Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Luminescent Tetraphenylethene-Cored, Carbazole- and Thiophene-Based Microporous Polymer Films for the Chemosensing of Nitroaromatic Analytes.

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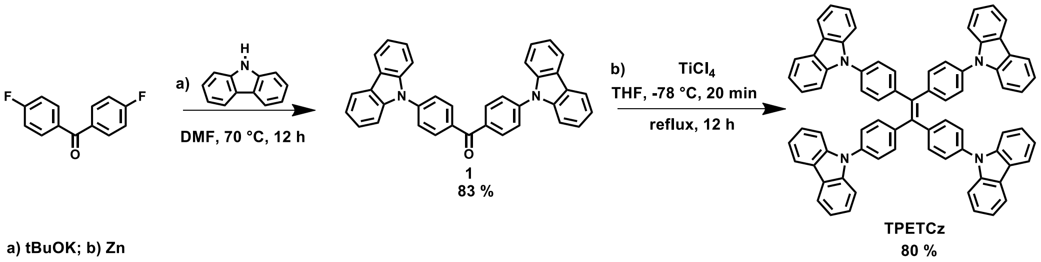
Materials and Methods

Monomers and bulk polymers

All reagents and chemicals were purchased from commercial suppliers, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were obtained on Bruker Avance 400 and III 600 machines. APLI mass spectra were recorded on a Bruker Daltronik micrOTOF system (KrF*-Laser ATLEX-SI, ATL Wermelskirchen), MALDI-TOF mass spectra on a Bruker Reflex TOF, and field desorption (FD) mass spectra on a VG Instruments ZAB2-SE-FPD. Thermogravimetric analyses were carried out under argon flow on a Mettler Toledo TGA/DSC1 STAR System. ^{13}C{^{1}H} cross-polarization magic-angle spinning (CPMAS) spectra were recorded at 50.33 MHz using a Bruker AVANCE III 200 NMR spectrometer with a contact time of 3 ms, averaging 8192 transients at a relaxation delay of 4 s. All experiments were carried out at room temperature using a standard Bruker 2.5 mm double resonance MAS probe spinning at 20 kHz, typical $\pi/2$-pulse lengths of 2.5 μs and SPINAL64 proton decoupling (200.15 MHz; $10\pi/12$ pulse set to 4.2 μs) at rather modest power levels of 46.5 Watt (^{13}C) and 19 Watt (^{1}H), respectively. The ^{13}C spectra were referenced with respect to tetramethylsilane (TMS) using solid adamantane as secondary standard (29.46 ppm for ^{13}C). UV-vis and FT-IR spectra were recorded on a JASCO V-670 and FT/IR-4200, respectively. Photoluminescence spectra were obtained on a HORIBA Scientific FluoroMax-4 Spectrofluorometer connected to a Quanta-Phi integrating sphere for determination of PL quantum yields. Optical measurements were carried out under aerobic conditions at room temperature. A Tousimis Samdri-795 system was used for washing the bulk polymers with supercritical carbon dioxide. Nitrogen and krypton adsorption-desorption isotherms were recorded on a BEL Japan Inc Belsorp-max system at 77 K. A maximum relative pressure of 0.6 was set for measurements with Kr gas. All samples were dried on a Belprep-vac II at 140 °C and ~ 2 Pa overnight prior to the gas sorption measurements.

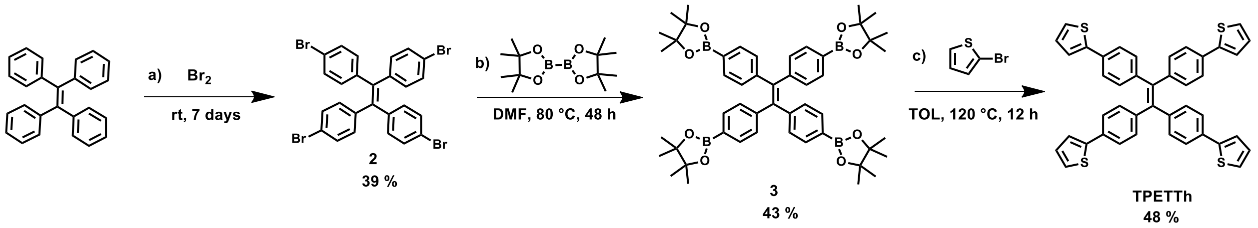


Synthesis of bis[4-(carbazol-9-yl)phenyl]methanone (1)

In a 100 mL round flask, carbazole (3.07 g, 18.33 mmol) was dissolved in anhydrous DMF (30 mL). After adding potassium tert-butoxide (2.16 g, 19.25 mmol), the mixture was heated up to 70 °C for 10 min and then bis(4-fluorophenyl)methanone (2.00 g, 9.17 mmol) in DMF (20 mL) were added. The mixture was stirred for additional 12 h. After cooling down to room temperature, the crude was poured into ice-water, filtered and recrystallized from acetone to give a yellow product, yield: 3.89 g (83 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ: 8.24-8.18 (m, 8H), 7.84 (d, J = 8.50 Hz, 4H), 7.63 (d, J = 8.23 Hz, 4H), 7.55-7.48 (m, 4H), 7.42-7.36 (m, 4H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ: 194.38, 141.60, 140.00, 135.53, 131.82, 126.30, 126.20, 123.56, 120.68, 120.39, 109.80; MS (APLI) 512.171 [512.189] (M^+).

Synthesis of 1,1,2,2-tetra[4-(carbazol-9-yl)phenyl]ethene (TPETCz)

To a solution of bis[4-(carbazol-9-yl)phenyl]methanone (1.50 g, 2.93 mmol) in dry THF (50 mL), zinc dust (0.46 g, 7.03 mmol) was added followed by the addition of titanium(IV) chloride (0.67 g, 3.52 mmol) after cooling to -78 °C. After stirring for 20 min under argon, the reaction mixture was warmed up to room temperature and then heated up to reflux for 12 h. Next, the reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with brine and water, and finally dried over magnesium sulfate. After solvent evaporation, the residue was washed with dichloromethane resulting in a white solid, yield: 1.16 g (80 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ: 8.21-8.15 (m, 8H), 7.60-7.53 (m, 16H), 7.49 (d, J = 8.05 Hz, 8H), 7.42-7.36 (m, 8H), 7.35-7.29 (m, 8H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ: 141.85, 140.99, 140.48, 136.14, 132.81, 126.23, 126.10, 123.12, 120.23, 120.05, 109.68; MS (MALDI TOF) 992.3 [992.4] (M^+).



b) Pd(PPh$_3$)$_4$, KOAc; c) water, n-BuOH, Pd(PPh$_3$)$_4$, Na$_2$CO$_3$

Synthesis of 1,1,2,2-tetra(4-bromophenyl)ethene (2)

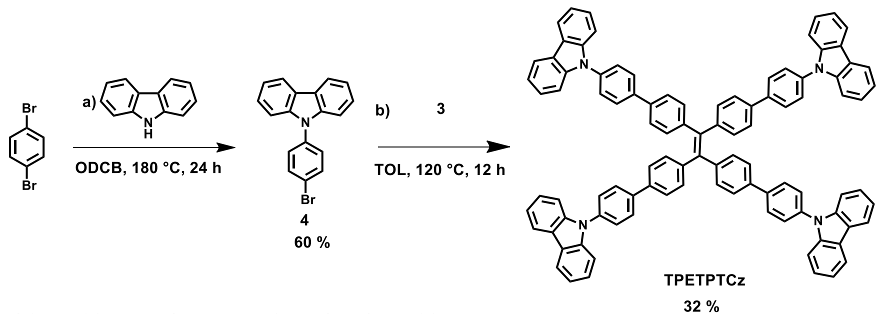
An evaporation plate with 1,1,2,2-tetraphenylethene (20 g, 60.20 mmol) and bromine (10 mL) was placed in a slightly open desiccator for 7 days (bromine was refilled whenever needed). The brownish product was recrystallized from a dichloromethane / methanol (2:1) mixture to give a white solid, yield: 15.17 g (39 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.29 (d, *J* = 8.5 Hz, 8H), 6.86 (d, *J* = 8.5 Hz, 8H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ 141.3, 139.4, 132.6, 131.1, 121.0; MS (APLI) 647.781 [647.795] (M^+).

Synthesis of 1,1,2,2-tetra[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethene (3)

1,1,2,2-Tetra(4-bromophenyl)ethene (7.00 g, 10.80 mmol), potassium acetate (8.48 g, 86.0 mmol), bis(pinacolato)diboron (12.07 g, 47.5 mmol) and anhydrous DMF (90 mL) were placed in a two-necked round bottom flask under argon atmosphere and stirred for 15 minutes. After addition of tetrakis(triphenylphosphine)palladium(0) (0.62 g, 0.54 mmol) in DMF (10 mL), the mixture was stirred under exclusion of light at 100 °C for 48 hours. After cooling to room temperature, the mixture was quenched with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was recrystallized from a mixture of ethanol/dichloromethane to give a light yellow solid, yield: 3.90 g (43 %) ^{1}H NMR (600 MHz, $C_2D_2Cl_4$): δ 7.58-7.50 (m, 8H), 7.07-6.98 (m, 8H), 1.37 (s, 48H); ^{13}C NMR (141 MHz, $C_2D_2Cl_4$): δ 146.0, 141.2, 134.0, 130.3, 83.6, 24.8; MS (APLI) 834.472 [836.500] (M^+).

