

Supplementary Information for:

Polymer brush on surface with tunable hydrophilicity using SAM formation of zwitterionic 4-vinylpyridine-based polymer†

P. Murugan,^a P. Ramar,^{a,b} Asit Baran Mandal,^{b,c} and Debasis Samanta^{*a,b}

^a*Polymer Science & Technology Department, CSIR-Central Leather Research Institute (CSIR-CLRI),
Adyar, Chennai-600020, India. Fax: 91-44-24911589, Tel: 91 -44 24422059 E-mail: debasis@clri.res.in,
debasis.samanta@gmail.com*

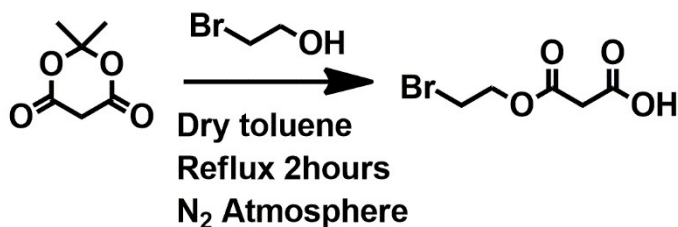
^b*Academy of Scientific and Innovative Research (AcSIR), India*

^c*CSIR-CGCRI, Kolkata, India*

Synthesis of 3-(2-bromoethoxy)-3-oxopropanoic acid (BEOPA)

We took it 50 ml single neck round bottom flask and degassed with N₂ gas. We added simultaneously 4000 mg (27.75 mmol) of Meldrum's acid in 20 ml of dry toluene and 2-bromo ethanol 3460 mg, 27.75 mmol under N₂ atmosphere. The reaction mixture was refluxed at 120 °C for 2 hours. After completion of the reaction, the reaction mixture was washed with 40 mL of saturated NaHCO₃ solution and separated out the aqueous layer. These aqueous layers acidified with Conc. HCl up to pH-4 and extracted with 200 ml ethyl acetate for two times. The organic layer was dried over with anhydrous Na₂SO₄ and we got light yellow colour viscose liquid. The organic compound was purified by column chromatography by using (100-200 mesh silica gel) gradient column chromatography (PE: CHCl₃- 5%, 10%) (Yield: 62%)^{1,2}

