Electronic Supplementary Material (ESI) for RSC Advances

Immobilization of Catalysts onto Poly(*p*-xylylene) Nanotubes

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Materials and Chemicals

water: deionized water (University of Bayreuth, PNS building)
poly(ethylene oxide): Acros, M_w = 300,000 g mol^{-1}
THF was freshly distilled from K, Et_2O was freshly distilled from K/Na, benzene was freshly distilled from Na and CH_2Cl_2 was distilled from P_2O_5. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Fluka, Alfa Aesar, or Acros.

Methods

General

All reactions involving air- or moisture-sensitive reagents were carried out in heat-gun-dried glassware under an argon atmosphere and were performed by using standard Schlenk techniques. **^{1}H NMR** and **^{13}C NMR** spectra were recorded on *a Bruker DPX-300* (^{1}H: 300 MHz, ^{13}C: 75 MHz), a *Varian Inova 500* (^{1}H: 500 MHz, ^{13}C: 125 MHz), or *Varian Unity plus 600* (^{1}H: 600 MHz, ^{13}C: 150 MHz). Chemical shifts δ in ppm are referenced to the solvent residual peak. Thin layer chromatography (TLC) was carried out on *Merck silica gel 60 F254* plates; detection by UV or dipping into a solution of $KMnO_4$ (1.5 g), $NaHCO_3$ (5.0 g) in H_2O (400 mL) followed by heating. Flash chromatography (FC) was carried out on *Merck silica gel 60* (40 – 63 µm) at about 1.5 bar. All solvents for FC and extraction were destilled before use. **HRMS**

(m/z) were performed using a *Bruker MicroTof* and a *LTQ Orbitrap XL* (nanospray inlet, 1.1 KV, resolution: 30000). **IR-spectra** were recorded on a *Digilab FTS 4000*, equipped with a *Specac MKII* Golden Gate Single Reflection ATR System. **GC** analysis were carried out on a *Hewlett Peckard HP 6890 Series* equipped with a *HP 5 column* (30 m x 0.32 mm, flim thickness 0.25 µm) using hydrogen as carrier gas.

Chemical Vapor Deposition Setup

For the CVD process, a 90 cm long quartz glass tube was connected to a cylindrical deposition chamber (borosilicate glass) of 5.5 cm inner diameter and a 8 cm long vaporization chamber (borosilicate glass) using ground glass joints. The deposition chamber was connected to three cold traps followed by an oil vacuum pump (Edwards S Two Stage). The pressure was measured using a vacuum gauge (Edwards Pirani 1001 and Pirani Gauge PRL10). Both the vaporization chamber and the glass tube were placed in a 115 cm long oven (Pyrolus AT) featuring three 38 cm long, individually controllable furnaces (vaporization zone, pyrolysis chamber, and transportation zone). The deposition chamber was kept outside the oven at room temperature.

Scanning Electron Microscopy

Scanning electron micrographs were recorded on a JSM-7500F (JEOL). The preset *Plastics (with coating)* was selected, and the acceleration voltage was set to 2 kV. The column mode *SEM (r-Filter SM)* was used, and the probe current was set to LC 7. The corresponding software was PC-SEM (JEOL, version 2.0.0.8). In order to determine the average fiber diameter of a fiber mat, 100 fibers were measured using ImageJ (National Institute of Health, USA, version 1.44c).

Special apparatus used for the catalytic cycles and the functionalization of the nanotubes

Figure 1 special apparatus used for the functionalization of the nanotubes and the catalytic cycles.

General Procedures

General procedure for the immobilization of catalysts or ligands onto ethinyl-functionalized PPX-nanotubes by CuAAC (GP 1)

A special reactor (see figure X in the paper) was charged with ethinyl-functionalized poly-*para*-xylylene (PPX, 1 eq.) and flushed with argon for 1 h. THF (5 mL) and CuI (0.06 eq.) were added under an argon atmosphere. After 2 h the azide (2 eq.) dissolved in THF (1 mL) was added and the reaction mixture was stirred for 48 h at room temperature (RT). The modified PPX-nanotubes were rinsed with THF (10 x 5 mL). The washed nanotubes were dried under reduced pressure; conversion was determined by elemental analysis and gravimetrically.

