Electronic Supplementary Information for:

Immobilization Of Quaternized Polymers on Bacterial Cellulose by Different Grafting Techniques†

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Contents

S1. Measurements details

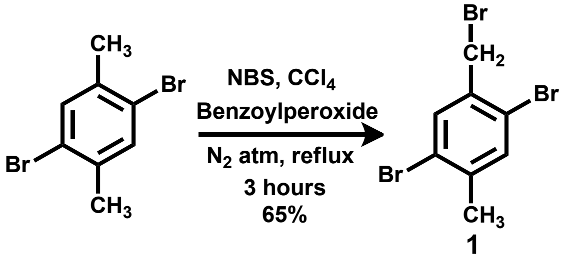
FT-IR spectra of solids, liquid compounds and films were recorded by using the JASCO-FT/IR-4200 type A spectrometer. The ^{1}H, ^{13}C, DEPT-135 and ^{31}P NMR spectra are recorded using a Bruker 400 MHz NMR spectrometer.The Solid state ^{13}C NMR spectra of powder formed BC and QBC surfaces were recorded at 400 MHz with Bruker Advance - III spectrometer and the CP/TOSS experiment with5000 scans and at a spinning speed of 5kHz on double resonance 4 mm MAS probe to get the side band free spectrum. UV-visible absorbance study for solution was carried out on Varian Carey 50 Bio UV−visible spectrophotometer. XRD patterns of polymer solids and BC surfaces were measured in Rigaku mini flex-II desktop instrument. Thermal stability of materials wasmeasured by Thermo gravimetric analysis (TGA), which were carried outinModel STA 449 F3 Jupiter NETZSCH Instruments, under N_2atmosphere. Differential Scanning Calorimetryexperiments were performed by using Netzsch DSC 214 Polyma with a heating rate at 10 °C/min under N_2 atmosphere. Elemental analysis was done in ElementarVario micro cube CHNS instrument. Thesmall angle X-ray scattering analysis of BC surfaces was recorded in antonparr SAXS space instrument (Instrument parameter: X-ray source-1.54 Å, SDD distance-120 mm, acquisition time-10 mins).Fluorescence images were captured by LEICA DMi8 fluorescence microscope instrument with 40X objective lens. SEMimages were captured on Carl Zeiss-ultra55. Atomic force microscopic (AFM) data were recorded for the surfaces on glass surfaces through Nova 1.0.26 RC1 atomic force microscope in semi-contact mode with NT-MDT solver software..The wettability of surface-bound polymers was measured through water contact angle measurement (Holmarc model HO-IAD-Cam-01B) and the mechanical property of BC surfaces were carried out by INSTRON 3369/J7257 tensile meter.

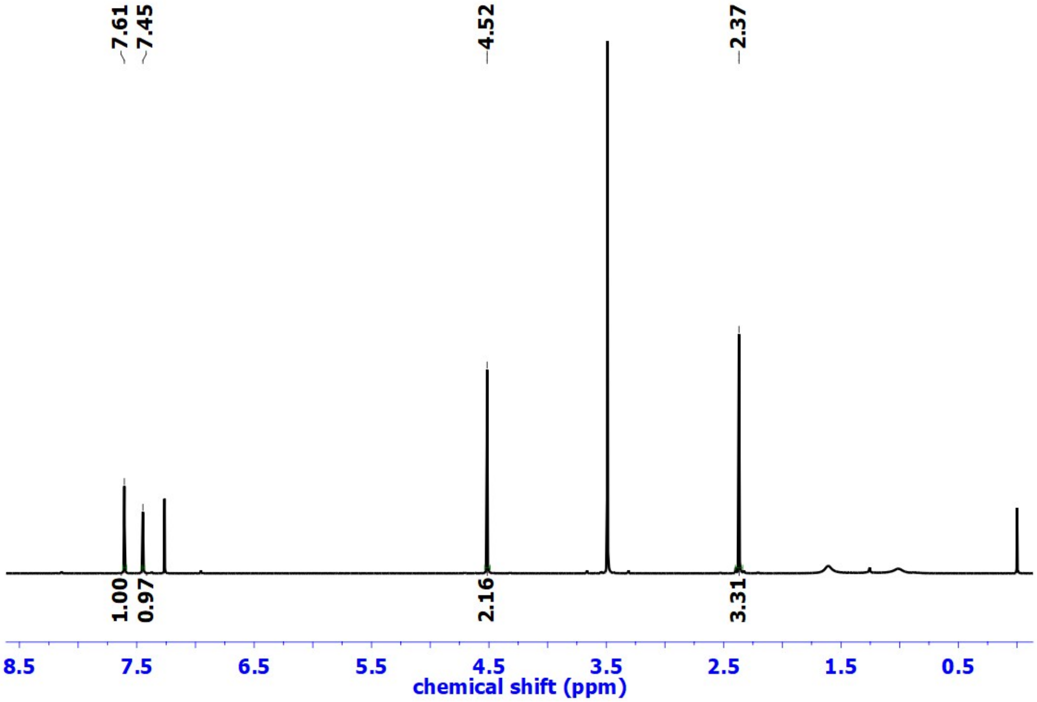
S2. Synthetic Procedure

S2.1. synthetic procedure of 1,4-dibromo-2-(bromomethyl)-5-methylbenzene (compound 1):

