Supporting Information

Supramolecular Polymers Based on Dative Boron-Nitrogen Bonds

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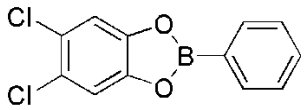
Content:

1. General

5-Bromo-2,2-dimethylbenzodioxole and 2-phenyl-1,3,2-benzodioxaborole were synthesized according to previously published procedures.[1-2] All other chemicals were obtained from commercial sources. All solvents were dried using a solvent purification system from Innovative Technologies, Inc. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra were obtained on a Bruker Avance (^{1}H: 400 MHz, ^{13}C: 100.6 MHz,^{19}F: 188.3 MHz ^{11}B: 128.4 MHz) in $CDCl_3$. ^{1}H chemical shifts are reported in parts per million δ (ppm) referenced to internal $CHCl_3$ (7.26 ppm). ^{13}C chemical shifts are reported in ppm and referenced to internal $CHCl_3$ (77.0 ppm). ^{19}F chemical shifts are reported in ppm and referenced to internal $CFCl_3$ (0.0 ppm). All spectra were recorded at room temperature unless otherwise indicated. Combustion analysis was performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. For the ITC titrations a VP-ITC apparatus (MicroCal) was used. Mass spectra were recorded with a Waters Q-TOF Ultima (ESI-TOF) instrument or a Shimadzu Axima-CFR plus (MALDI-TOF) instrument. Viscosity measurements were performed on a Thermo Scientific HAAKE RheoStress 1. The diffusion NMR (DOSY) experiments were carried out on a Bruker Avance NMR spectrometer (400 MHz). DOSY experiments were performed at 298 K (with temperature control turned on) using a bipolar gradient pulse pair with a spoil gradient pulse (stebpgp1s), with 32 incremental steps in the gradient strength ramped from 2% to 98% of the maximum gradient strength. 8 Scans per increment step and gradient pulse lengths of 1000 μs and 1500 μs for 10 mM and 100 mM solutions respectively. Pseudo-2D DOSY plots were processed with the standard Bruker software and the T1/T2 "vargrad" SlimFit fitting routine was used to determine the diffusion coefficients.

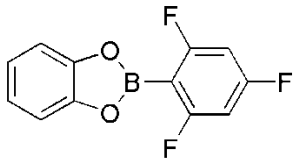
2. Synthesis of Dioxaboroles

A mixture of the corresponding catechol (1.0 mmol) and boronic acid (1.0 mmol) in toluene (45 mL) was heated under reflux using a Dean Stark apparatus for 4 h (overnight for the triisopropylphenyl boronate ester). After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by sublimation under vacuum.

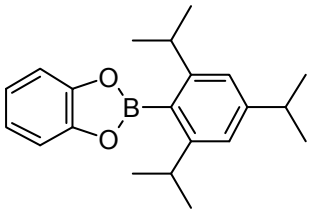


(101 mg, 38%). ^{1}H NMR ($CDCl_3$) δ 8.05 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.41 (s, 2H). ^{13}C NMR

($CDCl_3$) δ 147.7, 135.1, 132.9, 128.4, 126.3, 114.1 (B-C was not observed due to quadrupole broadening). ^{11}B NMR ($CDCl_3$) δ 33.0. Elemental anal. calc'd. for $C_{12}H_7BCl_2O_2$: C 54.41; H 2.66. Found: C 54.64; H 2.45.



(115 mg, 46%). ^1H NMR ($CDCl_3$) δ 7.38 (dd, J = 5.8 & 3.4 Hz, 2H), 7.17 (dd, J = 5.8 & 3.4 Hz, 2H), 6.76 (td, J = 9.0 & 1.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 168.5 (dt, J = 188.6 & 15.5 Hz), 165.9 (dt, J = 187.7 & 15.6 Hz), 147.8, 123.2, 112.9, 100.8 (m) (B-C was not observed due to quadrupole broadening). ^{19}F NMR ($CDCl_3$) δ -96.2 (t, J = 9.2 Hz, 2F), -100.8 (p, J = 9.5 Hz, 1F). ^{11}B NMR ($CDCl_3$) δ 30.3. Elemental anal. calc'd. for $C_{12}H_6BF_3O_2$: C 57.66; H 2.42. Found: C 58.13; H 2.05.



(175 mg, 54%). ^1H NMR ($CDCl_3$) δ 7.33 (dd, J = 5.8 & 3.2 Hz, 2H), 7.15 (dd, J = 5.8 & 3.2 Hz, 2H), 7.06 (s, 2H), 2.93 (sept, J = 7.03 Hz, 1H), 2.79 (sept, J = 6.8 Hz, 2H), 1.29 (d, J = 7.2 Hz, 6H), 1.25 (d, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$) δ 153.1, 151.2, 148.4, 122.6, 120.4, 112.7, 35.2, 34.6, 24.5, 23.9 (B-C was not observed due to quadrupole broadening). ^{11}B NMR ($CDCl_3$) δ 35.1. Elemental anal. calc'd. for $C_{21}H_{27}BO_2$: C 78.27; H 8.45. Found: C 78.45; H 8.67.

3. Titration procedures

NMR Titration Procedure: An NMR tube was prepared containing the boronate ester (3−10 mM) in either C_6D_6 or $CDCl_3$ (0.5 mL). Aliquots of stock solutions containing the boronate ester (identical concentration and solvent) and pyridine or DMAP (50−750 mM) were added and ^1H NMR spectra were recorded. The final N-donor concentrations were between 10 and 500 mM, depending on the strength of the dative B-N bond. The chemical shift values for the signal of a proton on the boronate ester were plotted versus N-donor concentration. The data was fitted with a non-linear least square curve-fitting program, WinEQNMR2,[3] using a 1:1 binding model.

ITC Titration Procedure: Freshly dried solvents (benzene, chloroform) were used for all titrations. The boronate esters and dimethylaminopyridine (DMAP) were weighed using an analytical precision balance, dissolved in a known volume of solvent, and loaded into the system for immediate analysis. Solutions used in the same titration experiment were made up from the same batch of solvent. The ITC experiments involved the titration of a solution of DMAP (4.65

mM for titrations with 2-phenyl-1,3,2-benzodioxaborole and 3.00 mM for titrations with 5,6-dichloro-2-phenyl-1,3,2-benzodioxaborole and 2-(2,4,6-trifluorophenyl)-1,3,2-benzodioxaborole) into a solution of the boronate ester (0.25 mM for titrations with 2-phenyl-1,3,2-benzodioxaborole and 0.30 mM for titrations with 5,6-dichloro-2-phenyl-1,3,2-benzodioxaborole and 2-(2,4,6-trifluorophenyl)-1,3,2-benzodioxaborole) at 298 K. The DMAP solution was added in 30 injections of 8 µL, separated by an interval of 240 sec between injections, with the exception of the first addition, which was 2 µL. Binding constants and enthalpies of binding were obtained by curve fitting of the titration data using the one-site binding model for 1:1 complexes implemented in the Origin 7.0 software provided by the manufacturer. In the experiments with 2-phenyl-1,3,2-benzodioxaborole the peak produced by the first injection and in the experiments with 5,6-dichloro-2-phenyl-1,3,2-benzodioxaborole and 2-(2,4,6-trifluorophenyl)-1,3,2-benzodioxaborole the peaks produced by the first two injections were discarded during data processing. Inflection points close to one were observed in all binding isotherms, which strongly indicate 1:1 stoichiometries for all complexes.