General procedure for the oxidation of benzyl alcohol using catalytic system A (GP 2)

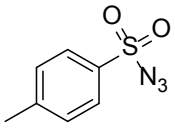
A solution (3.66 mL) of benzyl alcohol (0.40 M, 1.47 mmol, 1.0 eq.) and hexadecane (0.40 M, 1.47 mmol, 1.0 eq.; internal standard) in dichloromethane was mixed with a solution of KBr (*aq*., 0.5 M, 0.29 mL, 0.15 mmol, 0.1 eq.) at 0 °C. Then a solution of NaOCl (*aq*., 0.35 M, 5.24 mL, buffered by $NaHCO_3$ to pH 8.9, 1.83 mmol, 1.25 eq.) was added at 0 °C. The TEMPO-functionalized PPX-nanotubes (20.0 mg, 36.6 µmol, 2.5 mol% nitroxide) were fixed in a Teflon holder (see figure X in the paper) and dipped into the reaction mixture. By removal of the catalytic system A the reaction was stopped and the product was isolated by rinsing the fiber mat with dichloromethane (3 x 5 mL). The combined phases were separated and dried over $MgSO_4$. Conversion of the reaction was determined by GC analysis.

General procedure for the CuAAC by catalytic system B (GP 3)

For the CuAAC catalytic system **B** (72.0 mg, 12 µmol, 5 mol% copper) was fixed in a special apparatus and a solution of benzyl azide (**15**) (0.25 mmol, 1.0 q.) and phenyl propargyl ether (**14**) (0.27 mmol, 1.1 eq.) in dry methanol (5 mL) were added. In the first reaction cycle after longer storage time of the fiber mat, sodium L-ascorbate (5 mg, 0.02 mmol, 0.1 q.) was added to the solution to reduce oxidized Cu(II) to Cu(I). The reaction mixture was heated to 60 °C for 3 - 19 h. Subsequently, the sample mount and the tube material were washed several times with methanol and the washed tube material was dried carefully by passing an argon stream followed by drying under vacuum. After removing the solvent from the reaction mixture, the obtained residue was dissolved in $CDCl_3$ and yield was determined by ^{1}H-NMR-spectroscopy by using dibromomethane as an internal standard.

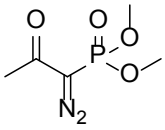
Preparation of starting materials

p-Toluenesulfonyl azide



According to *Regitz et al.*[1] NaN_3 (6.0 g, 31.6 mmol, 1.1 eq.) was dissolved in water (6 mL) and ethanol (9 mL). A heated 45 °C solution of *p*-toluenesulfonyl chloride (4.2 g, 22.1 mmol, 1.0 eq.) in ethanol (22 mL) was added and stirred for 2.5 h. After the reaction was finished the solvent was removed under reduced pressure. The residue was dissolved in water (20 mL) and extracted by dichloromethane (3 x 20 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford *p*-toluenesulfonyl azide as a white solid (6.1 g, 30.9 mmol, 98%). The product was used without further purification.

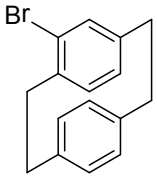
Dimethyldiazo-2-oxopropyl phosphonate (4)



NaH (60% in paraffin oil, 1.0 g, 25.3 mmol, 1.1 eq.) was dissolved in benzene at 0 °C (60 mL) and tetrahydrofurane (10 mL). A solution of dimethyl-2-oxopropylphosphonate (4.0 g, 24.1 mmol, 1.0 eq.) in benzene (20 mL) was added drop wise and the reaction mixture was stirred at 0 °C for 1 h. Then, *p*-toluenesulfonyl azide (5.0 g, 25.3 mmol, 1.05 eq.) was added and stirred for 2 h. The mixture was filtered over zelite and solvent was removed under reduced pressure. FC (pentane/EtOAc = 1:1) gave phosphonate **4** (3.2 g, 16.9 mmol, 72%) as a white solid.

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ = 3.78 (*d*, J = 11.9 Hz, 6H, 2 x OCH_3), 2.20 (*s*, 3H, CH_3). The physical data are in agreement with those reported in the literature.[2]

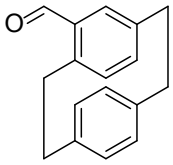
4-Bromo-[2.2]-*para*-cyclophane (2)



According to *Ernst et al.*[3] [2.2]-*para*-cyclophane **1** (4.0 g, 19.2 mmol, 1.0 eq.) and a catalytic amount of iron powder were dissolved in dichloromethane (90 mL) and carbon tetrachloride (30 mL). Bromine (1.0 mL, 19.2 mmol, 1.0 eq.) was added slowly under vigorous stirring. After 2 h the reaction mixture was quenched a solution of $NaHCO_3$ (*aq.*, *sat.*, 2 x 25 mL) and the phases were separated. The organic layer was extracted with water (25 mL), a solution of NaCl (*aq.*, *sat.*, 25 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. FC (pentane/ Et_2O) gave bromide **2** (5.2 g, 18.0 mmol, 94%) as a colorless solid.