The compound was prepared following a modified literature procedure[1]. In a clean and dry 100 mL single neck round bottom flask was charged 2,5-dibromo-p-xylene (2g, 7.75 mmol), 10 mg of benzoylperoxide and 30 mL of carbon tetrachloride and degassed with N_2 gas. 1.61g (9.09 mmol) of NBS was added and again reaction mass was degassed with N_2 gas. It was then refluxed for 3 hours followed by charging with 200 mL of water and 50 mL of chloroform. It was stirred for 15 min, organic layer was separated, dried with anhydrous sodium sulphate and distilled out the solvent. The resulting crude solid was purified by column chromatography using hexane solvent. Finally, we got pure white color solid (1.23g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz) Chemical shift : 7.61 (s, 1H, Ar-H), 7.45 (s, 1H, Ar-H), 4.52(s, 2H, bz-CH_2), and 2.37 (s, 3H, bz-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz) Chemical shift : 140.38, 136.13, 134.95, 134.42, 123.88, 122.83, 32.14, and 22.43 ppm.

Reaction Scheme.S1:





FigureS1:^{1}H NMR spectrum of 1,4-dibromo-2-(bromomethyl)-5-methylbenzene

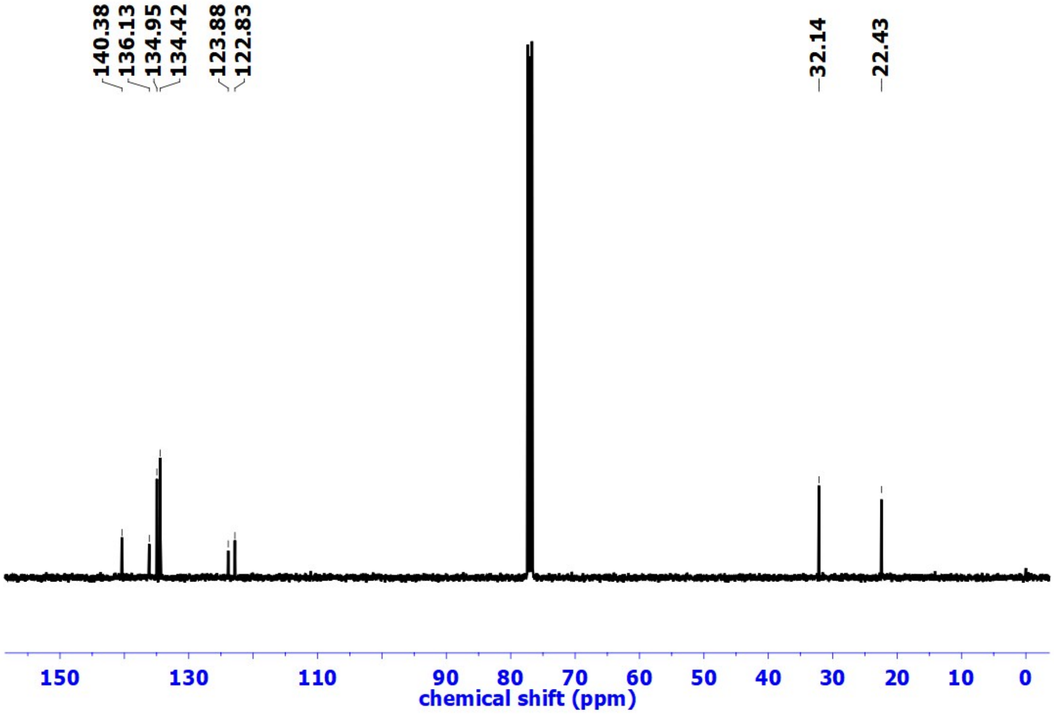


Figure S2: ^{13}C NMR spectrum of 1,4-dibromo-2-(bromomethyl)-5-methylbenzene

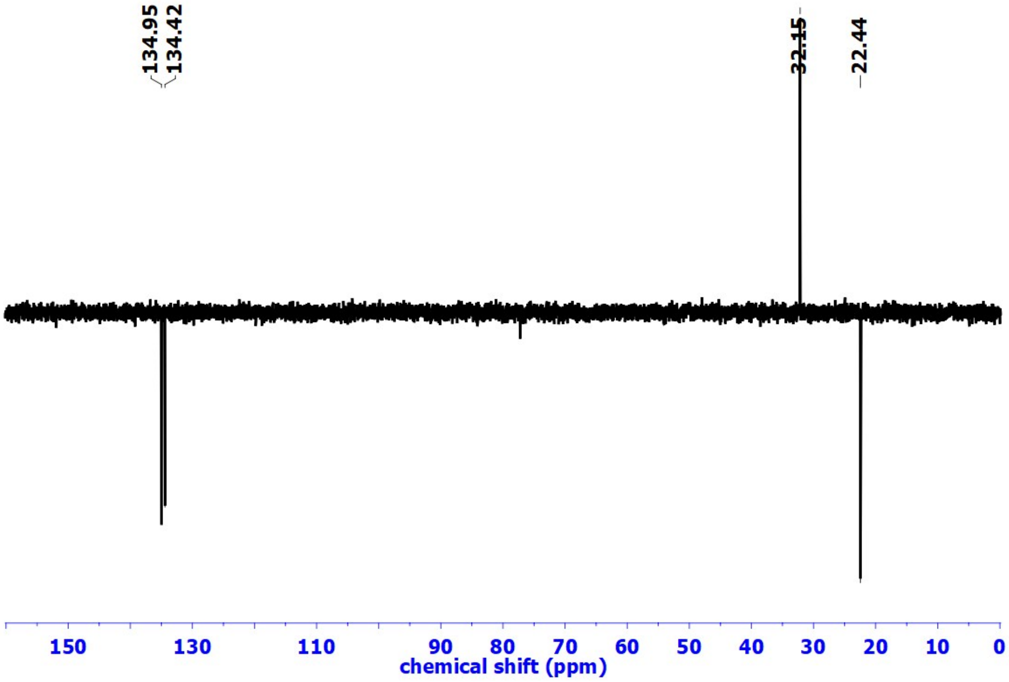
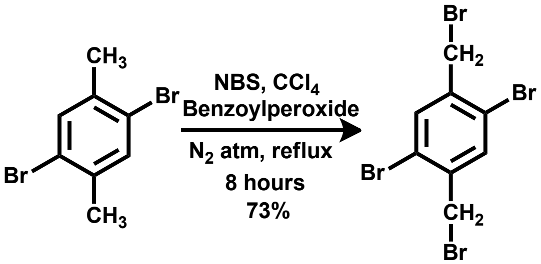


Figure S3: ^{13}C DEPTNMR spectrum of 1,4-dibromo-2-(bromomethyl)-5-methylbenzene

S2.2. synthetic procedure of 1,4-dibromo-2,5-bis(bromomethyl)benzene (compound 2):

In a clean and dry 100 mL single neck round bottom flask, was Charged 2,5-dibromo-p-xylene (2 g, 7.75 mmol), 20 mg of benzoyl peroxide and 50 mL of carbon tetrachloride and degassed with N_2 gas[1]. 3.22 g (18.18 mmol) of NBS was added and again reaction mass was degassed with N_2 gas. Then started heating at reflux condition (80^{0}C) and maintained the reaction condition for 8 hours in N_2 atmosphere. After completing the reaction, it was charged with 200 mL of water and 50 mL of chloroform and stirred for 15 minutes and organic layer was separated. The chloroform layer was dried with anhydrous sodium sulphate and distilled out the solvent. The crude solid was purified by column chromatography using 2% chloroform in hexane solvent mixture. Finally, we got pure white color solid (1.23 g, 65 %). ^1H NMR ($CDCl_3$, 400 MHz) Chemical shift : 7.66 (s, 2H, Ar-H), and 4.51(s, 4H, bz-CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz) Chemical shift : 139.01, 135.38, 123.31, and 31.48 ppm.

Reaction Scheme. S2:



2

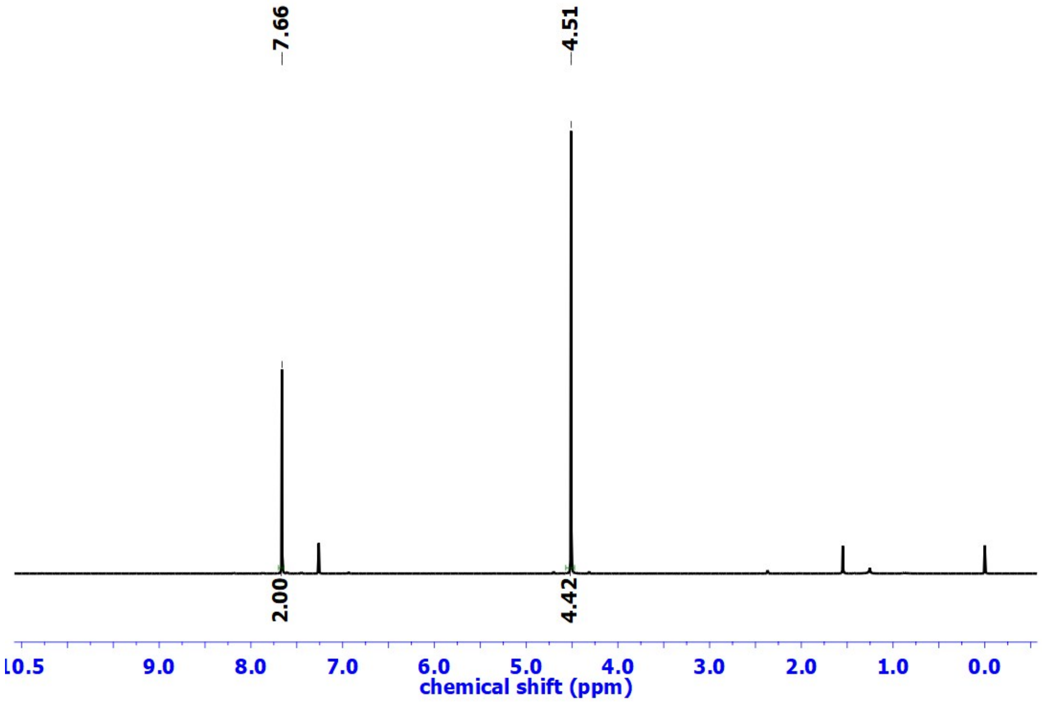


Figure S4: ^{1}H NMR spectrum of 1,4-dibromo-2,5-bis(bromomethyl)benzene

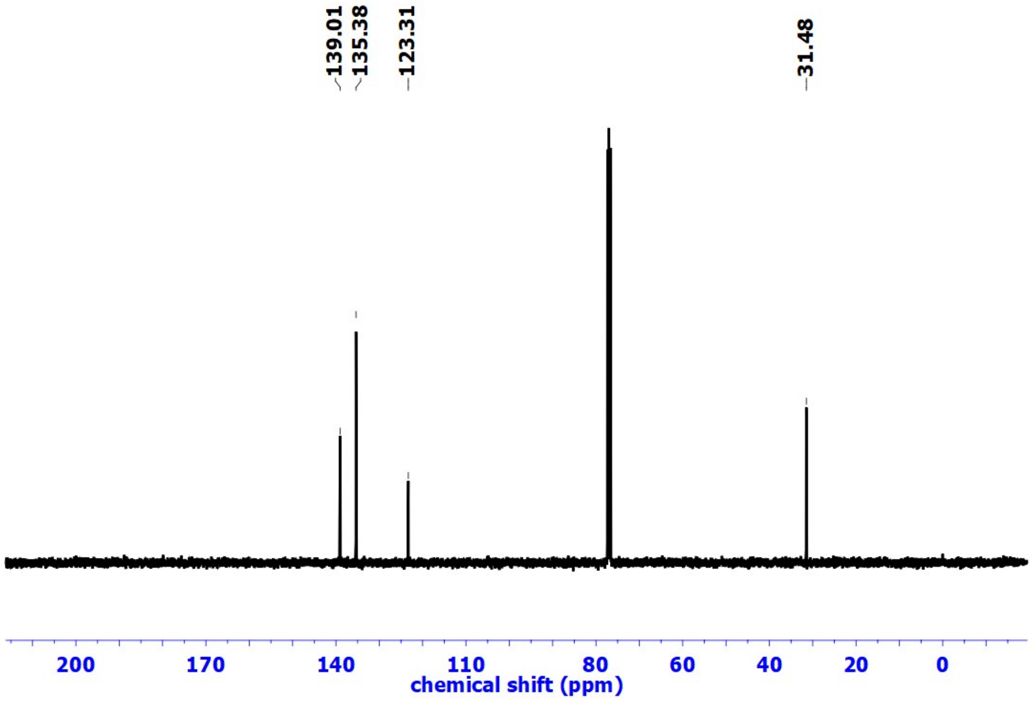


