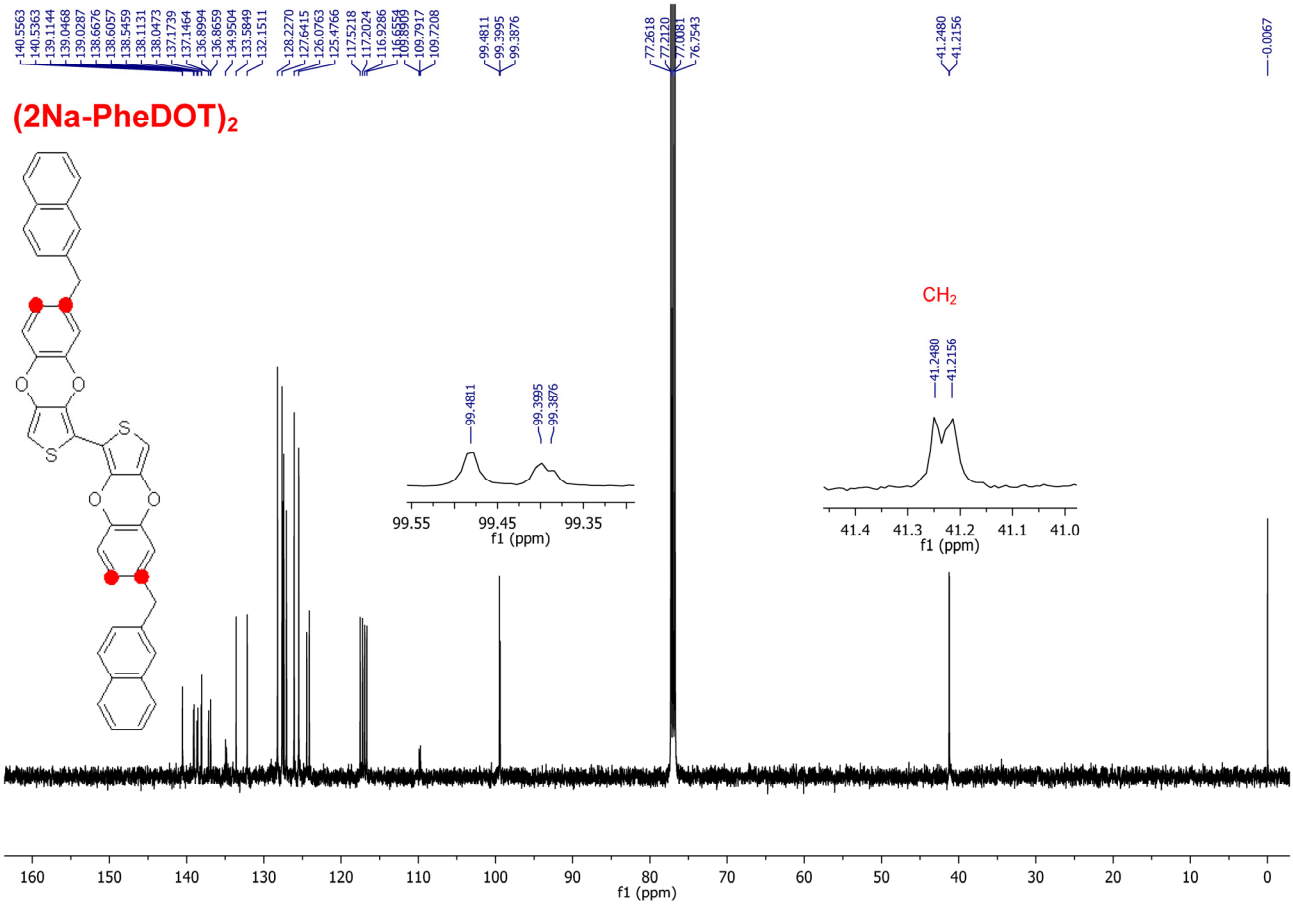

21
HO
OH
Exact mass: 300.12
m/z: 300.12 (100.0 %), 301.12 (23.0 %), 302.12 (2.9 %)
M+
300.27
316.29
356.33
371.25
386.38
425.14
283.37
253.44
265.42
239.43
215.43
m/z
Relative Abundance

