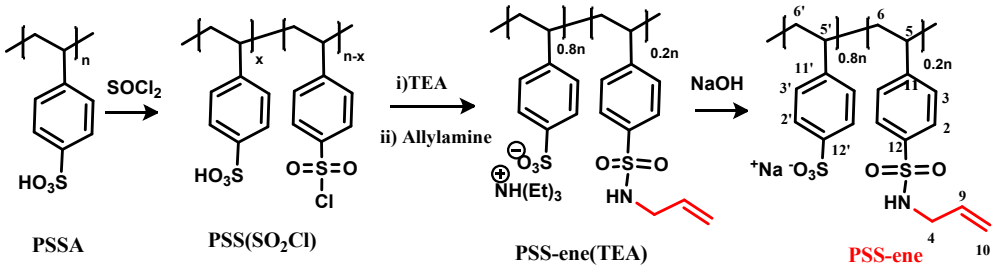
Supporting Information

From the Functionalization of Polyelectrolytes to the Development of a Versatile Approach to Polyelectrolyte Multilayer Films with Enhanced Stability

Thi-Thanh-Tam Nguyen*, Sabrina Belbekhouche, Pierre Dubot, Benjamin Carbonnier and Daniel Grande*

Experimental part

Functionalization of PSSA



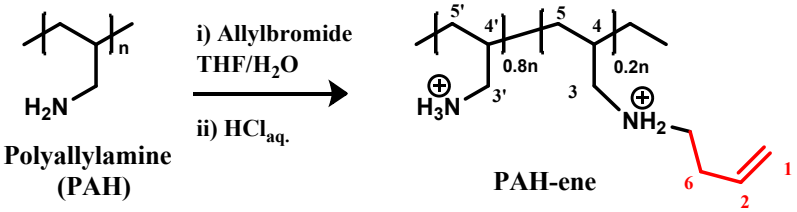
Poly(4-styrenesulfonic acid) (PSSA) solution was freeze-dried to remove completely water content. The resulting brown solid was ground into fine powder before being used for the functionalization.

In a 100 mL round flask, a mixture of fine powder PSSA (1.7 g, 9.24 mmol of repetitive monomer units, 1 eq.) and $SOCl_2$ (15 mL; 24.60 g ; 203.28 mmol ; 22 eq) was refluxed under argon during 2 h. The excess of $SOCl_2$was evaporated under reduced pressure to give intermediate PSS(SO_2Cl). Then, dimethylformamide (10 mL) and triethylamine (2.60 mL ; 1.87 g ; 18.5 mmol; 2 eq) were added. The mixture was stirred for 5 min before adding allylamine (0.17 ml ; 2.3 mmol; 0.25 eq). The mixture was stirred for further 3 h at room temperature under argon. Then, NaOH (10 mmol, 0.4 g in 10 mL water) was added. The resulting mixture was added dropwise into 100 mL of acetone followed by centrifugation to give a brown solid. The latter was redissolved in 10 mL of water and precicipated again in 100 mL of acetone. This step was repeated 2 times. The resulting solid was further purified by dialysis against water during 48 h. After freeze-drying, functionalized PSS-ene was obtained as a white yellowish solid (1.05 g, 60%) with a functionalization ratio of 20 % as confirmed by ^{1}H NMR.

^{1}H NMR (D_2O, 400 MHz): δ 7.52 (s, 2H, H^2), 6.50 (broad, 2H, H^3), 5.6 (broad, 0.2H, H^9), 5.1-4.8 (d, broad, 0.4H H^{10}), 3.43 (0.4H, H^4), 2.50-0.9 (broad, $H^{5+5'}$ and $H^{6+6'}$) ppm

^{13}C NMR (D_2O, 100 MHz,): δ 148.4 (borad, $C^{11+11'}$), 140.0 (broad, $C^{12+12'}$), 134.7 (C^9), 128.3 ($C^{2+2'}$), 125.4 ($C^{3+3'}$), 116.3 (C^{10}), 46.2 (C^4), 42.0 (C^{5+6}), 40.02 ($C^{5'+6'}$) ppm

Functionalization of PAH

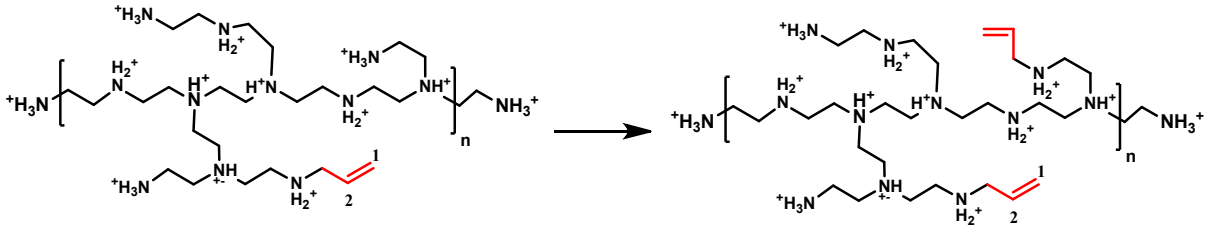


To an aqueous solution of neutral PAH 10 wt % (0.12 g of polymer, 2.07 mmol of repetitive monomer units, 1 eq.), THF (1mL) and allylbromide (50 mg, 36 µL, 0.41 mmol, 0.20 eq.) were added. The rereaction mixture was stirred overnight at room temperature and THF was removed by rotavapor under reduced pressure. Finally, 3 mL of 0.1 M HCl solution was added followed by water liophilization. PAH-ene was obtained as a light yellow solid (0.20 g, 95 %) with 20 % of functionalization ratio as confirmed by ^{1}H NMR. This product was stored at -20°C.