Synthesis of 1,1,2,2-tetra[4-(thiophen-2-yl)phenyl]ethene (TPETTh)

1,1,2,2-Tetra[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethene (2.00 g, 2.39 mmol), 2-bromothiophene (1.72 g, 10.52 mmol), sodium carbonate (2.28 g, 21.5 mmol), anhydrous toluene (20 mL), degasified butanol (12 mL) and degasified water (15 mL) were added to a two-necked round flask under argon atmosphere. After heating up to 80 °C, tetrakis(triphenylphosphine)palladium(0) (0.28 g, 0.24 mmol) in toluene (10 mL) was added to the mixture and refluxed under exclusion of light at 120 °C for 10 h. After cooling down to room temperature, the crude product was diluted with chloroform and washed with aqueous 2 N HCl. The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed by evaporation. The residue was purified by silica gel column chromatography (eluent: hexane/dichloromethane in a gradient from 6:1 to 4:1) to give a yellow solid, yield: 0.76 g (48 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.38 (d, *J* = 8.4 Hz, 8H), 7.28 (dd, *J* = 3.6, 1.0 Hz, 8H), 7.24 (dd, *J* = 5.1, 1.0 Hz, 8H), 7.07 (d, *J* = 8.4 Hz, 8H), 7.04 (dd, *J* = 5.1, 3.6 Hz, 8H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ 144.3, 143.0, 140.4, 132.6, 132.3, 128.5, 125.4, 125.2, 123.4; MS (APLI) 660.096 [660.107] (M^+).



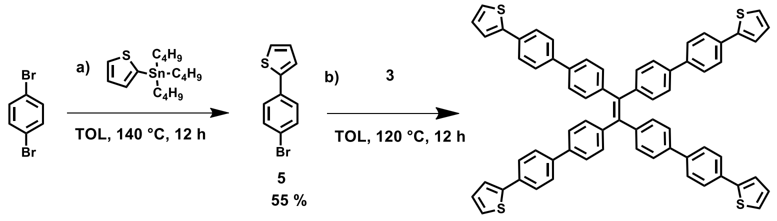
a) CuI, K_2CO_3, bipy; b) water, n-BuOH, $Pd(PPh_3)_4$, Na_2CO_3

Synthesis of 9-(4-bromophenyl)-carbazole (4)

1,4-Dibromobenzene (14.11 g, 59.8 mmol), carbazole (5.00 g, 29.9 mmol), copper(I)iodide (0.57 g, 2.99 mmol), potassium carbonate (37.2 g, 269 mmol), 2,2'-bipyridine (1.21 g, 7.77 mmol) and o-dichlorobenzene (70 mL) were added to a double-necked round flask under argon atmosphere and stirred under exclusion of light at 180 °C overnight. The hot reaction mixture was filtered over celite and washed with hot toluene. After solvent evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane) to give a white solid, yield: 5.793 g (60 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.80 - 7.75 (m, 2H), 7.51 - 7.40 (m, 6H), 7.34 (ddd, J= 8.0, 5.5, 1.4, 2H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ(ppm) 140.3, 136.5, 133.1, 128.4, 126.1, 123.2, 120.7, 120.3, 120.2,109.5; MS (APLI) 320.996 [321.015] (M^+).

Synthesis of 1,1,2,2-tetra[4'-(carbazol-9-yl)-[1,1'-biphenyl]-4-yl]ethene (TPEPTCz)

1,1,2,2-tetra[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethene (0.50 g, 0.60 mmol), 9-(4-bromophenyl)-carbazole (0.828 g, 2.57 mmol), sodium carbonate (0.570 g, 5.38 mmol), anhydrous toluene (20 mL), degasified butanol (12 mL) and degasified water (15 mL) were added to a two-necked round flask under argon atmosphere. After heating up to 80 °C, tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.06 mmol) in toluene (10 mL) was added and the mixture refluxed under exclusion of light at 120 °C for 10 h. After cooling down to room temperature, the crude product was diluted with chloroform and washed with aqueous 2 N HCl. The organic phase was dried over anhydrous magnesium sulfate and the solvent removed by evaporation. The residue was purified by silica gel column chromatography (eluent: hexane/dichloromethane 7:3) to give a yellow solid, yield: 0.25 g (32 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 8.17 (d, *J* = 7.8 Hz, 8H), 7.95 – 7.85 (m, 8H), 7.71 – 7.58 (m, 16H), 7.54 – 7.41 (m, 16H), 7.40 – 7.25 (m, 16H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ 143.0, 140.6, 139.3, 137.7, 137.6, 136.5, 132.1, 128.1, 127.0, 126.2, 126.0, 123.1, 120.2, 120.0, 109.8; MS (MALDI TOF) 1297.612 [1297.516] (M^+).



TPETPTTh
50 %

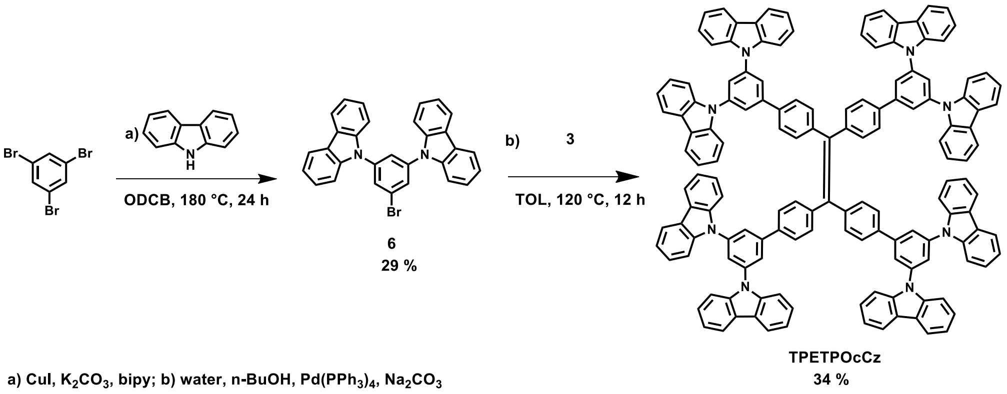
a) $Pd(PPh_3)_4$; b) water, n-BuOH, $Pd(PPh_3)_4$, Na_2CO_3

Synthesis of 2-(4-bromophenyl)thiophene (5)

1,4-Dibromobenzene (4.00 g, 16.96 mmol), tributyl(thiophen-2-yl)stannane (3.16 g, 8.48 mmol) and dry toluene (10 mL) were added to a 20 ml microwave vial under argon atmosphere. After adding tetrakis(triphenylphosphine)palladium(0) (0.49 g, 0.424 mmol) in 5 ml dry toluene, the mixture was stirred under exclusion of light at 140 °C for 10 h. The crude was purified by silica gel column chromatography (eluent: hexane) to give a white solid, yield: 1.13 g (55 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ H 7.55-7.47 (m, 4H), 7.35-7.32 (m, 2H), 7.11 (dd, *J* = 5.0, 3.7, 1H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ 142.8, 133.2, 131.9, 128.2, 127.3, 125.4, 123.6, 121.1; MS (FD) 240.2 [239.132] (M^+).

Synthesis of 1,1,2,2-tetra[4'-(thiophen-2-yl)-(1,1'-biphenyl)-4-yl]ethene (TPEPTTh)

1,1,2,2-Tetra[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethene (0.70 g, 0.84 mmol), 2-(4-bromophenyl)thiophene (0.86 g, 3.60 mmol), sodium carbonate (0.80 g, 7.53 mmol), anhydrous toluene (20 mL), degasified butanol (12 mL) and degasified water (15 mL) were added to a two-necked round flask under argon atmosphere. After heating up to 80 °C, tetrakis(triphenylphosphine)palladium(0) (0.10 g, 0.08 mmol) in toluene (10 mL) was added to the mixture and the mixture refluxed under exclusion of light at 120 °C for 10 h. After cooling down to room temperature, chloroform was added to the crude product. The mixture was washed with aqueous 2 N HCl, the organic phase was filtrated and finally washed with chloroform to give a greenish solid, yield: 0.41 g (50 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.69-7.63 (m, 16H), 7.50-7.38 (m, 8H), 7.39-7.35 (m, 4H), 7.34-7.31 (m, 4H), 7.26-7.15 (m, 8H), 7.14-7.10 (m, 4H); MS (APLI) 964.228 [964.233] (M^+).