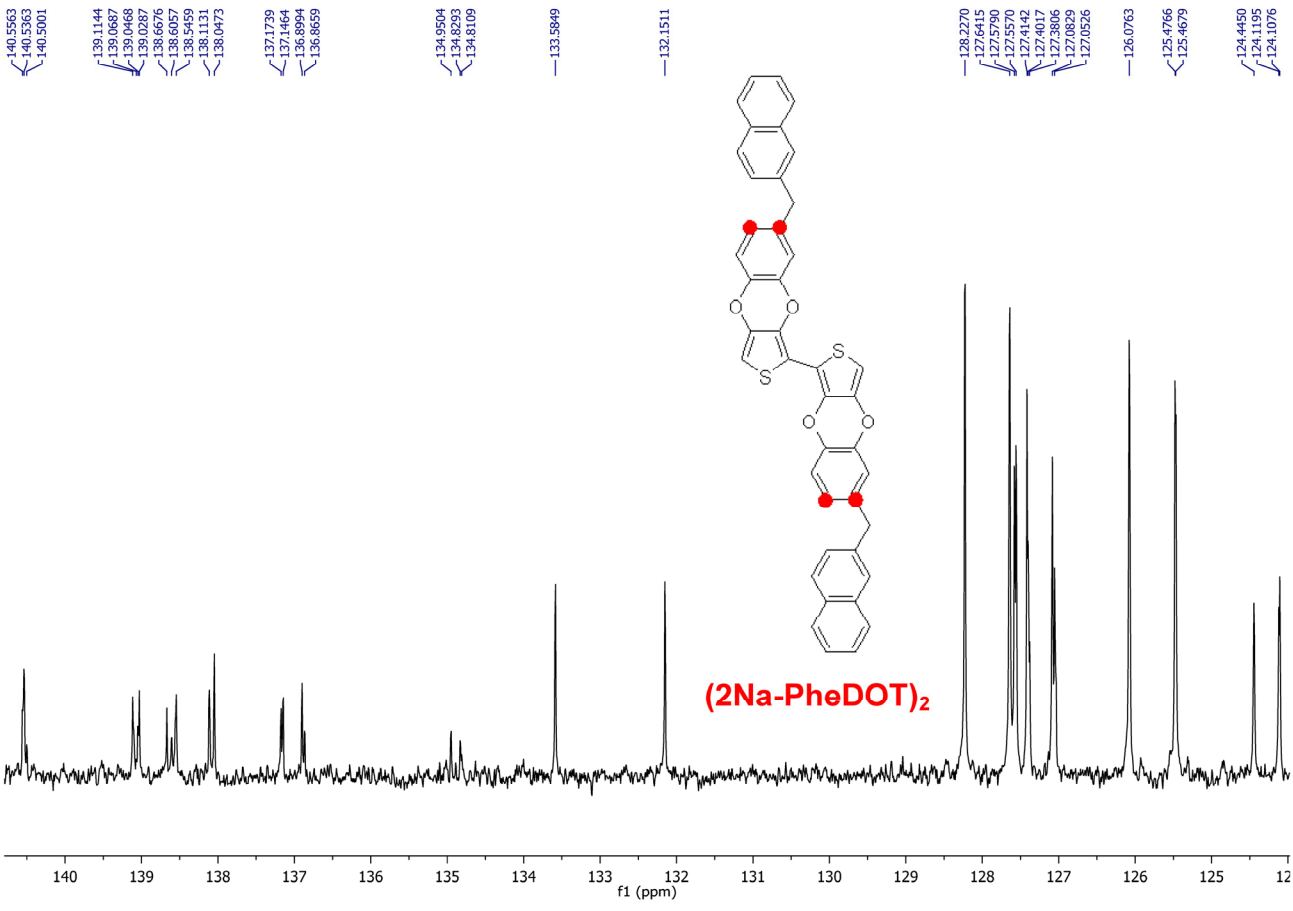

anthracene (9H)
benzene (3H)
thiophene-2,5
CH2
1H NMR in CDCl3
9Ant-PheDOT
f1 (ppm)

