Supporting Information

Helical Polymer Based on Intramolecularly Hydrogen-Bonded Aromatic Polyamides

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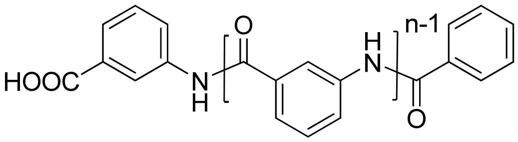
EXPERIMENTAL SECTION

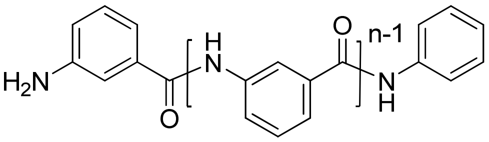
General: ^{1}H NMR and ^{13}C NMR spectra were taken on 500MHz Bruker instruments. NMR chemical shifts were reported as d values in ppm relative to TMS or deutrated solvent: $CDCl_3$ (7.26), DMSO-*d6* (2.50), TFA-d (11.50). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. Multiplets were reported over the range (in ppm) it appeared. N-methyl-2-pyrrolidone (NMP) was freshly distilled over calcium hydride. Pyridine (Py) was refluxed and distilled first over potassium hydroxide and then over calcium hydride. Triphenylphosphite (TPP) was freshly distilled under reduced pressure. All the above liquids were deaerated with nitrogen and stored under nitrogen atmosphere over molecular sieves. Lithium chloride (Fisher) was dried over $SOCl_2$ under reduced pressure while heating. Moisture sensitive reactions were performed under nitrogen atmosphere using flame-dried glassware and standard syringe/septa techniques. Extraction solvents were commercial grade. All glasswares were flame dried before use, and reactions were carried out under nitrogen atmosphere. Gel Permeation Chromatography (GPC) was carried out using an Agilent 1100 Series GPC Analysis System along with a mixed bed Plgel Mixed-C column from Polymer Labs. The eluent was DMF with 0.1% LiBr and a flow rate of 1.0 mL/min was used. The calibration was performed using poly(ethylene glycol) (PEG) based molecular weight standards. Circular dichroism (CD) spectroscopy was performed on a Jasco J-810 spectropolarimeter.

Synthesis and Characterization:



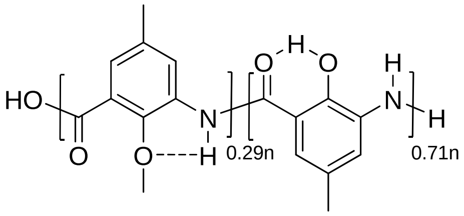
3

Synthesis of polymer 3: 0.685g (5mmol) of m-amino benzoic acid and 0.018g (0.15mmol) of benzoic acid in the mixed solvents of 15mL of NMP, 5mL of Py containing metal salts was heated at 100 degree Celsius. A warm solution of TPP in NMP was then introduced to the solution and the reaction mixture was then heated for 6 hours under nitrogen. After cooling, the reaction mixture was poured into 50mL of methanol, and the precipitate was then separated by filtration and was washed with methanol and dried under vacuum to yield 0.595g of polymer (100%). ^{1}H NMR (500 MHz, DMSO-d_6-4%LiCl) δ 10.88 (m, 1H), 8.44 (m, 1H), 8.02 (m, 1H), 7.92 (m, 1H), 7.37 (m, 1H). *Mn* = 4.17k (GPC). PDI = 1.87.