IR (Film): 3033*w*, 2958*w*, 2926*s*, 2888*m*, 2850*m*, 1894*w*, 1586*m*, 1543*m*, 1497*m*, 1476*m*, 1449*w*, 1432*m*, 1409*m*, 1391*s*, 1321*w*, 1238*w*, 1187*m*, 1156*w*, 1124*w*, 1092*w*, 1035*s*, 956*w*, 942*w*, 904*s*, 860*w*, 840*s*, 793*s*, 708*s*, 699*s*, 610*s*, 576*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ = 7.17 (*m*, 1H, Ar-*H*), 6.61 – 6.40 (*m*, 6H, Ar-*H*), 3.47 (*m*, 1H, CH_2CCBr), 3.28 – 3.16 (*m*, 1H, CH_2CCBr), 3.17 – 3.01 (*m*, 4H, 2 x CH_2), 2.98 – 2.75 (*m*, 2H, CH_2). The physical data are in agreement with those reported in the literature.[4]

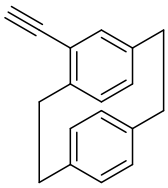
4-Formyl-[2.2]-*para*-cyclophane (3)



According to *Brink et al.*[5] bromide **2** (3.0 g, 10.4 mmol, 1.0 eq.) was dissolved in diethyl ether (70 mL) and a solution of *n*-butyl lithium (1.6 M in *n*-hexane, 13 mL, 20.8 mmol, 2.0 eq.) was added dropwise at 0 °C. The mixture was stirred for 2 h, followed by the addition of dimethyl formamide (1.6 mL, 20.8 mmol, 2.0 eq.). After 1.5 h the reaction was quenched by adding a solution of NH_4Cl (*aq.*, *sat.*, 45 mL). The phases were separated and the aqueous phase was extracted with diethyl ether (3 x 40 mL). The combined organic phases were dreid over $MgSO_4$ and the solvent was removed under reduced pressure. FC (pentane/Et_2O) gave aldehyde **3** (2.1 g, 8.7 mmol, 84%) as a colorless solid.

IR (Film): 3009*w*, 2952*w*, 2926*m*, 2889*w*, 2852*w*, 2747*w*, 1677*s*, 1589*m*, 1554*w*, 1497*w*, 1436*w*, 1410*w*, 1321*w*, 1283*w*, 1226*m*, 1181*w*, 1158*w*, 1142*m*, 1115*w*, 1102*w*, 977*w*, 943*w*, 907*m*, 874*m*, 795*s*, 773*m*, 742*w*, 719*s*, 659*w*, 635*s*, 623*s*, 574*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ = 9.95 (*s*, 1H, C*H*O), 7.01 (*d*, *J* = 2.0 Hz, 1H, Aryl-*H*), 6.73 (*dd*, *J* = 7.8, 2.0 Hz, 1H, Aryl-*H*), 6.63 – 6.53 (*m*, 3H, Aryl-*H*), 6.53 – 6.47 (*m*, 2H, Aryl-*H*), 6.40 (*qd*, *J* = 7.9, 1.8 Hz, 2H, CH_2CHO), 4.19 – 4.04 (*m*, 1H, CH_aCH$_b$CCCOH), 3.33 – 2.87 (*m*, 7H, CH$_a$CH_bCCCOH, 3 x CH_2). The physical data are in agreement with those reported in the literature.[6]

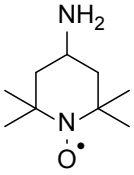
4-Ethinyl-[2.2]-*para*-cyclophane (5)



According to *Hopf et al.*[7] aldehyde **3** (3.0 g, 12.7 mmol, 1.0 eq.) and Cs_2CO_3 (8.3 g, 25.4 mmol, 2.0 eq.) were dissolved in methanol (250 mL). Then, phosphonate **4** (3.7 g, 19.1 mmol, 1.5 eq.) was added to the mixture and stirred for 4 h at 40 °C. The solvent was removed under reduced pressure and the residue was dissolved in water (100 mL) and pentane (100 mL). The phases were separated and the aqueous phase was extracted with pentane (3 x 75 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. FC (pentane/DCM = 30:1) gave alkyne **5** (2.4 g, 10.2 mmol, 80%) as a colorless solid.

