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Organoboronium-functionalized Polystyrenes as a New Class of Polycations

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Experimental Methods

Materials and General Methods. The compounds 2,2'-bipyridine (bipy), $NH_4[PF_6]$, and BBr_3 were purchased from Acros. All chemicals were used as received without further purification. Poly(4-trimethylsilylstyrene),[1] 4-*t*-butylphenyltrimethylstannane,[2] and $(CuMes)_n$[3] were prepared according to literature procedures. Reactions and manipulations involving reactive boron species were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents); chlorinated solvents and acetonitrile were distilled from CaH_2 and degassed via several freeze-pump-thaw cycles.

The 499.9 MHz ^1H, 125.7 MHz ^{13}C, 470.4 MHz ^{19}F, and 202.4 MHz ^{31}P NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 160.4 MHz ^{11}B NMR spectra were recorded with a boron-free probe using boron-free quartz NMR tubes. ^1H and ^{13}C NMR spectra were referenced internally to the solvent peaks, ^{19}F NMR spectra were referenced externally to α,α',α"-trifluorotoluene (0.05% in C_6D_6; $\delta = -63.73$), and the ^{11}B NMR spectra externally to $BF_3{\bullet}Et_2O$ ($\delta = 0$) in C_6D_6. MALDI-TOF measurements were performed on an Applied Biosystems 4800 Proteomics Analyzer in reflectron (+)-mode with delayed extraction. Benzo[a]pyrene was used as the matrix (20 mg/mL in toluene) and the samples were dissolved in MeOH (10 mg/mL), mixed with the matrix in a 1:10 ratio, and then spotted on the wells of a sample plate. Peptides were used for calibration (Des-Arg-Bradykinin (904.4681), Angiotensin I (1296.6853), Glu-Fibrinopeptide B (1570.6774), ACTH (clip 1-17) (2093.0867), ACTH (clip 18-39) (2465.1989), ACTH (clip 7-38) (3657.9294) with α-hydroxy-4-cyanocinnamic acid as the matrix. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

GPC analyses were performed in DMF / 20 mM $NH_4[PF_6]$ (0.5 mL/min) using a Waters Breeze system equipped with a 717 plus auto sampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. A series of Shodex Asahipak columns (GF-510 HQ, GF-310 HQ), which were kept in a column heater at 60 °C, were used for separation. The columns were calibrated with PS standards (Polymer Laboratories).

Caution! BBr_3 is toxic and corrosive and should be handled appropriately with great care. Fluorinated grease was used for ground glass joints in reactions involving boron tribromide.

Synthesis of poly(dipyridylmesitylstyrylboronium bromide) (P4-Mes). A solution of poly(4-trimethylsilylstyrene) (**P1**) (1.00 g, 5.67 mmol $SiMe_3$, $M_n = 15390$, $M_w = 17680$, $PDI = 1.15$ based on GPC-UV) in CH_2Cl_2 (30 mL) was added to a solution of BBr_3 (1.71 g, 6.83 mmol) in CH_2Cl_2 (20 mL) in a glove box. The reaction mixture was stirred at room temperature for 24 h. Copper mesityl (1.60 g, 8.76 mmol) in CH_2Cl_2 (20 mL) was added, and the mixture was kept stirring for 12 h. A yellow-orange precipitate formed, which was removed by filtration through celite on a medium fritted funnel. A solution of 2,2'-dipyridyl (4.00 g, 25.6 mmol) in CH_2Cl_2 (20 mL) was added drop-wise leading to a brownish suspension. After stirring for 12 h, the reaction mixture was poured into acetone (250 mL). The mixture was filtered to give an off-white solid, which was redissolved in methanol and dialyzed against methanol (Fisherbrand regenerated cellulose membrane with 6000 to 8000 Dalton molecular weight cut-off). The resulting solution was concentrated and precipitated into ether. The precipitate was collected on a filter paper and dried under high vacuum at 60 °C for 12 h to give the product as a light yellow solid. Yield: 1.88 g (71%). ^{1}H NMR (499.884 MHz, DMSO-d6) δ = 9.1, 8.8, 8.2 (very br, 8H, bipy-H), 7.0-6.0 (very br, 6H, styryl-H, Mes-H3,5), 2.4-0.8 (br, 12H, *p*-Me, *o*-Me, backbone H). ^{13}C NMR (125.699 MHz, DMSO-d6) δ = 144.6 137.3, 133, 130.4, 126.7 (br, aromatic C), 26.1, 22.0, 20.5 (*p*-Me, *o*-Me), backbone C n.r.. ^{11}B NMR (160.386 MHz, methanol-d4) δ = 3.6 ($w_{1/2}$ = 300 Hz).