^{1}H NMR (D_2O, 400 MHz) δ 5.97 (0.20 H^{2}), 5.55 (0.40 H^{1}), 3.73 (0.40 H^{6}), 3.05 (2H, ^{3}H+$^{3'}$H,), 2.06 (1H, ^{4}H+$^{4'}$H), 1.52 (2H, , ^{5}H+$^{5'}$H) ppm.

^{13}C NMR (D_2O, 100 MHz) δ 127.5 (^{1}C), 124.2 (^{2}C), 70.5 (^{6}C),54.4 (^{3}C), 50.6 ($^{3'}$C), 42.3 (^{5}C), 33.0 (broad, $^{5'}$C),30.0 (broad,$^{4'}$C), 23.7 (^{4}C) ppm.

Functionalization of branched PEI



A mixture of neutral branched PEI (10.3 g, ~240 mmol of repetitive ethyleneamine units, 1 eq.) in 50 mL dichloromethane was stirred until a homogeneous solution obtained. Then allylbromide (3mL, 35 mmols, 0.15 eq.) was added. The reaction mixture was stirred overnight at room temperature under argon adn then solvent was evaporated under reduced pressure. Then neutral functionalized PEI-ene was dissolved in 30 mL of distilled water, cooling to 0°C and acidified to pH= 4 using 1M HCl solution. Finally, water was removed by freeze-drying. Positively charged PEI-ene was obtained as a yellow solid (19.7 g, 97.2 %). This product was stored at -20°C.

^{1}H NMR (D_2O, 400 MHz) δ 6.00 (broad, ~ 0.15 H, H^{2}), 5.60 (broad, ~ 0.3 H, H^{1}),4.0-2.7 (broad, 4 H) ppm.

^{13}C NMR (D_2O, 100 MHz) δ 129.1 (C^{2}), 124.8 (C^{1}), 56.3, 50.0, 48.8, 45.0, 44.7, 43.4, 41.8, 36.4, 35.4 ppm.

Synthesis of PEG-diOMs

In a 250 mL flame dried round flask, PEG-1000 (15.4 g, 15.4 mmol, 1eq.), TEA (10.7 mL, 77 mmol, 5eq.) and 50 mL of dry $CHCl_3$ were added. The mixture, held at 0°C under argon, was added dropwise anhydrous methanesulfonyl chloride (3.6 ml, 46.2 mmol, 3eq.). The solution was stirred overnight at room temperature under argon. The solvent was evaporated under reduced pressure, then 50 mL of AcOE was added. The mixture was extracted with 10 wt % aqueous HCl (3x100 mL). The organic

layer was washed with distilled water (2 x 50 mL), saturated NaCl solution (50 mL), dried over magnesium sulfate and finally evaporated to afford intermediate PEG-diOMs as a yellowish oil (15 g, 96 %). This intermediate product was directly used for the next step without further purification.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.04(4 H, (O-CH_2-C**H**$_2$-OMs)), 3.60 (4H, O--C**H**$_2$-CH_2-OMs), 3.55(m, 80 H), 3.00(6 H, OMs) ppm.

^{13}C **NMR** ($CDCl_3$, 100 MHz) δ 37.5 (**C**H_3), 66.35, 69.04, 69.45, 70.56 ppm.

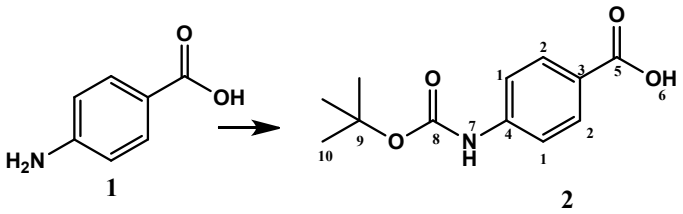
*Synthesis of **PEG-diSH***

A mixture of PEG-diOMs (9.6 g, ~ 9.6 mmol, 1eq.) and thiourea (4.4 g, 57.6 mmol, 6 eq.) in 20 mL of anhydrous THF was placed in a flame dried round flask and refluxed under argon during 9 hours. The reaction mixture was cooled to room temperature and then NaOH (3.84 g, 96 mmol, 10 eq, dissolved in 20 ml H_2O) was added. The mixture was again refluxed under argon overnight, cooled to room temperature. THF was evaporated under reduced pressure.The brute was diluted with 20 mL of distilled water and adjusted to pH 7 using 1 M HCl solution, extracted with methylene chloride (3 x 20 mL). The organic phases were washed with distilled water, saturated NaCl solution, dried over magnesium sulfate and filtered. The filtrate was evaporated to give di-thiolated poly(ethylene) glycol PEG-diSH as a colorless oil (8.0g, 94 %).

^{1}H-NMR δ ($CDCl_3$, 400 MHz) ^{1}H NMR 3.65 (116 H), 2.70 (q, 4H, C***H***$_2$-SH),1.60 (t, 2H, S***H***) ppm.

^{13}C **NMR** ($CDCl_3$, 100 MHz) δ 73.25 (O-**C**H_2-CH_2-SH), 70.97, 70.80, 70.62, 24.51 (O-CH_2-**C**H_2-SH) ppm.

