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Supporting Information towards:

Anhydrous proton conduction in porous organic networks

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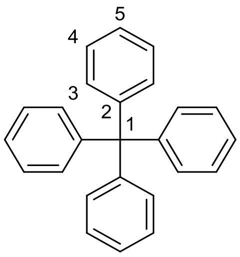
Linker Synthesis

Tetraphenylmethane[1]



Chemical Formula: $C_{25}H_{20}$
Molecular Weight: 320,43

15 g of trityl chloride (0.054 mol, 1 eq.) and 14.05 ml aniline (0.154 mol, 2.9 eq.) were heated up to 180 °C in a round flask with magnetic stirrer and condenser, until the reaction mixture turned into a violet solid. The heating process was extended for 10 more minutes. The solid was cooled down, crushed and resuspensed in 75 ml MeOH and 75 ml 2 *M* HCl. The Suspension was refluxed for 30 min., filtered and washed with water. After resuspending in ethanol the reaction mixture was cooled down to -30 °C and 15.8 ml sulfuric acid and 9.44 g of isopentylnitrite (0.081 mol, 1.5 eq.) were added under vigorous stirring. After stirring for 1 h at -10 °C, 26.9 ml of phosphinic acid (0.609 mol, 11 eq.) were added slowly and the reaction mixture was refluxed for 1.5 h. After cooling down, the solid was filtered, washed with DMF, H_2O and Ethanol and subsequently dried *in vacuo* to get a light brown powder. Further purification was not necessary but could be done by recrystallization in THF/methanol (1:1). Yield: 16.1 g (0.05 mol, 93 %). ^{1}H-NMR (500 MHz, DMSO-D6): δ [ppm] = 7.30 (t, 1H, H-4), 7.21 (t, 1H, H-5), 7.15 (d, 1H, H-3) (Figure S1). ^{13}C-NMR (500 MHz, DMSO-D6): δ [ppm] = 146.88 (C-2), 130.94 (C-3), 128.19 (C-4), 126.44 (C-5) (Figure S2). IR (ATR): ν [cm^{-1}] = 3037, 1588, 1489, 1186, 1077, 1033, 990, 967, 631, 523 (Figure S3).

^1H NMR

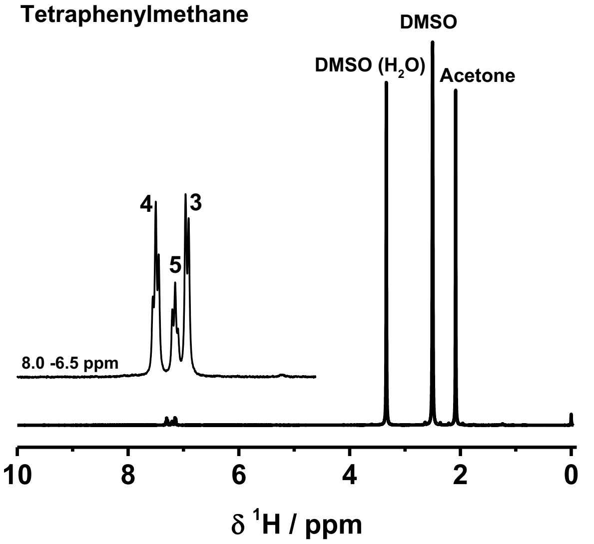


Figure S1: ^1H NMR spectrum of tetraphenylmethane measured in DMSO-d6.

^{13}C-NMR

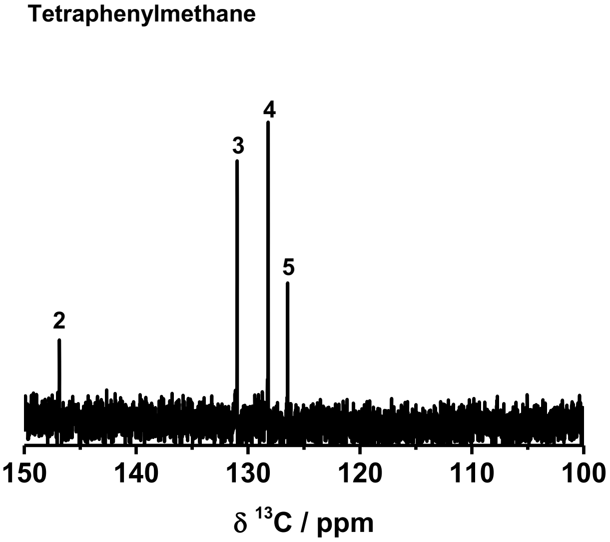


Figure S2: ^{13}C NMR spectrum of tetraphenylmethane measured in DMSO-d6.

IR

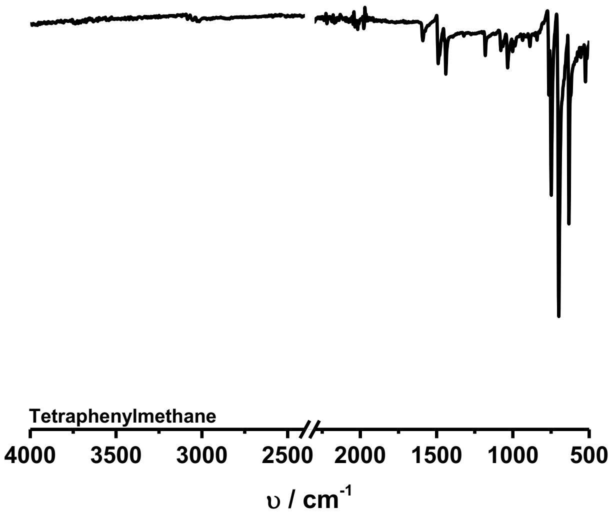
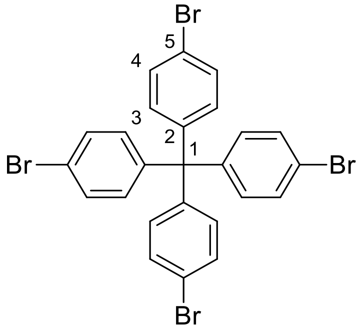


Figure S3: Infrared spectrum of tetraphenylmethane.

Tetrakis(4-bromophenyl)methane[2]



Chemical Formula: $C_{25}H_{16}Br_4$
Molecular Weight: 636,01

In a three necked vessel with magnetic stirrer, thermometer and condenser 10 g tetraphenylmethane (31.2 mmol, 1 eq.) were cooled in an ice bath. Now 99.8 g Br_2 (624 mmol, 20 eq.) were added dropwise. After cooling towards -78 °C, 140 ml ethanol (4.5 ml/mmol) were poured in and the mixture was allowed to reach room temperature overnight. Now sodiumdisulfide solution was added until the end of precipitation. The resulting solid was filtered, washed with H_2O and dried in an oven at 110 °C. Further purification was carried out performing recrystallization in a chloroform/ethanol mixture (1:1) to get a light brown solid. Yield: 12.9 g (20.3 mmol, 65 %). ^{1}H-NMR (500 MHz, DMSO-d6): δ [ppm] = 7.53 (d, 2H, H-4), 7.06 (d, 2H, H-3) (Figure S4). ^{13}C-NMR (500 MHz, DMSO-d6): δ [ppm] = 63.66 (C-1), 120.40 (C-5), 131.55 (C-3), 132.86 (C-4), 145.06 (C-2) (Figure S5). MS [M/z] = 279, 239, 636, 319, 555, 198. IR (ATR): ν [cm^{-1}] = 2960, 1569, 1486, 1393, 1181, 1072, 1005, 951, 908, 808, 750, 528, 507 (Figure S6).

^{1}H NMR

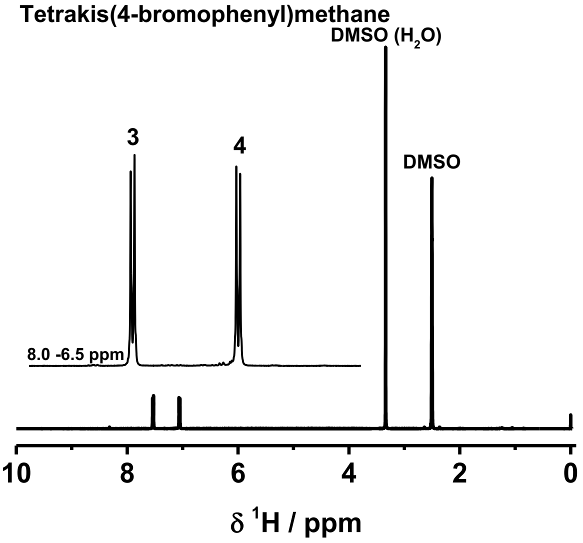


Figure S4: ^{1}H NMR spectrum of Tetrakis(4-bromophenyl)methane measured in DMSO.

^{13}C NMR

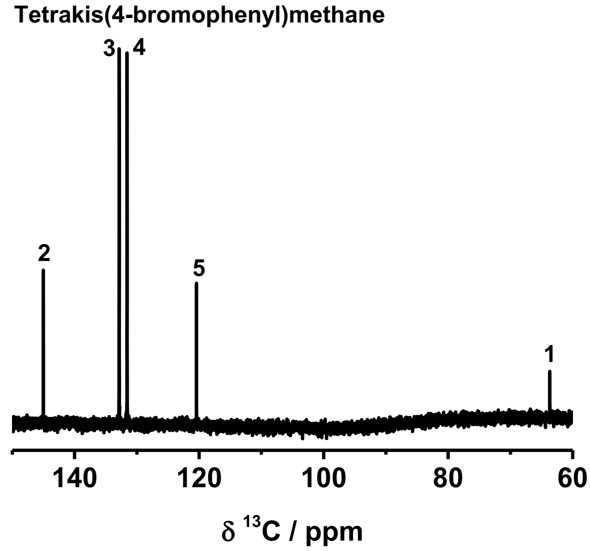


Figure S5: ^{13}C NMR spectrum of tetrakis(4-bromophenyl)methane measured in DMSO-d6.

IR

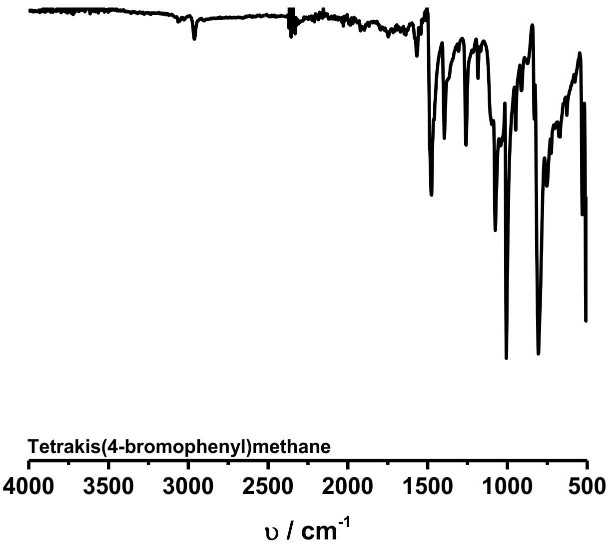
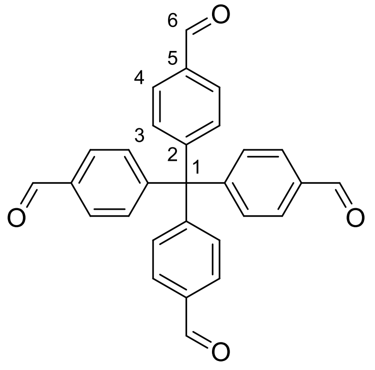


Figure S6: Infrared spectrum of tetrakis(4-bromophenyl)methane.

Tetrakis(4-formylphenyl)methane[3]



Chemical Formula: $C_{29}H_{20}O_4$
Molecular Weight: 432,47

Under argon atmosphere, 1.25 g of tetrakis(4-bromophenyl)methane ($1.97 \cdot 10^{-3}$ mol, 1 eq.) was dissolved in 75 ml dry tetrahydrofuran and cooled to -78 °C in a dry-ice/acetone bath. Now 10 ml *n*-BuLi (1.6 *M* in hexane, $1.6 \cdot 10^{-2}$ mol, 8 eq.) were added dropwise and the reaction mixture was stirred at -78 °C for further 7 h. Afterwards 5 ml dimethylformamide was added at -78 °C and the mixture was allowed to reach room temperature overnight. After addition of 1 *M* HCl, the mixture was extracted with dichloromethane (3x). The organic layers were combined, dried over $MgSO_4$, filtered and the solvent was evaporated. After performing flash column chromatographie with *n*-hexane/ethylacetate the product was obtained as white crystals. Yield: 0.246 g ($5.7 \cdot 10^{-4}$ mol, 29 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.92 (s, 1H, H-6), 7.76 (d, 1H, H-4), 7.37 (d, 1H, H-3) (Figure S7). ^{13}C NMR (500 MHz, $CDCl_3$): δ [ppm] = 191.5 (C-6), 151.2 (C-2), 134.8 (C-5), 131.2 (C-4), 129.7 (C-3), 66.3 (C-1) (Figure S8). IR (ATR): ν [cm^{-1}] = $2947\text{-}2715_{\text{mult.}}$, 1698, 1604, 1386, 1303, 1210, 1168, 1002, 795 (Figure S9).