Scheme. S1



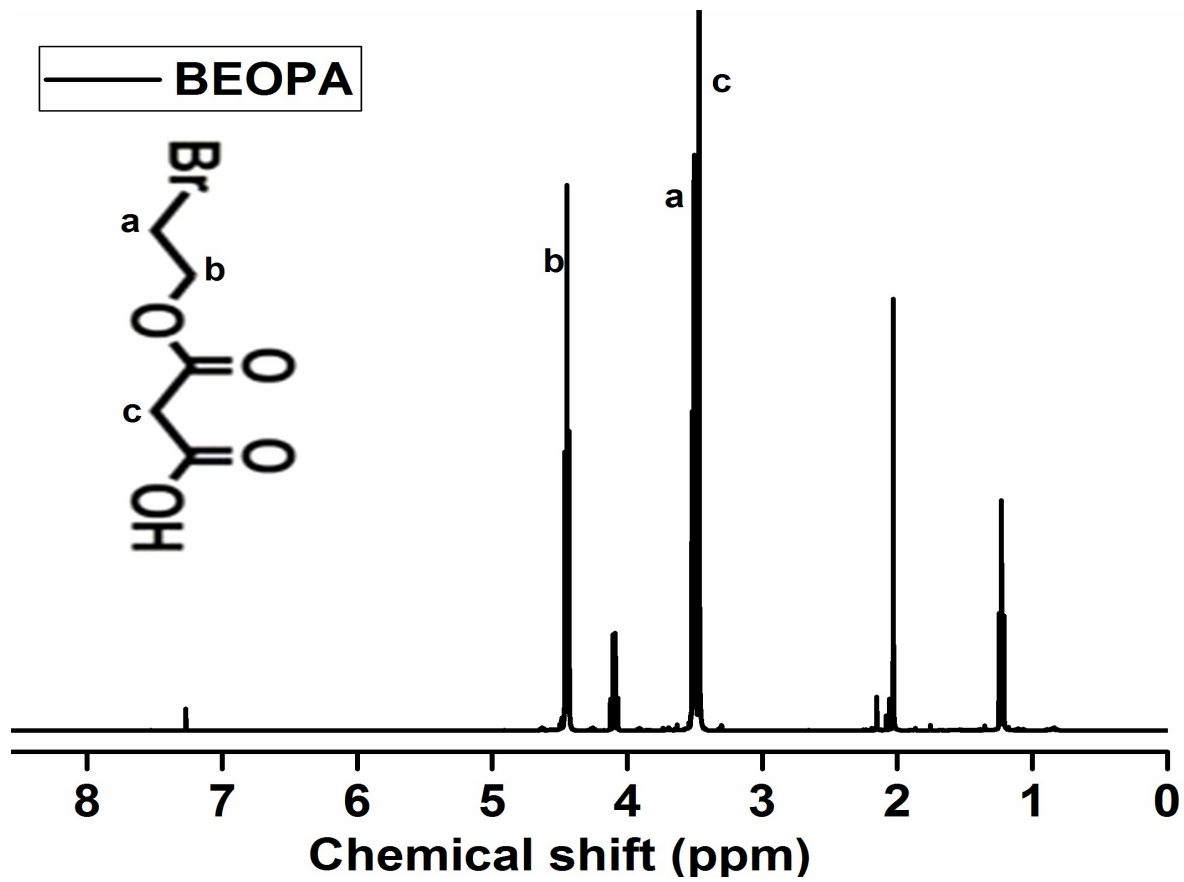


Fig. S1: ^1H NMR spectrum of 3-(2-bromoethoxy)-3-oxopropanoic acid (BEOPA)

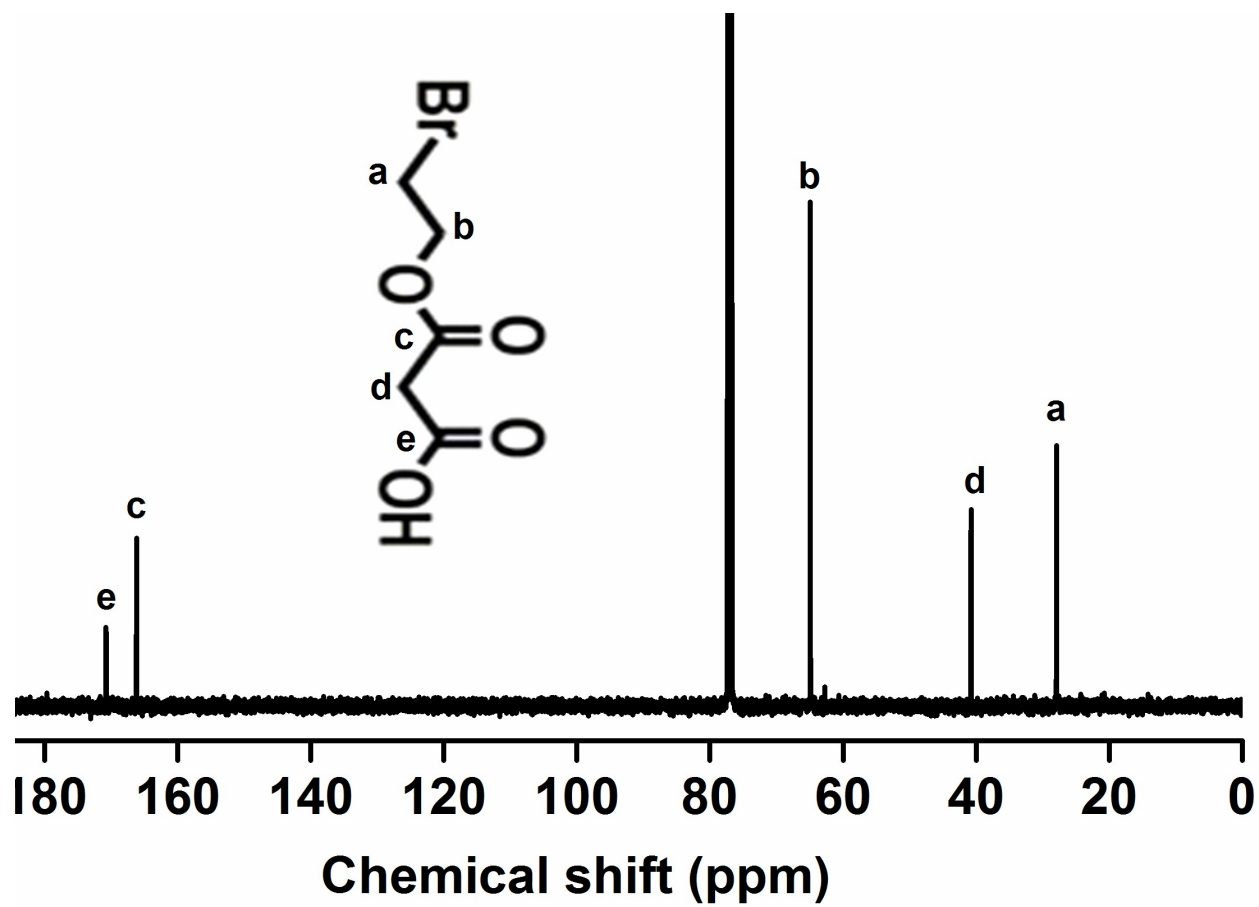


Fig. S2: ^{13}C NMR spectrum of 3-(2-bromoethoxy)-3-oxopropanoic acid (BEOPA)