Figure S5: ^{13}C NMR spectrum of 1,4-dibromo-2,5-bis(bromomethyl)benzene

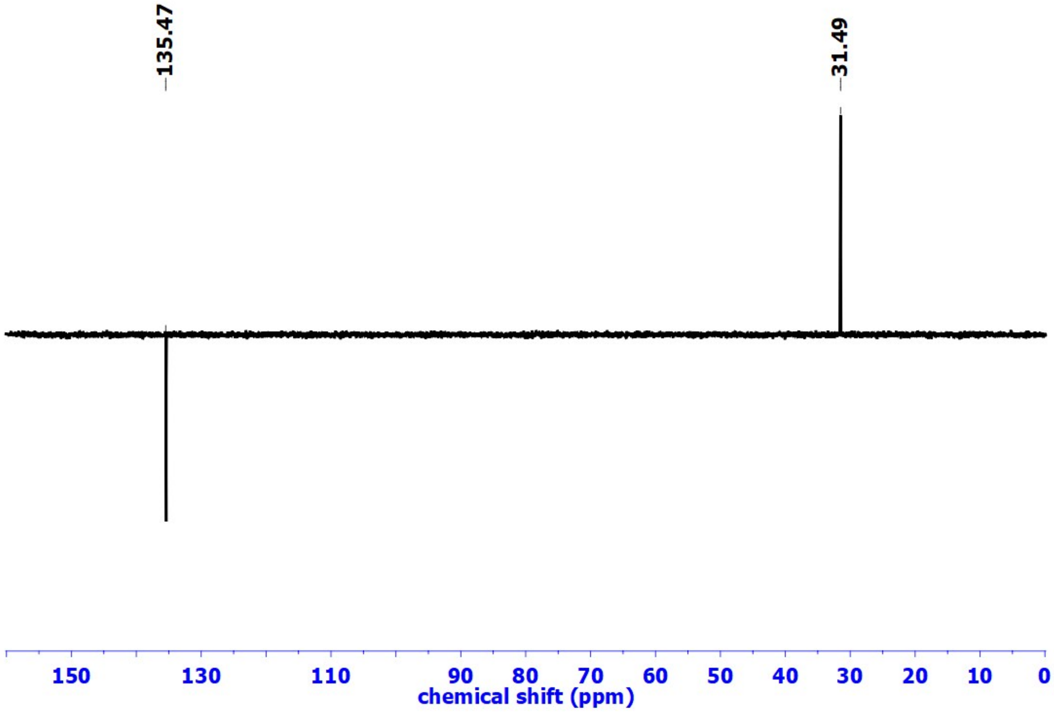
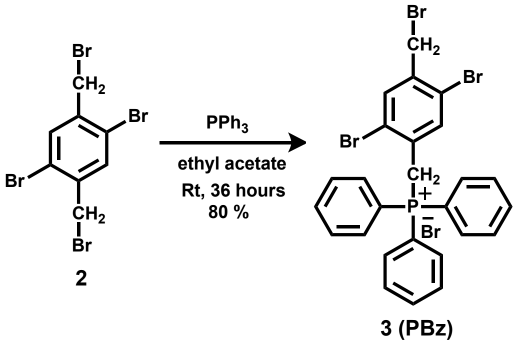