^{1}H NMR

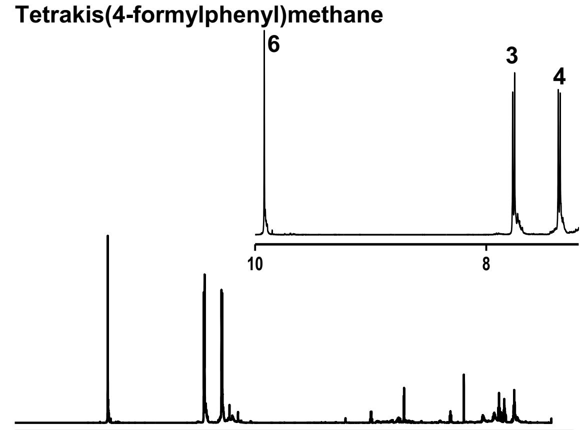


Figure S7: ^{1}H NMR Spectrum of tetrakis(4-formylphenyl)methane measured in $CDCl_3$.

^{13}C NMR

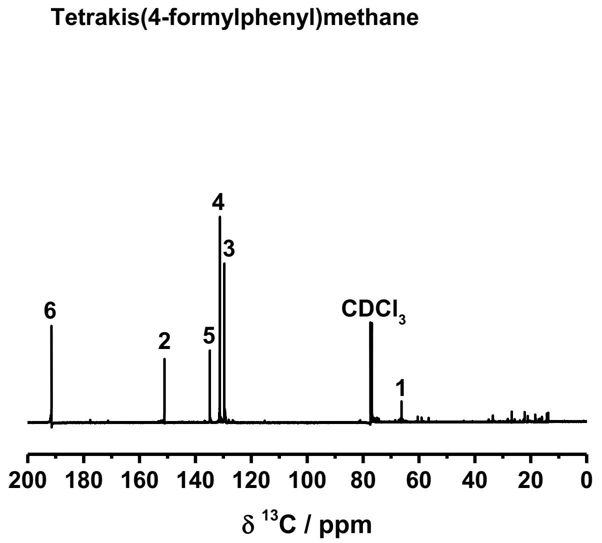


Figure S8: ^{13}C NMR spectrum of tetrakis(4-formylphenyl)methane measured in CDCl$_3$.

IR

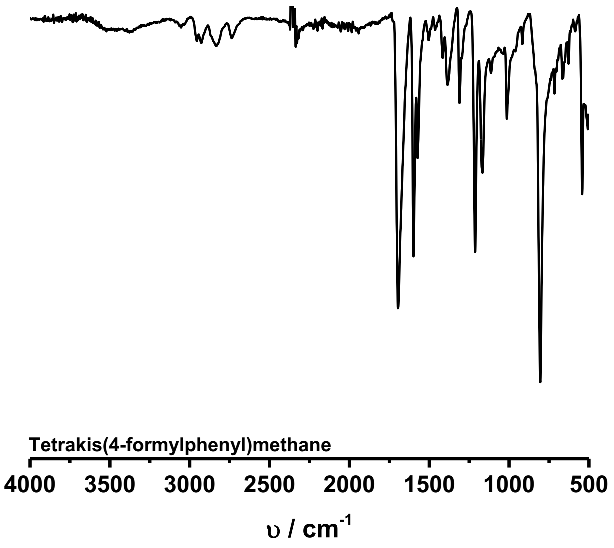
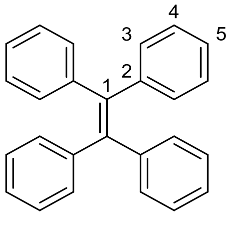


Figure S9: Infrared spectrum of tetrakis(4-formylphenyl)methane.

1,1,2,2-Tetraphenylethylene[4]



Chemical Formula: $C_{26}H_{20}$
Molecular Weight: 332,44

In a dry vessel, 5 g of benzophenone (0.027 mol, 1 eq.) was placed under Ar. 4.24 g Zn powder (0.065 mol, 2.4 eq.) and 100 ml dry tetrahydrofuran were added. The mixture was cooled towards -78 °C in a dry-ice/acetone bath and 3.6 ml of $TiCl_4$ (0.032 mol, 1.2 eq.) were added dropwise. After stirring at -78 °C for 20 minutes the mixture was allowed to reach room temperature and then refluxed for 14 h. After cooling down, the reaction mixture was poured into water and extracted with dichloromethane (4 x 100 ml). The organic layer was washed with brine and water, dried over $MgSO_4$ and filtered. After solvent evaporation the product was recrystallized from dichloromethane to give an off white powder. Yield 2.6 g ($7.83 \cdot 10^{-3}$ mol, 58 %). ^1H NMR (500 MHz, DMSO-d6): δ [ppm] = 7.45 (m, 1H, Ar-H), 7.12 (m, 1H, Ar–H), 6.96 (m, 1H, Ar-H) (Figure S10). ^{13}C NMR (500 MHz, DMSO-d6): δ [ppm] = 143.7 (C-2), 140.9 (C-1), 131.4 (C-3), 127.7 (C-4), 126.4 (C-5) (Figure S11). IR (ATR): ν [cm^{-1}] = 3023, 1598, 1493, 1443, 1167, 1076, 1021, 744, 690, 604, 564 (Figure S12).

^1H-NMR

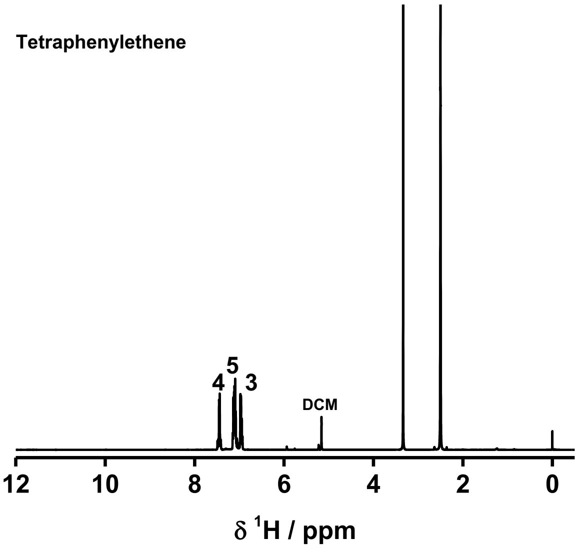


Figure S10: ^1H NMR spectrum of tetraphenylethene measured in DMSO-d6.

^{13}C-NMR

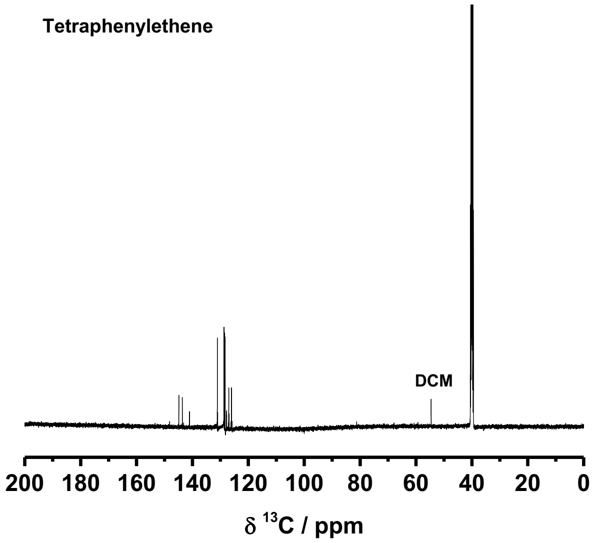


Figure S11: ^{13}C NMR spectrum of tetraphenylethe measured in DMSO-d6.

IR

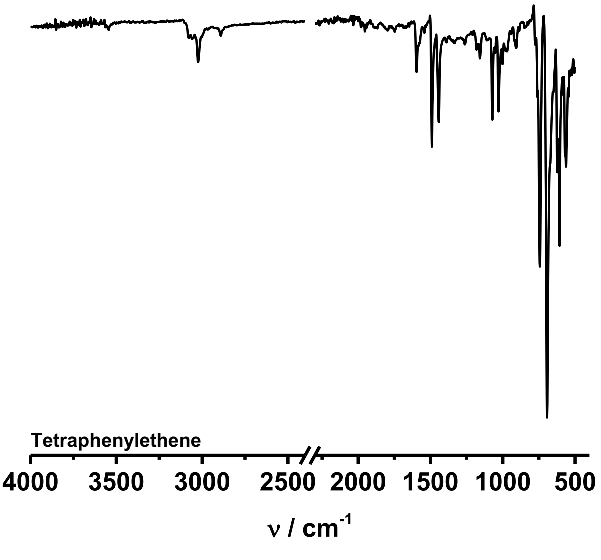
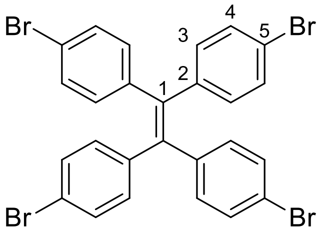


Figure S12: Infrared spectrum of tetraphenylethene.

1,1,2,2-Tetrabromophenylethylene



Chemical Formula: $C_{26}H_{16}Br_4$
Molecular Weight: 648,02

2 g of Tetraphenylethylene ($6.01\cdot10^{-3}$ mol, 1eq.) was placed in a vessel which and cooled in an ice bath. Now 6.2 ml of bromine (0.12 mol, 20 eq.) were added slowly. The mixture was now cooled towards -78 °C in a dry-ice/acetone bath, followed by the addition of 30 ml ethanol. The mixture was allowed to rise to room temperature overnight (18 h) and sodium thiosulfate solution was added. The resulting precipitate was filtered, washed with water and dried in an oven at 130 °C. After recrystallization in chloroform/methanol a white solid was obtained. Yield: 3,36 g ($5.19\cdot10^{-3}$ mol, 86 %). ^{1}H NMR (500 MHz, DMSO-d6): δ [ppm] = 7.4 (d, 1H, Ar–H), 6.9 (d, 1H, Ar–H) (Figure S13). ^{13}C NMR (500 MHz, DMSO-d6): δ [ppm] = 140.8 (C-2), 138.7 (C-1), 132.2 (C-3), 130.5 (C-4), 119.8 (C-5) (Figure S14). IR (ATR): ν [cm^{-1}] = 1937, 1559, 1473, 1262, 1194, 1090, 896, 827, 586 (Figure S15)

^{1}H NMR

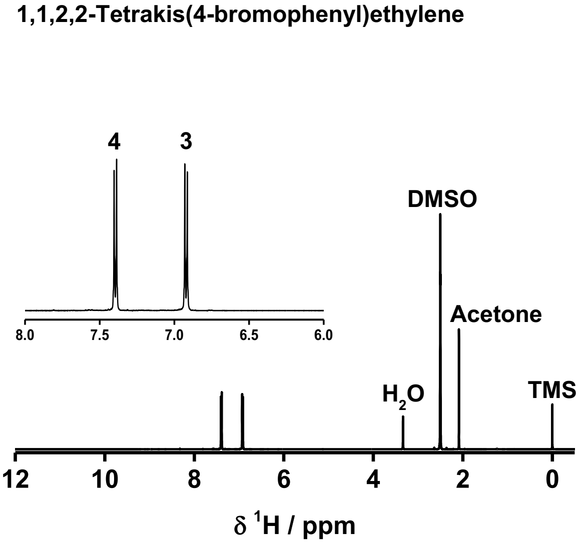


Figure S13: 1H NMR spectrum of tetrakis(4-bromophenyl)ethen measured in DMSO-d6.