4. NMR Titration Data

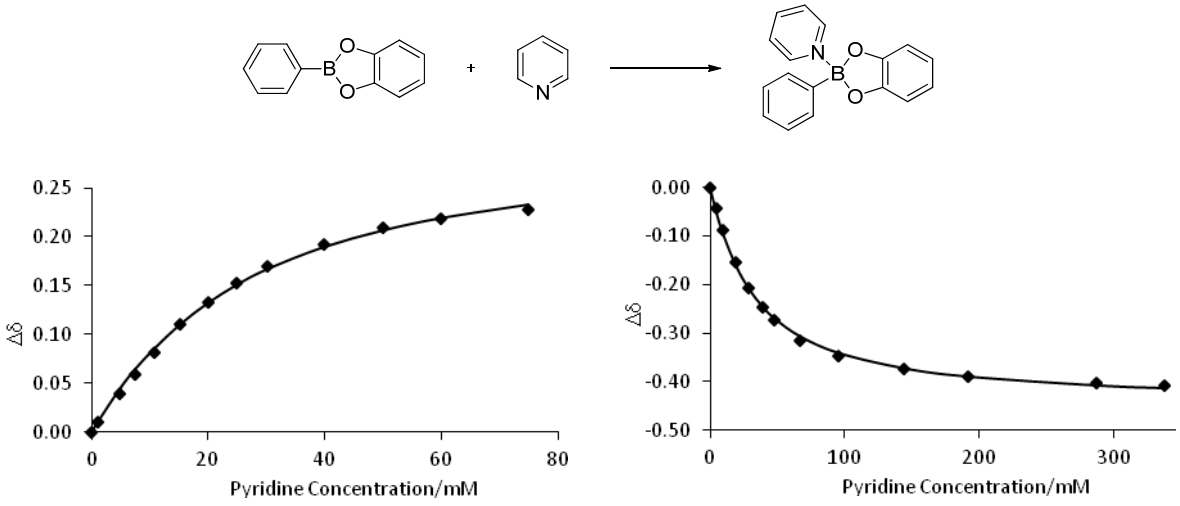


Figure S1: Titration of 2-phenyl-1,3,2-benzodioxaborole (10 mM) in C_6D_6 (left) and $CDCl_3$ (right) with pyridine. K_a = 5.1 (0.5) x 10^1 M^{-1} and 3.6 (0.3) x 10^1 M^{-1} respectively.

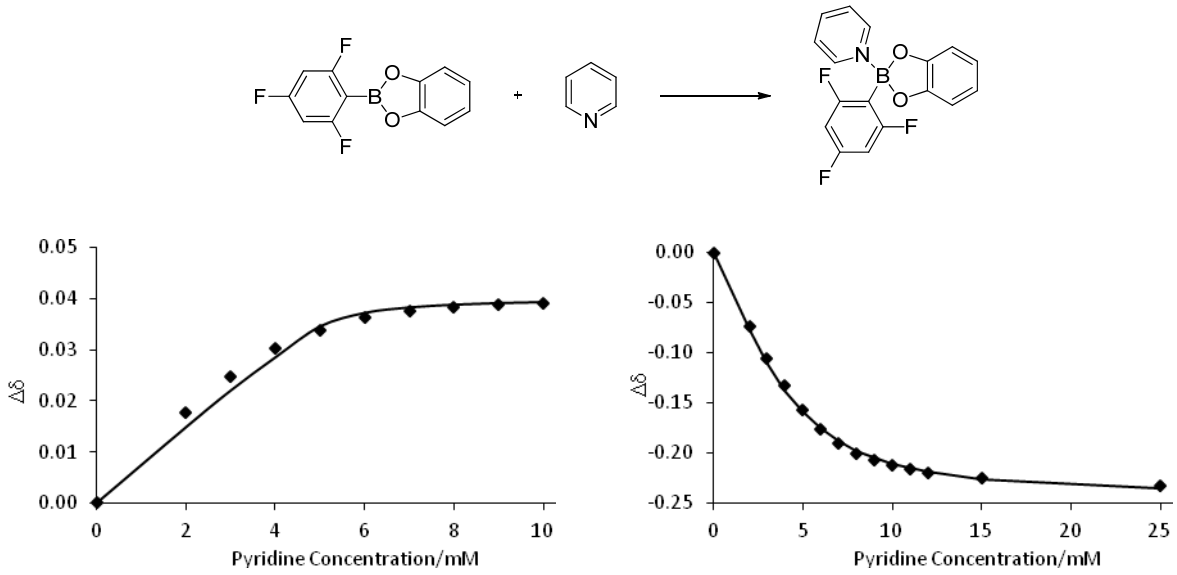


Figure S2: Titration of 2-(2,4,6-trifluorophenyl)-1,3,2-benzodioxaborole (5.0 mM) in C_6D_6 (left) and $CDCl_3$ (right) with pyridine. K_a = 8.8 (6.8) x 10^4 M^{-1} and 9.8 (1.1) x 10^3 M^{-1} respectively.

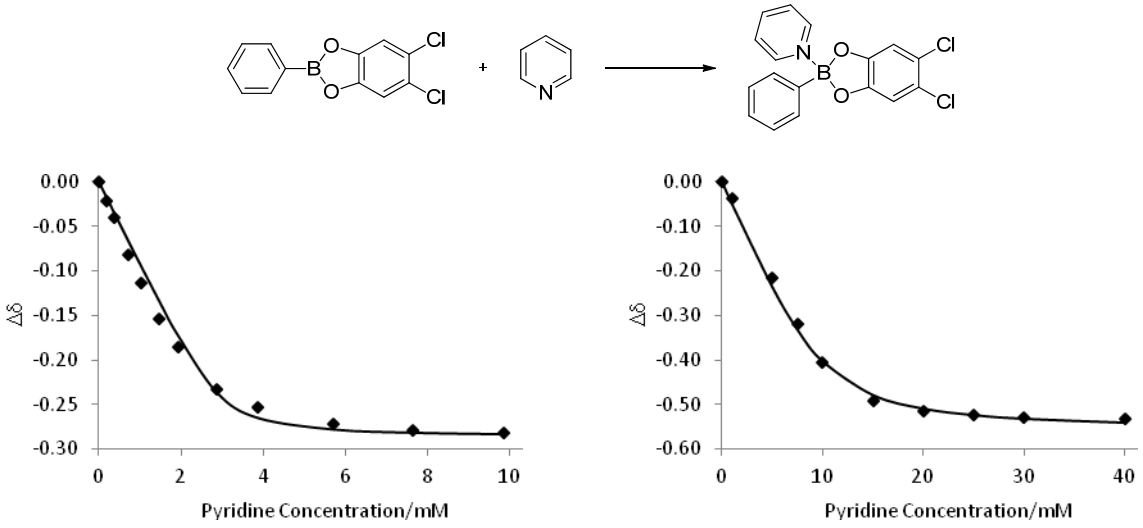


Figure S3: Titration of 5,6-dichloro-2-phenyl-1,3,2-benzodioxaborole, 3.0 mM in C_6D_6 (left) and 10 mM in $CDCl_3$ (right), with pyridine. K_a = 1.1 (0.7) x 10^4 M^{-1} and 9.1 (2.4) x 10^2 M^{-1} respectively.