IR (Film): 3300*m*, 3034*w*, 3012*w*, 2954*w*, 2929*m*, 2890*w*, 2852*w*, 2099*w*, 1676*w*, 1589*w*, 1500*w*, 1481*w*, 1449*w*, 1431*w*, 1411*w*, 1307*w*, 1206*m*, 1188*w*, 1154*w*, 1087*w*, 943*m*, 908*s*, 864*m*, 796*m*, 716*s*, 649*s*, 605*s*, 585*s*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ = 6.93 (*dd*, *J* = 7.8, 1.7 Hz, 1H, Aryl-*H*), 6.51 - 6.36 (*m*, 6H, Aryl-*H*), 3.51 (*ddd*, *J* = 13.0, 10.3, 2.8 Hz, 1H, $CH_aCH_bCH_2CCCCH$), 3.21 (*s*, 1H, CCCH), 3.20 - 3.10 (m, 1H, $CH_aCH_bCH_2CCCCH$)), 3.09 - 2.71 (*m*, 6H, 3 x CH_2). The physical data are in agreement with those reported in the literature. [7]

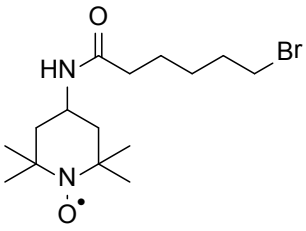
4-Amino-TEMPO



N-Acetamido-TEMPO **7** (8.0 g, 37.5 mmol, 1.0 eq.) and KOH (25.3 g, 450 mmol, 12.0 eq.) were dissolved in water (375 mL) and stirred for 72 h at reflux. After cooling down to rt K_2CO_3 was added (50 g, 360 mmol, 9.6 eq.) and the mixture was extracted with diethyl ether (3 x 150 mL). The organic phases were combined and dried over $MgSO_4$. By removal of the solvent under reduced pressure nitroxide (5.5 g, 32.3 mmol, 86%) was obtained as a red solid.

IR (Film): 3365*w*, 3301*w*, 2971*s*, 2934s, 2916*s*, 1641*w*, 1584*w*, 1461*s*, 1361*s*, 1332*m*, 1304*w*, 1243*s*, 1221*s*, 1178*s*, 1132*w*, 1088*w*, 1052*w*, 940*w*, 873*s*, 856*s*, 813*s*, 680*m*. **MS (ESI)**: *m/z* = 172 ($[M+H]^+$). **HRMS (ESI)**: calculated for $[C_9H_{19}N_2OH]^+$ *m/z* = 172.1570; found *m/z* = 172.1592. The physical data are in agreement with those reported in the literature.[8]

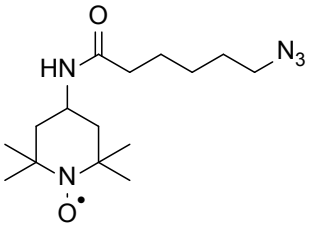
6-(1-Hydroxy-2,2,6,6-tetramethylpiperidine-4-ylcarbamoyl)bromhexane (8)



4-Amino-TEMPO (2.0 g, 11.7 mmol, 1.0 eq.) and trietyhlamine (2.74 g, 12.8 mmol, 1.1 eq.) were dissolved in dichloromethane. 6-Bromohexanoyl chloride (3.55 g, 35 mmol, 3.0 eq.) was added at 0 °C. The mixture was stirred for 1 h at rt, subsequently quenched with HCl (*aq*., 1 M, 15 mL) and extracted with dichloromethane (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. FC (DCM/MeOH = 20:1) gave nitroxide **8** (3.9 g, 11.1 mmol, 95%) as a red viscous oil.

IR (Film): 3329*m*, 3056*m*, 2937*m*, 2858*m*, 1639*s*, 1546*s*, 1448*m*, 1360*m*, 1300*m*, 1400*m*, 1178*m*, 1123*w*, 1087*w*, 1041*w*, 1003*w*, 936*w*, 841*w*, 724*m*, 692*m*, 620*m*, 576*w*. **MS (ESI)**: *m/z* = 370 ($[M+Na]^+$). **HRMS (ESI)**: calculated for $[C_{15}H_{28}BrN_2O_2Na]^+$ *m/z* = 370.1226; found *m/z* = 370.1219.

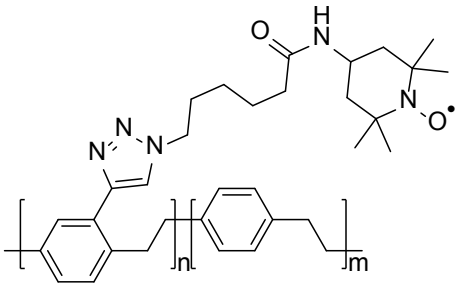
6-(1-Hydroxy-2,2,6,6-tetramethylpiperidine-4-ylcarbamoyl)azidohexane (9)



Nitroxide **8** (2.0 g, 5.7 mmol, 1.0 eq.) and NaN_3 (1.5 g, 23.0 mmol, 4.0 eq.) were dissolved ethanol (25 mL) and stirred for 16 h at reflux. The precipitation was filtered and the solvent removed under reduced pressure. The residue was dissolved in water (15 mL) and diethyl ether (10 mL) The phases were separated and the aqueous phase was extracted with diethyl ether (2 x 10 mL). The combined organic phases were dried over $MgSO_4$ and solvent was removed udner reduced pressure. Azide **9** (1.5 g, 4.9 mmol, 87%) was obtained as a red solid.