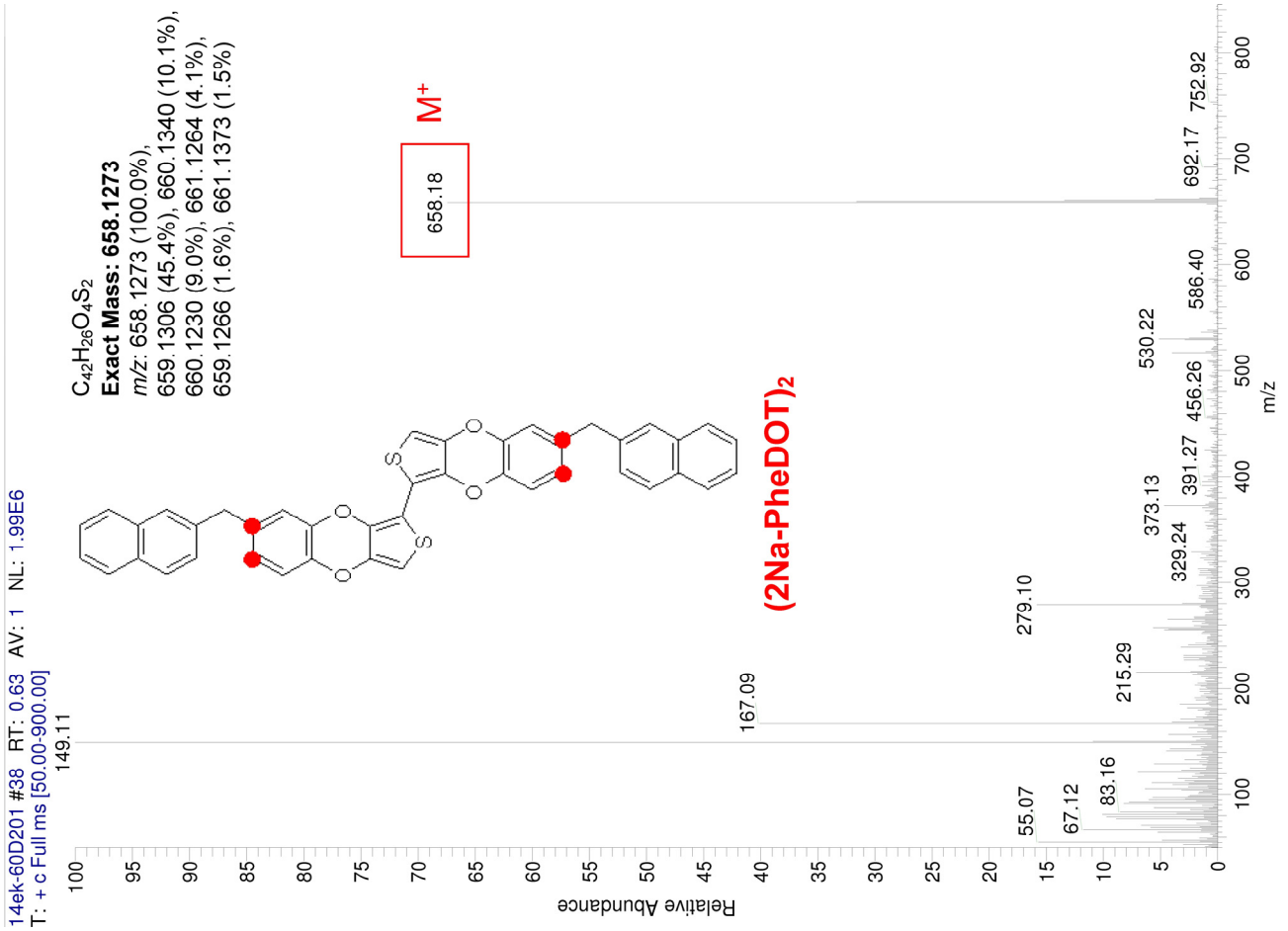

13C NMR in CDCl3
9Ant-PheDOT
CH2
f1 (ppm)