^{13}C NMR

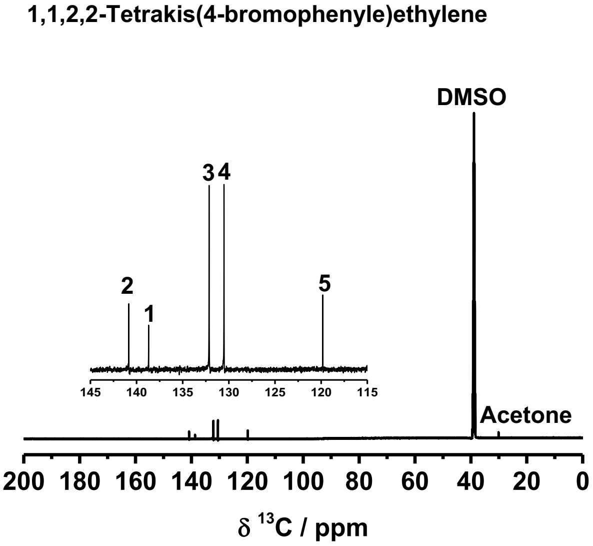


Figure S14: ^{13}C NMR spectrum of tetrakis(4-bromophenyl)ethene measured in DMSO-d6.

IR

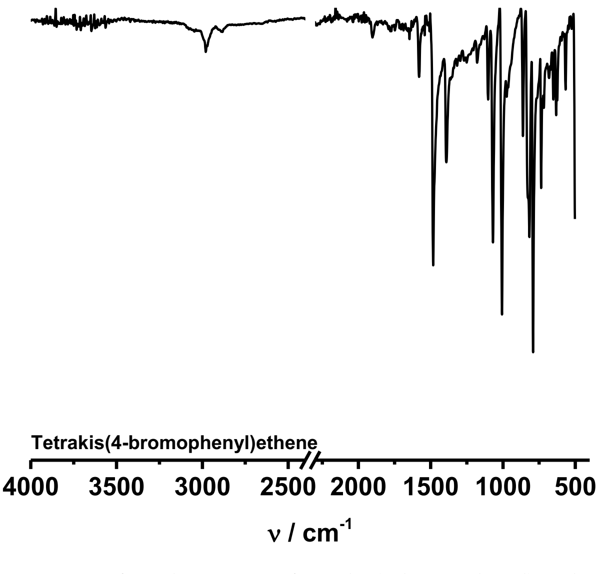
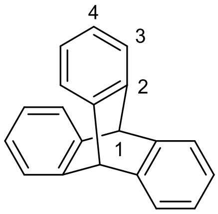


Figure S15: Infrared spectrum of tetrakis(4-bromophenyl)methane.

Triptycene



Chemical Formula: $C_{20}H_{14}$
Molecular Weight: 254,33

Under dry conditions 10 g of anthracene (0.056 mol, 1 eq.) was refluxed in 200 ml chloroform. After addition of 9.1 ml amyl nitrite (0.067 mol, 1.2 eq.), 8.46 g anthranilic acid (0.062 mol, 1.1 eq.) in 100 ml dry tetrahydrofuran was added dropwise over a time frame of 1.5 h. Afterwards, the reaction mixture was stirred under reflux for further 45 minutes. Now the solvent was evaporated and 5.5 g maleic anhydride (0.056 mol, 1 eq.) and 50 ml dioxane were added. The mixture was again refluxed for 1 h. The resulting solution was given in an ice cooled mixture of 150 ml H_2O, 150 ml MeOH and 25 g KOH and stirred for 5 minutes. The precipitate was filtered and washed with MeOH and Water. The solid was solved in 75 ml hot butanone and filtered. The filtrate was given in 100 ml MeOH and was stored in a freezer overnight for crystallisation. The resulting precipitate was filtered, washed with cold MeOH and dried in an oven at 130 °C to yield the product as white crystals. Yield: 3.01 g (0.012 mol, 21 %). ^{1}H NMR (500 MHz, DMSO-d6): δ [ppm] = 7.4 (m, 1H, Ar–H), 6.9 (m, 1H, Ar–H), 5.6 (s, 1H, H-1) (Figure S16). ^{1}H NMR (500 MHz, DMSO-d6): δ [ppm] = 146 (C-2), 125 (C-3), 124 (C-4), 53 (C-1) (Figure S17). IR (ATR): ν [cm^{-1}] = 3046, 2957, 1317, 1250, 1165, 1017, 794, 727, 618 (Figure S18).

^{1}H-NMR

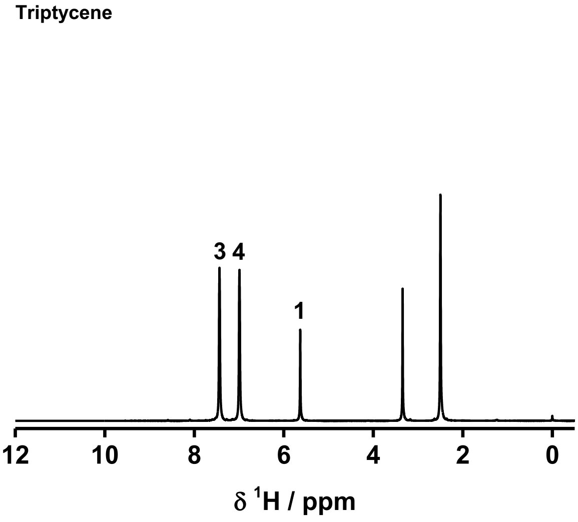


Figure S16: ^{1}H NMR spectrum of triptycene measured in DMSO-d6.

^{13}C NMR

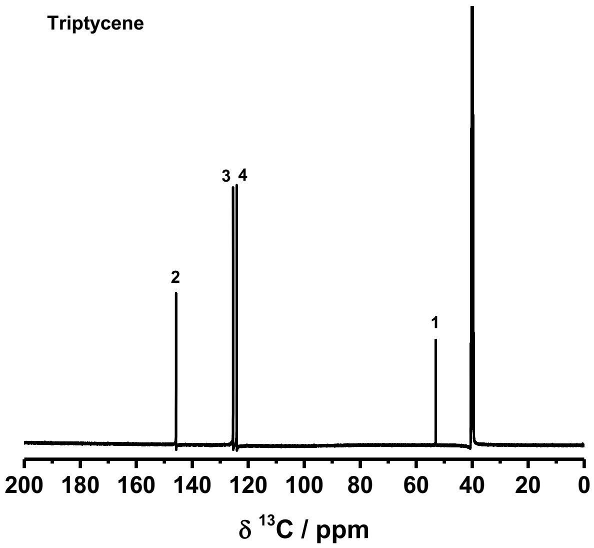


Figure S17: ^{13}C NMR spectrum of triptycene measured in DMSO-d6.

IR

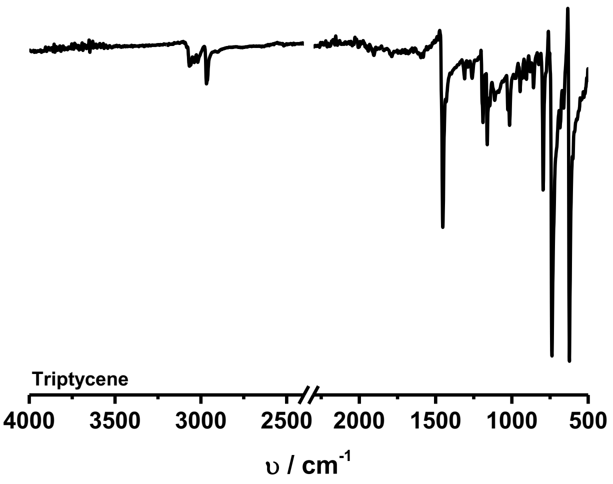
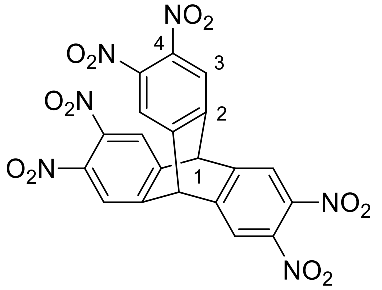


Figure S18: Infrared spectrum of triptycene.

Hexanitrotriptycene[5]



Chemical Formula: $C_{20}H_8N_6O_{12}$
Molecular Weight: 524,31

After combining 4.8 ml HNO_3 (100%) with 1.2 ml of sulfuric acid, 0.5 g triptycene ($1.97\cdot10^{-3}$ mol, 1 eq.) was added slowely. The resulting mixtures was refluxed overnight at 85 °C. After cooling down, the reaction was quenched in 300 ml H_2O and stirred for further 10 min., causing the precipitation of a white solid, which was then filtered and dried in an oven at 130 °C. Recrystallization from hot acetone yielded the product as white crystals. Yield: 0.27 g ($5.1\cdot10^{-4}$ mol, 26 %). ^{1}H NMR (500 MHz, DMSO-d6): δ [ppm] = 8.4 (m, 1H, H−3), 6.7 (m, 1H, H−1) (Figure S19). ^{13}C NMR (500 MHz, DMSO-d6): δ [ppm] = 148.1 (C-2), 140.6 (C-4), 124.0 (C-3), 51.1 (C-1) (Figure S20). IR (ATR): ν [cm^{-1}] = 3071, 1674, 1539, 1349, 1203, 902, 860, 778, 702, 522 (Figure S21).

^{1}H NMR

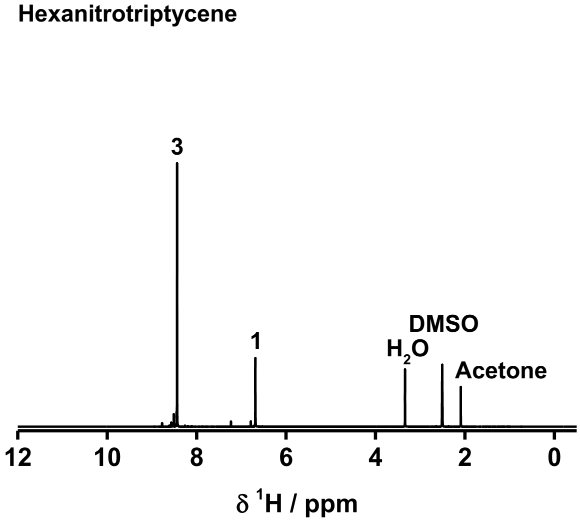


Figure S19: ^{1}H NMR spectrum of hexanitrotriptycene measured in DMSO-d6.

^{13}C NMR

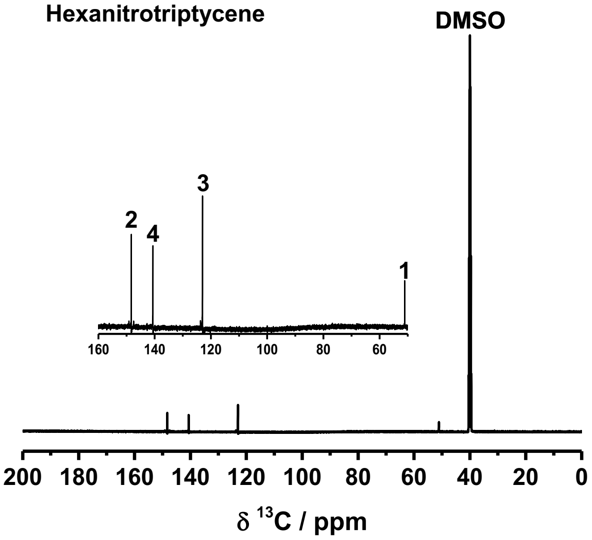


Figure S20: ^{13}C NMR spectrum of hexanitrotriptycene measured in DMSO-d6.

IR

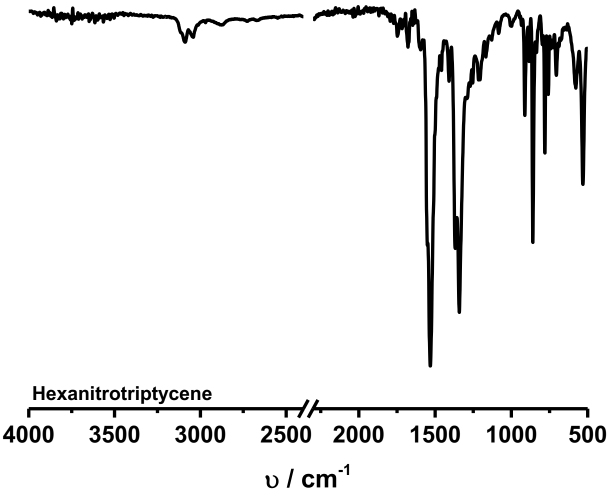
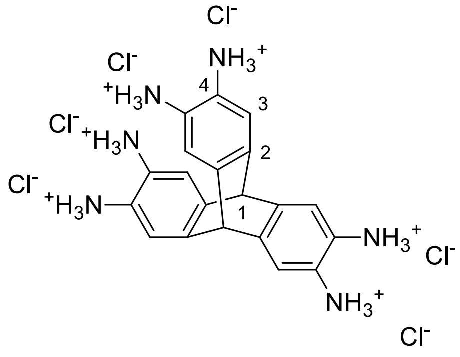


Figure S21: Infrared spectrum of hexanitrotriptycene.