IR (Film): 3298*w*, 3072*w*, 2986*m*, 2935*m*, 2864*w*, 2093*s*, 1642*s*, 1539*s*, 1460*m*, 1361*m*, 1298*m*, 1261*s*, 1241*s*, 1179*m*, 1110*w*, 976*w*, 897*w*, 725*m*, 637*m*, 564*s*. **MS (ESI)**: *m/z* = 333 ($[M+Na]^+$). **HRMS (ESI)**: calculated for $[C_{15}H_{28}N_5O_2Na]^+$ *m/z* = 333.2135; found *m/z* = 333.2138. **Elemental analysis** in % calculated for $C_{15}H_{28}N_5O_2$: C 58.04, H 9.09, N 22.56; found: C 57.69, H 9.15, N 22.30.

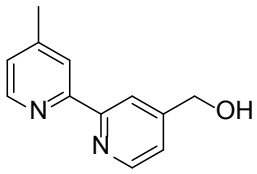
Synthesis of catalytic system A



According to **GP 1**, with TEMPO-azide **9** (40.0 mg, 129.0 µmol). Catalytic system A (31.7 mg) was isolated by intensive washing with THF and drying under reduced pressure. Elemental analysis revealed a degree of functionalization of 62% (calculated by the nitrogen content of the functionalized fiber mat).

Elemental analysis in % calculated for complete functionalization: C 73.03, H 8.17, N 12.90; found: C 68.74, H 7.21, N 8.00.

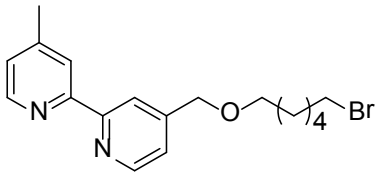
4-Hydroxymethyl-4´-methyl-2,2´-bipyridine (11)



According to *Åkermark et al.*[9] 4,4´-Dimethyl-2,2´-bipyridine **10** (2.0 g, 11.0 mmol, 1.0 eq.) was supended in 1,4-Dioxan (100 mL) and selenium dioxide (2.0 g, 18.0 mmol, 1.6 eq.) was added at rt vigorous under stirring. The mixture was heated for 24 h at reflux. After cooling down to rt the reaction mixture was treated carefully with $NaBH_4$ (0.4 g, 11 mmol, 1.0 eq.) und NaOH (*aq*., 2 M, 5 ml) at 0 °C. The precipitation was filtered and the solvent was removed under reduced pressure. Residuals were dissolved in chloroform and filtered again to remove selenium byproducts. FC (DCM/MeOH = 9:1) gave bipyridine **11** (1.1 g, 5.5 mmol, 50%) as a colorless solid.

IR (Film): 3154*m*, 3062*w*, 3006*w*, 2920*w*, 2880*w*, 2825*w*, 1598*s*, 1557*m*, 1457*m*, 1375*s*, 1321*m*, 1275*m*, 1246*m*, 1157*m*, 1111*m*, 1060*s*, 993*s*, 908*m*, 823*s*, 813*s*, 737*m*, 720*m*, 695*m*, 669*m*, 581*m*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.56 (*d*, *J* = 5.0 Hz, 1H, Aryl-*H*), 8.48 (*d*, *J* = 5.1 Hz, 1H, Aryl-*H*), 8.30 (*s*, 1H, Aryl-*H*), 8.18 (*d*, *J* = 1.7 Hz, 1H, Aryl-*H*), 7.34 – 7.23 (*m*, 1H, Aryl-*H*), 7.13 (*dd*, *J* = 5.2, 1.7 Hz, 1H, Aryl-*H*), 4.75 (*s*, 2H, C*H*$_2$OH), 3.95 (*br s*, 1H, CH$_2$O*H*), 2.42 (*s*, 3H, C*H*$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 155.8 (CH), 155.5 (CH), 151.7 (CH), 149.1 (CH), 148.7 (CH), 148.6 (CH), 124.9 (CH), 122.4 (CH), 121.3 (CH), 118.8 (CH), 63.4 (CH_2), 21.2 (CH_3). **MS (ESI)**: *m/z* = 223 ([M+Na]$^+$), 201 ([M+H]$^+$). **HRMS (ESI)**: calculated for $[C_{12}H_{12}N_2ONa]^+$ *m/z* = 223.0842; found *m/z* = 223.0844. The physical data are in agreement with those reported in the literature.[9]