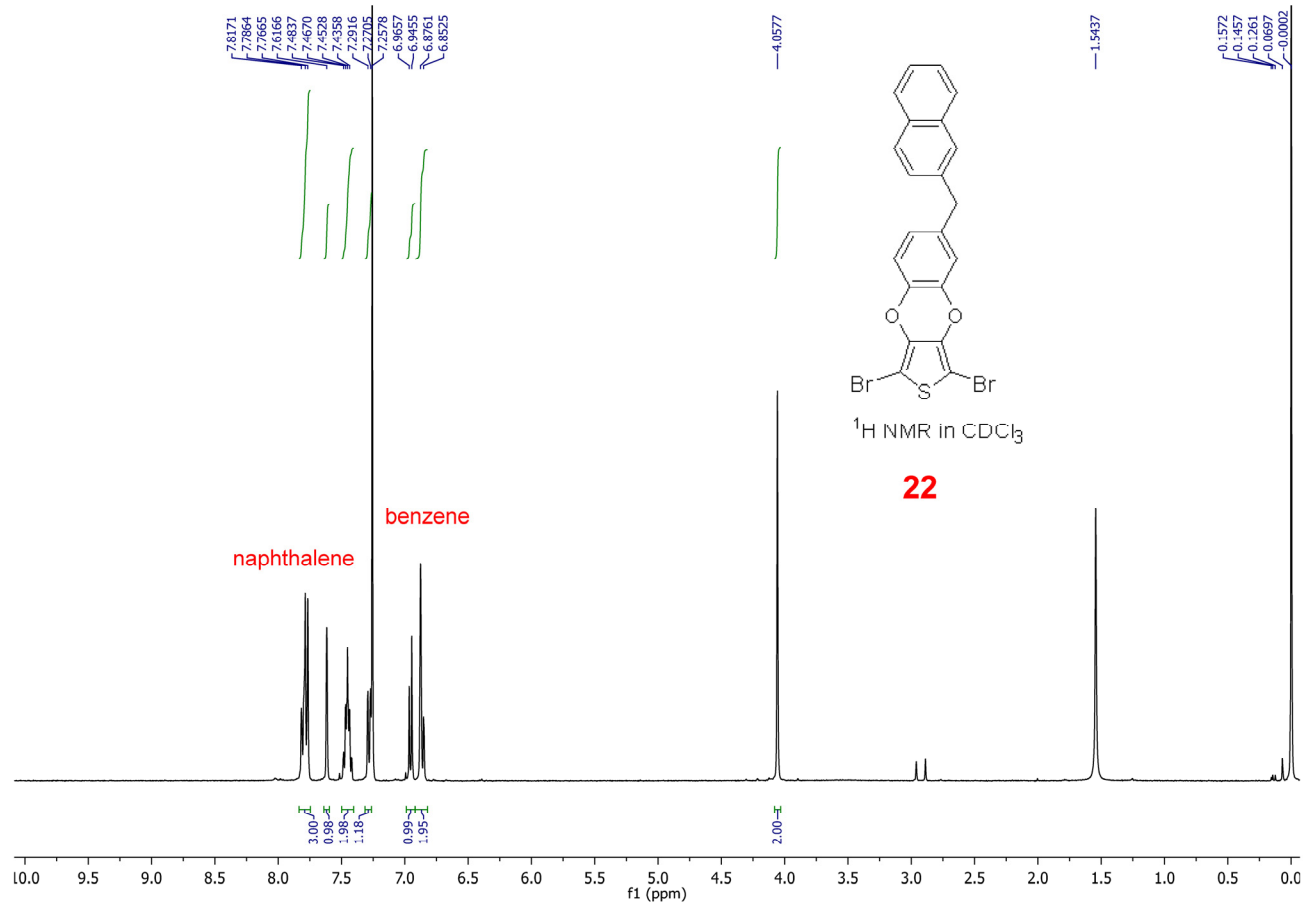

14EK-96E2 #83 RT: 1.21 AV: 1 NL: 4.17E7
T: + c Full ms [50.00-900.00]
M+
380.22
9Ant-PheDOT
Exact Mass: 380.09
m/z: 380.09 (100.0%), 381.09 (27.0%),
382.08 (4.5%), 382.09 (2.7%), 383.09 (1.2%)
Relative Abundance
m/z
265.30
191.46
51.15
69.30
89.28
138.45
165.44
226.40
252.31
305.46
365.39