*Synthesis of compound **2***

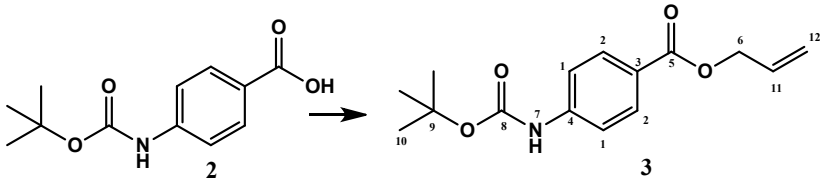


To a mixture of 4-aminobenzoic acid (5 g, 36.5 mmol, 1 eq.) in 100 mL of dioxane/water 2:1 (v/v) was added NaOH (1.45 g, 1 eq., dissolved in 21 mL distilled water) and then di-*t*-butyldicarbonate (12 g, 55 mmol, 1.5 eq.). The reaction mixture was stirred at room temperature during 24 hours followed by solvent removal under reduced pressure. Then, 200 mL of distilled water was added. The mixture was acidified slowly to pH 3 using a 1M HCl solution. The precipitate was filtered and dried under vacuum at 50 °C. Finally, excess of Boc_2O was removed just by simple trituration with dichloromethane affording pure product **2** as white solid with quantitative yield (8.5 g, 98 %).

^{1}H NMR (d_6-acetone, 400 MHz) : δ 8.79 (s, 1H, NH), 7.70 (d, 2H, ^{1}H), 7.98 (d, 2H, ^{2}H), 1.51 (s, 9 H, CH_3) ppm.

^{13}C NMR (D_6-acetone, 100 MHz): δ 167.50 (C^5), 153.46 (C^8), 145.05 (C^4), 131.79 (C^2), 124.91 (C^3), 118.28 (C^1), 80.81 (C^9), 28.02 (C^{10}) ppm.

*Synthesis of compound **3***

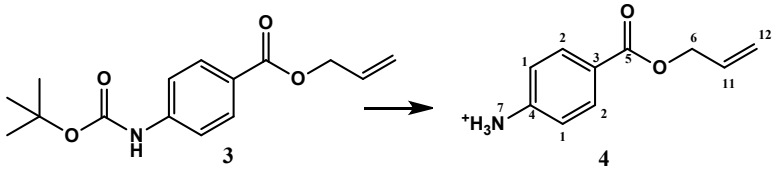


A mixture of **2** (5.6 g, 23.6 mmol, 1 eq.), potassium carbonate (8.1 g, 59 mmols, 2.5 eq) and tetrabutylammonium iodide (1.1 g, 2.95 mmol, 0.12 eq.) in 25 mL DMF was stirred at 40 °C and then allylbromide (2.45 mL, 28.3 mmol, 1.2 eq.) was added dropwise.The reaction mixture was stirred at room temperature overnight. The flask content was poured slowly into 200 mL of 3 M HCl solution. The precipitate was filtered to give a grey solid (m = 6.5 g). Further purification was done by precipitation of this solid in a mixture of solvents (acetone/H_2O) with acetone as good solvent and H_2O as bad solvent. Finally, the pure product **3** was obtained by simple trituration of the resulting solid in hexane (white solid, 3.5 g, 54 %).

^{1}H NMR (d_6-acetone, 400 MHz) : δ 0.97(H^7), 7.97(d, 2H, H^2), 7.68 (d, 2H, H^1), 1.50 (s, 9H, H^{10}), 5.35-5.10 (d, 2H,H^5), 4.55-4.54 (d, 2H,H^6) ppm.

^{13}C NMR (d_6-acetone, 100 MHz): δ 166.10 (C^5), 152.38 (C^8), 142.99 (C^4), 132.59 (C^{11}), 131.16 (C^2), 124.53 (C^3), 118.30 (C^{12}), 117.54 (C^1), 81.42 (C^9), 65.61 (C^6), 28.47 (C^{10}) ppm

*Synthesis of compound **4***

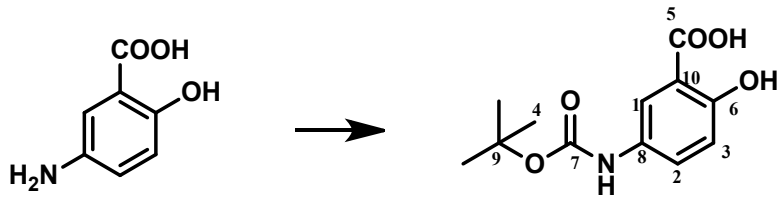


To a solution of **3** (2 g, 7.2 mmol) in THF (20 mL), 5 ml of 5M HCl aqueous solution was added.The reaction mixture was stirred at room temperature during 3 hours. The solvent was evaporated under reduced pressure affording **4** as a brown solid (1.50, 99 %)

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.86 (d, 2H, H^1), 6.60 (d, 2H, H^2), 6.02 (m, 1H,H^{11}), 5.40-5.23 (dd, 2H, H^{12}), 4.76 (d, 2H,H^6), 4.13 (s, broad, H^7) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.56 (C^5), 151.22 (C^4), 132.89 (C^{11}), 131.85 (C^2), 119.66 (C^3), 117.88 (C^1), 113.95 (C^{12}), 65.12 (C^6) ppm