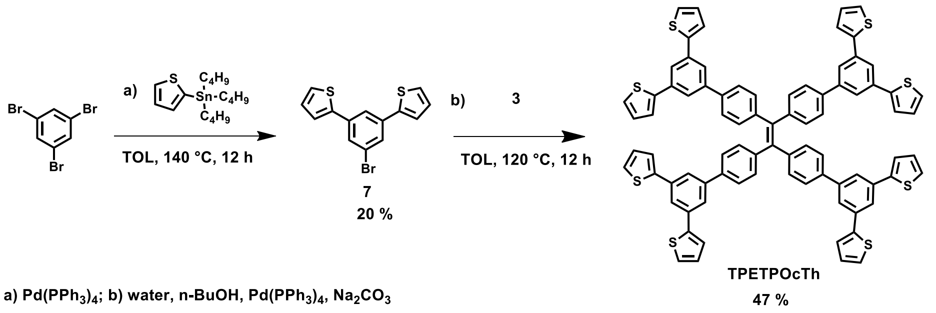


Synthesis of 9,9'-(5-bromo-1,3-phenylene)bis(carbazole) (6)

1,3,5-Tribromobenzene (7.00 g, 22.2 mmol), carbazole (7.44 g, 44.5 mmol), copper(I)iodide (0.85 g, 4.5 mmol), potassium carbonate (27.7 g, 200 mmol), 2,2'-bipyridine (1.74 g, 11.1 mmol) and o-dichlorobenzene (70 mL) were added to a double-necked round flask under argon atmosphere and stirred under exclusion of light at 180 °C for 10 h. The hot reaction mixture was filtered over celite and washed with hot toluene. After solvent evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane) to give a white solid, yield: 3.11 g (29 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 8.18 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 2H), 7.83 (t, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 4H), 7.53 – 7.48 (m, 4H), 7.40 – 7.35 (m, 4H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ 140.2, 140.0, 128.4, 126.4, 124.1, 123.5, 123.5, 120.8, 120.5, 109.6; MS (APLI) 488.054 [488.072] (M^+).

Synthesis of 1,1,2,2-tetra[3',5'-di(carbazol-9-yl)-(1,1'-biphenyl)-4-yl]ethene (TPEPOcCz)

1,1,2,2-Tetra[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethene (0.50 g, 0.60 mmol), 9,9'-(5-bromo-1,3-phenylene)bis(carbazole) (1.25 g, 2.57 mmol), sodium carbonate (0.57 g, 5.38 mmol), anhydrous toluene (20 mL), degasified butanol (12 mL) and degasified water (15 mL) were added to a two-necked round flask under argon atmosphere. After heating up to 80 °C, tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.06 mmol) in toluene (10 mL) was added. The mixture was refluxed under exclusion of light at 120 °C for 10 h. After cooling down to room temperature, the crude product was diluted with chloroform and washed with aqueous 2 N HCl. The organic phase was dried over anhydrous magnesium sulfate and the solvent was evaporated. The resulting residue was purified by silica gel column chromatography (eluent: hexane/dichloromethane 6:4) to give a yellow solid, yield: 0.40 g (34 %). ^{1}H NMR (600 MHz, $C_2D_2Cl_4$): δ 8.18 (d, *J* = 7.8 Hz, 16H), 7.93 (d, *J* = 1.8 Hz, 8H), 7.77 (t, *J* = 1.8 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 24H), 7.47-7.40 (m, 16H), 7.35-7.28 (m, 24H); ^{13}C NMR (141 MHz, $C_2D_2Cl_4$): δ 143.9, 143.6, 140.4, 140.3, 140.3, 139.4, 136.9, 132.1, 126.5, 126.2, 123.8, 123.3, 120.4, 120.4, 109.6; MS (APLI) 1957.127 [1957.747] (M+).



Synthesis of 2,2'-(5-bromo-1,3-phenylene)dithiophene (7)

1,3,5-Tribromobenzene (3.00 g, 9.53 mmol), tributyl(thiophen-2-yl)stannane (7.11 g, 19.06 mmol) and dry toluene (10 mL) were added to a 20 ml microwave vial under argon atmosphere. After adding tetrakis(triphenylphosphine)palladium(0) (0.15 g, 0.13 mmol) in toluene (5 mL), the mixture was stirred under exclusion of light at 140 °C for 10 h. The crude product was purified by silica gel column chromatography (eluent: hexane) and sublimation (100 °C, 10^{-2} torr) to give yellow crystalline needles, yield: 0.60 g (20 %). ^{1}H NMR (600 MHz, $C_2D_2Cl_4$): δ 7.74 (t, *J* = 1.6 Hz, 1H), 7.66 (d, *J* = 1.6 Hz, 2H), 7.40 – 7.37 (m, 4H), 7.13 (dd, *J* = 5.1, 3.6 Hz, 2H); ^{13}C NMR (141 MHz, $C_2D_2Cl_4$): δ 142.3, 137.0, 128.7, 127.8, 126.5, 124.8, 123.7, 122.4; MS (APLI) 321.913 [321.931] (M^+).

Synthesis of 1,1,2,2-tetra[3',5'-di(thiophen-2-yl)-(1,1'-biphenyl)-4-yl]ethene (TPEPOcTh)

1,1,2,2-Tetra[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethene (0.32 g, 0.41 mmol), 2,2'-(5-bromo-1,3-phenylene)dithiophene (0.57 g, 1.77 mmol), sodium carbonate (0.39 g, 3.71 mmol), anhydrous toluene (20 mL), degasified butanol (12 mL) and degasified water (15 mL) were added to a two-necked round flask under argon atmosphere. After heating up to 80 °C, tetrakis(triphenylphosphine)palladium(0) (0.05 g, 0.04 mmol) in toluene (10 mL) was added and the mixture refluxed under exclusion of light at 120 °C for 10 h. After cooling down to room temperature, the crude product was diluted with chloroform and washed with aqueous 2 N HCl. The organic phase was dried over anhydrous magnesium sulfate and the solvent was evaporated. The resulting residue was purified by silica gel column chromatography (eluent: hexane/dichloromethane 6:1 to 3:1) to give a white solid, yield: 0.25 g (47 %). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.79 (d, *J* = 1.4 Hz, 4H), 7.75 (d, *J* = 1.5 Hz, 8H), 7.55 (d, *J* = 8.3 Hz, 8H), 7.44 (dd, *J* = 3.5, 0.9 Hz, 8H), 7.35 (dd, *J* = 5.1, 0.8 Hz, 8H), 7.31 (d, *J* = 8.3 Hz, 8H), 7.13 (dd, *J* = 5.0, 3.6 Hz, 8H); ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ 143.5, 143.1, 141.8, 140.4, 138.0, 135.3, 132.0, 128.1, 126.4, 125.3, 123.8, 123.6, 122.3; MS (APLI) 1292.988 [1292.183] (M^+).

Synthesis of bulk polymers by oxidative coupling with iron(III)chloride

All monomers were chemically polymerized in a similar procedure as described here for the TPEPOcCz monomer: 1,1,2,2-tetra[3',5'-di(carbazol-9-yl)-(1,1'-biphenyl)-4-yl]ethene (0.10 g, 0.051 mmol) was dissolved in anhydrous chloroform (20 mL) and added dropwise to a suspension of iron(III) chloride (0.21 g, 1.29 mmol) in anhydrous chloroform (30 mL) under argon atmosphere. The resulting mixture was stirred at room temperature for one day. After addition of methanol (100 mL), the mixture was stirred for one more hour. The resulting precipitate was collected by filtration and washed with methanol. The powder was treated with aqueous hydrochloric acid (37 %) for 2 h, filtered off and washed with water and methanol. After Soxhlet extraction with methanol and THF for 24 h, the product was treated with ethanol (p.a.) for three days and finally washed with supercritical carbon dioxide. PTPETPOcCz was isolated as yellow powder, yield: 0.084 g (84 %). PTPETCz as yellow powder (99 %), PTPETTh as orange powder (73 %), PTPEPTCz was obtained as yellow powder (80 %), PTPEPTTh as dark yellow powder (85 %), and finally PTPEPOcTh as yellow powder (99 %).

Electrochemical polymerization and characterization

Dichloromethane (HPLC grade) was refluxed over phosphorus pentoxide for 3 h and distilled. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, ≥ 99 %) was purchased from Alfa Aesar. Borontrifluoride diethyletherate (BFEE, ≥ 46.5 % BF_3), nitrobenzene (NB, analytical standard), 1,3-dinitrobenzene (DNB, analytical standard) and 2,4,6-trinitrophenol (TNP, ≥ 98%, moistened with water) were purchased from Sigma-Aldrich; 1,3,5-trinitrobenzene (TNB, neat) from Supelco; 4-nitrotoluene (NT, 99 %) from Across; and 4-nitrophenol (NP, 99 %) from ABCR. Potassium chloride (KCl, ≥ 99.5 %, ACS) was purchased from Roth. Indium tin oxide-coated transparent electrodes on glass (ITO, ≤ 20 Ohm m^{-2}) were purchased from pgo. For electrochemical polymerization and characterization, an electrochemical workstation PAR VersaSTAT 4 was used in combination to a three-electrode cell. The AFM images were recorded on an atomic force microscope Bruker diInnova operated in tapping mode. Average surface roughness and thickness of the films were extracted from the topography images.