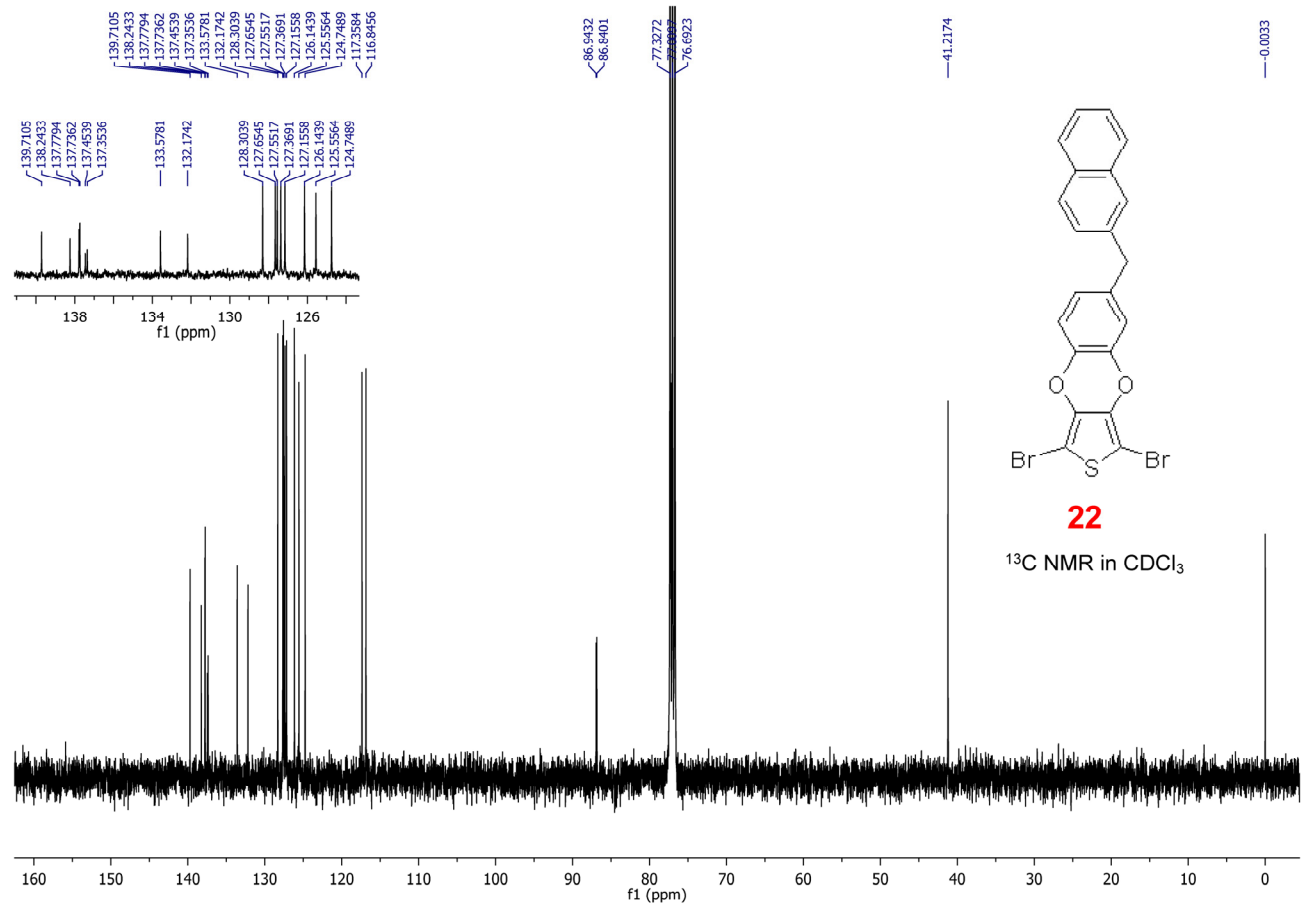

naphthalene (14H)
benzene (6H)
thiophene (2H)
2 x CH2
(2Na-PheDOT)2
f1 (ppm)