Synthesis of compound ***6***



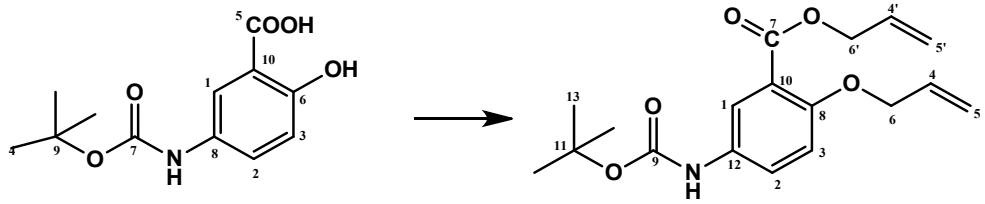
5 **6**

Into a 200 mL round flask was introduced 2-hydroxy-5-aminobenzoic acid (10 g, 65.3 mmol, 1 eq), a mixture Dioxane /water (50 ml /100 mL), Boc_2O (17.0 g, 78.4 mmol, 1.20 eq) and NaOH (3.28 g, 81.6mmol, 1.25 eq). The mixture was stirred at room temperature for 4 hours followed by solvent removal by rotavapor under reduced pressure. The resulting solid was dissolved in dichloromethane and filtered to remove all impurities (insoluble in dichloromethane). The resulting filtrate was concentrated and redissolved in acetone followed by filtration to remove all impurities insoluble in acetone. The filtrate was concentrated to afford pure **6** as a white solid (15.5 g, 94 %).

^{1}H NMR (d_6-acétone, 400 MHz): δ 10.83 (s, broad, COOH), 8.36 (s, large, NH), 8,19 (s,1H, H^1) 7.67 (d,1H , H^2), 6,91 (d, 1H, H^3), 2.06 (s, broad, OH), 1.48 (s, 9H, H^4) ppm

^{13}C NMR (d_6-acétone, 100 MHz): δ 172.71 (C^5), 158.63 (C^6), 154.06 (C^1), 132.46 (C^8), 128.02 (C^2), 120.61 (C^1), 118.14 (C^9), 112.71 (C^3), 80.12 (C^{10}), 28.60 (C^4) ppm.

Synthesis of compound 7



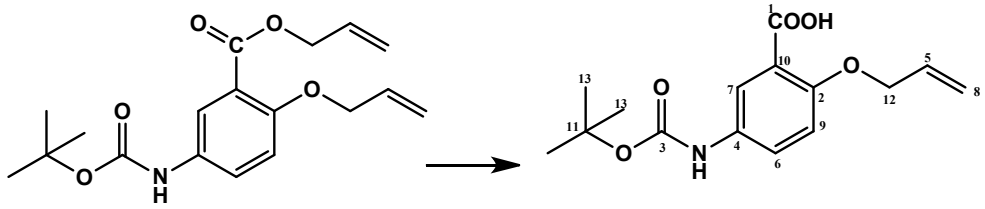
6 **7**

Into a 100 mL round flask was introduced acid **6** (1.70 g, 6.72 mmol, 1eq), K_2CO_3 (4.64 g, 33.6 mmol, 5 eq), tetrabutylammoniumbromide (0.43 g, 1.34 mmol, 0.2 eq), allylbromide (2.90 mL, 4.07 g, 33.60 mmol; 5 eq) and15 mL DMF. The reaction mixture was stirred at 50°C under argon overnight, cooled to room temperature. The flask content was poured slowly into 200 mL of 0.5 M HCl solution, the mixture was extracted with ethyl acetate (3x 50 mL). The organic phases were washed with a saturated NaCl solution (30 mL), dried over $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure to afford the desired product **7** as yellowish oil (2.03 g, 91 %). This product (almost pure) was used without further purification.

^{1}H NMR(d_6-acetone, 400 MHz): δ 8.04-2.99-2.89 (DMF), 7.68 (s, 1H, H^1), 7.60 (s, 1H, H^2), 6.91-6.89 (d,1H, H^3), 6.48 (s, 1H, NH), 5.98 (m, 1H, H^4-$H^{4'}$), 5.3 (m, 2H, $H^{5'}$), 5.2 (m, 2H, H^5), 4.79-4.78 (d, 2H, $H^{6'}$), 4.58-4.57 (d, 2H, H^6), 2.19 (CH_3CO), 1.50 (s, 9H, Boc) ppm

^{13}C NMR (d_6-acetone, 100 MHz): δ 165.77 (C^7), 154.40 (C^8), 153.26 (C^9), 133.1 (C^{12}), 133.02 (C^4 – $C^{4'}$), 132.45 (C^2), 131.66 (C^5-$C^{5'}$), 120.97 (C^1), 118.46-117.75 (C^3), 115.06 (C^{10}), 80.72 (C^{11}), 70.49 (C^6), 65.94 ($C^{6'}$), 28.65(C^{13}) ppm

*Synthesis of compound **8***



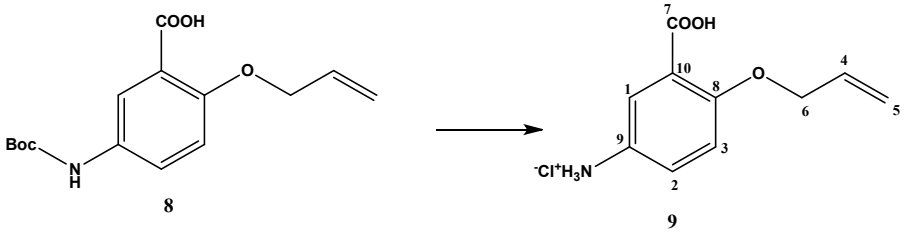
7 **8**

To a mixture of **7** (2.2 g, 6.6 mmol, 1 eq.) in 30 mL MeOH, NaOH (0.6g, 15 mmol, 2.8 eq dissolved in 10 ml distilled water.) was added. The mixture was refluxed overnight and cooled to room temperature followed by MeOH removal. The resulting mixture was neutralized to neutral pH with a 1M HCl solution. The resulting precipitates was solubilized in DCM,dried over $MgSO_4$ and then filtered. The filtrate was evaporated under reduced pressure and purified on silica gel based column chromatography with gradient of eluent (DCM 100 % to a mixture of DCM/MeOH (95/5) v/v). The pure product **8** was isolated as a pinkish-white solid (1.6 g; 83 %).