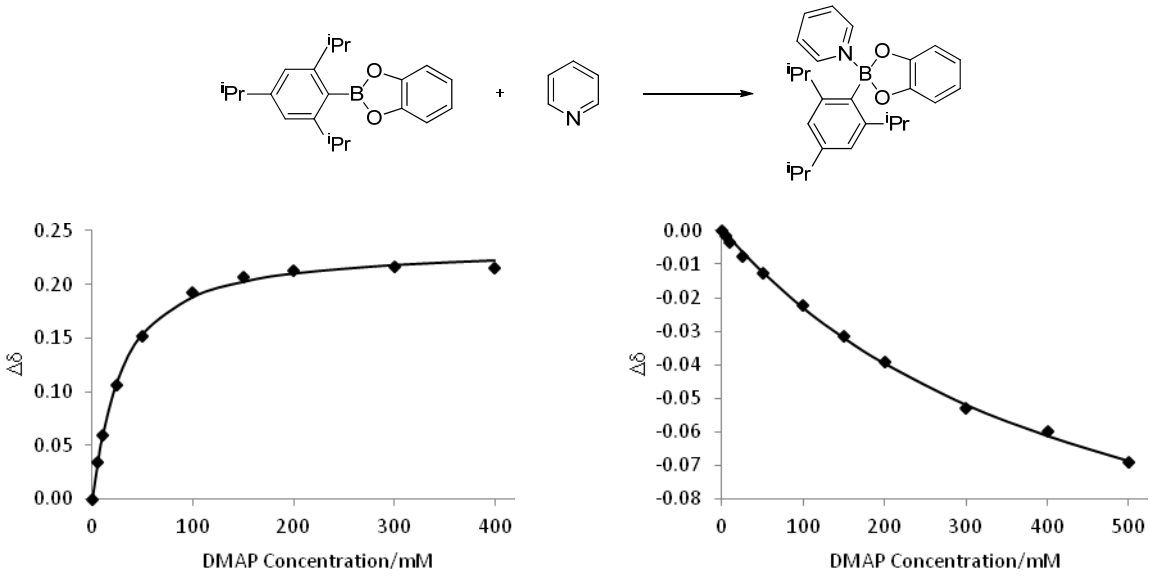


Figure S4: Titration of 2-(2,4,6-triisopropylphenyl)-1,3,2-benzodioxaborole (10 mM) in C_6D_6 (left) and $CDCl_3$ (right) with dimethylaminopyridine. K_a = 4.4 (0.5) x 10^1 M^{-1} and 2.2 (0.2) M^{-1} respectively.

5. ITC Titration Data

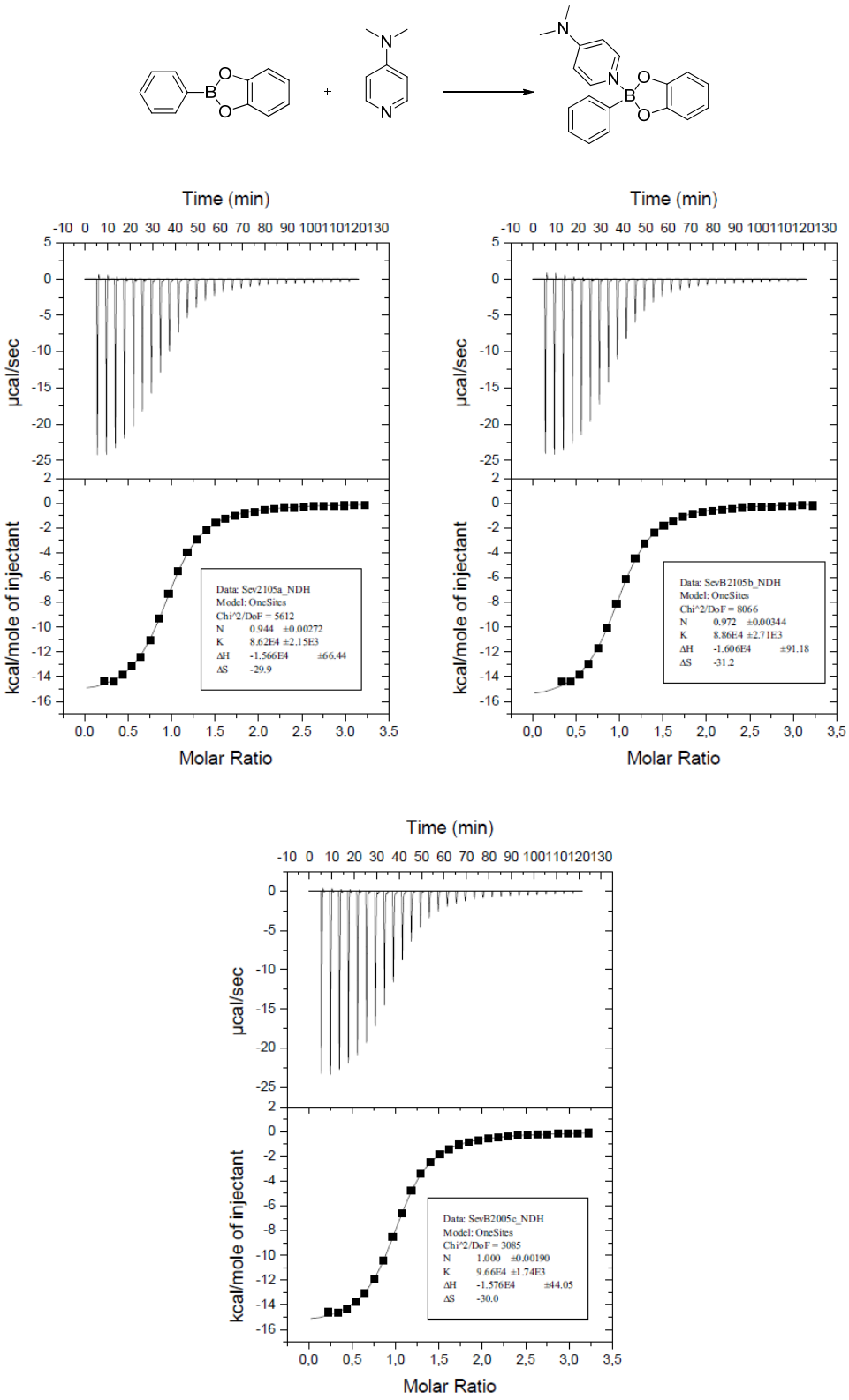


Figure S5: ITC measurements in benzene. K_a(av.) = 9.1 (0.4) x 10^4 M^{-1}.