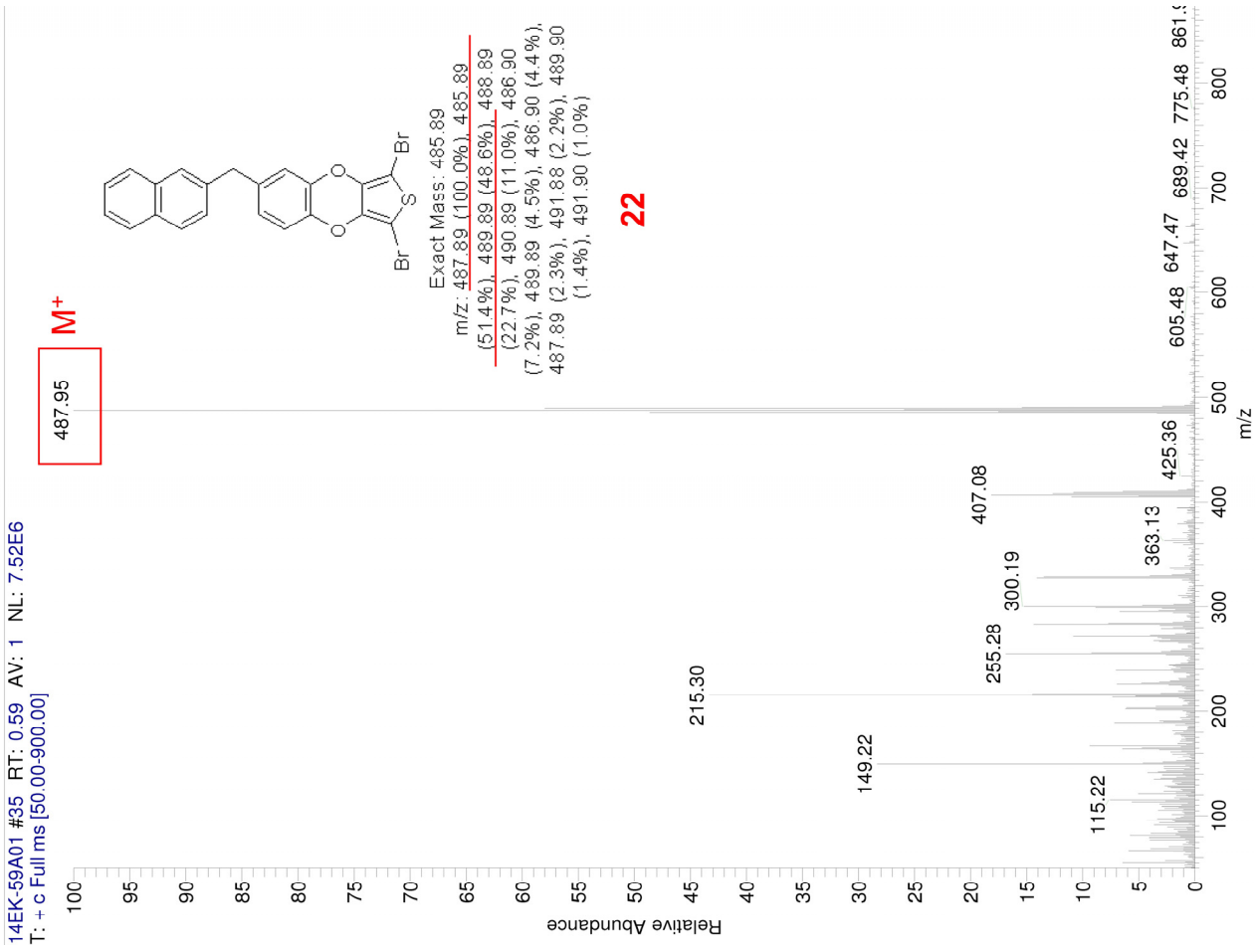

(2Na-PheDOT)2
CH2
99.55
99.45
99.35
f1 (ppm)
41.4
41.3
41.2
41.1
41.0
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

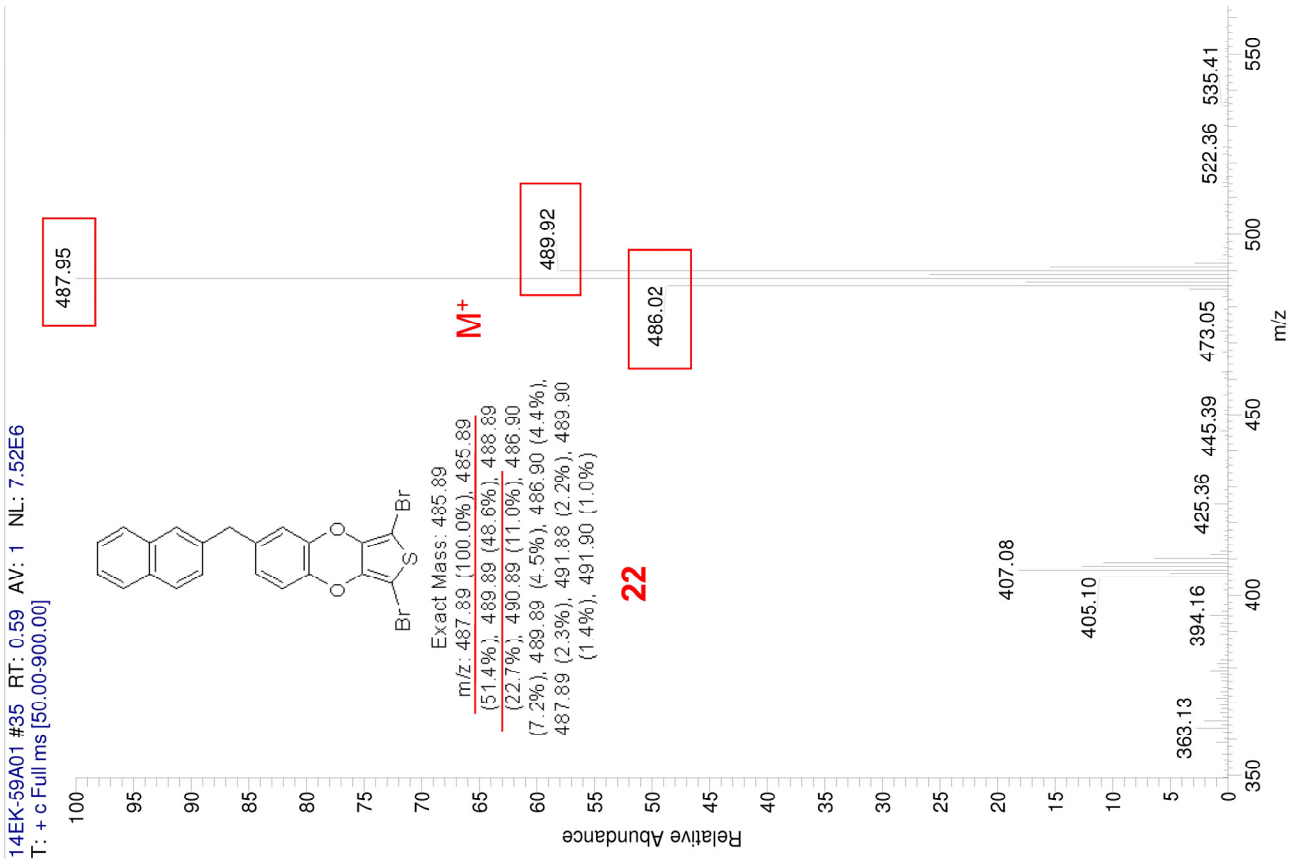

(2Na-PheDOT)2
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
12
f1 (ppm)