Conversion to poly(dipyridylmesitylstyrylboronium hexafluorophosphate). Poly(dipyridylmesitylstyrylboronium bromide) (0.35 g, 0.75 mmol boronium groups) in methanol (5 mL) was added into $NH_4[PF_6]$ (0.36 g, 2.2 mmol) in H_2O (100 mL). The resulting suspension was stirred for 1 h at room temperature. A white solid was collected on a filter paper and then washed extensively with water followed by hexanes. The product was dried under high vacuum at 60 °C. Yield: 0.31 g (77%). ^{1}H NMR (499.890 MHz, acetonitrile-d3) δ = 8.6, 7.9, 7.3, 6.7, 5.9 (v br, aromatic H), 2.2-1.0 (br, *p*-Me, *o*-Me, backbone). ^{13}C NMR (125.697 MHz, acetonitrile-d3) δ = 146.1, 144.9, 139.6, 134.2, 131.8, 130.5, 129.9, 125.0 (br, aromatic C), 46-40 (backbone C), 28-20 (v br, *p*-Me, *o*-Me). ^{11}B NMR (160.384 MHz, acetonitrile-d3) δ = 4.7 ($w_{1/2}$ = 520 Hz). ^{19}F NMR (470.367 MHz, acetonitrile-d3) δ = –72.6 (d, $^1J_{PF}$ = 708 Hz, $[PF_6]^-$). ^{31}P NMR (202.394 MHz, DMSO-d6) δ = –144.2 (sept, $^1J_{PF}$ = 709 Hz, $[PF_6]^-$). Elemental analysis for $\{C_{27}H_{26}BF_6N_2P\}_n$: calcd C 60.70, H 4.90, N 5.24; found C 61.40, H 4.89, N 5.30%.

SYNTHESIS OF MODEL COMPOUNDS

Synthesis of dipyridyl(*t*-butylphenyl)(mesityl)boronium bromide (M4-Mes). In a glove box, 4-dibromoboryl-1-*t*-butylbenzene (0.25 g, 0.82 mmol) in CH_2Cl_2 (20 mL) was added to a solution of copper mesityl (1.66 g, 0.91 mmol) in CH_2Cl_2 (20 mL), and the reaction mixture was stirred at room temperature for 1 h. An orange precipitate formed and the volume was reduced to ca. 2 mL. Hexanes (40 mL) were added and the mixture was stirred for 1 h. The solid was filtered off, and a colorless oil was obtained after evaporation of hexanes. The residue was redissolved in CH_2Cl_2 (30 mL) and a solution of 2,2'-dipyridyl (0.32 g, 2.05 mmol) in CH_2Cl_2 (10 mL) was added to give a clear yellow solution. After stirring for 1 h, the reaction mixture was concentrated and precipitated into hexanes to give a light yellow solid that was dried under high vacuum. Yield: 0.35 g (87%). ^{1}H NMR (499.896 MHz, DMSO-d6) δ = 9.30 (d, ^3J = 8.0 Hz, 2H, bipy-H3,3'), 9.20 (d, ^3J = 6.0 Hz, 2H, bipy-H6,6'), 8.86 (pst, ^3J = 8.0 Hz, 4H, bipy-H4,4'), 8.25 (pst, ^3J = 7.5 Hz, 2H, bipy-H5,5'), 7.20, 6.90 (2 x d, ^3J = 8.5 Hz, 2 x 2H, tBuPh-H2,6 and tBuPh-H3,5), 6.77 (br s, 2H, mesityl-H3,5), 2.17 (s, 3H, *p*–Me), 1.48 (br s, 6H, *o*-Me), 1.17 (s, 9H, *t*-Bu). ^{13}C NMR (125.707 MHz, DMSO-d6) δ = 149.4 (tBuPh-C4), 145.1 (bipy-C4,4'), 144.9 (bipy-C2,2'), 144.3 (bipy-C6,6'), 144.1 (br, tBuPh-C1), 143.2 (br, Mes-C2,6), 137.3 (Mes-C4), 133.7 (br, Mes-C1), 130.4 (Mes-C3,5), 129.6 (bipy-C5,5'), 129.3, 125.1 (tBuPh-C2,6 / tBuPh-C3,5), 124.2 (bipy-3,3'), 34.0 ($Me_3\mathit{C}$), 31.0 (Me_3C), 24.1 (br, *o*-Me), 20.3 (*p*-Me). ^{11}B NMR (160.386 MHz, DMSO-d6) δ = 8 ($w_{1/2}$ = 1520 Hz). MALDI-TOF MS (+ reflectron mode): m/z (Da) = 419.2555 (calcd for $[C_{29}H_{32}BN_2]^+$ 419.2658.