Electrochemical polymerization and characterization on Pt disc electrodes

10 mL of 0.1 mM solutions of the carbazole- or thiophene-based monomers were prepared in dichloromethane or BFEE / dichloromethane (1:4), respectively, using 0.1 M $TBABF_4$ as supporting electrolyte. The solutions were placed in a three-electrode cell under argon atmosphere at 25 °C. A platinum disc electrode (Pt, 1 mm diameter) was used as working electrode (WE), a platinum wire as counter electrode (CE), and Ag°/$AgNO_3$ (0.01 M $AgNO_3$ / 0.1 M TBAP, 0.56 V vs NHE) as reference electrode (RE). Multiple cyclic voltammograms were repeatedly recorded in a potential range from -1.0 V to 1.2 V (TPETCz, TPETPTCz, TPETPOcCz, TPETPTTh, and TPETPOcTh) or -1.0 V to 1.4 V (TPETTh) with a scan rate of 0.1 Vs^{-1}. The resulting deposits on Pt were placed as WE in 0.1 M monomer-free solutions of $TBABF_4$ in dichloromethane. Multiple cyclic voltammograms at different scan rates from 0.005 to 0.20 Vs^{-1} were recorded in the potential range from 0 V to 1.1 V (TPETCz, TPETPTCz, and TPETPOcCz) or 1.0 V (TPETTh, TPETPTTh, and TPETPOcTh).

Electrochemical polymerization on ITO electrodes for porosity measurements and optical characterization

10 mL of the monomers solutions were placed in a three-electrode cell. ITO (~ 1.5 cm x 1.2 cm deposited area) on glass and a platinum gauze (2.5 cm x 1.2 cm area), separated by 1 cm, were used as WE and CE, respectively (Ag°/$AgNO_3$ as RE). For krypton gas sorption measurements, thick films were produced by applying an oxidative potential of 1.2 V (TPETCz, TPETPTCz, TPETPOcCz, TPETPTTh, and TPETPOcTh) or 1.4 V (TPETTh) for 20 min. Afterwards, a potential of -1.0 V was applied for 120 s in order to dedope the deposits. After rinsing the deposits with acetonitrile and dichloromethane, they were dried for 20 min at 100 °C. The collection of ca. 2 mg of material was necessary for reliable BET measurements. For morphological characterization, carbazole-based MPN films on ITO were prepared by applying ten voltammetric cycles in the potential range of -1.0 V to 1.1 V at scan rate of 0.01 Vs^{-1}. After rinsing the films with acetonitrile and dichloromethane, they were dried for 20 min at 100 °C.

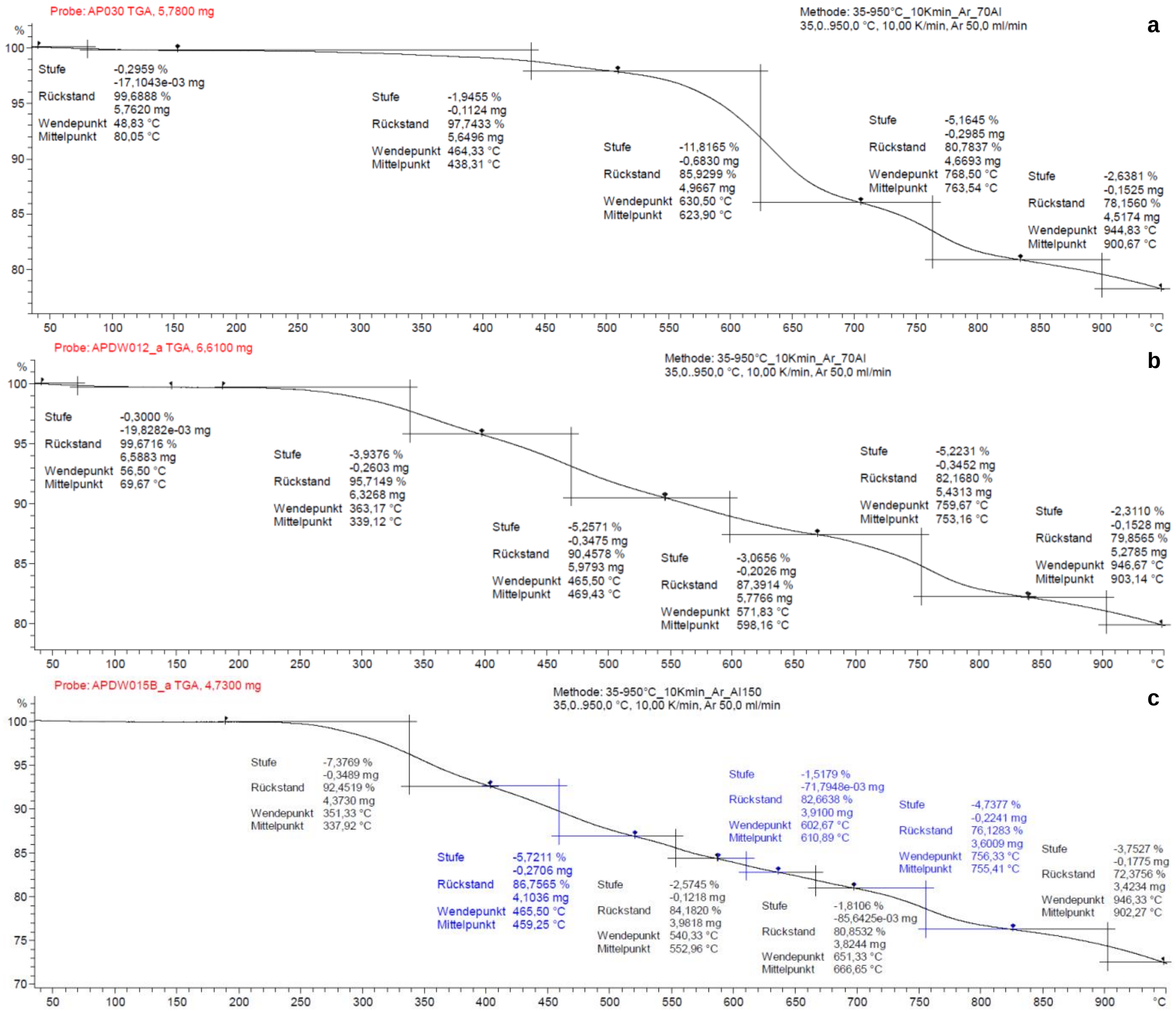


Figure S1. TGA plotes of the bulk MPNs (made by $FeCl_3$ oxidation): PTPETCz (a), PTPETPTCz (b), and PTPETPOcCz (c).