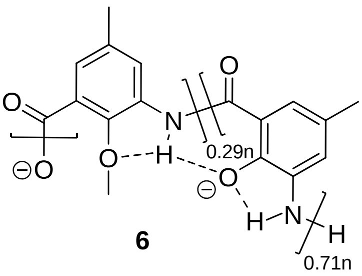
4

Synthesis of polymer 4: 0.685g (5mmol) of m-amino benzoic acid and 0.014g (0.15mmol) of aniline in the mixed solvents of 15mL of NMP, 5mL of Py containing metal salts was heated at 100 degree Celsius. A warm solution of TPP in NMP was then introduced to the solution and the reaction mixture was then heated for 6 hours under nitrogen. After cooling, the reaction mixture was poured into 50mL of methanol, and the precipitate was then separated by filtration and was washed with methanol and dried under vacuum to yield 0.595g of polymer (100%). ^{1}H NMR (500 MHz, DMSO-d_6-4%LiCl) δ 10.85 (m, 1H), 8.44 (m, 1H), 8.03 (m, 1H), 7.91 (m, 1H), 7.38 (m, 1H). *Mn* = 4.98k (GPC). PDI = 1.95.



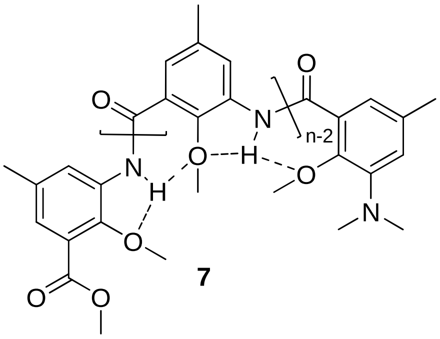
5

Synthesis of polymer 5: 0.091g (0.5mmol) of 3-amino-2-methoxy-5-methylbenzoic acid in 2.0mL of NMP containing 0.081g of lithium chloride was heated at 100 degree Celsius. A warm solution of TPP in NMP was then introduced to the solution and the reaction mixture was then heated for 6 hours under nitrogen. After cooling, the reaction mixture was poured into 10mL of water, and the precipitate was then separated by filtration. The solid was then washed with hot methanol and dried under vacuum to yield 0.060 mg of product (78.4%). ^{1}H NMR (500 MHz, $CDCl_3$: TFA-d=1:1) δ 8.32-7.09 (m, 2nH), 4.02 (m, 0.87nH), 2.42 (m, 3nH). *Mn* = 3.75k (GPC). PDI = 1.72.



6

Synthesis of polymer 6: 0.078g (0.5mmol of monomer) of polymer **5** was dissolved in 2.0mL of DMF. To the solution was added 14.2mg (0.36mmol) of NaOH and was stirred for 30min at room temperature. The solvent was then evaporated and the residue was dried under vacuum (100%). ^{1}H NMR (500 MHz, DMSO) δ 8.20 (m, nH), 7.22 (m, nH), 3.83 (m, 0.87nH), 2.34 (m, 3nH). *Mn* = 2.07k (GPC). PDI = 1.52.