^{1}H NMR (d_6-acetone, 400 MHz, 298 K): δ 10.94 (s, 1H, COOH), 6.98 (s, 1H, H^7), 6.96 (s, 1H, H^6), 6.06 (d, 1H, H^9), 6.03 (s, 1H, NH), 5.47 (m, 1H, H^5), 5.40 (m, 2H, H^8), 4.74 (s, 9H, Boc) ppm.

^{13}C NMR (d_6-acetone, 100 MHz, 298 K): δ 165.44 (COOH), 153.20 (C^2), 153.18 (C^3), 133.83 (C^4), 131.54 (C^5), 125.93 (C^6), 123.89 (C^7), 121.08 (C^8), 118.79 (C^9), 114.46 (C^{10}), 81.32 (C^{11}), 71.89 (C^{12}), 28.80 (C^{13}) ppm.

*Synthesis of compound **9***

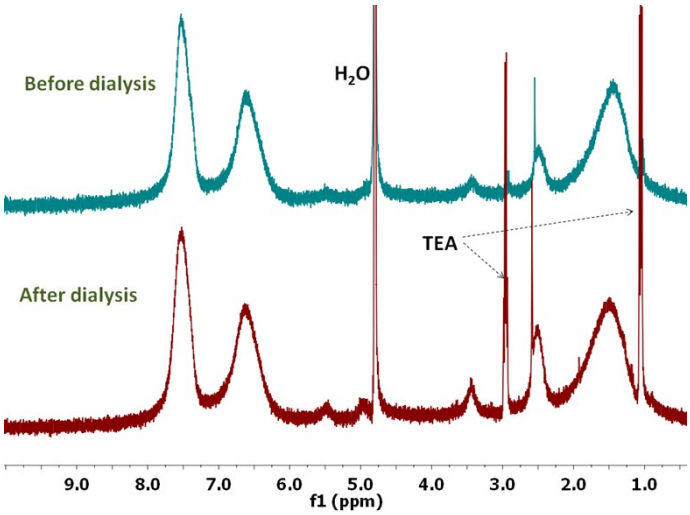


8 **9**

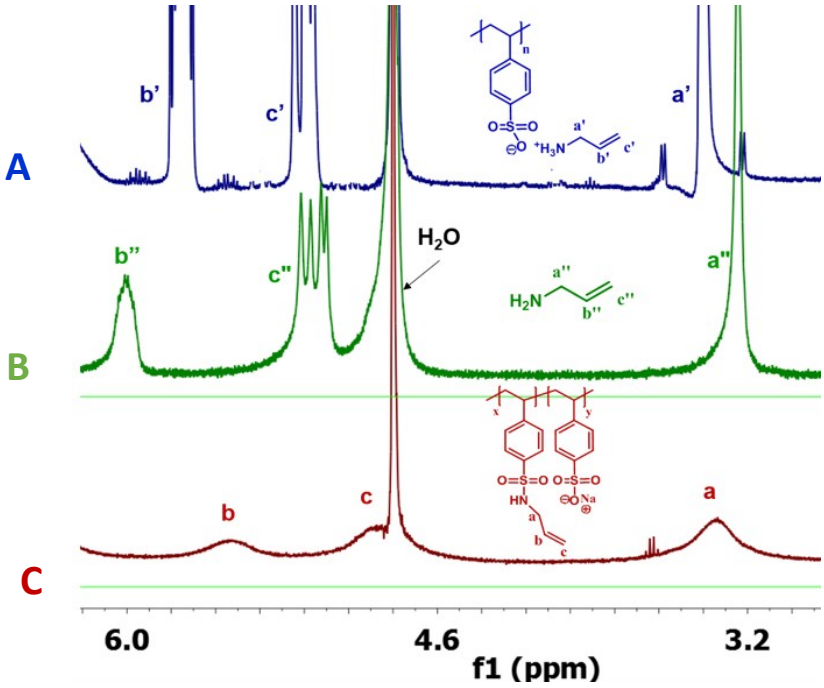
To a mixture of acid **8** (2.2 g, 7.5 mmol) in THF (20 mL), 5 ml of 5 M HCl aqueous solution was added. The reaction mixture was stirred for 2 hours followed by solvent removal under reduced pressure by rotavapor. Anilinium derivative **9** was obtained as a brown solid (2.3 g, 100 %).

^{1}H NMR (MeOD, 400 MHz) : δ 7.67(s,1H, H^1), 7.40-7.38-7.37 (m, 1H, H^2), 7.11-7.09 (d, 1H, H^3), 5.94-5.91-5.90-5.87 (m, 1H, H^4), 5.35-5.10 (d, 2H, H^5), 4.55-4.54 (d, 2H, H^6) ppm.