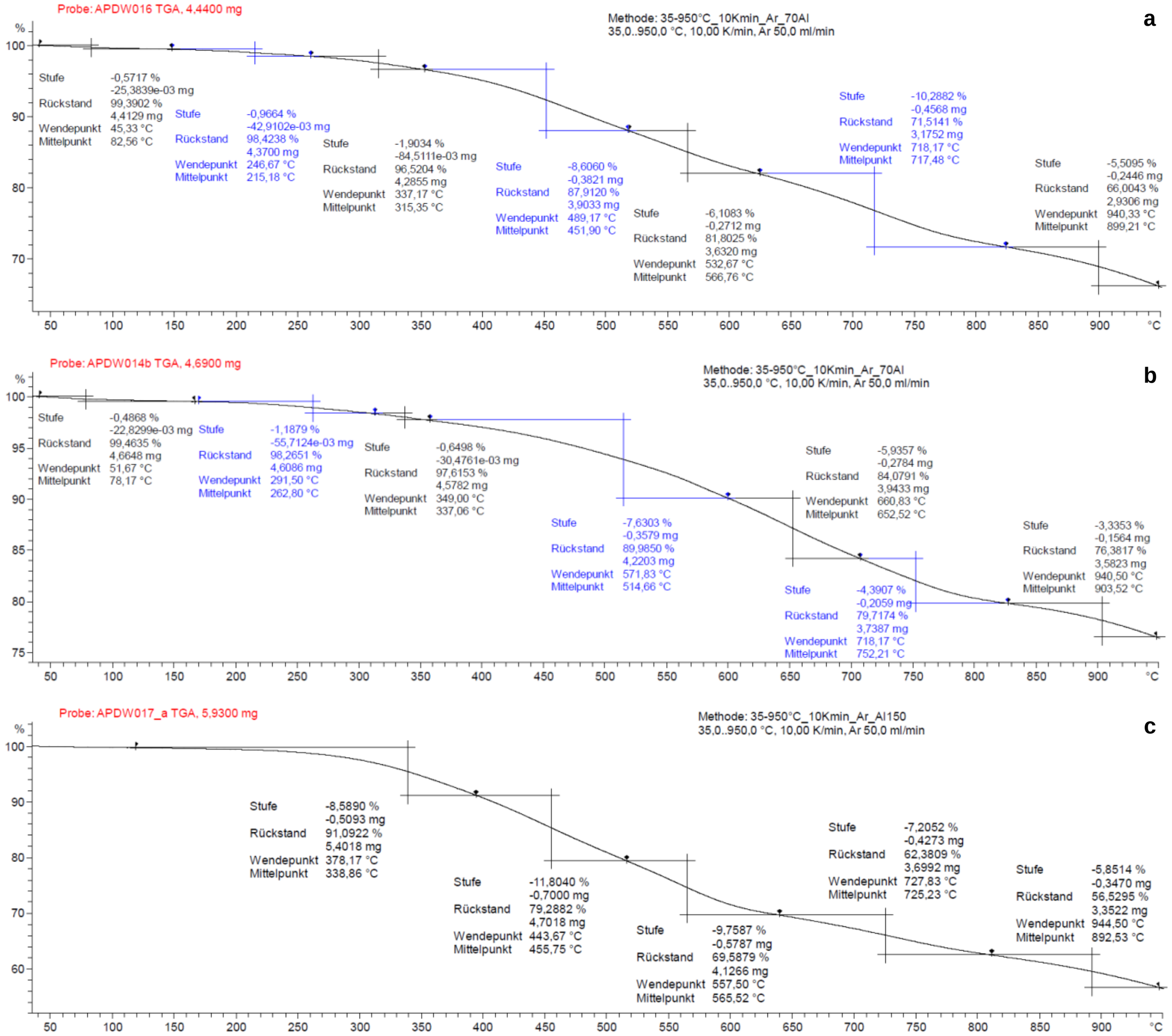


Figure S2. TGA plots of the bulk MPNs (made by $FeCl_3$ oxidation): PTPETTh (a), PTPETPTTh (b), and PTPETPOcTh (c).

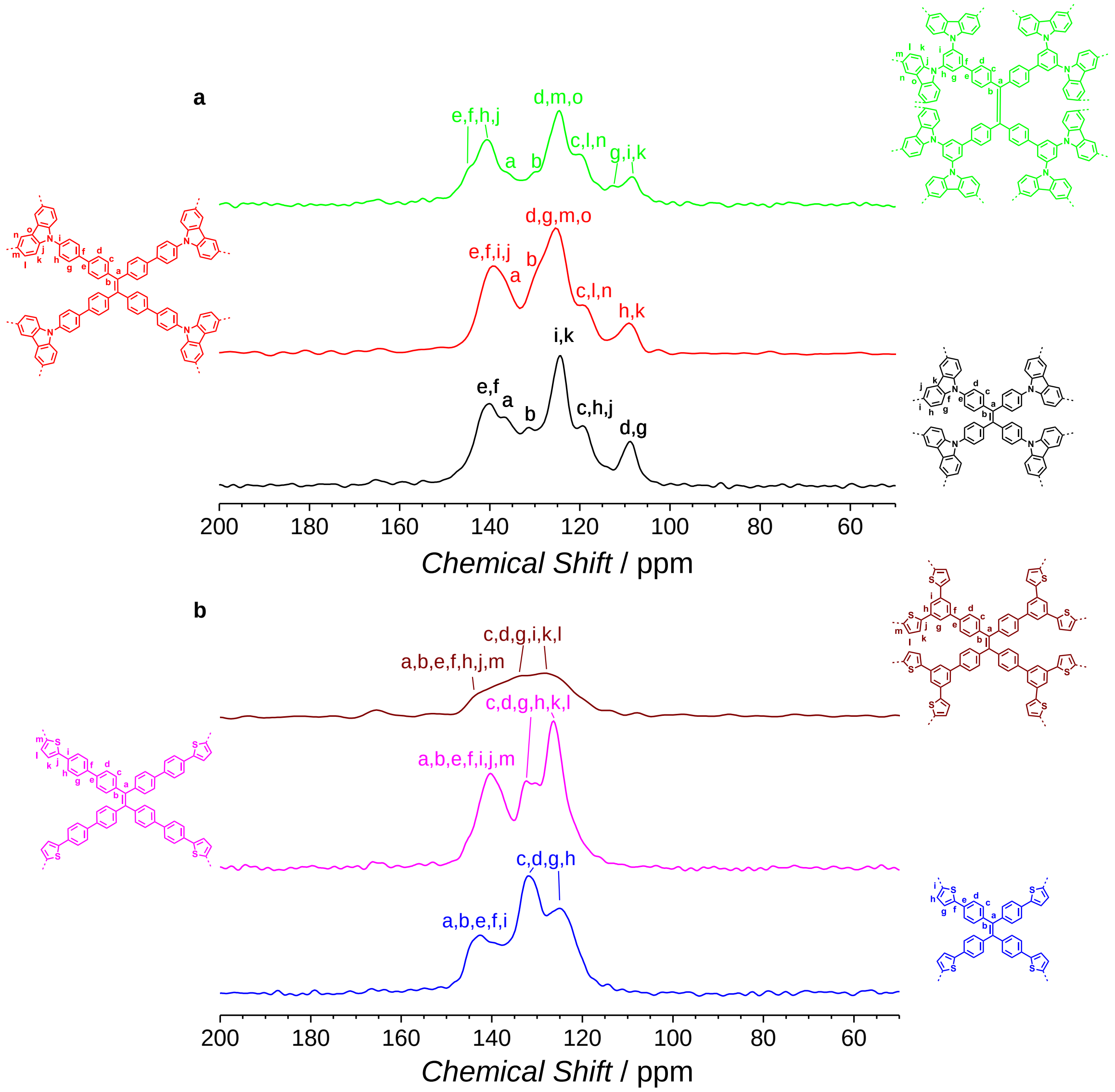


Figure S3. $^{13}C\{^1H\}$ CPMAS NMR spectra of the carbazole-based (a) and thiophene-based (b) bulk polymers.

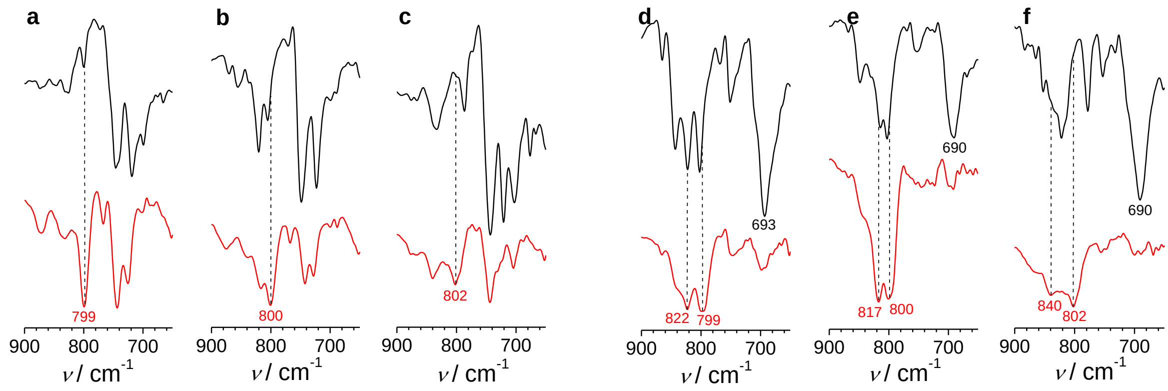


Figure S4. FT-IR spectra of the monomers (black lines): TPETCz (a), TPETPTCz (b), TPETPOcCz (c), TPETTh (d), TPETPTTh (e), TPETPOcTh (f); and the corresponding bulk polymers (red lines).