Hexaaminotriptycene-hexachloride[6]



Chemical Formula: $C_{20}H_{26}Cl_6N_6$
Molecular Weight: 563,18

0.14 g of hexanitrotriptycene ($2.5 \cdot 10^{-4}$ mol, 1 eq.) and 1.86 g $SnCl_2 \cdot 2H_2O$ were suspended in 50 ml ethanol. After addition of 6.6 ml concentrated HCl (32 %) the mixture was refluxed for 24 h. The resulting solid was filtrated, washed with HCl and dried in an oven at 130 °C overnight to yield yellow platelets. Yield: 0.10 g ($1.8 \cdot 10^{-4}$ mol, 72 %). ^{1}H NMR (500 MHz, D_2O): δ [ppm] = 7.14 (s_{br}, 1H, H−3), 5.4 (s_{br}, 1H, H−1) (Figure S22). ^{13}C NMR (500 MHz, D_2O): δ [ppm] = 141.6 (C-2), 125.3 (C-4), 117.2 (C-3), 50.2 (C-1) (Figure S23). IR (ATR): ν [cm^{-1}] = 2968, 1559, 1473, 1262, 1194, 1090, 896, 827, 586 (Figure S24).

^{1}H-NMR

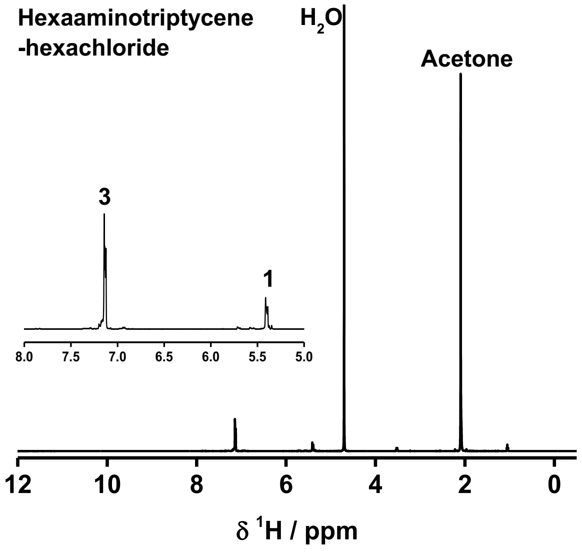


Figure S22: ^{1}H NMR spectrum of hexaaminotriptycene hexachloride measured in D_2O.

^{13}C- NMR

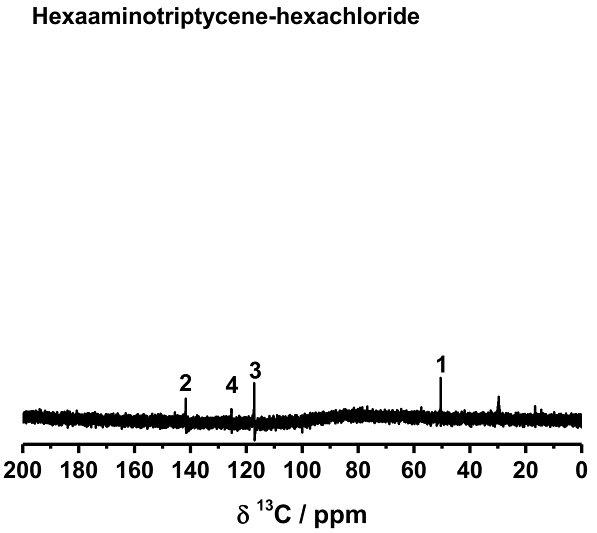


Figure S23: ^{13}C NMR spectrum of hexaaminotriptycene hexachloride measured in D_2O.

IR

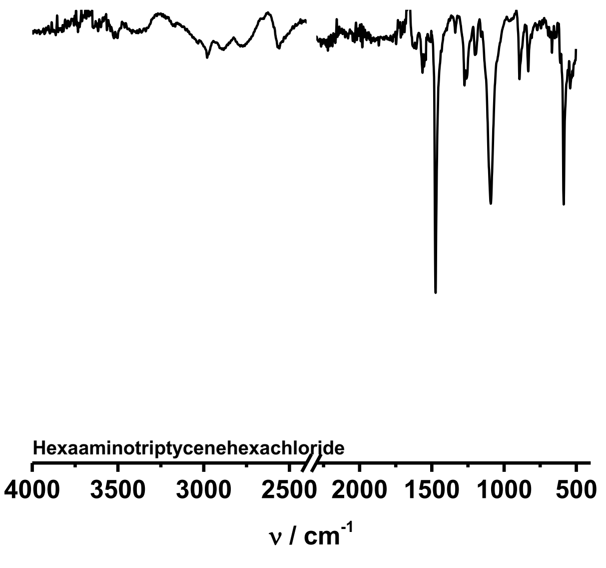
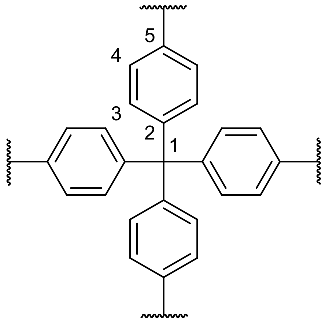


Figure S24: Infrared spectrum of hexaaminotriptycene hexachloride.

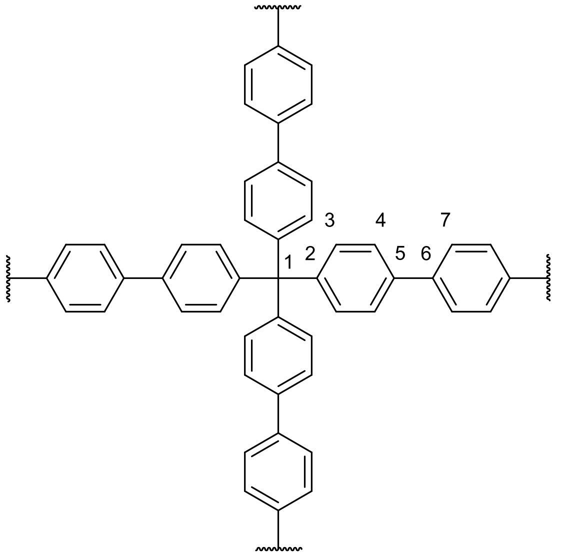
Polymer Synthesis

PON-1



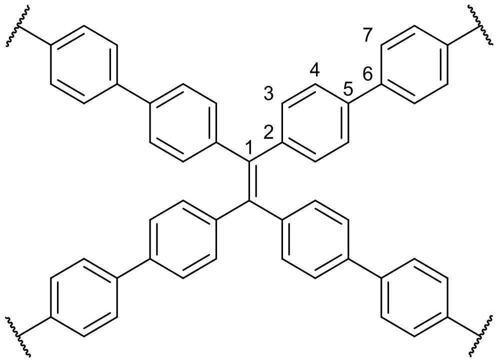
50 ml dry DMF (27 ml/mmol), 1.35 g 2,2-bipyridiyl (8.64 mmol, 1.2 eq.), 2 g Ni(cod)$_2$ (7.27 mmol, 1 eq.), 0.8 ml cyclooctadiene (8.4 mmol, 1.2 eq.), 50 ml dry THF (21 ml/mmol) and 1.16 g tetrakis(4-bromophenyl)methane (1.82 mmol, 0.22 eq.) were placed in a dry vessel under Ar and stirred for 22 h at room temperature. The mixture was cooled to 0 °C and 50 mL 6 *M* HCl were added dropwise and stirred overnight (8 h). The resulting solid was filtered, washed with MeOH. Further purification was done via a *Soxhlet* apparatus with MeOH/THF (1:1) for 16 h to yield the product as an off white powder. Yield: 0.59 g (1.85 mmol; 99 %). ^{13}C NMR (CP-MAS, 12.5 kHz): δ [ppm] = 145.9 (C-2), 139, 34 (C-5), 131 (C-4), 125.3 (C-3), 64.6 (C-1) (Figure 2). CHN$_{\text{Found}}$: C [89.04], H [5.13], N [0.73]. CHN$_{\text{Calc.}}$: C [94.90], H [5.10], N [0.00]. IR (ATR): ν [cm^{-1}] = 3022, 1602, 1448, 1399, 1336, 1260, 1196, 1069, 1006, 917, 816 (Figure S27)

PON-2



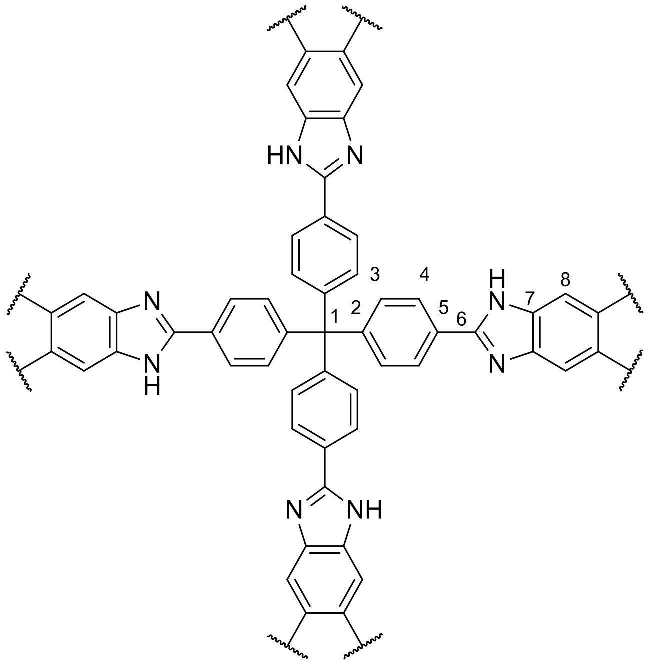
A mixture of 45 ml THF and 5 ml 2 *M* aqueous K$_2$CO$_3$ were refluxed while purged with Ar for 45 min. After cooldown, the mixture was poured in a vessel with 0.41 g tetrakis(4-bromophenyl)methane ($6.5 \cdot 10^{-4}$ mol, 1 eq.), 0.216 g benzene-1,4-diboronic acid ($1.3 \cdot 10^{-3}$ mol, 2eq.), 0.008 g Pd(PPh$_3$)$_4$ ($6.5 \cdot 10^{-6}$ mol, 0.01 eq.), 0.006 g 1,1'-bis(diisopropylphosphino)ferrocene ($1.3\cdot10^{-5}$ mol, 0.02 eq.) under dry conditions. The reaction mixtures were refluxed at 100 °C under static Ar atmosphere for 19 h. After cooling down, the resulting solid was filtered, washed with acetone and dried in an oven. Further purification via *Soxhlet* extraction with tetrahydrofuran/methanol (1:1) gave a grey solid. Yield: 0.30 g ($6.54\cdot10^{-4}$ mol, 67 %). ^{13}C NMR (CP-MAS, 12.5 kHz): δ [ppm] = 146 (C-2), 139 (C-3, C-5), 131 (C-6), 127 (C-4, C-7), 64 (C-1) (Figure 2). CHN$_{\text{Found}}$: C [78.73], H [4.44], N [0.26]. CHN$_{\text{Calc.}}$: C [94.84], H [5.16], N [0.00]. IR (ATR): ν [cm^{-1}] = 3022, 1598, 1484, 1395, 1255, 1167, 1078, 1002, 799, 736 (Figure S27).