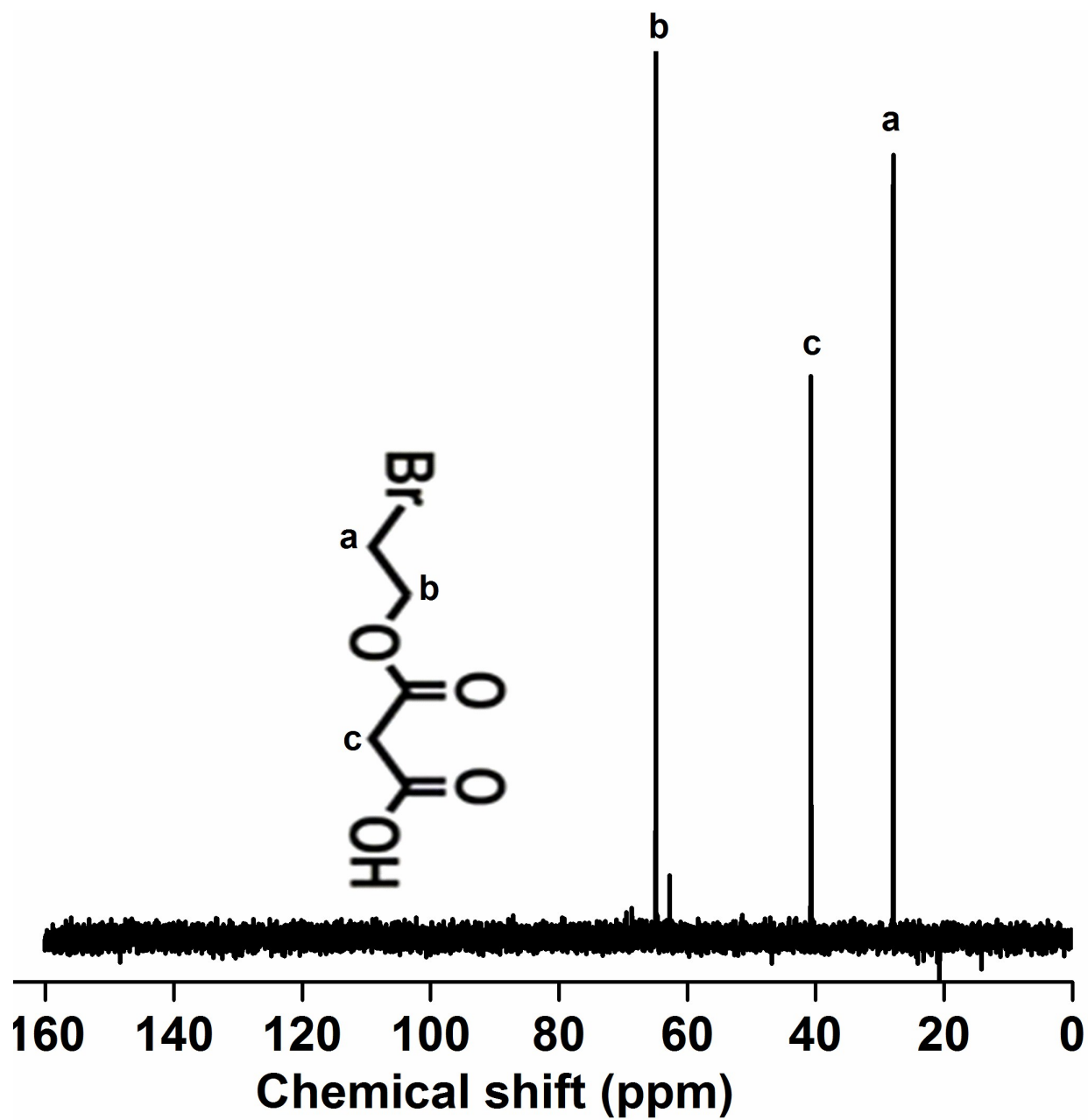


Fig.S3: DEPT NMR spectrum of 3-(2-bromoethoxy)-3-oxopropanoic acid (BEOPA)

