Electronic Supplementary Information

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), NH₄[PF₆], and BBr₃ were purchased from Acros. All chemicals were used as received without further purification. Poly(4-trimethylsilystyrene),¹ 4-t-butylphenyltrimethylstannane,² and (CuMes)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. Hydrocarbons 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 CaH₂ and degassed via several freeze-pump-thaw cycles.

The 499.9 MHz ¹H, 125.7 MHz ¹³C, 470.4 MHz ¹⁹F, and 202.4 MHz ³¹P NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 160.4 MHz ¹¹B NMR spectra were recorded with a boron-free probe using boron-free quartz NMR tubes. ¹H and ¹³C NMR spectra were referenced internally to the solvent peaks, ¹⁹F NMR spectra were referenced externally to α,α',α''-trifluorotoluene (0.05% in C₆D₆; δ = -63.73), and the ¹¹B NMR spectra externally to BF₄•Et₂O (δ = 0) in C₆D₆. 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 NH₄[PF₆] (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! BBr₃ 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-trimethylsilystyrene) (P1) (1.00 g, 5.67 mmol SiMe₃, Mₙ = 15390, Mₜ = 17680, PDI = 1.15 based on GPC-UV) in CH₂Cl₂ (30 mL) was added to a solution of BBr₃ (1.71 g, 6.83 mmol) in CH₂Cl₂ (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 CH₂Cl₂ (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 CH₂Cl₂ (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%). 1H 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). 13C NMR (125.699 MHz, DMSO-d6) δ = 146.4, 137.3, 133, 130.4, 126.7 (br, aromatic C), 26.1, 22.0, 20.5 (p-Me, o-Me), backbone C n.r. 11B NMR (160.386 MHz, methanol-d4) δ = 3.6 (w, ν2 = 300 Hz).

Conversion to poly(dipyriddyldimesitylstyrylboronion hexafluorophosphate). Poly(dipyriddyldimesitylstyrylboronion bromide) (0.35 g, 0.75 mmol boronium groups) in methanol (5 mL) was added into NH4[PF6] (0.36 g, 2.2 mmol) in H2O (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%). 1H 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). 13C NMR (125.367 MHz, acetonitrile-d3) δ = 146.1, 144.9, 139.6, 134.2, 131.8, 129.9, 125.0 (br, aromatic C), 46-40 (backbone C), 28-20 (v br, p-Me, o-Me). 11B NMR (160.384 MHz, acetonitrile-d3) δ = 4.7 (w, ν2 = 520 Hz). 19F NMR (470.367 MHz, acetonitrile-d3) δ = −72.6 (d, JPF6 = 708 Hz, [PF6]−). 31P NMR (202.394 MHz, DMSO-d6) δ = −144.2 (sept, JPF6 = 709 Hz, [PF6]−). Elemental analysis for {C27H26BF6N2P}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 dipyriddyldi(t-butylphenyl)(mesityl)boronion bromide (M4-Mes). In a glove box, 4-dibromoboryl-1-t-butylbenzene (0.25 g, 0.82 mmol) in CH2Cl2 (20 mL) was added to a solution of copper mesityl (1.66 g, 0.91 mmol) in CH2Cl2 (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 CH2Cl2 (30 mL) and a solution of 2,2’-dipyridyl (0.32 g, 2.05 mmol) in CH2Cl2 (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%). 1H NMR (499.896 MHz, DMSO-d6) δ = 9.30 (d, J = 8.0 Hz, 2H, bipy-H3,3’), 9.20 (d, J = 6.0 Hz, 2H, bipy-H6,6’), 8.86 (s, pst, J = 8.0 Hz, 4H, bipy-H4,4’), 8.25 (p, J = 7.5 Hz, 2H, bipy-H5,5’), 7.20, 6.90 (2 x d, J = 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). 13C 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 (Me3C), 31.0 (Me3C), 24.1 (br, o-Me), 20.3 (p-Me). 11B NMR (160.386 MHz, DMSO-d6) δ = 8 (w, ν2 = 1520 Hz). MALDI-TOF MS (+ reflectron mode): m/z (Da) = 419.2555 (calcd for [C23H32BN1]11B 419.2658.

Synthesis of di(t-butylphenyl)dipyriddyldiboronion bromide (M4-Ph). Under nitrogen protection, a solution of 1-trimethylstanny1-4-t-butylbenzene (0.26 g, 0.88 mmol) in CH2Cl2 (30 mL) was slowly added to a solution of 4-dibromoboryl-1-t-butylbenzene (0.25 g, 0.82 mmol) in CH2Cl2 (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 CH3CN (20 mL) and the resulting solution was added dropwise into a solution of 2,2’-dipyridyl (0.25 g, 1.60 mmol) in CH3CN (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 °C. Yield: 0.41 g (97%). $^1$H NMR (499.895 MHz, DMSO-d$_6$) $\delta$ = 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 (psr, $^3$J = 7.7 Hz, 2H, bipy-H4,4$'$), 8.17 (psr, $^3$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-d$_6$) $\delta$ = 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$_3$C), 31.0 (Me$_3$C). $^{11}$B NMR (160.386 MHz, DMSO-d$_6$) $\delta$ = 8 ($^{2}J_{11B}$ = 1280 Hz). MALDI-TOF MS (+ reflectron mode): m/z (Da) = 433.2740 (calcd for [C$_{30}$H$_{34}$BN$_2$]+ 433.2815.