PON-3



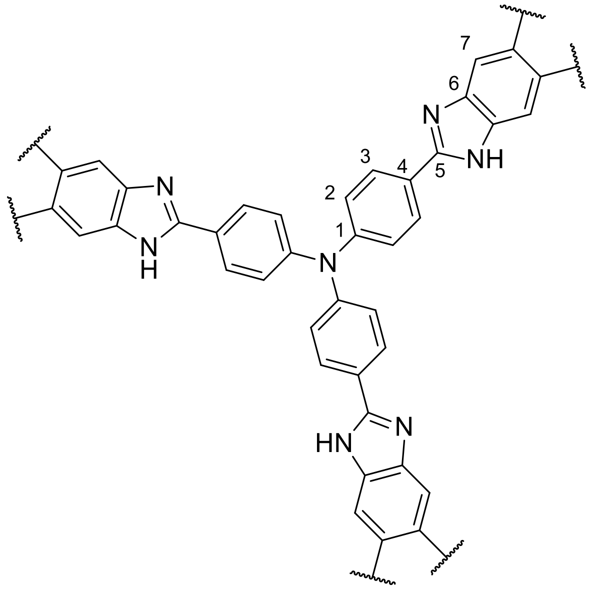
0.50 g of tetrakis(4-bromophenyl)ethene ($7.72\cdot10^{-4}$ mol, 1 eq.) and 0.26 g of benzene-1,4-diboronic acid were dissolved in a mixture of 135 ml dimethylformamide and 15 ml 1 *M* K_2CO_3. The resulting solution was now degassed by freeze pump thaw cycles (4x). Now 0.120 g of $Pd(PPh_3)_4$ ($1.04\cdot10^{-4}$, 0.13 eq.) was added and the mixtures was stirred at 90 °C for 23 h under static Ar atmosphere. The resulting solid was filtered, washed with water, methanol and acetone and dried in an oven at 130 °C. Further purification via *Soxhlet*-extraction with tetrahydrofuran/methanol (1:1) gave a green solid. Yield: 0.359 g ($7.46\cdot10^{-4}$ mol, 65 %). ^{13}C NMR (CP-MAS, 12.5 kHz): δ [ppm] = 140_{br} (C-5; C-1; C-2), 132_{br} (C-3), 127_{br} (C-6, C-4, C-7) (Figure 2). CHN$_{\text{Found}}$: C [75.80], H [5.13], N [0.73]. CHN$_{\text{Calc.}}$: C [94.97], H [5.03], N [0.00]. IR (ATR): ν [cm^{-1}] = 3401, 1613, 1486, 1435, 1359, 1270, 1017, 814 (Figure S27).

PON-4



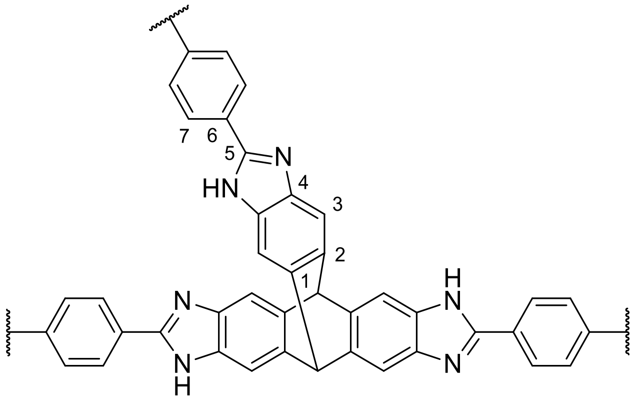
In a dry vessel 0.32 g of 1,2,4,5-benzenetetramine tetrahydrochloride ($1.1\cdot10^{-3}$ mol, 2 eq.) was dissolved in 40 ml dry DMF and cooled to -50 °C in a dry-ice/acetone bath. Now 0.24 g of tetrakis(4-formylphenyl)methane ($5.5\cdot10^{-4}$ mol, 1 eq.) in 20 ml dry DMF were added dropwise and the reaction mixture was slowly allowed to rise to room temperature. After stirring for 21 h under a static Ar atmosphere, the reaction mixture was flushed with air for 10 minutes, sealed and heated in an oven for 4 days. The resulting solid was filtered and washed with DMF, acetone, 1*M* HCl, 1*M* NaOH, H_2O and acetone, respectively. After *Soxhlet* extraction with DCM/acetone (1:1) for 22 h, the brown polymer was dried in vacuo at 120 °C. Yield: 0.274 g ($4.32\cdot10^{-4}$ mol, 79 %). ^{13}C NMR (CP-MAS, 12.5 kHz): δ [ppm] = 152 (C-6), 147 (C-2), 142 (C-7), 128_{br} (C-3, C-4, C-5), 99 (C-8), 65 (C-1) (Figure 2). ^{15}N NMR (CP-MAS, 5.0 kHz): δ [ppm] = -237 (-NH-), -148 (-N-) (Figure 2). CHN_{Found}: C [73.12], H [4.50], N [15.27]. $CHN_{Calc.}$: C [78.45], H [3.69], N [17.85]. IR (ATR): ν [cm^{-1}] = 3401, 1613, 1486, 1435, 1359, 1270, 1017, 814 (Figure S27).

PON-5



In a dry vessel 0.65 g of 1,2,4,5-Benzenetetramine tetrahydrochloride ($1.52 \cdot 10^{-3}$ mol, 1.5 eq.) was dissolved in 40 ml dry DMF and cooled to -60 °C in a dry ice/acetone bath. Now 0.5 g of tris(4-formylphenyl)amine ($1.52 \cdot 10^{-3}$ mol, 1 eq.) in 20 ml dry DMF were added dropwise and the reaction mixture was slowly allowed to rise to room temperature. After stirring for 16 h under a static Ar atmosphere, the reaction mixtures was put under air for 10 minutes, sealed and heated in an oven for 5 days. The resulting solid was filtered and washed with DMF, acetone, 1*M* HCl, 1*M* NaOH, H_2O and acetone, respectively. After *Soxhlet* extraction with DCM/acetone (1:1) for 22 h, the black material was dried in vacuo at 120 °C. Yield: 0.884 g ($1.86 \cdot 10^{-3}$ mol, 99 %). ^{13}C-NMR (CP-MAS, 20.0 kHz): δ [ppm] = 152 (C-5), 148 (C-1), 141 (C-6), 128_{br} (C-2, C-3, C-4), 106 (C-7) (Figure 2). ^{15}N-NMR (CP-MAS, 10 kHz) = -149 (-N=), -241(-NH-), -276 (NR_3) (Figure 2). CHN_{found} [%] = 65.8 (C), 4.2 (H, 17.9 (N); $CHN_{calc.}$ [%]: 70.3 (C), 4.3 (H), 19.3 (N). IR (ATR): ν [cm^{-1}] = 3393, 1593, 1479, 1276, 1188, 1098, 1022, 946, 832, 731 (Figure S27).

PON-6



In a dry vessel 0.1 g of 2,3,6,7,14,15-Hexaaminotriptycene hexachloride ($1.74\cdot10^{-4}$ mol, 1 eq.) was dissolved in 30 ml dry DMF and cooled to -40 °C in a dry-ice/acetone bath. Now 0.034 g of terephthalaldehyde ($2.5\cdot10^{-4}$ mol, 1.5 eq.) in 20 ml dry DMF were added dropwise and the reaction mixture was slowly warmed to room temperature. After stirring for 21 h under static Ar atmosphere, the reaction mixtures was flushed with air for 10 minutes, sealed and heated in an oven for 4 days. The resulting solid was filtered and washed with DMF, acetone, 1*M* HCl, 1*M* NaOH, H_2O and acetone, respectively. After *Soxhlet* extraction with DCM/acetone (1:1) for 22 h, the yellow polymer was dried in vacuo at 120 °C. Yield: 0.053 g ($1.098\cdot10^{-4}$ mol, 65 %). ^{13}C NMR (CP-MAS, 12.5 kHz): δ [ppm] = 151 (C-5), 141 (C-2, C-4), 131 (C-6), 128 (C-7), 113 (C-3), 106 (C-3), 55 (C-1) (Figure 2). ^{15}N NMR (CP-MAS, 10.0 kHz): δ [ppm] = -236 (-NH-), -146 (-N-)(Figure 2). $\mathrm{CHN_{Found}}$: C [67.80], H [4.35], N [14.70]. $\mathrm{CHN_{Calc.}}$: C [79.16], H [3.53], N [17.31]. IR (ATR): ν [$\mathrm{cm^{-1}}$] = 3401, 1617, 1427, 1350, 1325, 1186, 1020, 843, 755, 602 (Figure S27).

Incorporation of Imidazol

For the incorporation of imidazole, the respective polymer was placed on a septum within a glas tube and primary dried for ca. 30 min. Afterwards imidazole was molten and introduced, by vacuum evaporation.

Figure S25: Apparatus for gas phase incorporation of imidazole.

Polymer Analytic

Pore size distribution

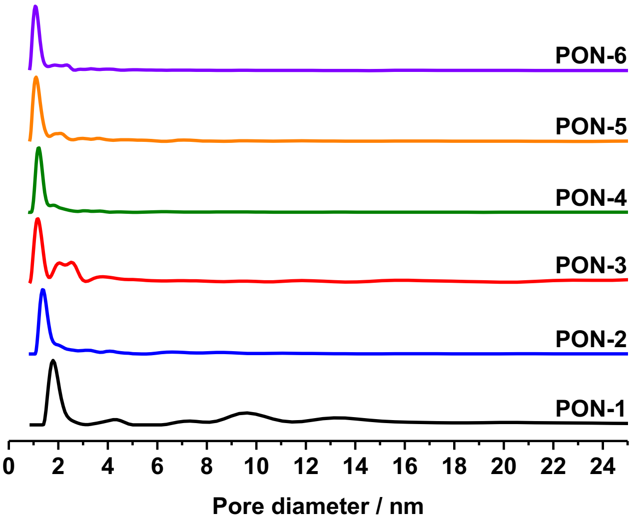


Figure S26: Pore size distribution estimated by argon physisorption isotherms at 87 K.

Infrared Spectroscopy

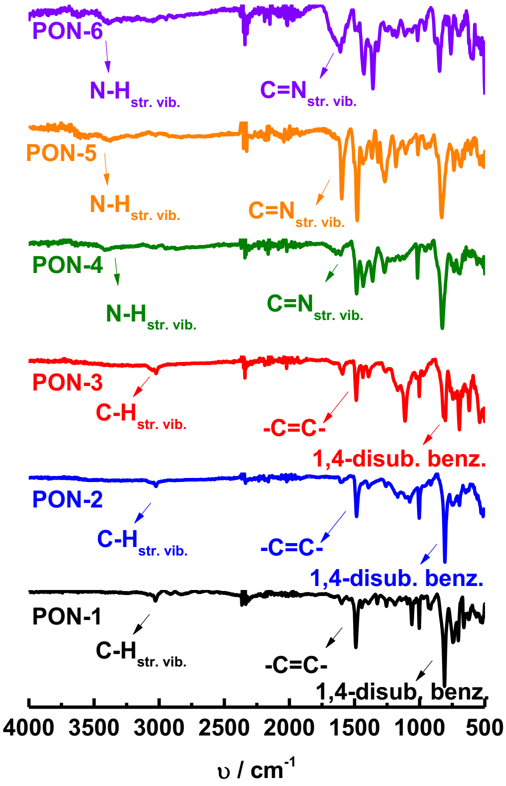


Figure S27: Infrared spectra of PON-1 – PON-6.

Networks after loading with imidazole

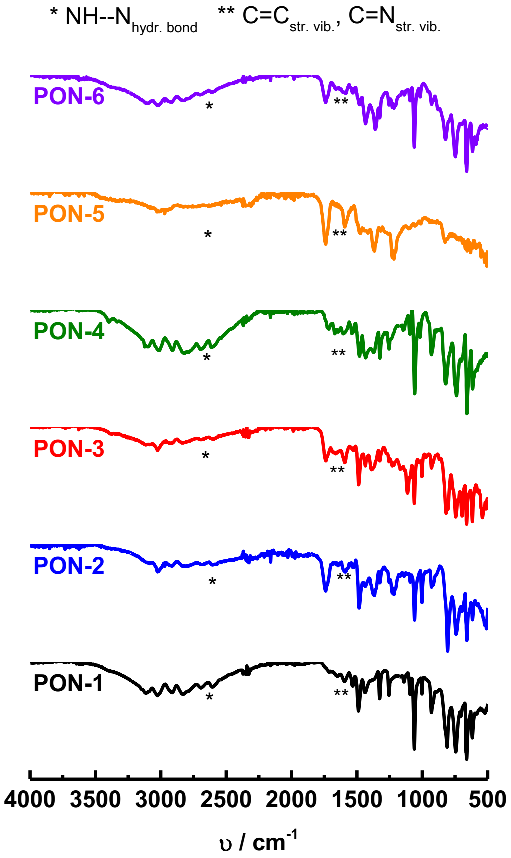


Figure S28: Infrared spectra of PON-1 - PON-6 after loading with imidazole.