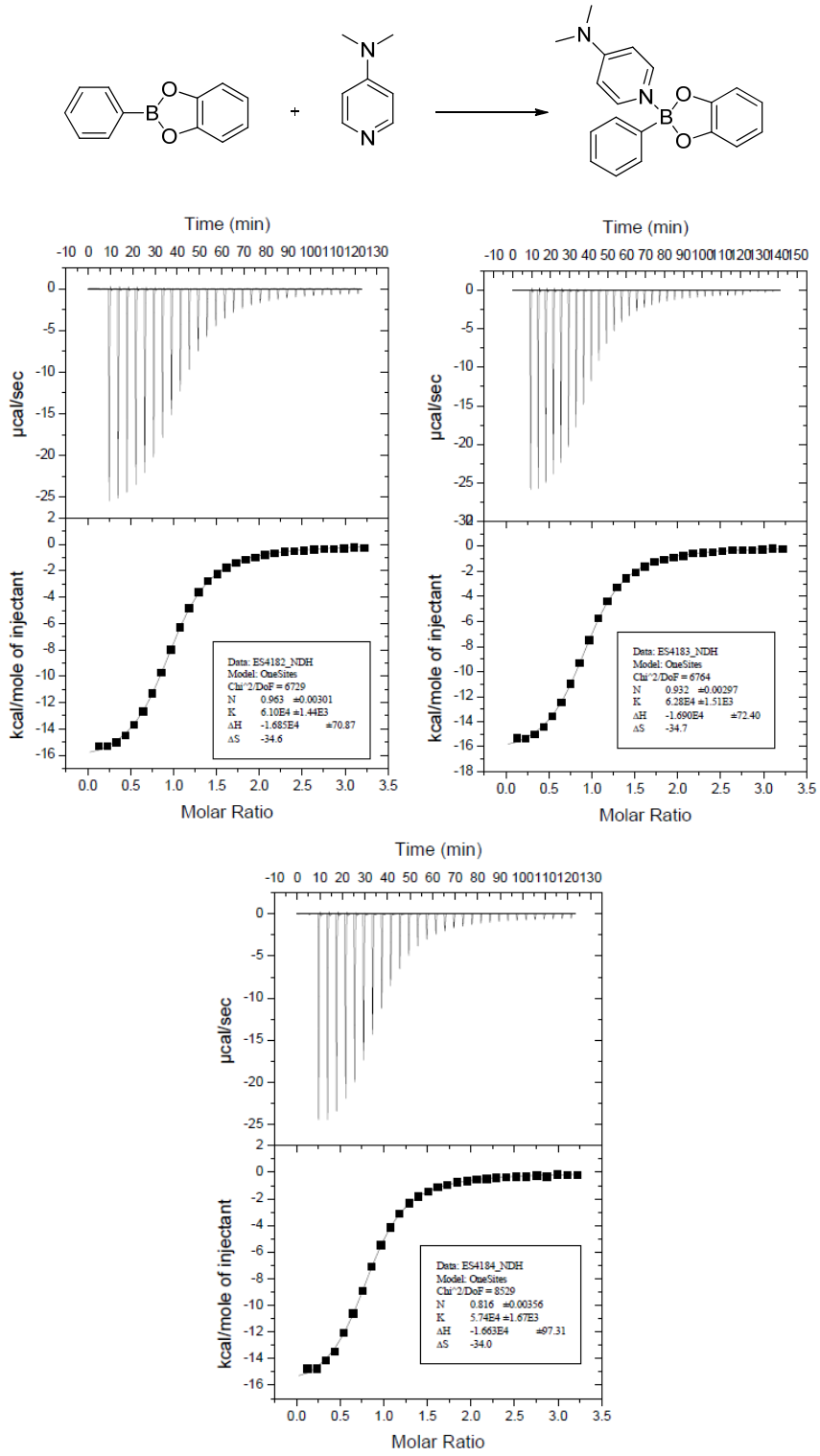


Figure S6: ITC measurements in chloroform. K_a(av.) = 6.0 (0.2) x 10^4 M^{-1}

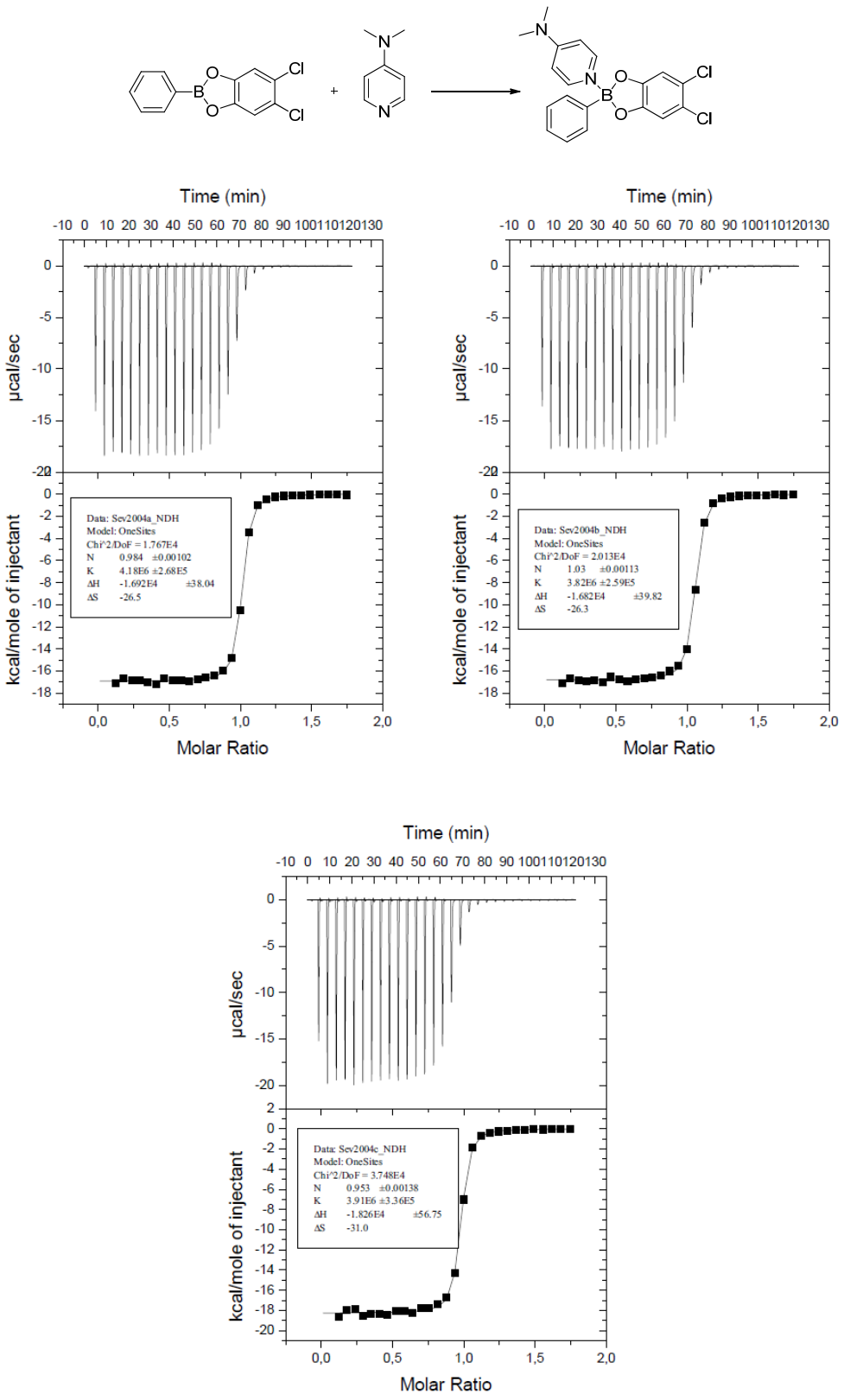


Figure S7: ITC measurements in benzene. K_a(av.) = 4.0 (0.1) x 10^6 M^{-1}.