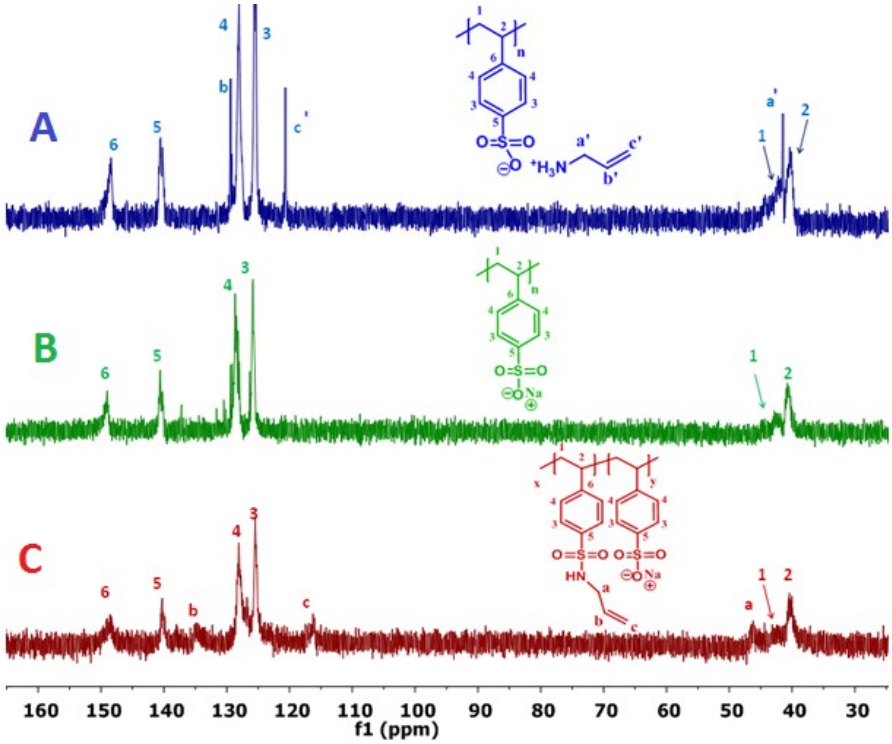
^{13}C NMR (MeOD, 100 MHz): δ 168.75 (C^7), 159.83 (C^8), 134.09 (C^4), 129.50 (C^1), 127.71 (C^9), 124.65 (C^2), 123.63 (C^3), 118.79 (C^{10}), 116.75 (C^5), 71.21(C^6) ppm.



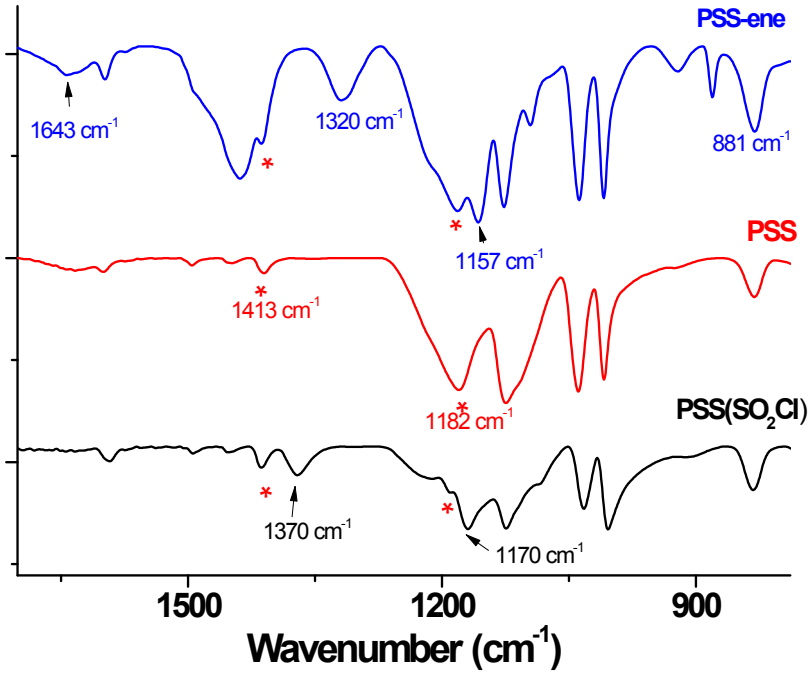
SI Fig. 1 : Comparison of ^{1}H NMR (D_2O) spectra of PSS-ene before and after dialysis



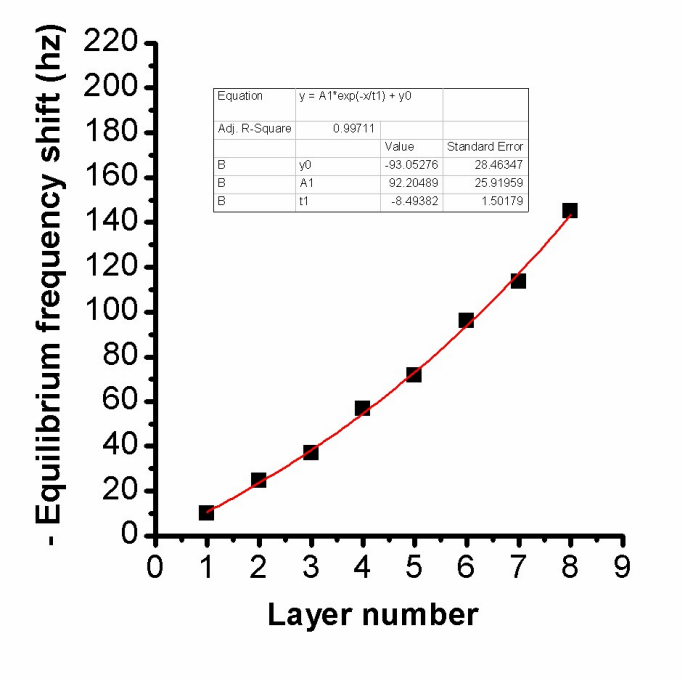
SI Fig. 2: Comparison of ^{1}H NMR (D_2O) spectra of allylammonium-PSS salt (A), free allylamine (B) and PSS-ene (C)