Thermogravimetric analysis

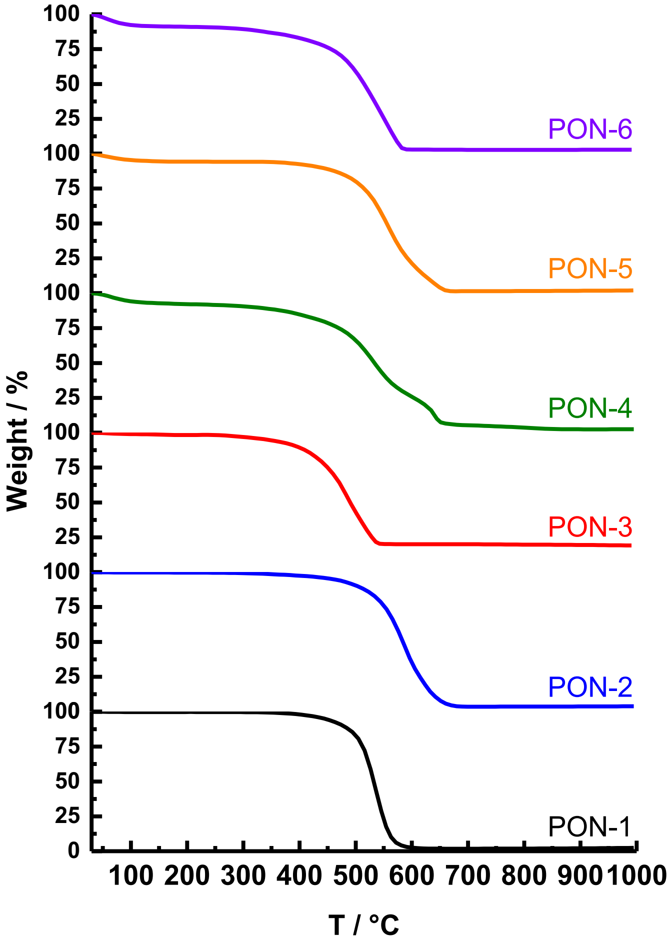


Figure S29: Decomposition curves taken from thermogravimetric analysis of PON-1 - PON-6.

Networks after loading with imidazole

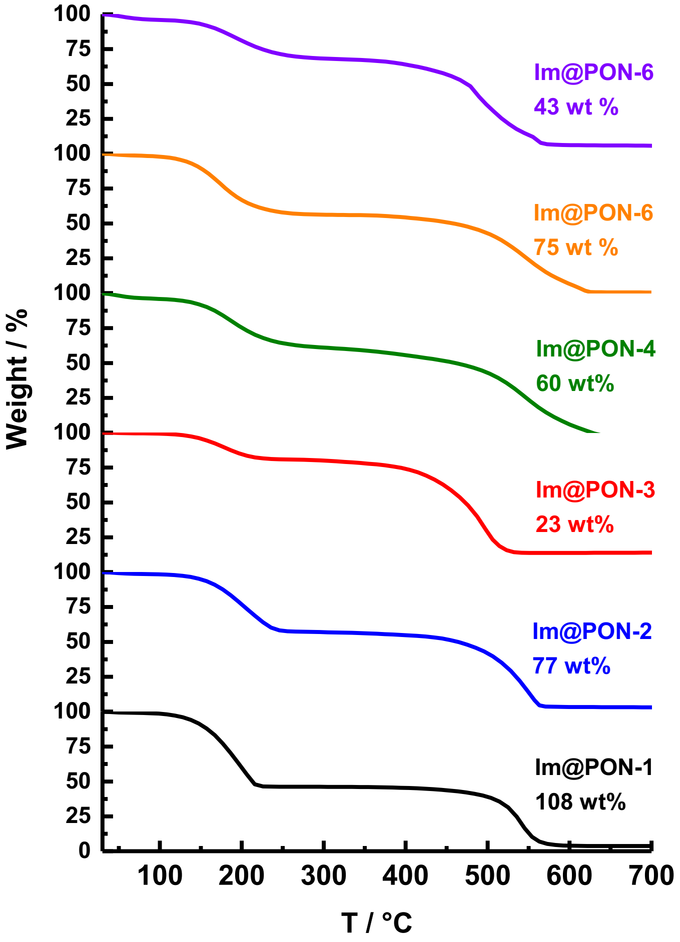


Figure S30: Decomposition curves from thermogravimetric analysis of PON-1 - PON-6, respectively, after loading with imidazole. The decrease of the curve around from 150 to 200 °C is assigned to the removement of imidazole.

Powder X-ray diffraction

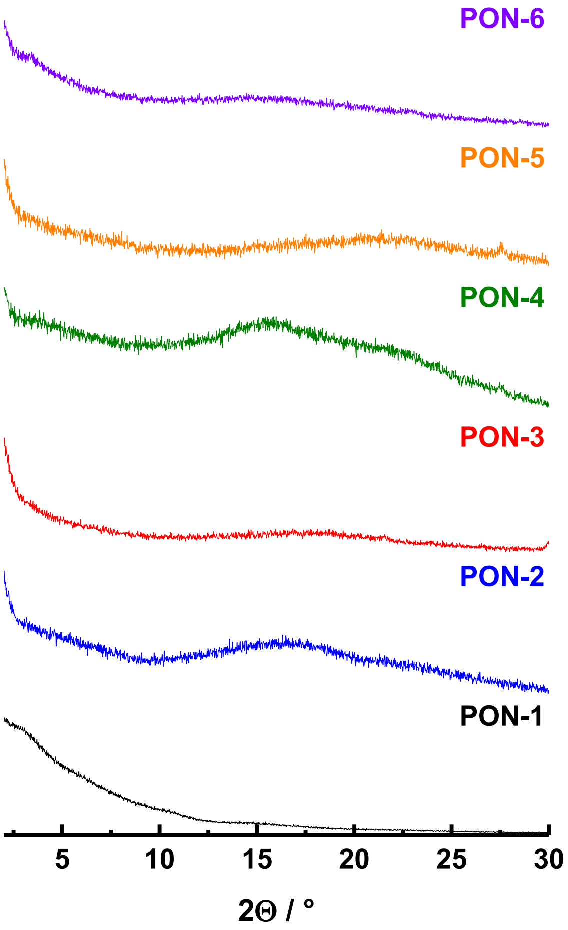


Figure S31: Powder x-ray diffractograms of PON-1 - PON-6.

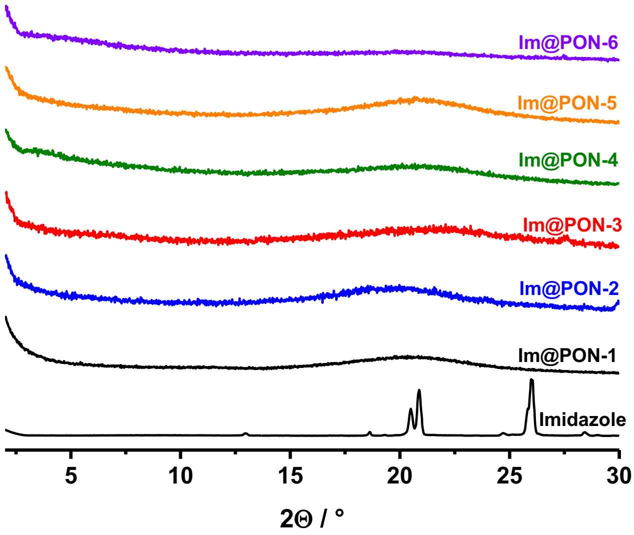


Figure S32: PXRDs of PON-1 - PON-6 after loading with imidazole.

Differential scanning calorimetry

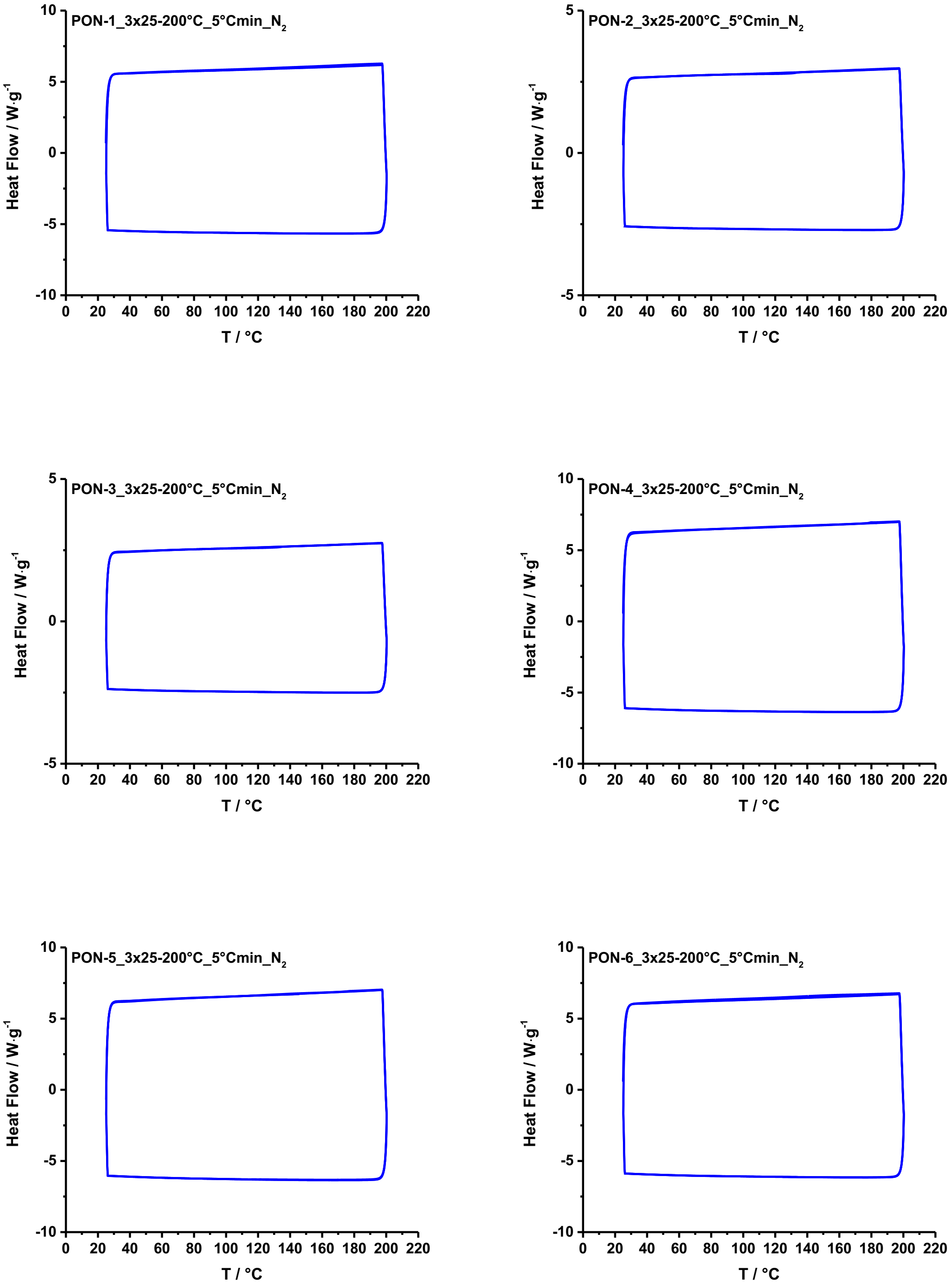


Figure S 33: DSC curves of PON-1 - PON-6 in a temperature range of 25 – 200 °C. The temperature range was cycled for three times to ensure the samples persistence.

Electrochemical impedance spectroscopy

Fitting procedure

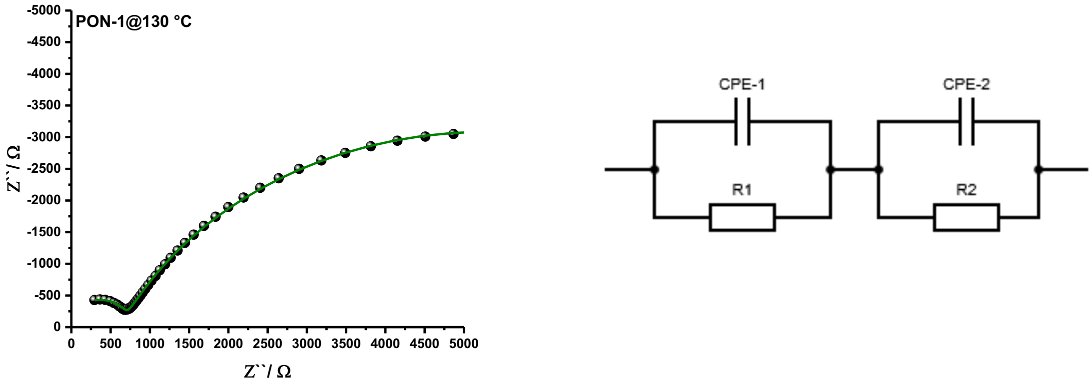


Figure S 34: Nyquist plot of PON-1 at 130 °C (left) fitted with the depicted equivalent circuit (right).

With:

Resistance (R): $Z = R$

Constant Phase Element (CPE):

$$Z = \frac{1}{T(i\omega)^P}$$

Fit-Parameters CPE-T, CPE-P

Table S 1: Fitting parameters for PON-1 at 130 °C.