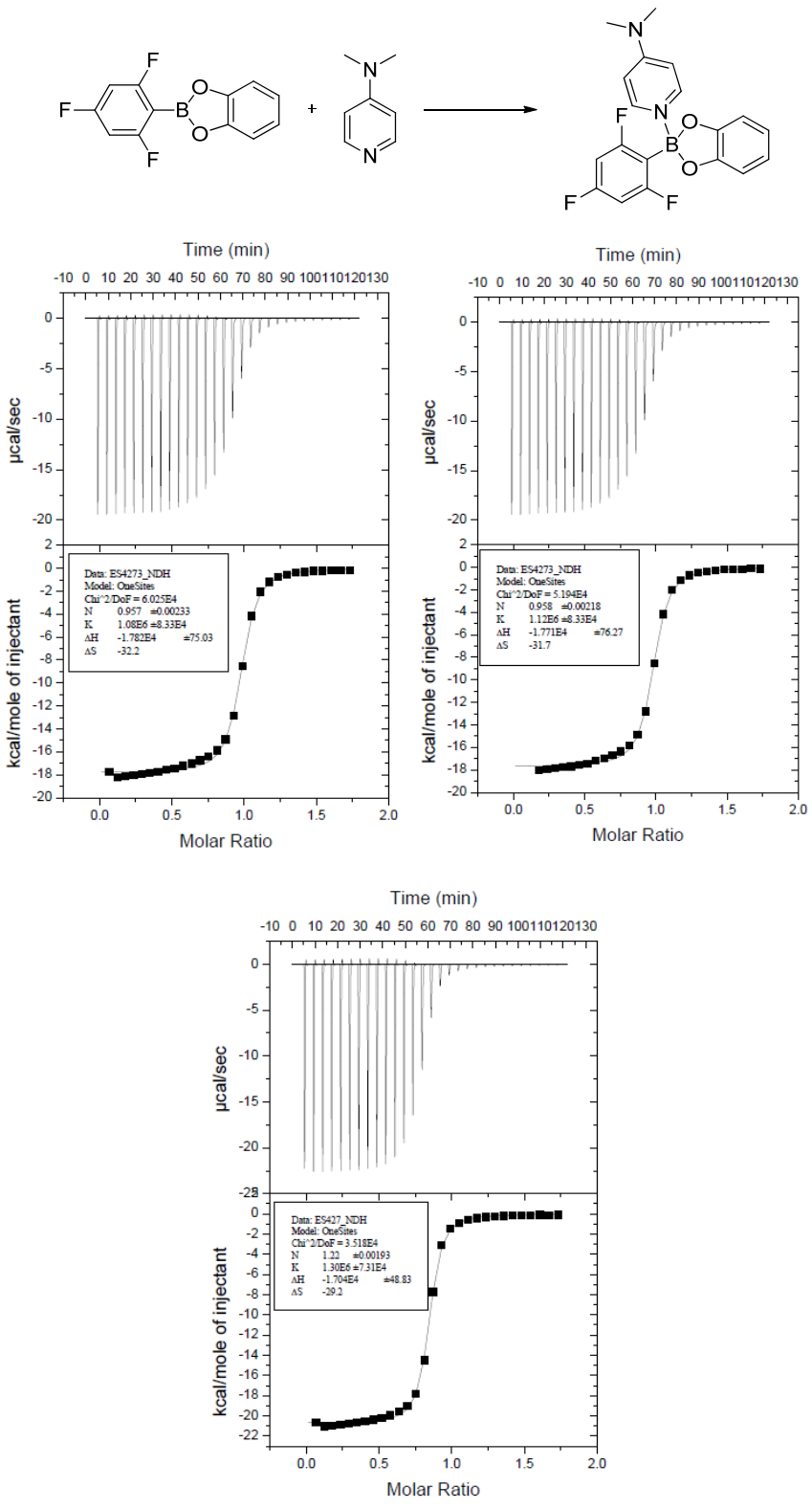


Figure S8: ITC measurements in benzene. K_a(av.) = 1.3 (0.2) x 10^6 M^{-1}

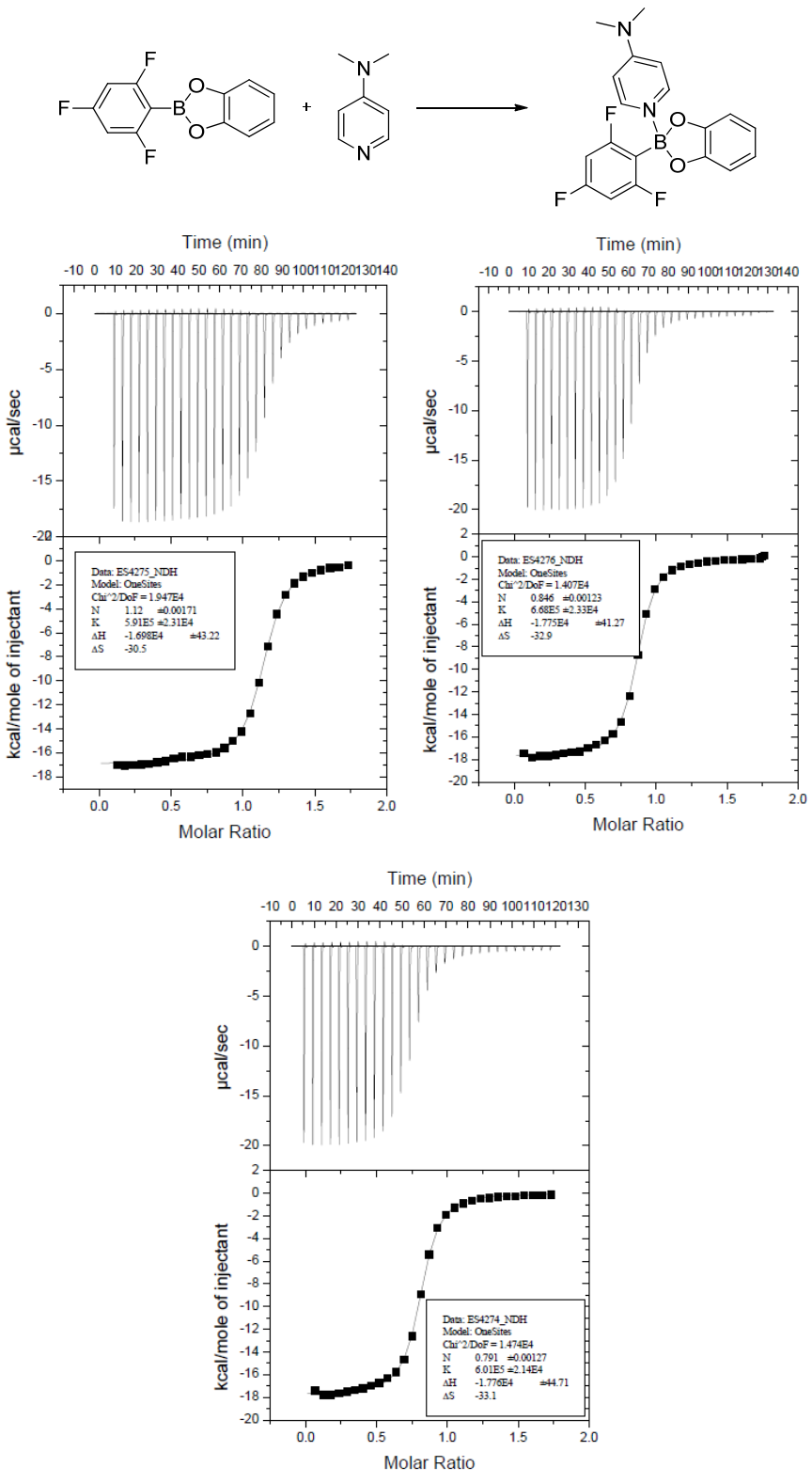
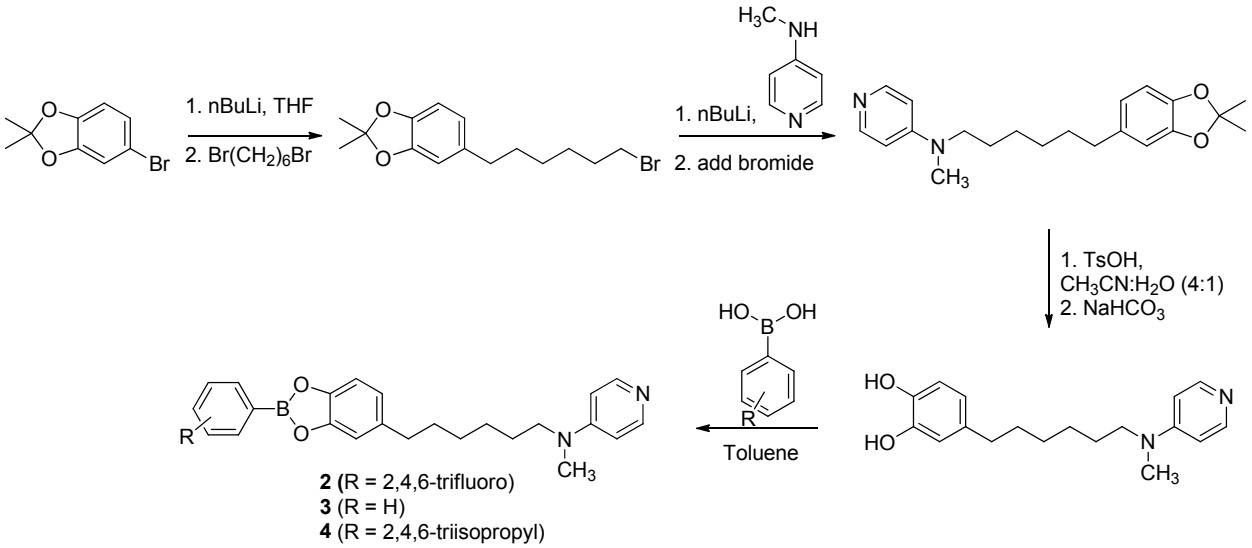


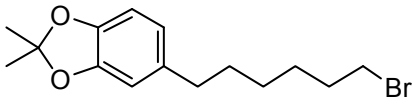
Figure S9: ITC measurements in chloroform. K_a(av.) = 6.2 (0.3) x 10^5 M^{-1}

6. Monomer Syntheses

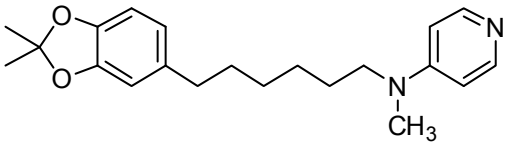


Scheme S1: Synthesis of the monomers **2**, **3** and **4**.

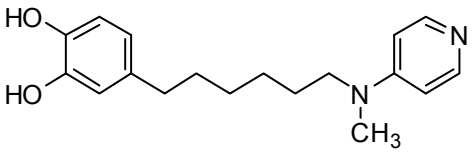
5-(6-Bromohexyl)-2,2-dimethylbenzodioxole



A solution of 5-bromo-2,2-dimethylbenzodioxole (2.0 g, 8.7 mmol) in THF (20 mL) was cooled to -78 °C and nBuLi (4.2 mL, 10.5 mmol, 2.5 M in hexanes) was added slowly via syringe. After stirring the solution at -78 °C for 2 h, dibromohexane (2.96 mL, 19.1 mmol) was added in one batch and the reaction was allowed to warm slowly to RT and stirred overnight. The reaction was quenched with H_2O (20 mL), the aqueous layer was separated and extracted with Et_2O (3 x 25 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. Excess dibromohexane was distilled off under vacuum. The product was further purified by column chromatography (Si_2O, 5% EtOAc in hexane) to give pure 5-(6-bromohexyl)-2,2-dimethylbenzodioxole (1.9 g, 71%). ^{1}H NMR ($CDCl_3$) δ 6.63 (d, J = 8.0 Hz, 1H), 6.57-6.50 (m, 2H), 3.40 (t, J = 6.8 Hz, 2H), 2.51 (t, J = 7.7 Hz, 2H), 1.85 (p, J = 7.2 Hz, 2H), 1.61 (s, 6H), 1.60-1.51 (m, 2H), 1.49-1.42 (m, 2H), 1.38-1.32 (m, 2H). ^{13}C ($CDCl_3$) δ 147.3, 145.3, 135.7, 120.3, 117.4, 108.6, 107.8, 35.5, 34.0, 32.7, 31.5, 28.2, 28.0, 25.8. HRMS (MALDI-TOF): Calc'd for $C_{15}H_{21}BrO_2$, 312.0722; Found, 312.0522