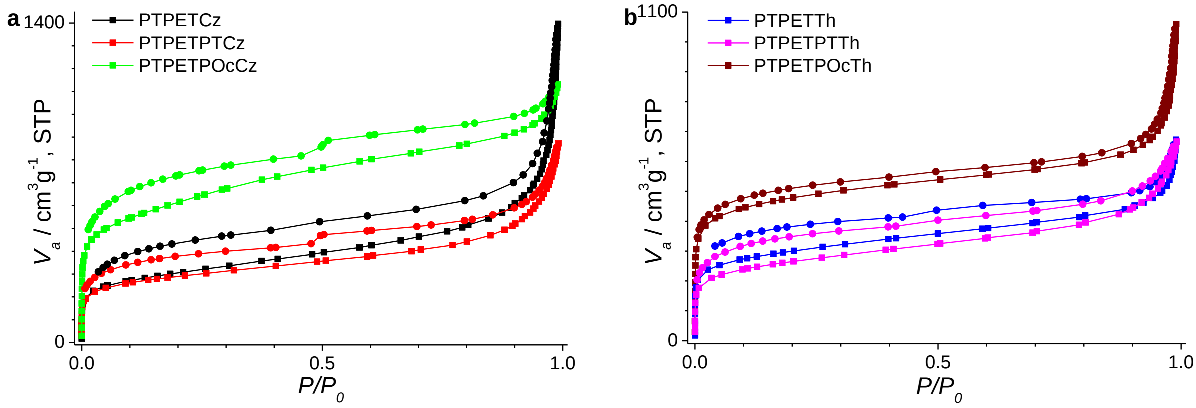


Figure S5. Nitrogen gas sorption isotherms of chemically synthesized carbazole-based (a), and thiophene-based (b) bulk MPNs.

Table S1. Porosity data, gas uptake (at 298 K) and gas sorption selectivities of the six bulk MPNs synthesized by oxidative coupling with iron(III) chloride.

Polymer	Pore volume[a] $[cm^3g^{-1}]$	Gas uptake [%]				Selectivity[c]	
		CO_2	N_2	CH_4	H_2[b]	CO_2/N_2	CO_2/CH_4
PTPETCz	1.13	5.71	1.23	0.80	0.45	8.0	2.6
PTPETPTCz	0.95	6.21	1.22	0.80	0.36	11.1	2.8
PTPETPOcCz	1.51	8.95	2.04	1.15	0.44	13.0	2.8
PTPETTh	0.75	5.95	1.24	0.79	0.36	10.6	2.7
PTPETPTTh	0.78	5.33	1.09	0.68	0.30	11.2	2.8
PTPETPOcTh	1.08	8.11	1.80	1.09	0.48	10.8	2.7

[a] Determined at $P/P_0 = 0.95$; [b] Measured at 77 K; [c] Calculated by applying Henry's law.[S1]

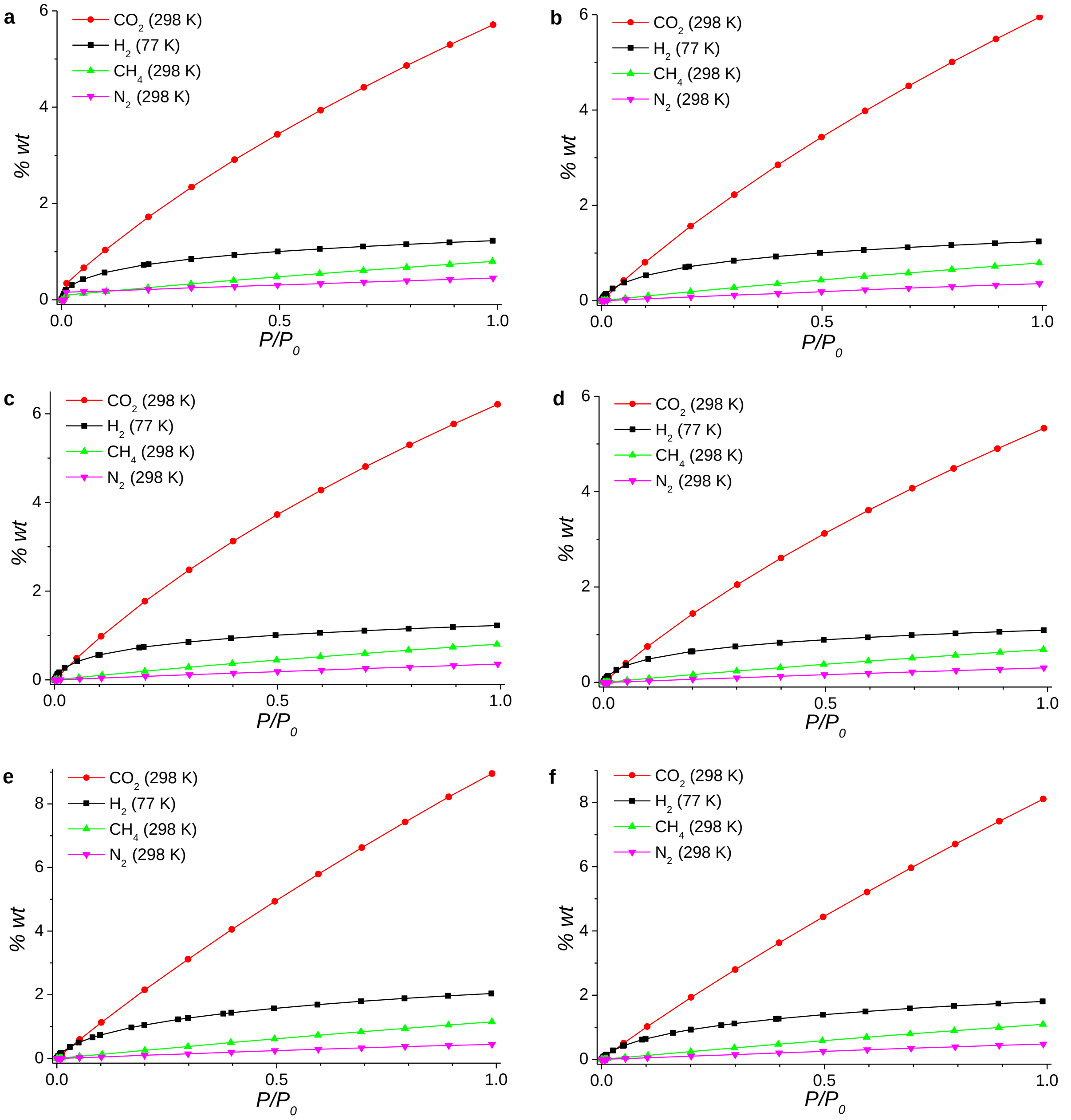


Figure S6. Gas adsorption isotherms for the bulk MPNs for PTPETCz (a), PTPETTh (b), PTPETPTCz (c), PTPETPTTh (d), PTPETPOcCz (e), and PTPETPOcTh (f).