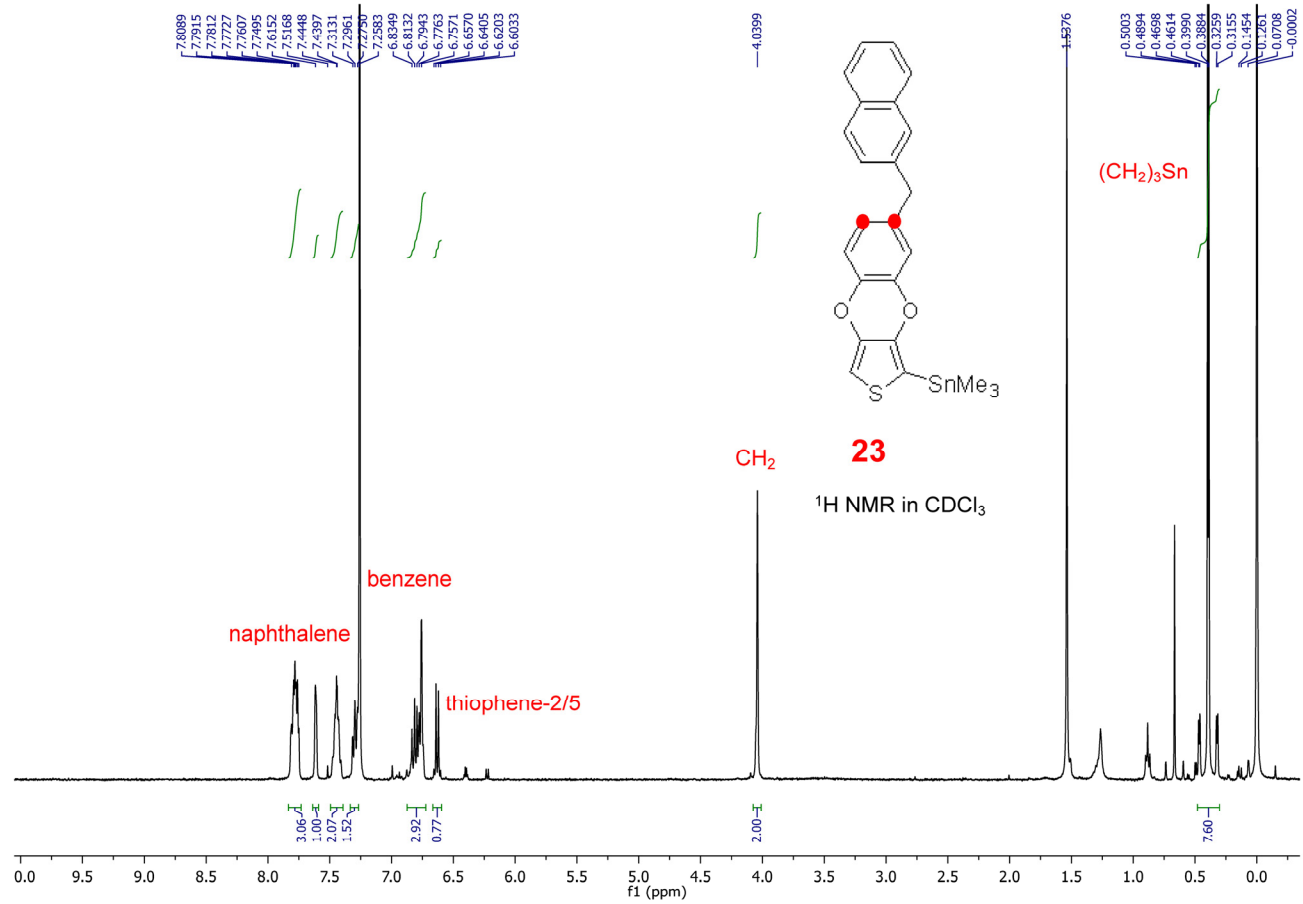

14ek-60D201 #38 RT: 0.63 AV: 1 NL: 1.99E6
T: + c Full ms [50.00-900.00]
149.11
167.09
215.29
279.10
329.24
373.13
391.27
456.26
530.22
586.40
692.17
752.92
658.18
M+
(2Na-PheDOT)2
C42H26O4S2
Exact Mass: 658.1273
m/z: 658.1273 (100.0%), 659.1306 (45.4%), 660.1340 (10.1%), 660.1230 (9.0%), 661.1264 (4.1%), 659.1266 (1.6%), 661.1373 (1.5%)
55.07
67.12
83.16
Relative Abundance
m/z


naphthalene
benzene
Br
Br
S
O
O
1H NMR in CDCl3
22
f1 (ppm)


139.7105
138.2433
137.7794
137.7362
137.4539
137.3536
133.5781
132.1742
128.3039
127.6545
127.5517
127.3691
127.1558
126.1439
125.5564
124.7489
117.3584
116.8456
86.5432
86.8401
77.3272
76.6923
41.2174
-0.0033
f1 (ppm)
Br
S
Br
22
13C NMR in CDCl3