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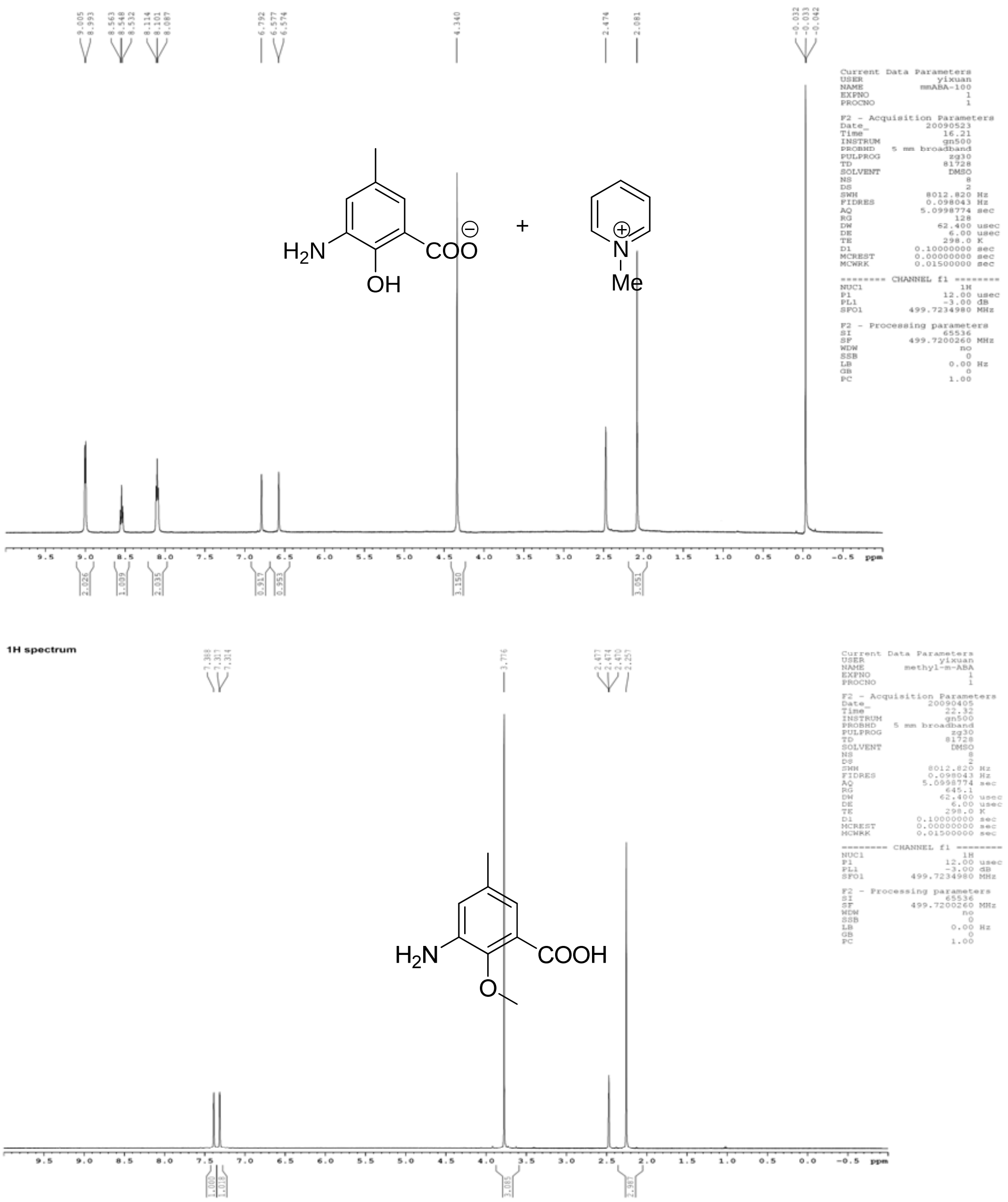
Synthesis of polymer 7: 0.078g (0.5mmol of monomer) of polymer **5** was dissolved in DMF with 0.69g of K_2CO_3. The mixture was kept at 60 degree Celsius and then 0.252mL of Me_2SO_4 was added within 12 hours. After cooling, DMF was evaporated and the polymer was participated in water to yield 62mg of product (76.1%). ^{1}H NMR (500 MHz, $CDCl_3$: TFA-d=1:1) δ 8.24 (m, nH), 7.69 (m, nH), 3.98 (m, 3nH), 3.90 (s, 3H), 3.25 (s, 6H), 2.43 (m, 3nH). (500 MHz, DMSO) δ 10.28 (m, nH), 8.19 (m, nH), 7.43 (m, nH), 4.00 (s, 3H), 3.88 (m, 3nH), 3.07 (s, 6H), 2.33 (m, 3nH). *Mn* = 2.43k (GPC), 2.37k (NMR). PDI = 1.47.

UV measurements: Polymer **5**, **6** and **7**(1.0 mg) was placed in a 20-mL flask equipped with a stopcock. 20 mL of DMSO was then added to keep the concentration of polymers as 0.05 mg/ml. Pure DMSO solvent was used as blank.