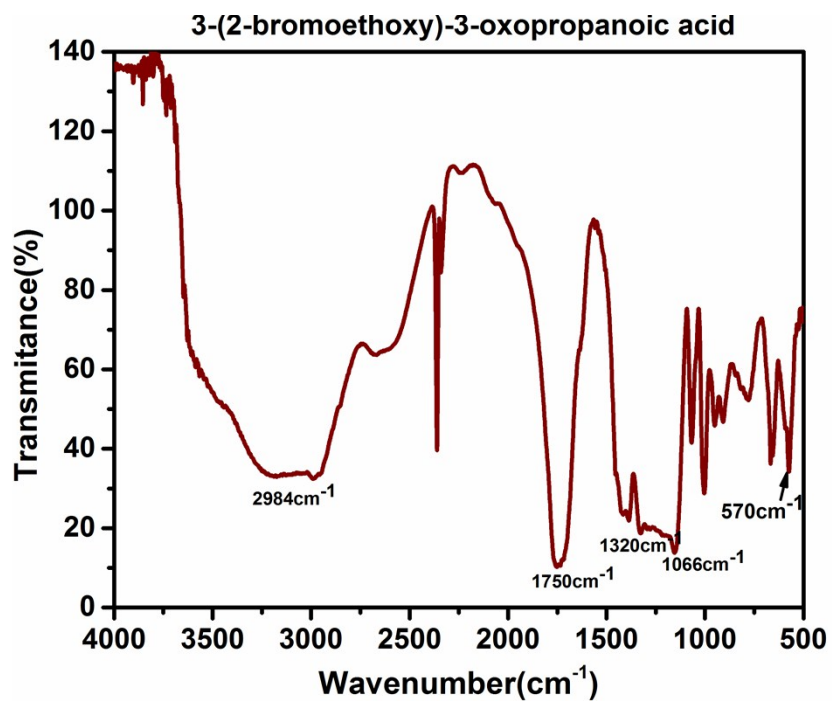


Fig. S4: FT-IR spectrum of 3-(2-bromoethoxy)-3-oxopropanoic acid (BEOPA)