14EK-59A01 #35 RT: 0.59 AV: 1 NL: 7.52E6
T: + c Full ms [50.00-900.00]
487.95
M+
Exact Mass: 485.89
m/z: 487.89 (100.0%), 485.89 (51.4%), 489.89 (48.6%), 488.89 (22.7%), 490.89 (11.0%), 486.90 (7.2%), 489.89 (4.5%), 486.90 (4.4%), 487.89 (2.3%), 491.88 (2.2%), 489.90 (1.4%), 491.90 (1.0%)
22
Br
Br
S
O
O
Relative Abundance
m/z
215.30
149.22
115.22
255.28
300.19
407.08
363.13
425.36
605.48
647.47
689.42
775.48

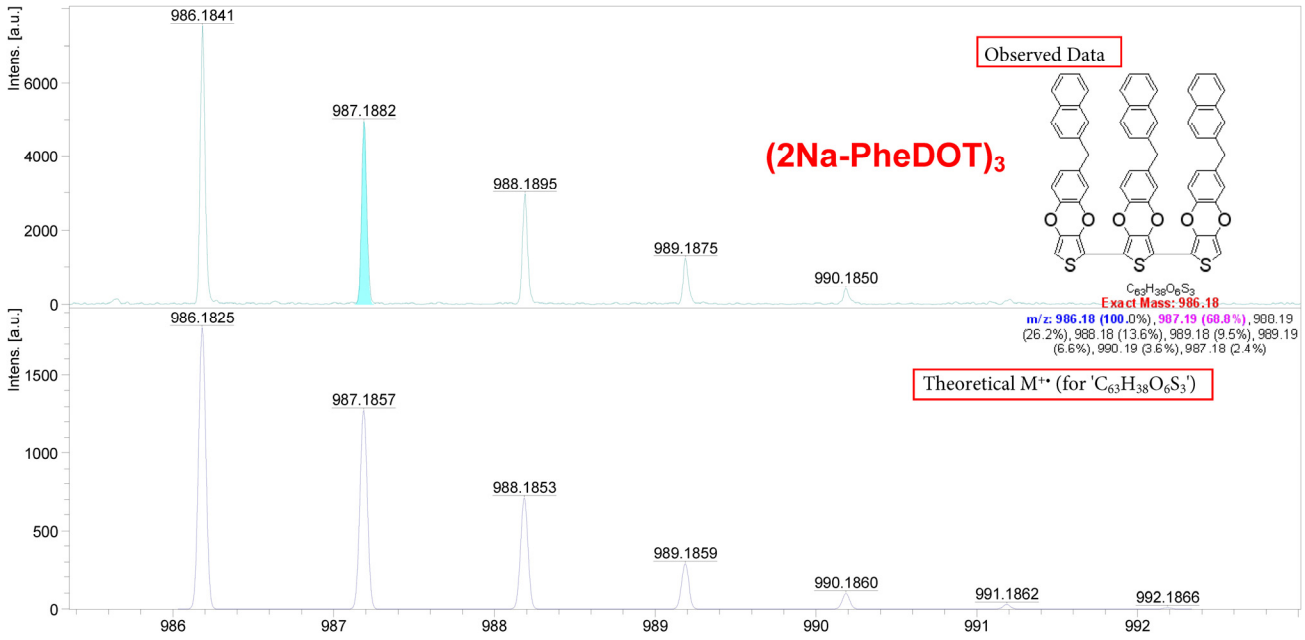

14EK-59A01 #35 RT: 0.59 AV: 1 NL: 7.52E6
T: + c Full ms [50.00-900.00]
487.95
489.92
486.02
407.08
405.10
363.13
394.16
425.36
445.39
473.05
522.36
535.41
M+
Exact Mass: 485.89
m/z: 487.89 (100.0%), 485.89 (51.4%), 489.89 (48.6%), 488.89 (22.7%), 490.89 (11.0%), 486.90 (7.2%), 489.89 (4.5%), 486.90 (4.4%), 487.89 (2.3%), 491.88 (2.2%), 489.90 (1.4%), 491.90 (1.0%)
22
Br
Br
S
O
O
Relative Abundance
m/z


naphthalene
benzene
thiophene-2/5
CH2
(CH2)3Sn
SnMe3
23
1H NMR in CDCl3
f1 (ppm)

EPSRC UK National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2017\August\BANMUR-3LKE3-UR-B\0_M9\1\1SRef

Comment 1 14EK-63C1 MW=986?? PosRef DCM [1:49] (Terth;DCM) (PPG-725; Dith;DCM+NaAOc)



ultrafleXtreme MALDI Date of Acquisition 2017-08-30T14:11:27.716+01:00 Printed 30/08/2017 14:15:49