CD measurements: For CD measurements of polymer **4**, **5** and **7** with chiral acid, the polymer (1.0 mg) was placed in a 10-mL flask equipped with a stopcock. 20 equivalent of (S)- or (R)-acids in DMSO was added to the flask and DMSO was then added to the flask to keep the concentration of polymer as 0.5 mg/ml. The same amount of (S)- or (R)-acids in DMSO was transferred to another 10-mL flask and diluted with DMSO, giving solution of the acids as control. For CD measurements of polymer **3**, **5**, **6**, **7** with chiral amine, the polymer (1.0 mg) was placed in a 10-mL flask equipped with a stopcock. 1 equivalent of acetic acid and 20 equivalent of (S)- or (R)- amines in DMSO was added to the flask and DMSO was then added to the flask to keep the concentration of polymer as 0.5 mg/ml. The same amount of acetic acid and (S)- or (R)- amines in DMSO was transferred to another 10-mL flask and diluted with DMSO, giving solution of the amines as control. The CD spectra of these solutions were taken with a 0.1-cm quartz cell. The contribution of chiral inducers to the CD spectra was then subtracted from the originally observed data.



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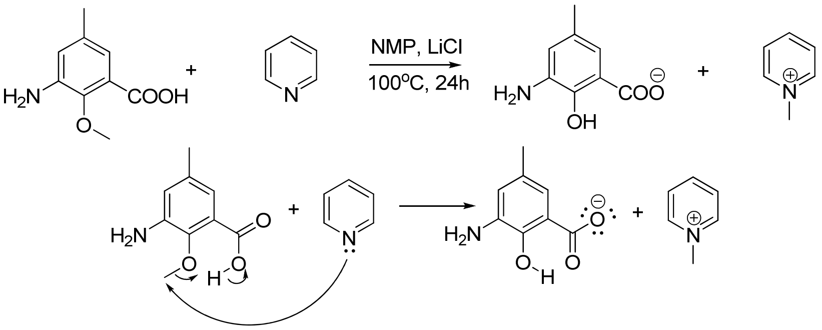
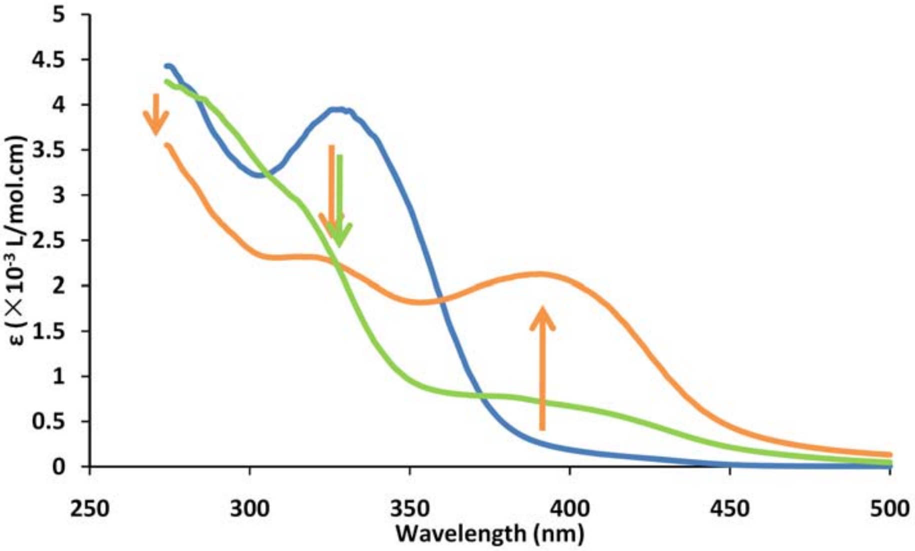
Scheme.S1 NMR spectra of product of model reaction and monomer **1**



Scheme S2. Model reaction of demethylation and proposed mechanism



Scheme. S3 UV-Vis spectra of solutions of polymer **5** (blue), **6** (orange) and **7** (green) in DMSO (0.05mg/mL) at 25 °C.