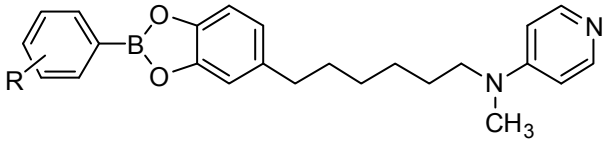


A solution of 4-methylaminopyridine (519 mg, 4.8 mmol) in THF (10 mL) was cooled to 0 °C and nBuLi (2.3 mL, 5.8 mmol, 2.5 M in hexanes) was added slowly via syringe. After stirring the solution at 0 °C for 2 h, a solution of 5-(6-bromohexyl)-2,2-dimethylbenzodioxole (1.0 g, 3.2 mmol) in THF (5 mL) was added at 0 °C. The reaction was then allowed to warm slowly to RT and stirred overnight. The reaction was quenched with H_2O (15 mL), the aqueous layer was separated and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The product was purified by column chromatography on deactivated silica gel (20% acetone in CH_2Cl_2) to give pure N-(6-(2,2-dimethylbenzodioxol-5-yl)hexyl)-N-methylpyridin-4-amine (710 mg, 65%). ^{1}H NMR ($CDCl_3$) δ 8.18 (dd, J = 5.2 & 1.6 Hz, 2H), 6.62 (d, J = 8.2 Hz, 1H), 6.56-6.54 (m, 2H), 6.45 (dd, J = 5.2 & 1.6 Hz, 2H), 3.30 (t, J = 7.5 Hz, 2H), 2.95 (s, 3H), 2.50 (t, J = 7.7 Hz, 2H), 1.66 (s, 6H), 1.61-1.53 (m, 4H), 1.39-1.31 (m, 4H). ^{13}C ($CDCl_3$) δ 153.2, 149.8, 147.3, 145.3, 135.7, 120.3, 117.4, 108.5, 107.8, 106.3, 51.4, 37.4, 35.6, 31.6, 28.9, 26.8, 26.6, 25.8. HRMS (ESI-TOF): Calc'd for $C_{21}H_{28}N_2O_2$ x H^+, 341.2229; Found, 341.2215.