Figure S6: ^{13}C DEPT NMR spectrum of 1,4-dibromo-2,5-bis(bromomethyl)benzene

S2.3. Synthetic procedure of (2,5-dibromo-4-(bromomethyl)benzyl)triphenyl phosphonium bromide (compound 3PBz):

We took a 50 mL round bottom flask and charged 500 mg (1.18 mmol) of compound 2, 321.77 mg (1.22 mmol) of triphenylphosphine and 20 mL of ethyl acetate and it was tightly closed with lid. The reaction medium was maintained at room temperature for 36 hours[2]. After that the reaction mass was filtered and washed with ethyl acetate. The crude solid was dissolved in chloroform and reprecipitated with diethyl ether. We got white solid (80%) after drying at 60°C for 6 hours. ^{1}H NMR ($CDCl_3$, 400 MHz) Chemical shift: 7.82-7.64 (m, 16H, Ar-H), 7.46 (s, 1H, Ar-H), 5.81(d, 2H, bz-CH_2), and 4.45 (s, 2H, CH_2-P^+-$(C_6H_5)_3(Br^-)$) ppm. ^{13}C NMR ($CDCl_3$, 100.64 MHz) Chemical shift: 140.38, 136.13, 134.95, 134.42, 123.88, 122.83, 32.14, and 22.43 ppm. ^{31}P NMR ($CDCl_3$, 202 MHz) chemical shift: 24.66 (s, 1P, P^+-$(C_6H_5)_3(Br^-)$). FT-IR (KBr) Stretching frequency: 3130, 2910, 2844, and 1647 cm^{-1}.

Reaction Scheme. S3:



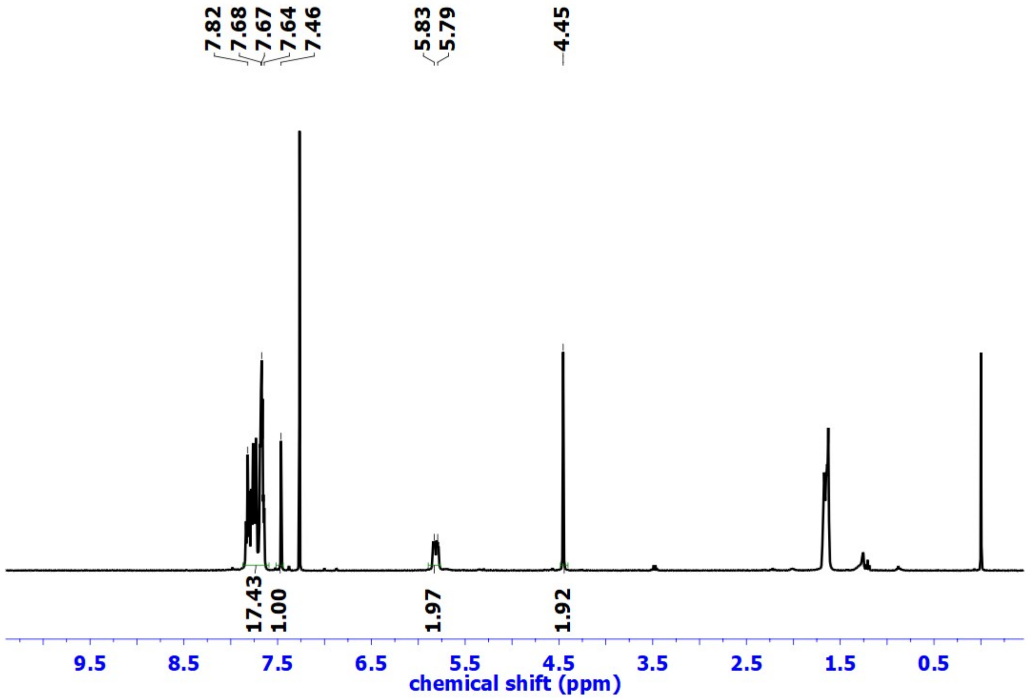


Figure S7: ^{1}H NMR spectrum of (2,5-dibromo-4-(bromomethyl)benzyl)triphenylphosphonium bromide