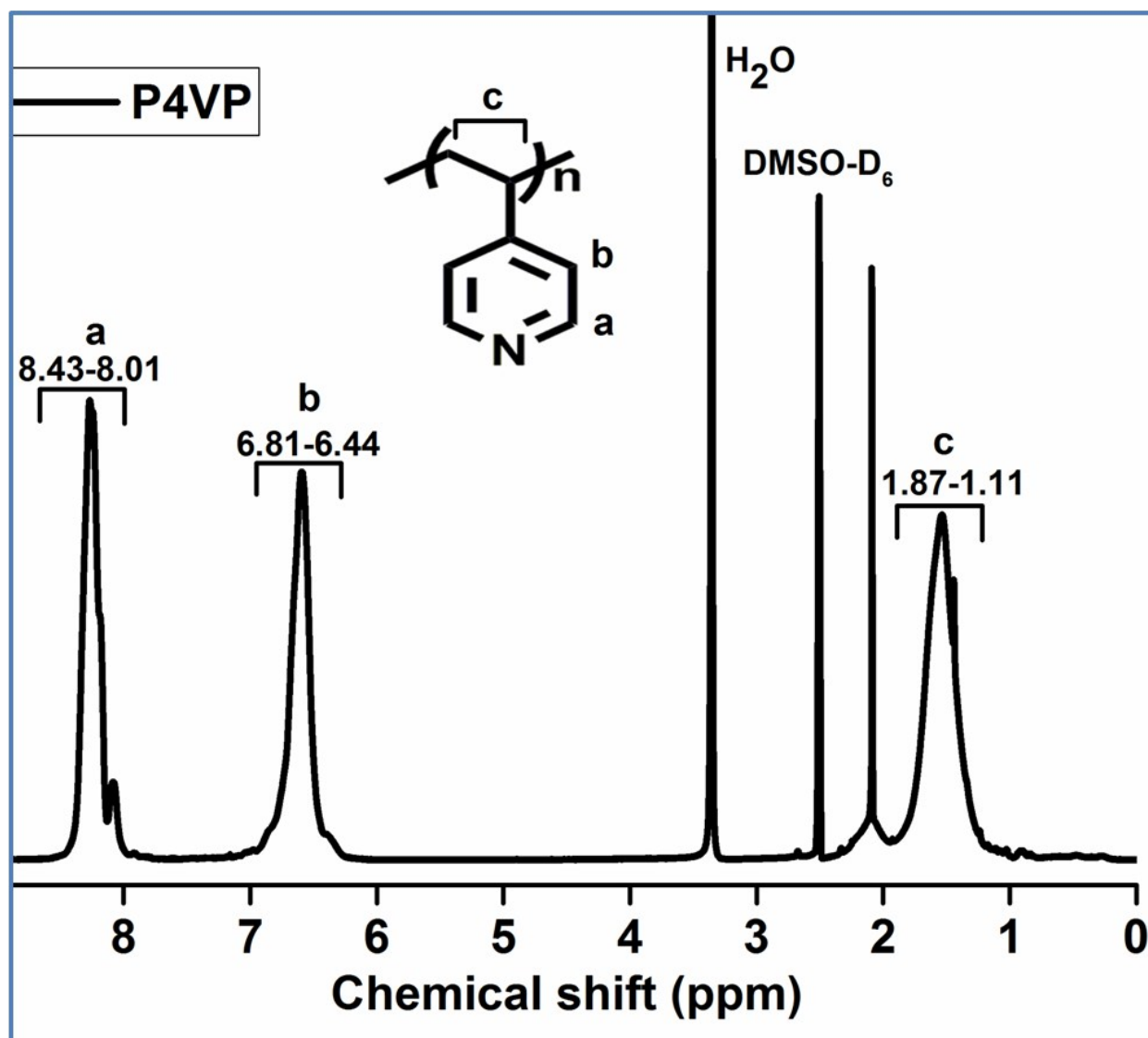


Fig. S5: ^1H NMR spectrum of poly 4-vinylpyridine (P4VP)

Scheme. S2: Attempted quaternization of poly4-vinylpyridine with 1-octanoic acid. (control reaction-P4VPOA)
(Failure)

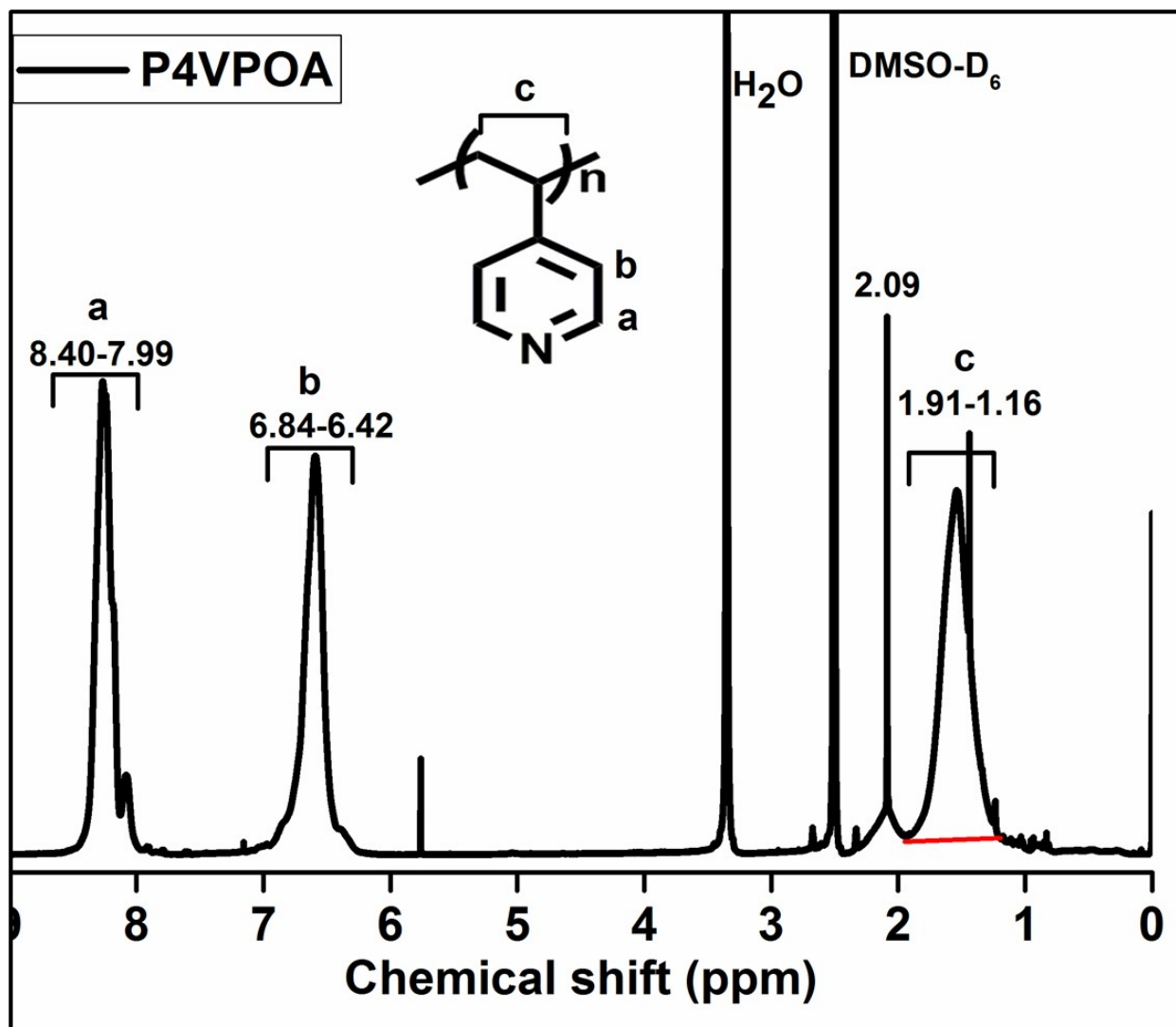
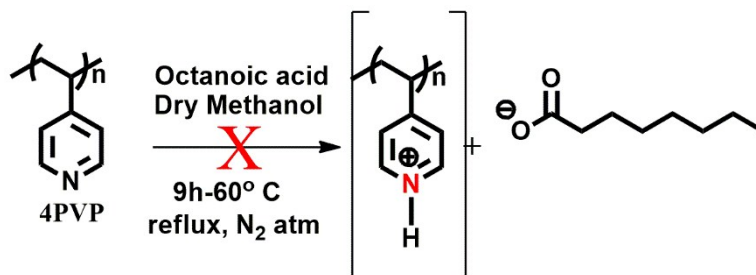