A solution of N-(6-(2,2-dimethylbenzodioxol-5-yl)hexyl)-N-methylpyridin-4-amine (600 mg, 1.76 mmol) and p-toluenesulfonic acid monohydrate (1.67 g, 8.80 mmol) in CH_3CN:H_2O (4:1) (60 mL) was heated under reflux for 48 h. The solution was then cooled to RT and the solvent was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (25 mL) and washed with saturated aqueous $NaHCO_3$ (40 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The product was purified by column chromatography on deactivated silica gel (10% MeOH in CH_2Cl_2) to give pure 4-(6-(methyl(pyridin-4-yl)amino)hexyl)benzene-1,2-diol as an oil (409 mg, 77%). When this oil was dissolved in CH_2Cl_2 and subsequently re-evaporated under vacuum, an off white solid resulted. ^{1}H NMR ($CDCl_3$) δ 8.11 (d, J = 5.8 Hz, 2H), 6.76 (d, J = 7.9 Hz, 1H), 6.62 (s, 1H), 6.59-6.43 (m, 3H), 3.32 (t, J = 7.4 Hz, 2H), 2.96 (s, 3H), 2.45 (t, J = 7.4 Hz, 2H), 1.58-1.51 (m, 4H), 1.37-1.28 (m, 4H). ^{13}C ($CDCl_3$) δ 154.2, 147.2, 145.0, 143.1, 134.2, 119.5, 115.0, 114.6, 106.6, 51.5, 37.7,

35.1, 31.3, 28.6, 26.6, 26.5. HRMS (ESI-TOF): Calc'd for $C_{18}H_{24}N_2O_2$ x H^+, 301.1916; Found, 301.1927.



A solution of 4-(6-(methyl(pyridin-4-yl)amino)hexyl)benzene-1,2-diol (0.25 mmol) and the corresponding phenylboronic acid (0.25 mmol) in toluene (50 mL) was stirred under reflux for 4 h (24 h for polymer **4**). The solution was then cooled to RT and the solvent was evaporated under vacuum. The residue was dissolved in $CHCl_3$ (10 mL) and filtered using an Acrodisc syringe filter through a polytetrafluoroethylene (PTFE) membrane and 0.45 μm pore size. The filtrate was evaporated under vacuum to give the pure monomer.

R = 2,4,6-trifluoro (**2**) (95 mg, 87%) ^{1}H NMR ($CDCl_3$, 100 mM, 50 °C) δ 8.23 (bd, J = 5.7 Hz, 2H), 6.69 (d, J = 7.72 Hz, 1H), 6.64 (s, 1H), 6.52-6.41 (m, 5H), 3.29 (bt, J = 7.2 Hz, 2H), 2.95 (s, 3H), 2.47 (bt, J = 7.3 Hz, 2H), 1.57-1.52 (m, 4H), 1.32-1.24 (m, 4H). ^{13}C ($CDCl_3$, 100 mM, 50 °C) δ 166.2 (ddd, J = 14.7 & 19.1 & 245.9 Hz), 162.7 (dt, J = 16.2 & 246.1 Hz), 155.6, 151.4, 149.5, 142.5, 133.1, 118.4. 110.1, 109.1, 106.3, 99.6 (ddd, J = 2.4 & 24.1 & 33.1 Hz), 52.1, 37.9, 35.6, 31.3, 28.6, 26.5 (B-C was not observed due to quadrupole broadening). ^{19}F ($CDCl_3$, 100 mM, 50 °C) δ -112.0 (bs, 1F), -101.4 (bs, 2F). ^{11}B ($CDCl_3$, 100 mM, 50 °C) δ 9.05. HRMS (ESI-TOF): Calc'd for $C_{24}H_{24}BF_3N_2O_2$ x H^+, 441.1966; Found, 441.1970.

R = H (**3**) (116 mg, 86%) ^{1}H NMR ($CDCl_3$, 100 mM, 50 °C) δ 8.19 (bd, J = 7.5 Hz, 2H), 7.52 (d, J = 6.5 Hz, 2H), 7.28-7.21 (m, 3 H), 6.70 (d, J = 7.7 Hz, 1H), 6.65 (s, 1H), 6.46-6.41 (m, 3H), 3.25 (t, J = 7.4 Hz, 2H), 2.90 (s, 3H), 2.50 (t, J = 7.7 Hz, 2H), 1.61-1.48 (m, 4H), 1.37-1.30 (m, 4H). ^{13}C ($CDCl_3$, 100 mM, 50 °C) δ 155.4, 152.1, 150.1, 142.8, 133.0, 131.8, 127.5, 127.2, 118.3, 110.1, 109.1, 106.2, 52.0, 37.9, 35.6, 31.2, 28.6, 26.6, 26.4 (B-C was not observed due to quadrupole broadening). ^{11}B ($CDCl_3$, 100 mM, 50 °C) δ 11.1. HRMS (ESI-TOF): Calc'd for $C_{24}H_{27}BN_2O_2$ x H^+, 387.2248; Found, 387.2253.

R = 2,4,6-triisopropyl (**4**) (97 mg, 66%) ^{1}H NMR ($CDCl_3$) δ 8.31 (d, J = 6.5 Hz, 2H), 7.46 (s, 1H), 7.29-7.23 (m, 3H), 7.03 (d, J = 9.2 Hz, 1H), 6.66 (d, J = 6.5 Hz, 2H), 3.53 (t, J = 7.5 Hz,

2H), 3.21-3.11 (m, 6H), 2.84 (t, J = 7.5 Hz, 2H), 1.88-1.76 (m, 4H), 1.6 (m, 4H), 1.50 (d, J = 6.8 Hz, 6H), 1.44 (d, J = 6.8 Hz, 12H). ^{13}C ($CDCl_3$) δ 153.8, 153.2, 150.2, 149.2, 148.1, 147.2, 136.4, 121.3, 120.4, 111.8, 111.2, 106.3, 51.6, 37.5, 35.7, 34.4, 34.4, 31.8, 28.9, 26.8, 26.6, 24.6, 23.9 (B-C was not observed due to quadrupole broadening). ^{11}B ($CDCl_3$) δ 31.5. HRMS (ESI-TOF): Calc'd for $C_{33}H_{45}BN_2O_2 + H^+$, 513.3658; Found, 513.3654.