Element	Value	Error	Error %
R2	9326	73.00	0.78
CPE2-T	6.43^{-8}	1.48^{-9}	2.45
CPE2-P	0.74	2.04^{-3}	0.27
R1	577	2.38	0.4
CPE1-T	9.26^{-12}	6.10^{-13}	6.59
CPE1-P	1,12	3.96^{-4}	0.35

With the resistance value (R) of the first semicircle and the pellet parameters (l = length, A=area) calculation of the relative conductivity is done as follows:

$$\kappa = \frac{l}{R \cdot A}$$

⇔

$$\kappa = \frac{0.15\ cm}{577\ \Omega\ \cdot 0.5027\ cm^2}$$

⇔

$$\kappa = 5{,}17\ \cdot 10^{-4}\ S\ \cdot cm^{-1}$$

PON-1

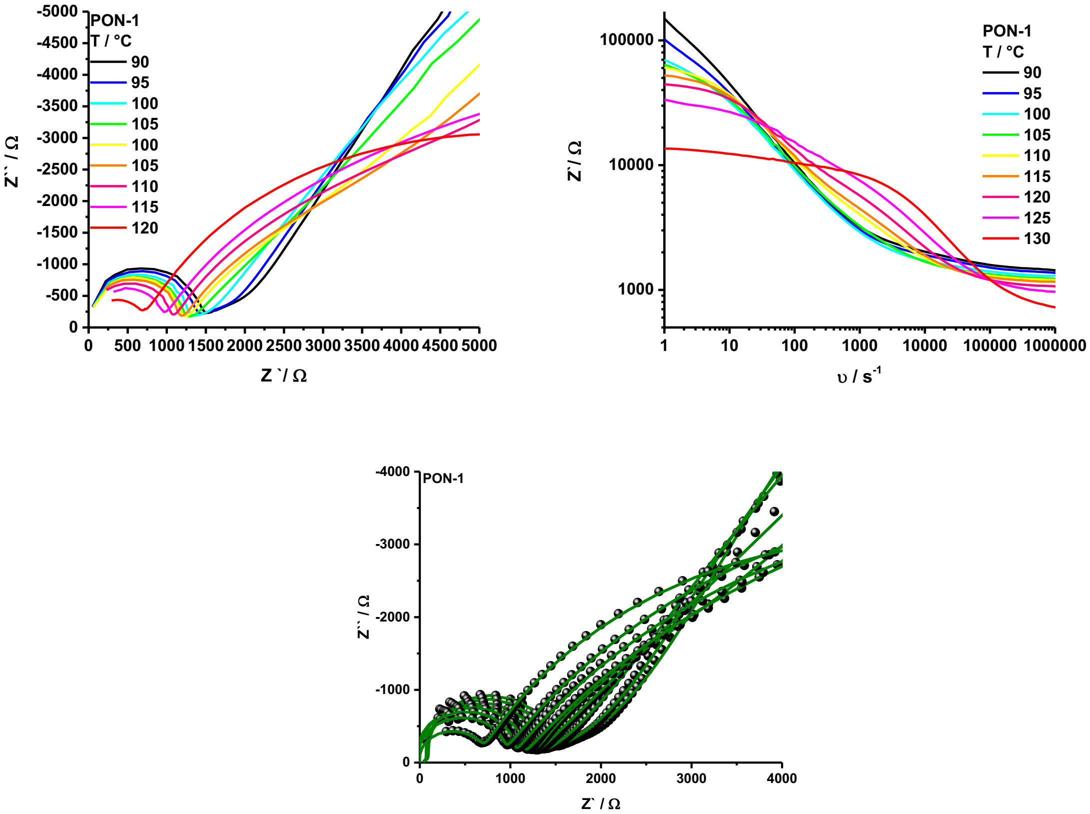


Figure S35: Nyquist (left) and Bode (right) plots of PON-1 measured on a temperature range between 90 °C and 130 °C with a perturbation signal of 20 mV. Nyquist plots with observed data (black circles) and corresponding fits (solid green lines) based on the described equivalent circuit (bottom).

Table S 2: Impedance values found for PON-1 and the respective conductivities (Pellet parameters: A = 0.5027 cm^2, l =0.15 cm).

T / K	Z\`/ Ohm	κ / S·cm^{-1}
363	1560	$1.91\cdot10^{-4}$
368	1440	$2.07\cdot10^{-4}$
373	1301	$2.29\cdot10^{-4}$
378	1181	$2.53\cdot10^{-4}$
383	1060	$2.82\cdot10^{-4}$
388	1075	$2.78\cdot10^{-4}$
393	971	$3.07\cdot10^{-4}$
398	857	$3.48\cdot10^{-4}$
403	577	$5.17\cdot10^{-4}$

PON-2

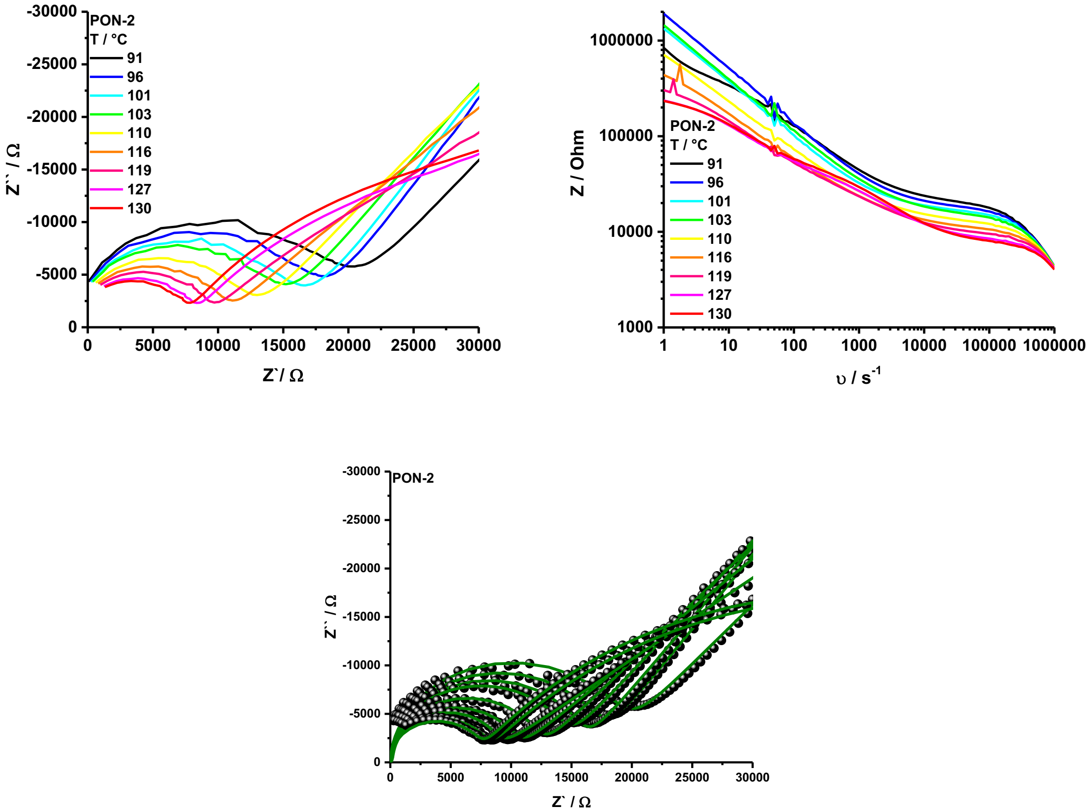


Figure S36: Nyquist (left) and Bode (right) plots of PON-2 measured on a temperature range between 90 °C and 130 °C with a perturbation signal of 10 mV. Nyquist plots with observed data (black circles) and corresponding fits (solid green lines) based on the described equivalent circuit (bottom).

Table S 3: Impedance values found for PON-2 and the respective conductivities (Pellet parameters: A = 0.5027 cm^2, l =0.23 cm).

T / K	**Z` / Ohm**	**κ / S·cm^{-1}**
364	18995	$2.41 \cdot 10^{-5}$
369	17011	$2.69 \cdot 10^{-5}$
374	15888	$2.88 \cdot 10^{-5}$
376	14069	$3.25 \cdot 10^{-5}$
383	12107	$3.78 \cdot 10^{-5}$
389	9665	$4.73 \cdot 10^{-5}$
392	7941	$5.76 \cdot 10^{-5}$
400	6741	$6.79 \cdot 10^{-5}$

PON-3

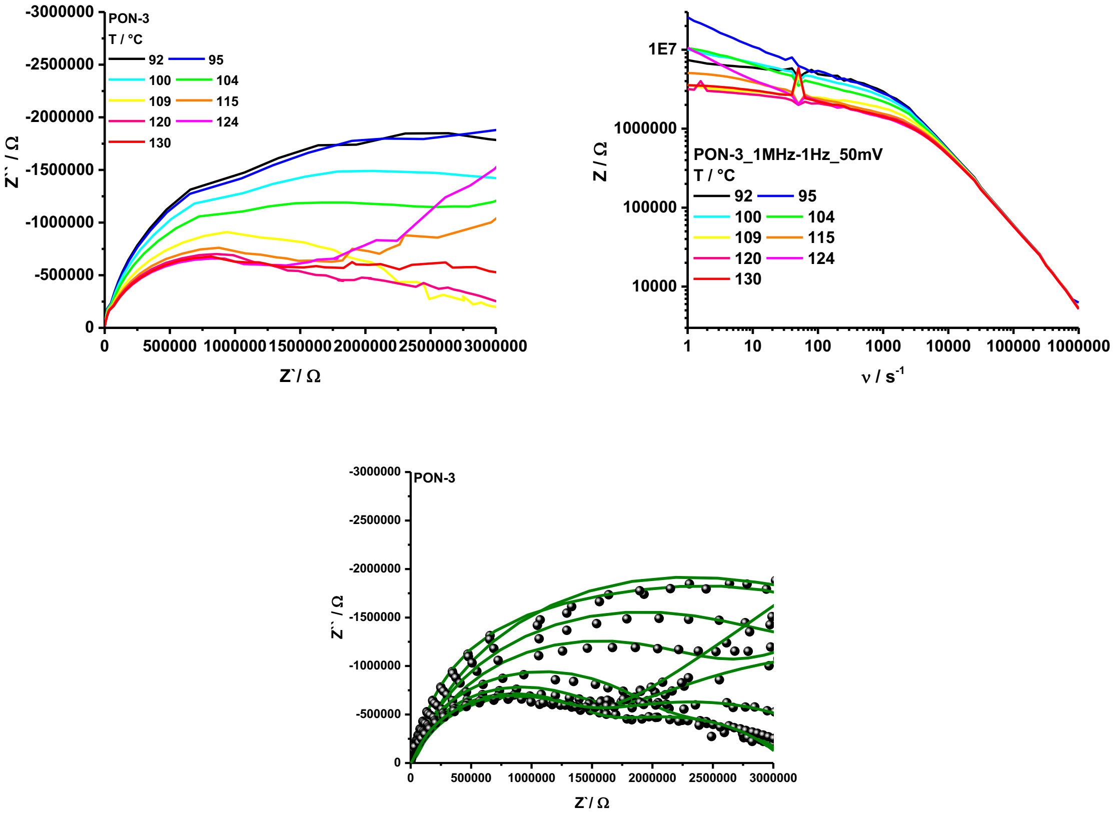


Figure S37: Nyquist (left) and Bode (right) plots of PON-3 measured on a temperature range between 90 °C and 130 °C with a perturbation signal of 50 mV. Nyquist plots with observed data (black circles) and corresponding fits (solid green lines) based on the described equivalent circuit (bottom).