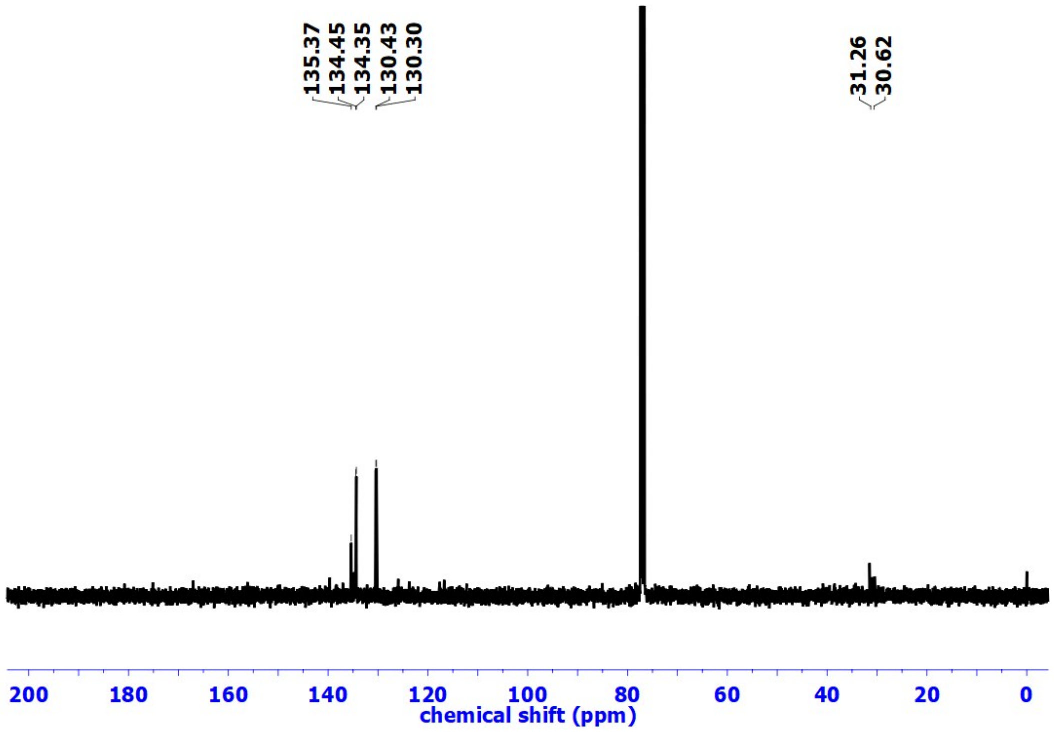


Figure S8: ^{13}C NMR spectrum of (2,5-dibromo-4-(bromomethyl)benzyl)triphenylphosphonium bromide