7. Chain Stopper Experiment

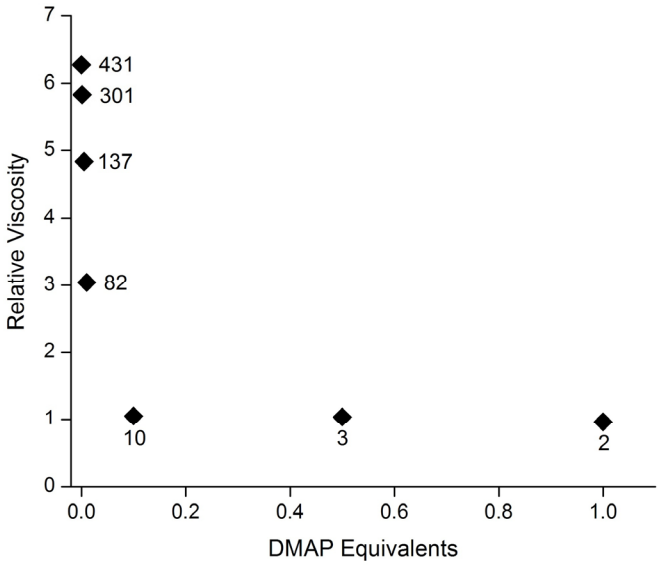


Figure S10: Relative viscosity (η_r) of a solution of monomer **2** (75 mM) in $CHCl_3$ with increasing mole fraction of DMAP. The average degree of polymerization (DP, in monomeric units), calculated using the equation given below, are labeled for each mole fraction of DMAP.

Equation for calculation the the average degree of polymerization (DP) for different mole fractions of the chain stopper:

$$DP(x) = \frac{n(DP_o)}{n(1-x) + x(DP_o)}$$

8. ^{1}H NMR Study

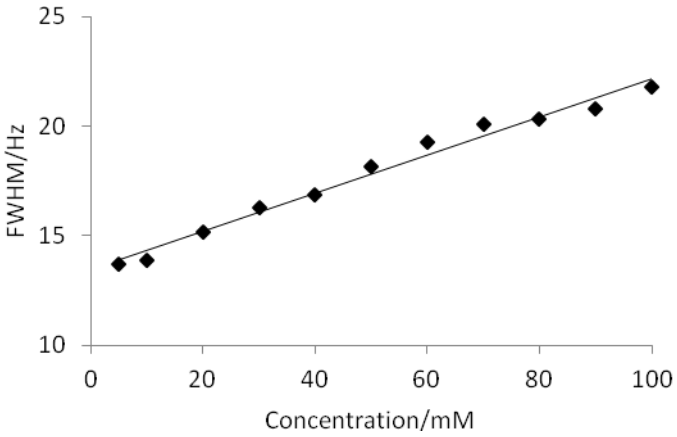


Figure S11: ^{1}H NMR peak broadening of the pyridyl signals of monomer **2** with increasing concentration in $CDCl_3$.

9. Diffusion Ordered Spectroscopy (DOSY)

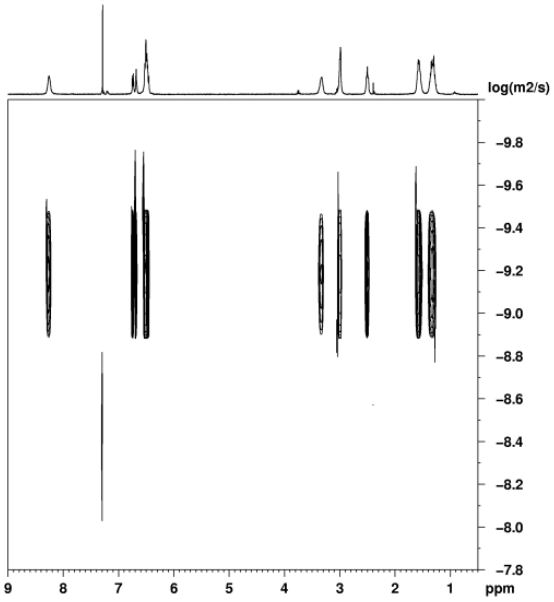


Figure S12: DOSY ^{1}H NMR of monomer **2** (100 mM) in $CHCl_3$.

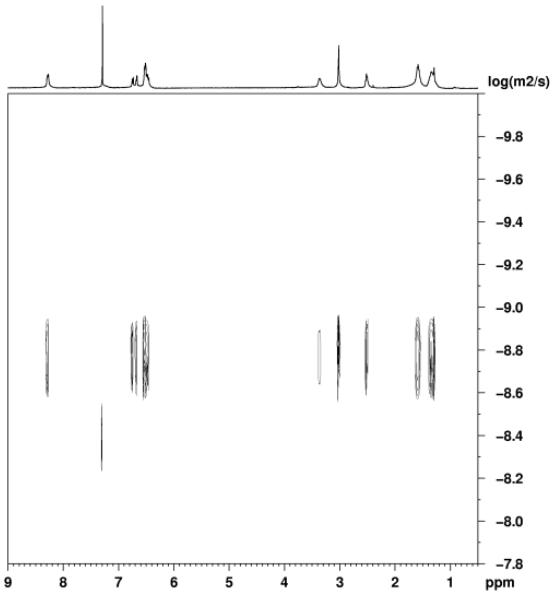


Figure S13: DOSY ^{1}H NMR of monomer **2** (10 mM) in $CHCl_3$.

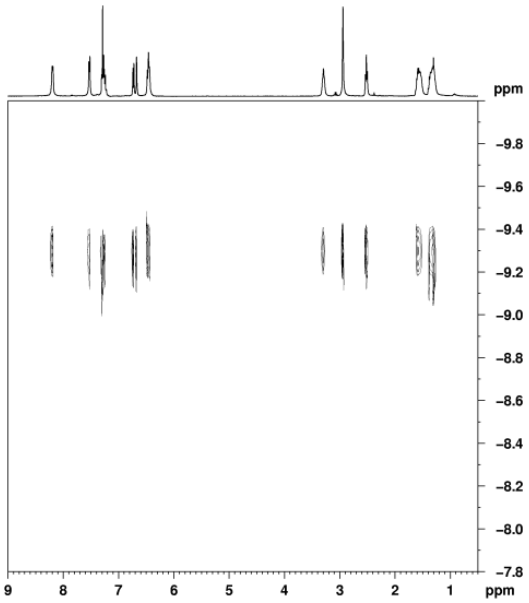


Figure S14: DOSY ^{1}H NMR of monomer **3** (100 mM) in $CHCl_3$.

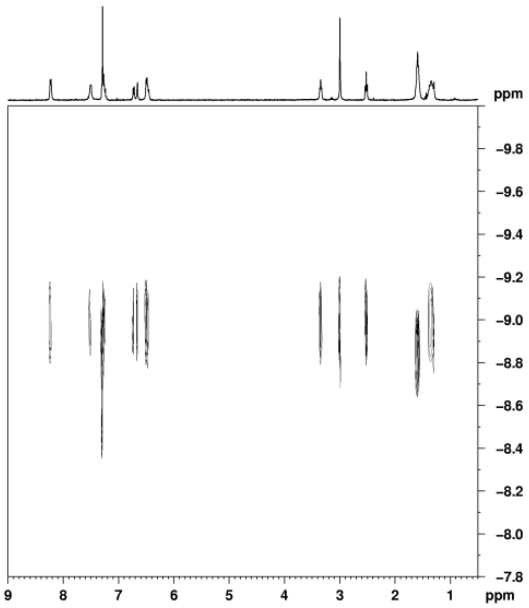


Figure S15: DOSY ^{1}H NMR of monomer **3** (10 mM) in $CHCl_3$.

10. References

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