4-(((6-Bromohexyl)oxy)methyl)-4`-methyl-2,2`-bipyridine (12)

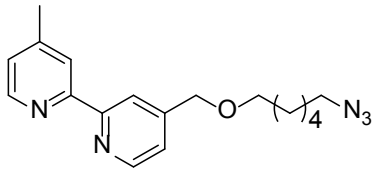


Bipyridine **11** (0.5 g, 2.5 mmol, 1.0 eq.) was dissolved in tetrahydrofurane (10 ml). NaH (0.2 g, 3.7 mmol, 1.5 eq.) was added slowly under stirring. The reaction mixture was added droppwise into a solution of 1,6-dibromohexane (2.3 ml, 15.0 mmol, 6.0 eq.) in tetrahydrofurane (5 mL) and stirred for 1 h. After removal of the solvent under reduced pressure bromide **12** (0.6 g, 1.5 mmol, 61%) was isolated by FC (DCM/MeOH = 9:1) as a colorless solid.

IR (Film): 3180*m*, 3008*w*, 2934*m*, 2744*w*, 1597*s*, 1557*m*,1445*s*, 1373*s*, 1327*m*, 1285*m*, 1247*m*, 1216*m*, 1158*w*, 1108*m*, 1074*m*, 1037*s*, 992*m*, 927*w*, 897*m*, 848*m*, 819*s*, 667*m*, 642*m*, 576*s*, 525*s*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.63 (*d*, *J* = 5.0 Hz, 1H, Aryl-*H*), 8.52 (*d*, *J* = 4.9 Hz, 1H, Aryl-*H*), 8.30 (*s*, 1H, Aryl-*H*), 8.22 (*s*, 1H, Aryl-*H*), 7.40 – 7.27 (*m*, 1H, Aryl-*H*), 7.19 – 6.97 (*m*, 1H, Aryl-*H*), 4.58 (*s*, 2H, CC*H*$_2$O), 3.51 (*t*, *J* = 6.4 Hz, 2H, C*H*$_2$Br), 3.39 (*t*, *J* = 6.8 Hz, 2H, OC*H*$_2$CH$_2$), 2.42 (*s*, 3H, CC*H*$_3$), 1.85

(*q*, *J* = 6.9 Hz, 2H, CH_2CH$_2$Br), 1.64 (*q*, *J* = 6.6 Hz, 2H, OCH$_2$CH_2), 1.52 – 1.35 (*m*, 4H, 2 x CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 156.0 (C), 155.7 (C), 149.4 (CH), 149.1 (CH), 149.0 (C), 148.2 (C), 124.8 (CH), 122.1 (CH), 121.9 (CH), 119.5 (CH), 71.6 (CH_2), 71.0 (CH_2), 33.9 (CH_2), 32.9 (CH_2), 29.7 (CH_2), 28.1 (CH_2), 25.5 (CH_2), 21.3 (CH_3). . **MS (ESI)**: *m/z* = 363 ([M+H]$^+$). **HRMS (ESI)**: calculated for $[C_{18}H_{23}BrN_2OH]^+$ *m/z* = 363.1067; found *m/z* = 363.1064.

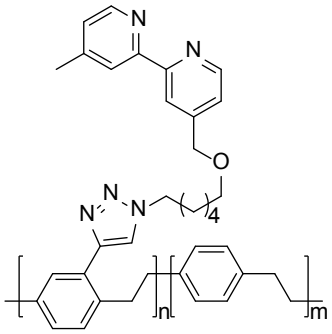
4-(((6-Azidohexyl)oxy)methyl)-4`-methyl-2,2`-bipyridine (13)



Bromide **12** (300 mg, 0.8 mmol, 1 eq.) and NaN_3 (210 mg, 3.3 mmol, 4 eq.) were dissolved in ethanol (10 mL) and stirred for 24 h at reflux. After cooling to rt the solvent was removed under reduced pressure and the residue was dissolved in water (15 mL) and dichloromethane (15 mL). Phases were separated and the aqueous phase was extracted with dichloromethane (2 x 15 mL). The combined organic phases were were dried over $MgSO_4$ and the solvent removed under reduced pressure. FC (DCM/MeOH = 20:1) gave azide **13** (250 mg, 0.77 mmol 96%) as a colorless oil.