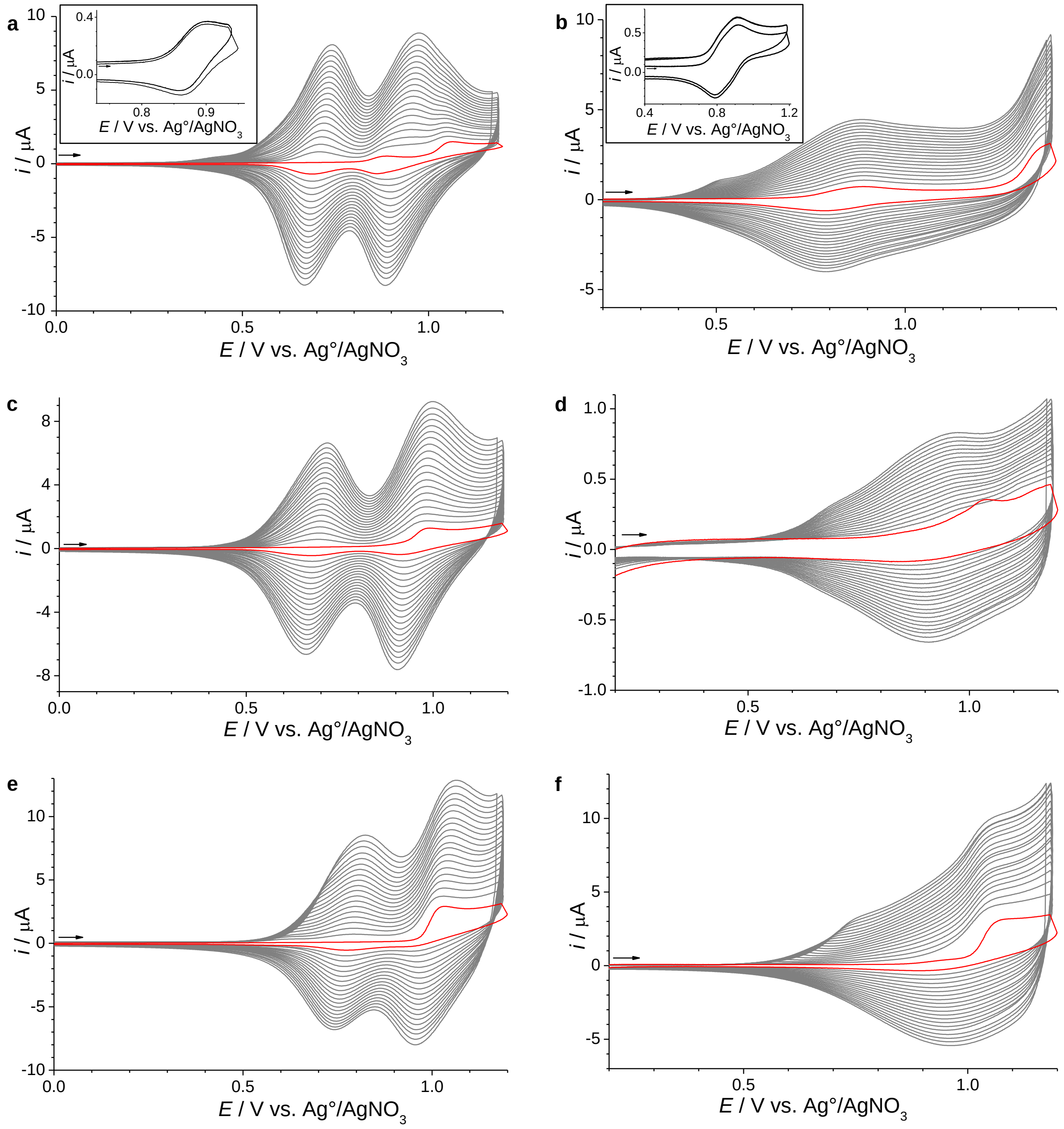


Figure S7. Twenty cyclic voltammograms at Pt disc electrodes carried out for 0.1 mM solutions of TPETCz (a), TPETTh (b), TPETPTCz (c), TPETPTTh (d), TPETPOcCz (e), and TPETPOcTh (f) in dichloromethane for the carbazole-based monomers or in BFEE/dichloromethane (1:4) mixtures for the thiophene-based monomers. 0.1 M TBABF$_4$ was used as supporting electrolyte. Cyclic voltammograms were recorded from -1.0 V to 1.2 V (a,c,e), 0 V to 1.4 V (b), or 0 V to 1.2 V (d, f) with a scan rate of 0.10 Vs^{-1}. The insets show the cyclic voltammograms in a narrower potential window for the reversible peaks for TPETCz (a) and TPETTh (b).

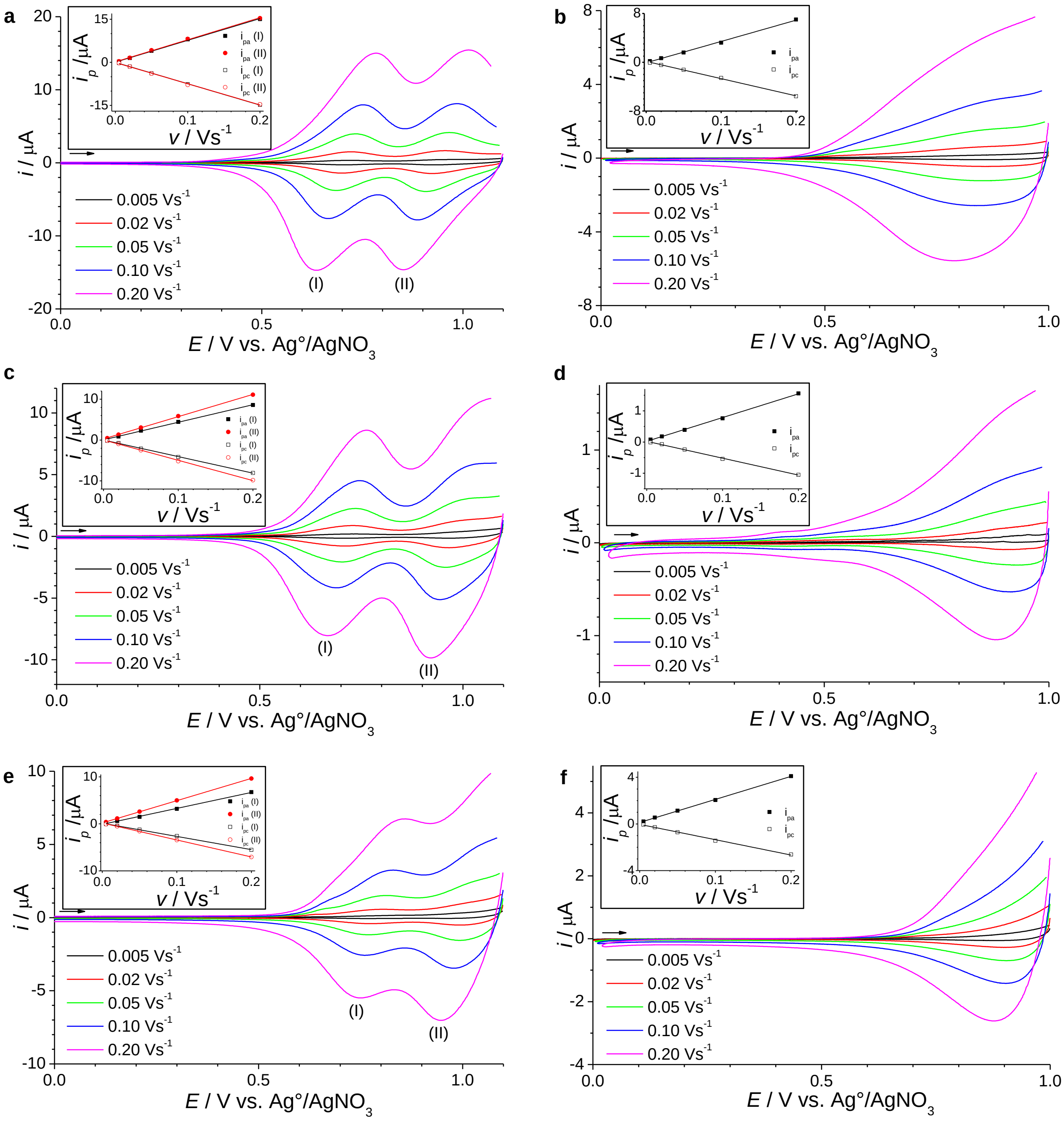


Figure S8. Cyclic voltammograms for PTPETCz (a), PTPETTh (b), PTPETPTCz (c), PTPETPTTh (d), PTPETPOcCz (e), and PTPETPOcTh (f) deposits on Pt disc electrodes in monomer-free dichloromethane containing 0.1 M TBABF$_4$ as supporting electrolyte. CVs were recorded from 0 V to 1.1 V (a,c,e) or 1.0 V (b,d,f) at different scan rates from 0.005 to 0.20 Vs^{-1}. The films were prepared as described in the caption of Figure S7. The insets demonstrate the linear dependence of peaks current and scan rate.