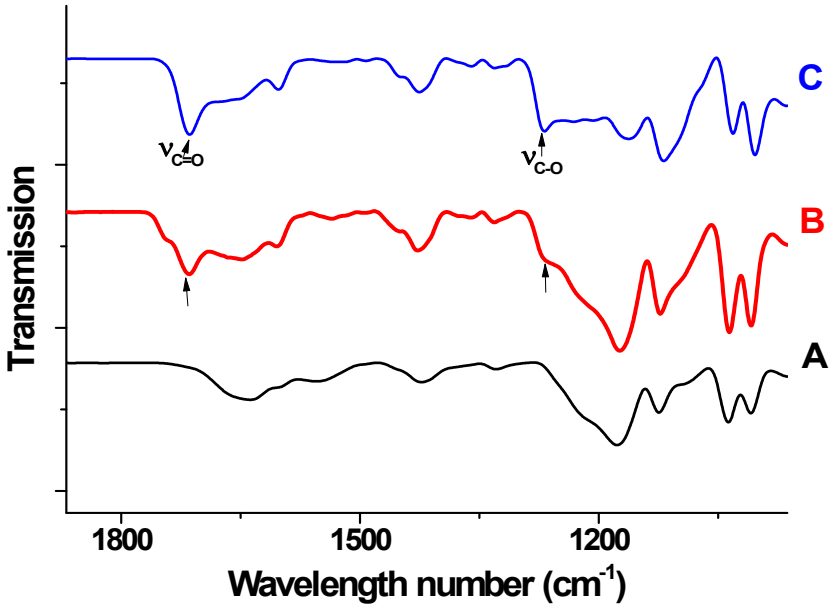
SI Fig. 3: Comparison of ^{13}C NMR (D_2O) spectra of allylammonium-PSS salt (A), PSS (B), and PSS-ene (C).



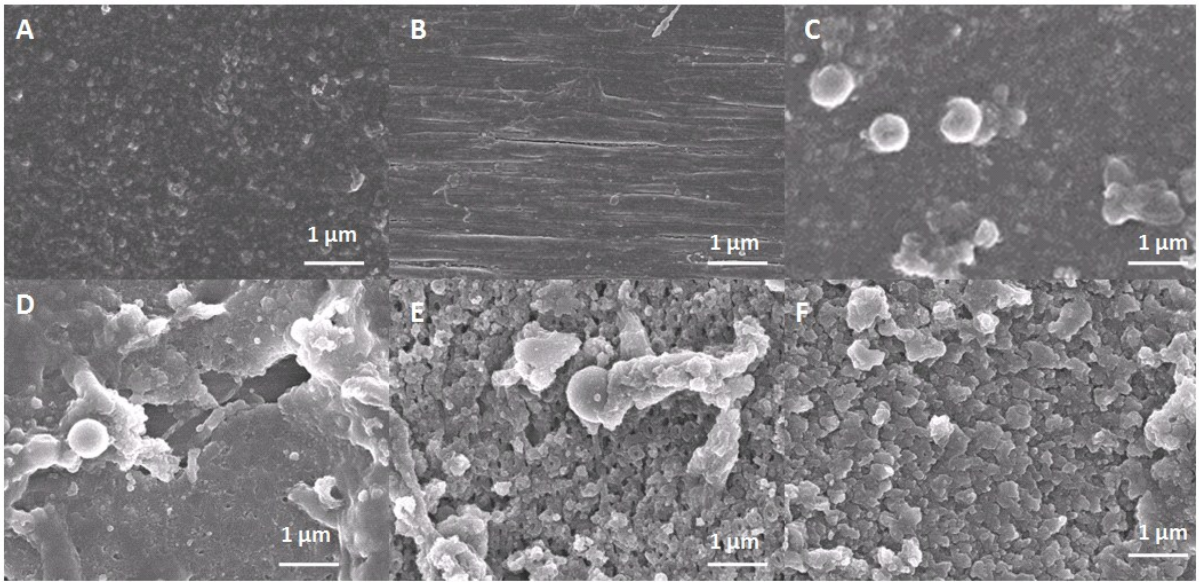
SI Fig. 4: FTIR spectra of three different PSS derivatives: (top) PSS-ene; (middle) PSS and (bottom) PSS(SO_2Cl). (*) indicate characteristic bands from unmodified PSS