Fig. S6: ¹H NMR spectrum of control reaction (P4VPOA)

Scheme. S3: Attempted quaternization of poly4-vinylpyridine with 3-(2-bromoethoxy)-3-oxopropanoic acid (QP4VPA)

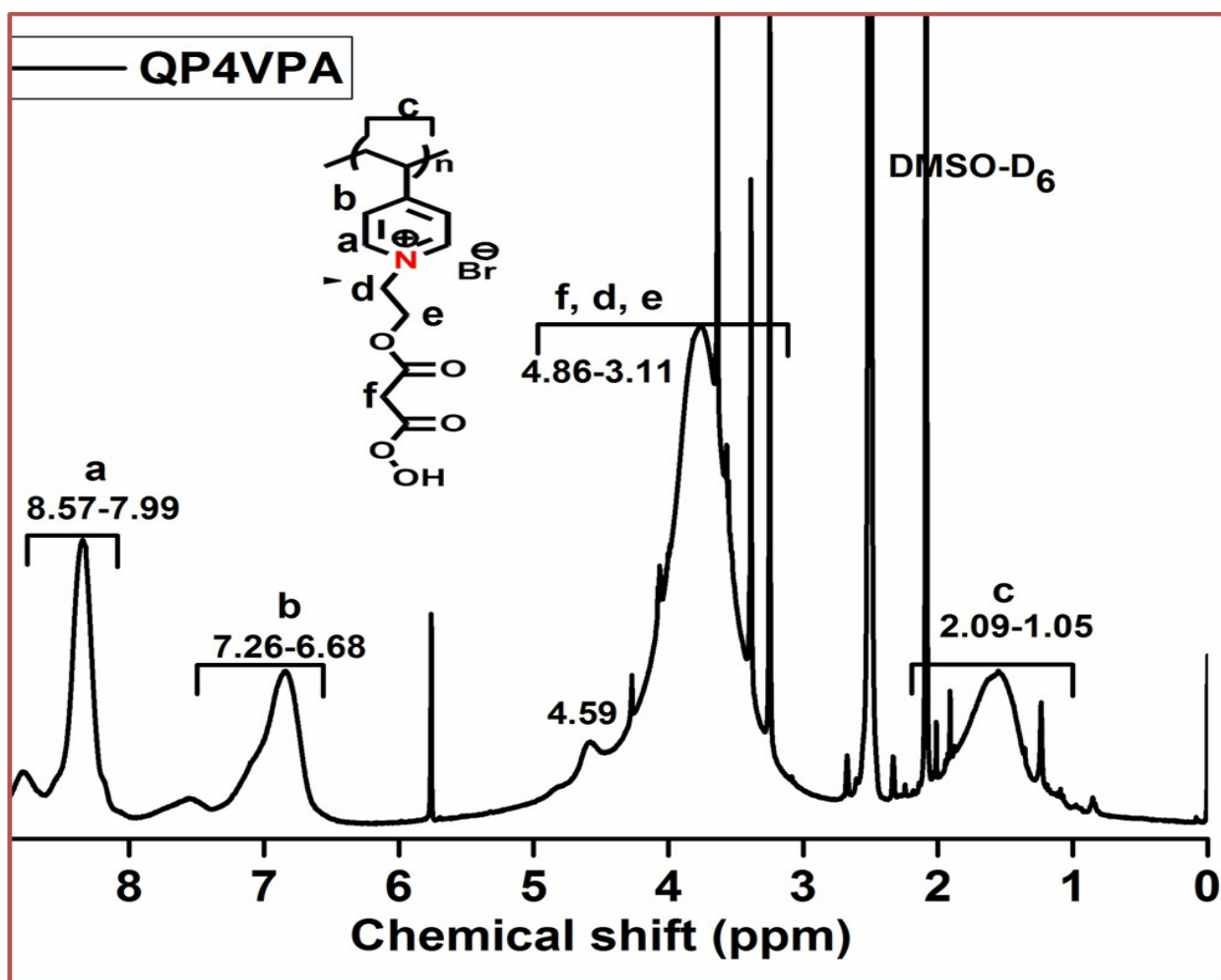
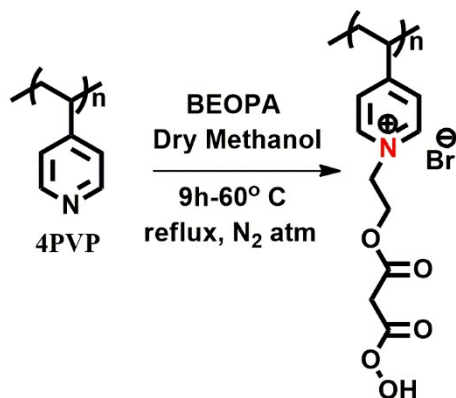