IR (Film): 2935*m*, 2860*m*, 2092*s*, 1729*w*, 1596*s*, 1555*m*, 1458*m*, 1376*m*, 1252*s*, 1182*w*, 1101*s*, 991*m*, 900*w*, 822*s*, 744*w*, 670*m*, 588*w*. **^{1}H-NMR** (300 MHz, $CDCl_3$, 300 K): δ = 8.64 (*d*, *J* = 5.0 Hz, 1H, Aryl-*H*), 8.53 (*d*, *J* = 4.9 Hz, 1H, Aryl-*H*), 8.31 (*s*, 1H, Aryl-*H*), 8.23 (*s*, 1H, Aryl-*H*), 7.33 (*d*, *J* = 4.9 Hz, 1H, Aryl-*H*), 7.13 (*d*, *J* = 4.9 Hz, 1H, Aryl-*H*), 4.59 (*s*, 2H, CCH_2O), 3.53 (*t*, *J* = 6.4 Hz, 2H, CH_2N$_3$), 3.26 (*t*, *J* = 6.9 Hz, 2H, OCH_2CH$_2$), 2.44 (*s*, 3H, CCH_3), 1.64 (*m*, 4H, CH_2CH$_2$N$_3$, OCH$_2$CH_2), 1.52 – 1.33 (*m*, 4H, 2 x CH$_2$). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K): δ = 156.4 (C), 155.9 (C), 149.3 (CH), 149.0(CH), 148.9 (C), 148.1 (C), 124.7 (CH), 122.0 (CH), 121.8 (CH), 119.4 (CH), 71.5 (CH_2), 70.9 (CH_2), 51.4 (CH_2), 29.6 (CH_2), 28.8 (CH_2), 26.6 (CH_2), 25.8 (CH_2), 21.2 (CH_3). **MS (ESI)**: *m/z* = 326 ([M+H]$^+$), 348 ([M+Na]$^+$). **HRMS (ESI)**: calculated for $[C_{18}H_{23}N_5ONa]^+$ *m/z* = 348.1795; found *m/z* = 348.1799.

Synthesis of catalytic system B



According to **GP 1**, with bipyridine-derivate **13** (150.0 mg, 461.0 µmol). Catalytic system B (72.0 mg) was isolated by intensive washing with THF and drying under reduced pressure. Elemental analysis revealed a degree of functionalization of 27% (calculated by the nitrogen content of the functionalized fiber mat).

Elemental analysis in % calculated for complete functionalization: C 73.03, H 8.17, N 12.90; found: C 69.94, H 7.81, N 3.48.

Literature

[1] M. Regitz, J. Hocker, A. Liedhegener, *Org. Synth.* 1968, **48**, 36.

[2] W. R. F. Goundry, J. E. Baldwin, V. Lee, *Tetrahedron* 2003, **59**, 1719.

[3] L. Ernst, L. Wittkowski, *Eur. J. Org. Chem.* 1999, **7**, 1653.

[4] J. W. Graskemper, B. Wang, L. Qin, K. D. Neumann, S. G. DiMagno, *Org. Lett.* 2011, **13**, 3158.

[5] M. Brink, *Synthesis* 1975, **12**, 807.

[6] H. Nandivada, H.-Y. Chen, J. Lahann, *Macromol. Rapid Commun.* 2005, **26**, 1794.

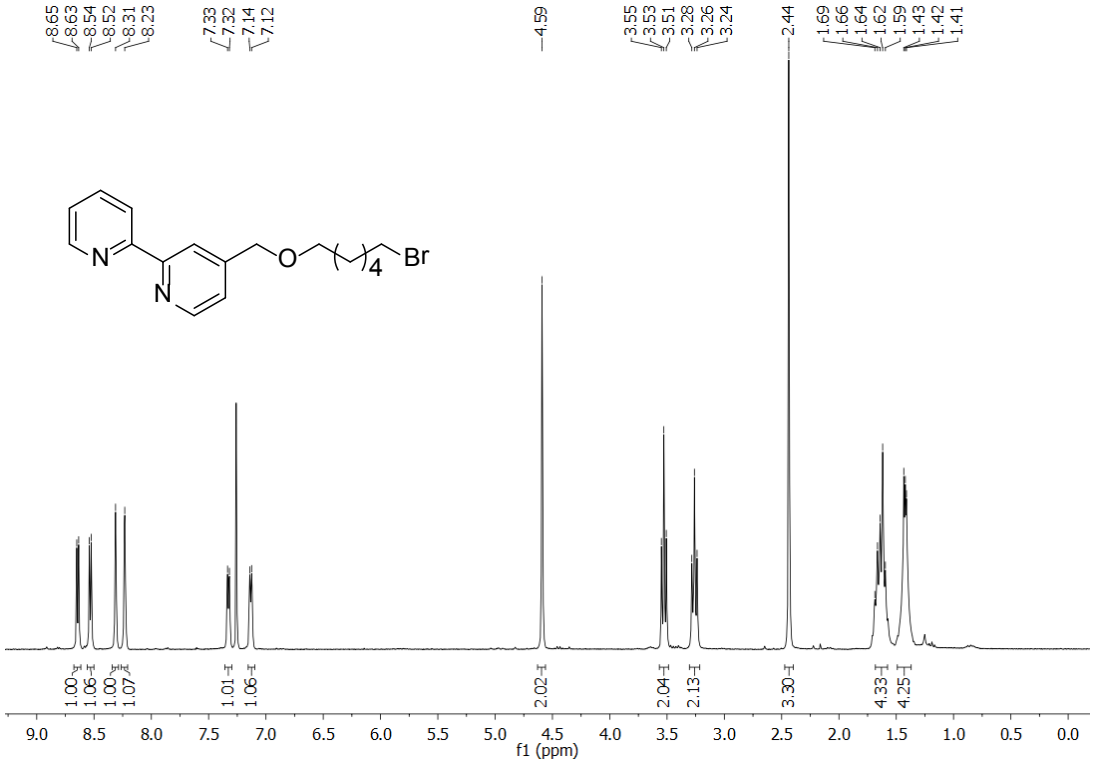
[7] L. Bondarenko, I. Dix, H. Hinrichs, H. Hopf, *Synthesis* 2004, **16**, 2751.