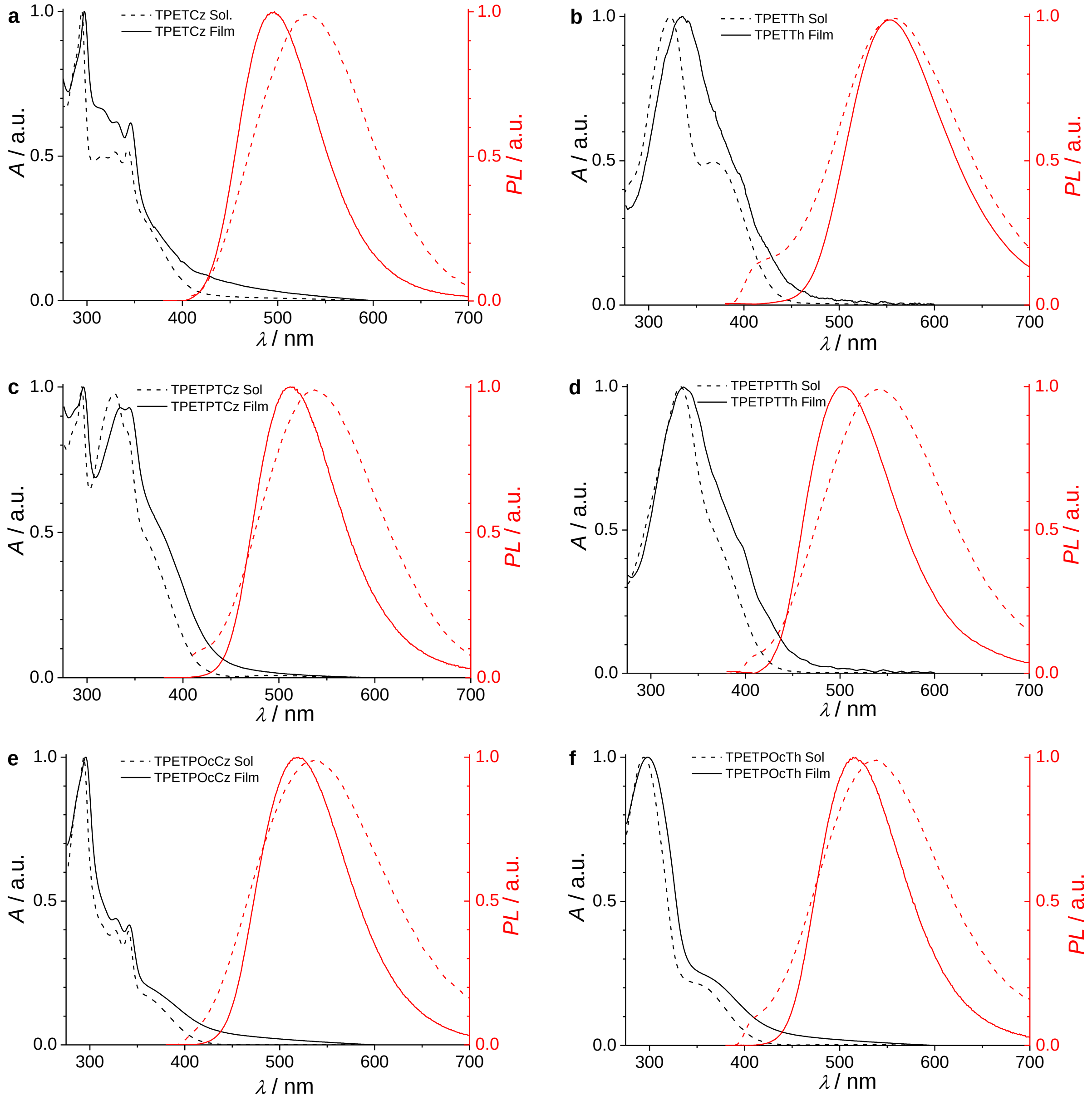


Figure S9. Absorption (black lines) and photoluminescence (red lines) spectra of the monomers: TPETCz (a), TPETTh (b), TPETPTCz (c), TPETPTTh (d), TPETPOcCz (e), and TPETPOcTh (f) in diluted chloroform solutions (dashed lines) and in the solid state (films) on quartz, solid lines).

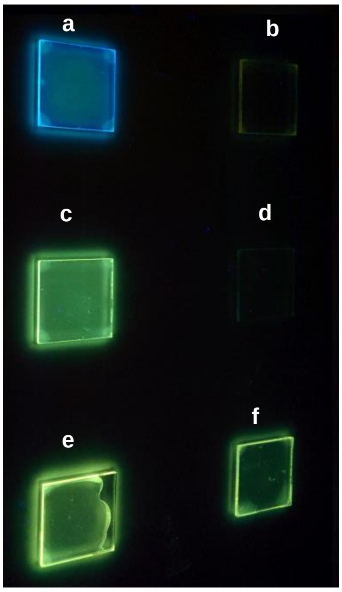


Figure S10. Photographs of monomer films of TPETCz (a), TPETTh (b), TPETPTCz (c), TPETPTTh (d), TPETPOcCz (e), and TPETPOcTh (f) on quartz plates upon excitation at 364 nm with an UV lamp.

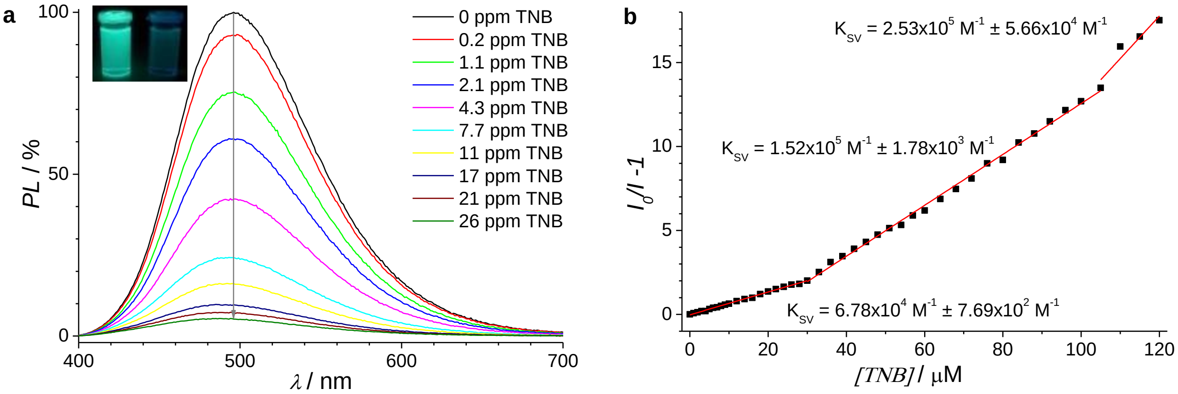


Figure S11. Photoluminescence spectra (a) of a 0.01 mM TPETPOcCz dispersion in THF/water (1:9) upon excitation at 340 nm, and Stern-Volmer plot of the PL intensity at 497 nm (b) by addition of different amounts of TNB.

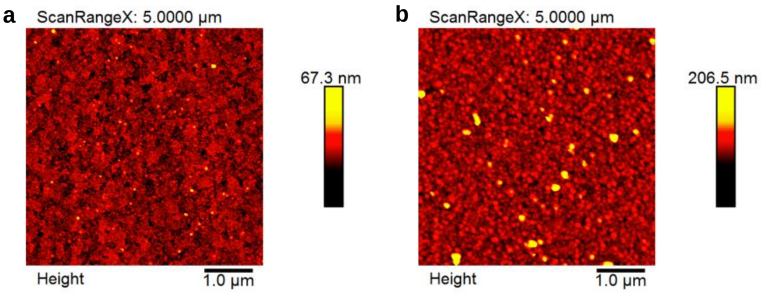


Figure S12. Tapping mode AFM images of MPN films on ITO: PTPETCz (a), PTPETPTCz (b), and PTPETPOcCz (c). The films were electrochemically prepared from a 0.1 mM solution of the monomers in dichloromethane using 0.1 M $TBABF_4$ as supporting electrolyte. Ten consecutive voltammetric cycles in the range from -1.0 V to 1.1 V were applied with a scan rate of 0.10 Vs^{-1}.

Table S2. Average roughness, thicknesses and PL-QYs for excitation at 340 nm of electrogenerated carbazole-based MPN films on ITO (for the preparation see the caption of Figure S12).

MPN films	Rq (nm)	Thickness (nm)	PL λ_{max} Film [nm]	PL-QY Film [%]
PTPETCz	4.0	25	527	3.9
PTPETPTCz	13.0	50	542	11.5
PTPETPOcCz	7.7	75	529	3.1

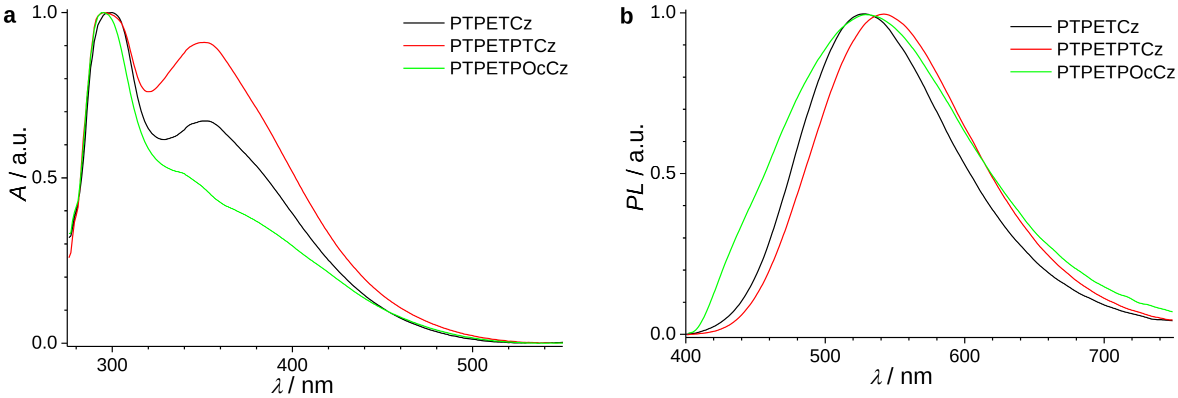


Figure S13. Absorption (a) and photoluminescence (b) spectra of the carbazole-based MPN films on ITO.

Table S3. Sensitivity values for detection of TNT from the literature using different techniques and sensory materials.

Technique	Sensory Material	Sensitivity	Reference
Differential pulse voltammetry	MCM-41	0.4 ppb TNT	S2
Differential pulse voltammetry	TCAC EP film	0.1 ppm TNT	S3
Liner scan voltammetry	PTPTCz	22 ppb TNT	S4
Fluorescence quenching	PSpCz	5 ppb TNT	S5
Fluorescence quenching	Polymer 1	5 ppb TNT	S6
Fluorescence quenching	PTPETPOcCz	1 ppm TNT	This study
Fluorescence quenching	polyTPECz	2 ppm TNP	S7
Ion mobility spectrometry	-	ppt levels TNT	S8
Mass spectrometry	-	0.3ppt TNT	S9
OFET	rr-P3HT/SXFA	500 ppt	S10

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