Fig. S7: ¹H NMR spectrum of model reaction (QP4VPA)

Scheme. S4: Attempted quaternization of poly4-vinylpyridine with 3-(2-bromoethoxy)-3-oxopropanoic acid and 3-iodopropyltrimethoxysilane (QP4VPSA)

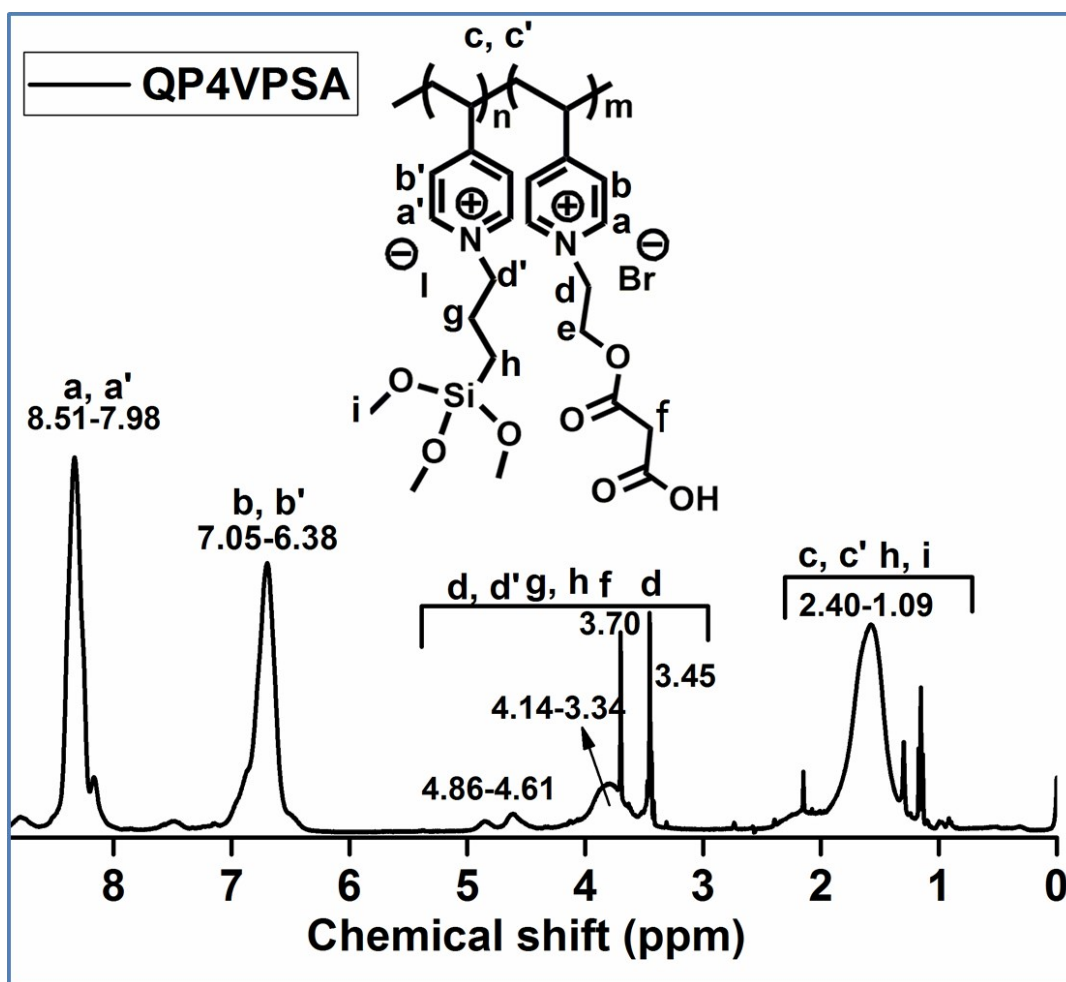
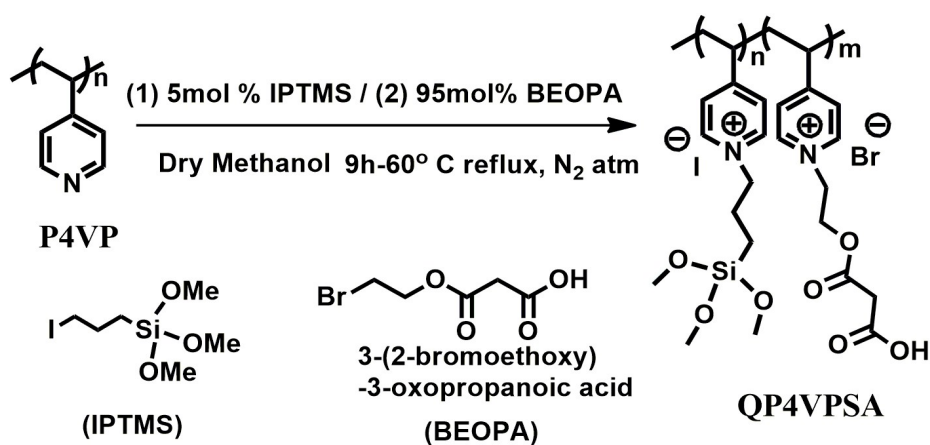