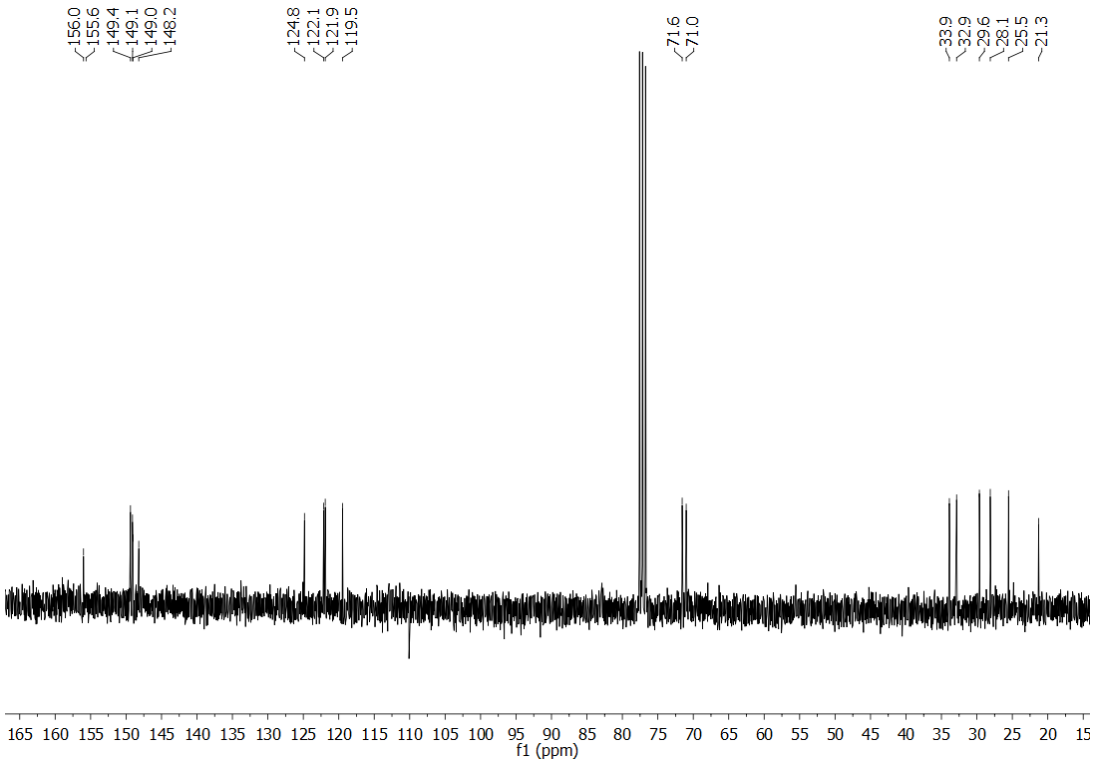
[8] J. Zakrzewski, J. Hupko, K. Kryczka, *Monatshefte für Chemie / Chemical Monthly* 2003, **134**, 843.

[9] Katja E. Berg, A. Tran, Mary K. Raymond, M. Abrahamsson, J. Wolny, S. Redon, M. Andersson, L. Sun, S. Styring, L. Hammarström, H. Toftlund, B. Åkermark, *Eur. J. Inorg. Chem.* 2001, **12**, 1019.

^{1}H-NMR- and ^{13}C-NMR-spectra of all new compounds:

4-(((6-Bromohexyl)oxy)methyl)-4`-methyl-2,2`-bipyridine (12)





4-(((6-Azidohexyl)oxy)methyl)-4`-methyl-2,2`-bipyridine (13)