Table S 4: Impedance values and the respective conductivities found for PON-3 (Pellet parameters: A = 0.5027 cm^2*, l =0.25 cm).*

T / **K**	**Z`/** **Ohm**	**κ /** **S·cm^{-1}**
365	$4.51\cdot10^{-6}$	$5.54\cdot10^{-8}$
368	$4.12\cdot10^{-6}$	$6.06\cdot10^{-8}$
373	$3.41\cdot10^{-6}$	$7.33\cdot10^{-8}$
377	$2.29\cdot10^{-6}$	$1.09\cdot10^{-7}$
382	$1.83\cdot10^{-6}$	$1.37\cdot10^{-7}$
388	$1.42\cdot10^{-6}$	$1.76\cdot10^{-7}$
393	$1.36\cdot10^{-6}$	$1.84\cdot10^{-7}$
397	$1.20\cdot10^{-6}$	$2.08\cdot10^{-7}$

PON-4

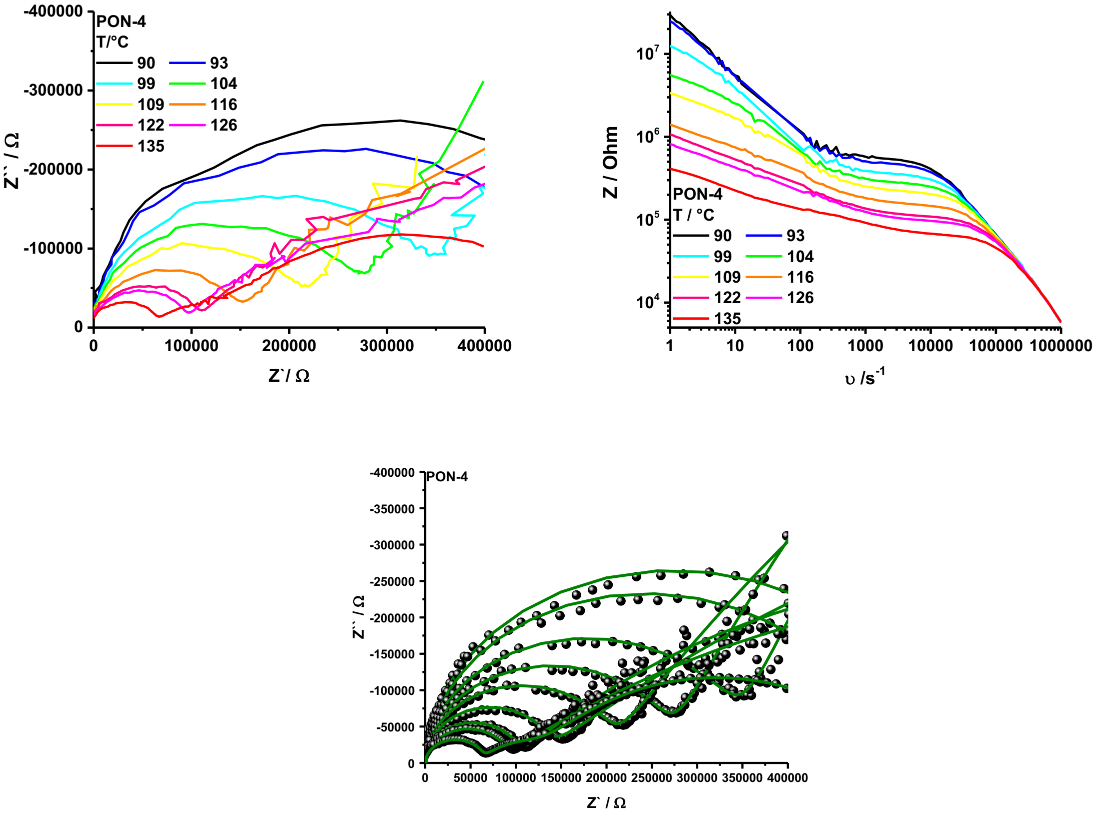


Figure S38: Nyquist (left) and Bode (right) plots of PON-4 measured on a temperature range between 90 °C and 130 °C with a perturbation signal of 10 mV. Nyquist plots with observed data (black circles) and corresponding fits (solid green lines) based on the described equivalent circuit (bottom).

Table S 5: Impedance values and the respective conductivities found for PON-4 (Pellet parameters: A = 0.5027 cm², l =0.30 cm).

T / K	Z\`/ Ohm	κ / S·cm^{-1}
363	507840	1.18·10^{-6}
366	448110	1.33·10^{-6}
372	327400	1.82·10^{-6}
377	255510	2.34·10^{-6}
382	195750	3.05·10^{-6}
389	135960	4.39·10^{-6}
395	105300	5.67·10^{-6}
399	93489	6.38·10^{-6}
408	61432	9.71·10^{-6}

PON-5

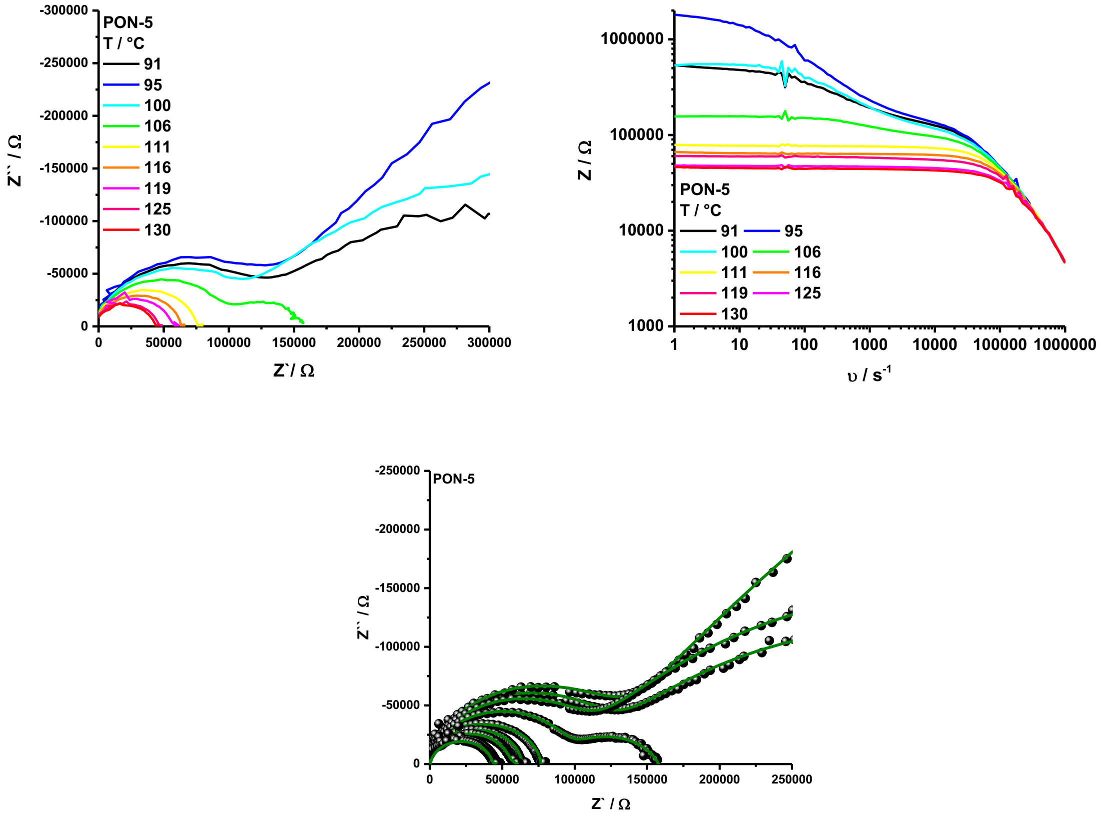


Figure S39: Nyquist (left) and Bode (right) plots of PON-5 measured on a temperature range between 90 °C and 130 °C with a perturbation signal of 10 mV. Nyquist plots with observed data (black circles) and corresponding fits (solid green lines) based on the described equivalent circuit (bottom).

Table S 6: Impedance values and the respective conductivities found for PON-5 (Pellet parameters: A = 0.5027 cm², l =0.40 cm).

T / K	**Z` / Ohm**	**κ / S·cm^{-1}**
364	113300	7.02·10^{-6}
368	115540	6.89·10^{-6}
373	99957	7.96·10^{-6}
379	94459	8.42·10^{-6}
384	73708	1.08·10^{-5}
389	63409	1.26·10^{-5}
392	56429	1.41·10^{-5}
398	43897	1.81·10^{-5}
403	41940	1.90·10^{-5}

PON-6

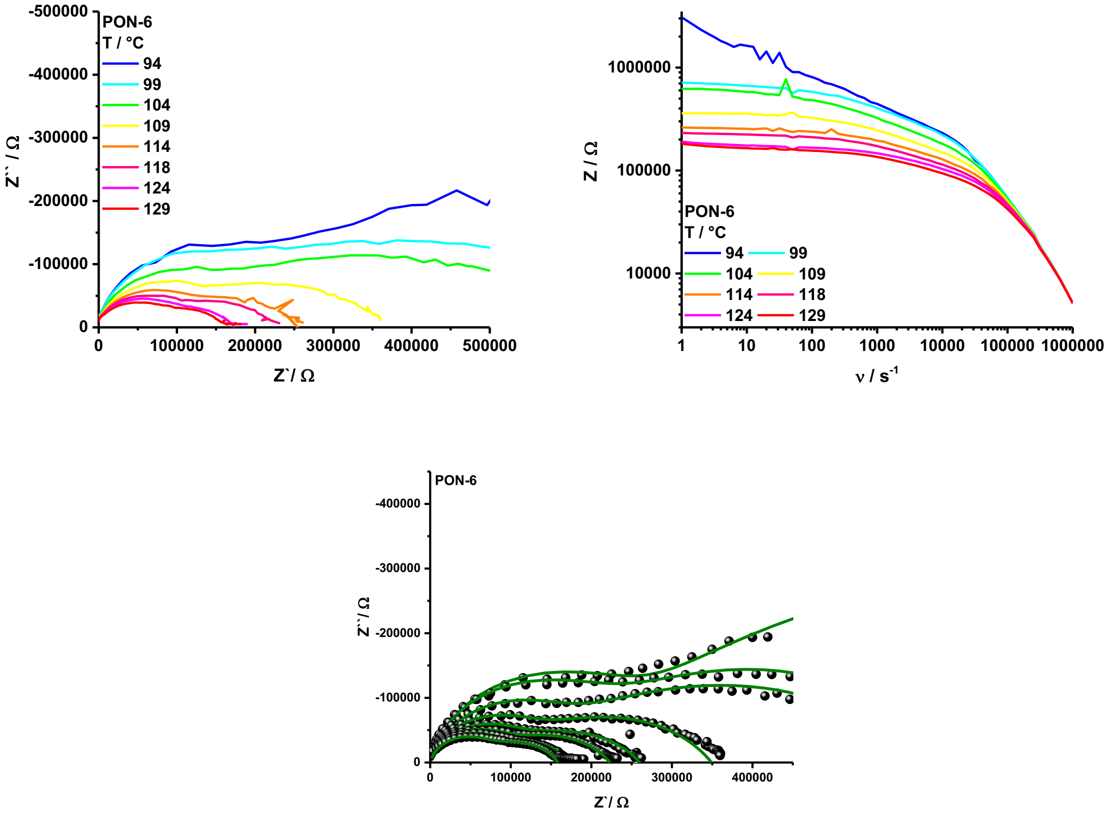


Figure S40: Nyquist (left) and Bode (right) plots of PON-6 measured on a temperature range between 90 °C and 130 °C with a perturbation signal of 10 mV. Nyquist plots with observed data (black circles) and corresponding fits (solid green lines) based on the described equivalent circuit (bottom).

Table S 7: Impedance values and the respective conductivities found for PON-5 (Pellet parameters: A = 0.5027 cm2, l =0.15 cm).

T / K	Z\`/ Ohm	κ / S·cm^{-1}
367	208180	$1.43 \cdot 10^{-6}$
372	183340	$1.63 \cdot 10^{-6}$
377	144060	$2.07 \cdot 10^{-6}$
382	116740	$2.56 \cdot 10^{-6}$
387	98770	$3.02 \cdot 10^{-6}$
391	84472	$3.53 \cdot 10^{-6}$
397	72242	$4.13 \cdot 10^{-6}$
402	61263	$4.87 \cdot 10^{-6}$

Arrhenius Plot

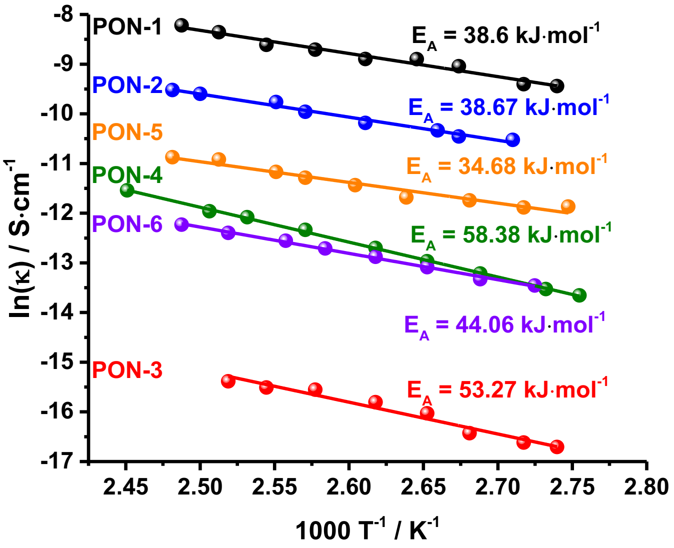


Figure S 41: Arrhenius Plots of all polymers.

Literatur

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