S3. Polymer characterization

S3.1. NMR spectra of P4VP, QP4VP-Bz and QP4VP-PBz polymer

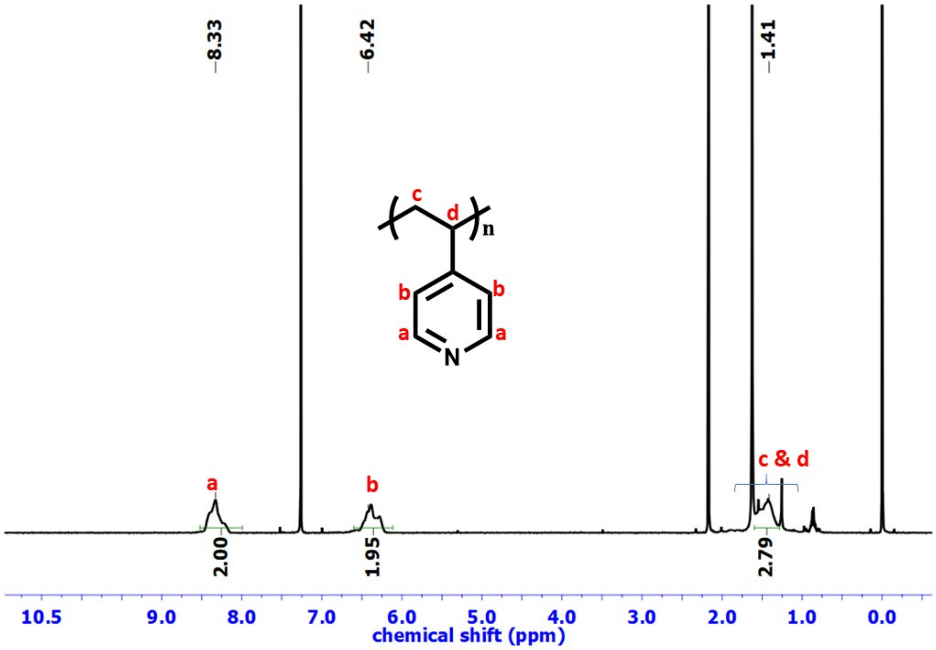


Figure S9: ^{1}H NMR spectrum of poly-4-vinyl pyridine (P4VP) polymer

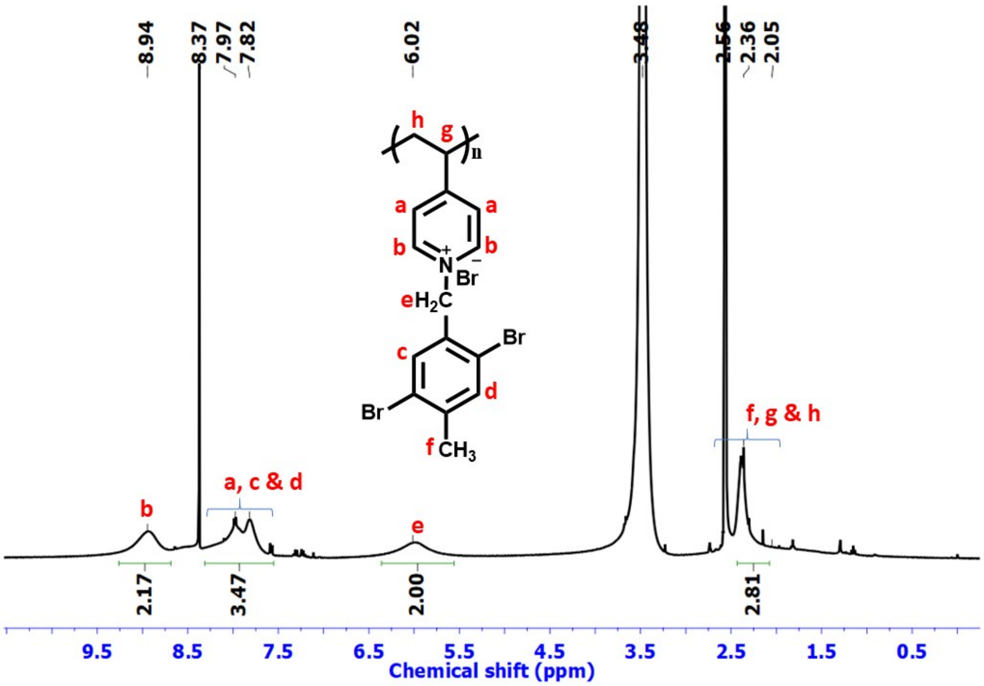


Figure S10: ^{1}H NMR spectrum of QP4VP-Bz polymer

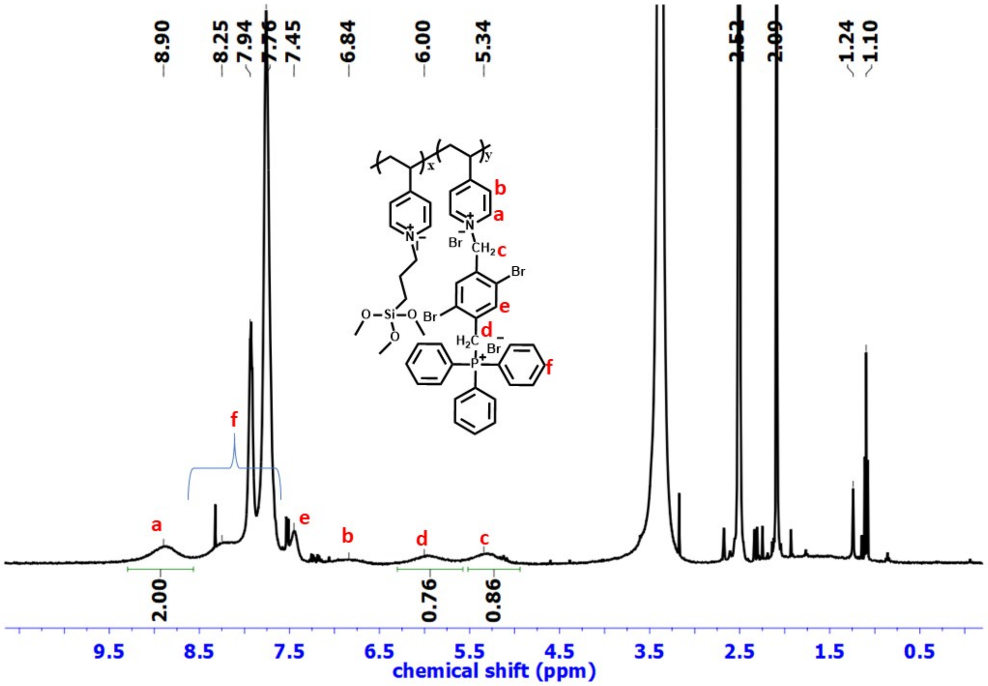


Figure S11: ^{1}H NMR spectrum of QP4VP-PBz polymer

S3.2. Fluorescence microscope analysis of QP4VP-PBz polymer

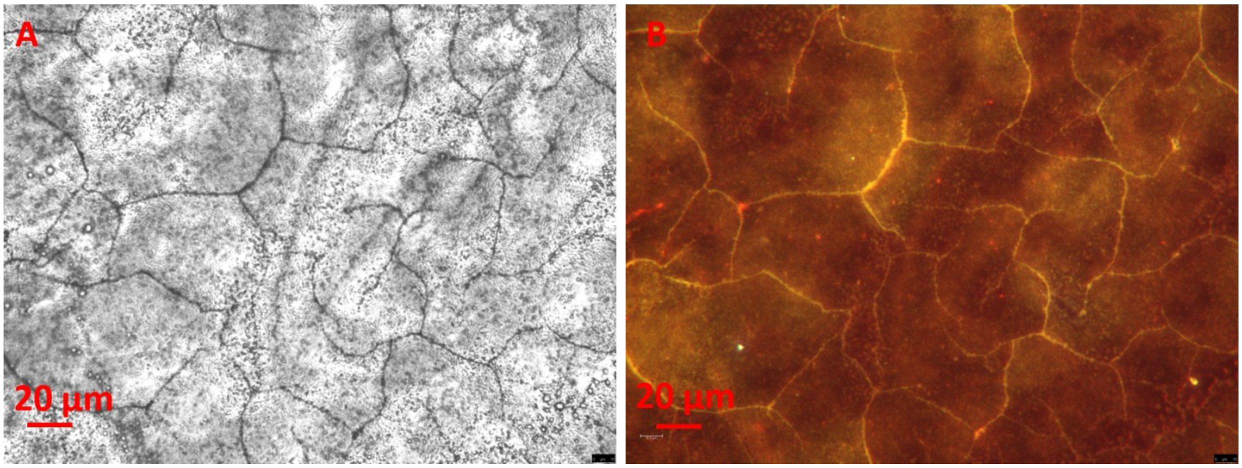


Figure S12. (A) Bright field image and (B) fluorescence image of QP4VP-PBz polymerthin film (in glass surface) using 40X objective lensin 365 nm excitation.

S4. Bacterial cellulose surface characterization:

S4.1. CHNS Elemental analysis