Synthesis of di(t-butylphenyl)dipyridylboronium bromide (M4-Ph). Under nitrogen protection, a solution of 1-trimethylstannyl-4-*t*-butylbenzene (0.26 g, 0.88 mmol) in CH_2Cl_2 (30 mL) was slowly added to a solution of 4-dibromoboryl-1-*t*-butylbenzene (0.25 g, 0.82 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 2 h. The mixture was dried under high vacuum at room temperature. The white residue was redissolved in CH_3CN (20 mL) and the resulting solution was added dropwise into a solution of 2,2'-dipyridyl (0.25 g, 1.60 mmol) in CH_3CN (20 mL). A white precipitate formed immediately. After stirring for 1 h, the supernatant was removed and the white crystalline residue was washed three times with cold acetonitrile (2 mL). A second crop of product was obtained from the supernatant and acetonitrile extracts upon concentration and precipitation into ether. The white solids were dried under high vacuum at 60 ºC. Yield: 0.41 g (97%). ^{1}H NMR (499.895 MHz, DMSO-d6) δ = 9.20 (d, ^{3}J = 8.0 Hz, 2H, bipy-H3,3'), 9.09 (d, ^{3}J = 5.5 Hz, 2H, bipy-H6,6'), 8.79 (pst, ^{3}J = 7.7 Hz, 2H, bipy-H4,4'), 8.17 (pst, ^{3}J = 6.7 Hz, 2H, bipy-H5,5'), 7.32 (d, ^{3}J = 8.0 Hz, 4H, tBuPh-H2,6 / tBuPh-H3,5), 7.08 (d, ^{3}J = 8.0 Hz, 4H, tBuPh-H2,6 / tBuPh-H3,5), 1.24 (s, 18H, *t*-Bu). ^{13}C NMR (125.689 MHz, DMSO-d6) δ = 150.4 (tBuPh-C4), 145.5 (bipy-C2,2'), 145.0, 144.1 (bipy-C4,4',6,6'), 139.2 (tBuPh-C1), 132.4 (tBuPh-C2,6), 129.1 (bipy-C5,5'), 124.9 (Ph-C3,5), 123.7 (bipy-C3,3'), 34.2 (Me_3C), 31.0 (Me_3C). ^{11}B NMR (160.386 MHz, DMSO-d6) δ = 8 ($w_{1/2}$ = 1280 Hz). MALDI-TOF MS (+ reflectron mode): m/z (Da) = 433.2740 (calcd for $[C_{30}H_{34}BN_2]^+$ 433.2815.

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