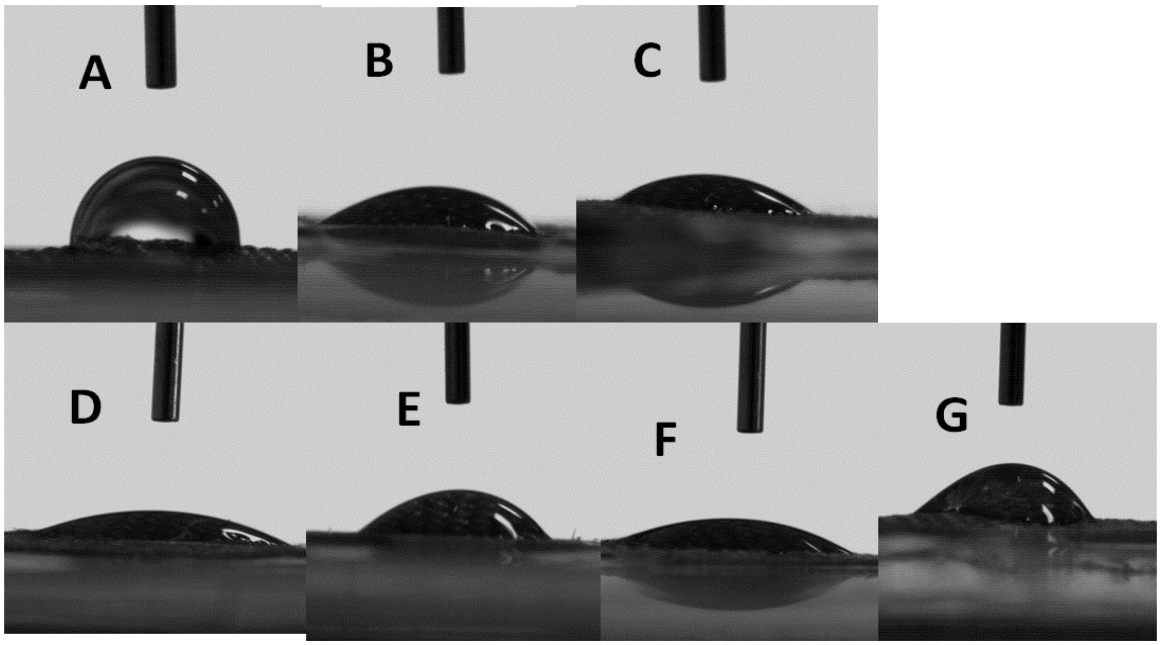
SI Fig. 5: Equilibrium frequency shift as a function of number of layers PAH-ene/PSS-ene deposited, according to QCM measurements.



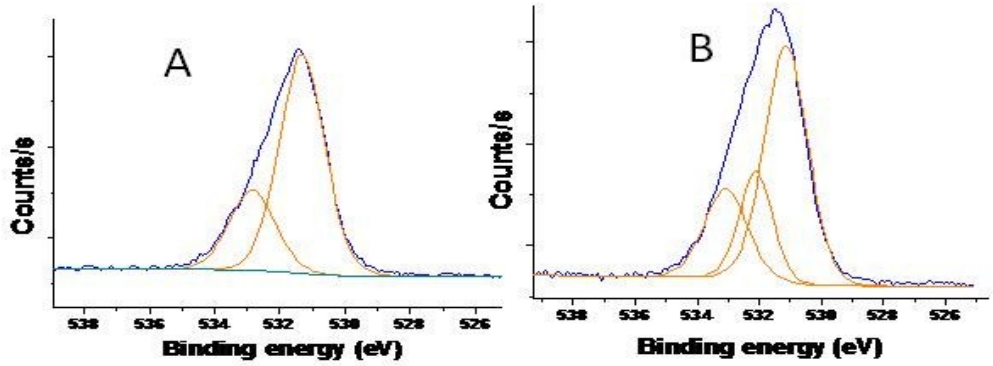
SI Fig. 6: FTIR spectra of pristine AMX membrane (A), AMX modified with anilinium derivative **4** after washing with distilled water and with EtOH (B), and AMX modified with anilinium derivative **4** after washing with distilled water (C). The arrows indicate new bands, as compared to the spectrum of pristine AMX membrane.



SI Fig. 7: SEM images of AMX membrane after different steps of modification: (A) pristine AMX membrane; (B) AMX-ene (AMX after chemical reduction of aryldiazonium salt derived from **4**); (C) AMX-ene after deposition of the first PSS-ene layer; (D) AMX-ene + 1 bilayer (PSS-ene/PAH-ene) ; (E) AMX-ene + $(PSS\text{-}ene/PAH\text{-}ene)_2$; (F) : AMX-ene + $(PSS\text{-}ene/PAH\text{-}ene)_7$.



SI Fig. 8: WCA images of membranes after differents stages of treatment. (A) AMX-ene; (B) uncrosslinked AMX-ene modified with $(PSS\text{-}ene/PAH\text{-}ene)_{5,5}$; (C) crosslinked AMX-ene modified with $(PSS\text{-}ene/PAH\text{-}ene)_{5,5}$ using PEG-diSH as a crosslinker; (D) crosslinked AMX-ene$(PSS\text{-}ene/PAH\text{-}ene)_{5,5}$ with PEG-diSH as crosslinker after immersion in an acidic solution (pH 1) for 10 days; (E) blank experiment: uncrosslinked AMX-ene modified with $(PSS\text{-}ene/PAH\text{-}ene)_{5,5}$ after immersion in an acidic solution (pH 1) for 10 days; (F) crosslinked AMX-ene modified with $(PSS\text{-}ene/PAH\text{-}ene)_{5,5}$ using PEG-diSH as a crosslinker after immersion in a saturated NaCl solution for 10 days; (G) blank experiment: uncrosslinked AMX-ene modified with $(PSS\text{-}ene/PAH\text{-}ene)_{5,5}$ after immersion in a saturated NaCl solution for 10 days.



SI Fig. 9: High resolution XPS spectra in the O1s region of AMX-ene modified with uncrosslinked (PSS-ene/PAH-ene) $_{5.5}$ film (A) and AMX-ene modified with crosslinked (PSS-ene/PAH-ene)$_{5.5}$ film (**B).**

SI Table 1: Ratios of S2p from different sulfur-containing species present on modified AMX membranes after different stages of treatment.

Figure 9	**Main peak (166- 171 eV) S2p from -SO_3^- & -SO_2NH- groups**	**Additional peak (162-165 eV) S2p from - SH and -C-S-C- groups**
A	100 %	0 %
B	89.5 %	10.5 %
C	93.5 %	6.5 %
D	91.8 %	8.20 %
E	100 %	0 %