Fig. S8: ¹H NMR spectrum of QP4VPSA polymers

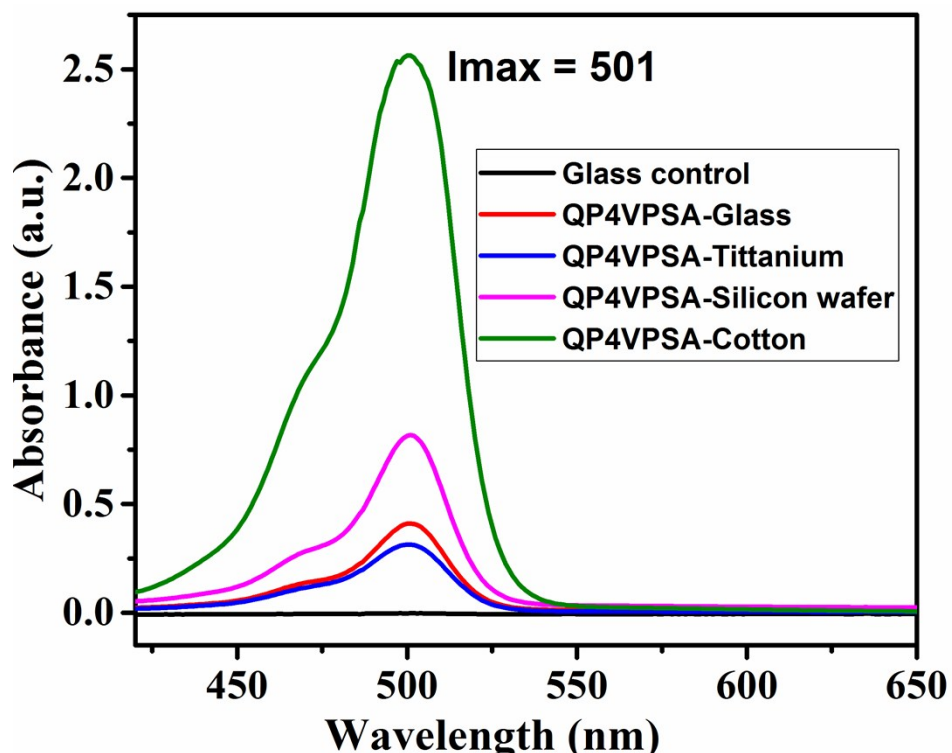


Fig. S9. UV-vis spectra of desorbed fluorescein salt solution after treatment of polymeric SAM on the surface with fluorescein salt followed by treatment with 0.5 mol % were hexadecyltrimethylammonium bromide solutions.

Reference:

1. P. Witte, F. Beuerle, U. Hartnagel, R. Lebovitz, A. Savouchkina, S. Sali, D. Guldi, N. Chronakis and A. Hirsch, *Organic & Biomolecular Chemistry*, 2007, **5**, 3599-3613.
2. O. Bouloussa, F. Rondelez and V. Semetey, *Chem. Commun.*, 2008, 951-953.