Table S1. Elemental composition of BC materials (beforeandafter reaction)

S.NO	Surfaces	N (%)	C (%)	H (%)
1	BC	0.0000	43.0547	7.1972
2	BCTMS	0.0000	36.6759	6.1382
3	QBC	2.1814	39.3293	5.5315
4	QBCP	1.1241	41.4146	5.6794

S4.2. SEM images of BC and BCC surfaces:

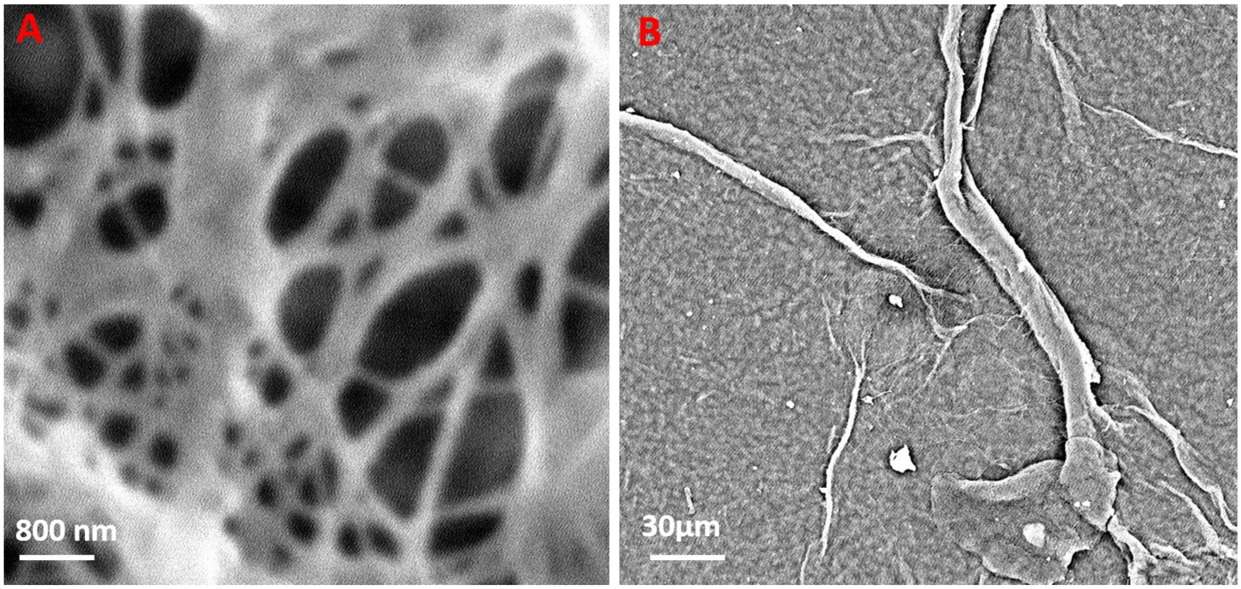


Figure S13: SEM images of (A) BC and (B) BCC surfaces

S4.3. Procedure for calculating the density of quaternary ammonium groups on the pristine (BC and BCC) and polymer functionalized surfaces (QBC, QBCC, QBCP and QBCCP):

We took pristine surfaces (BC and BCC), “graft to” surfaces (QBC and QBCC) and “direct graft” surfaces (QBCP and QBCCP) with size 1 cm **x** 1 cm square shape in the 100 mL glass beaker. Then 20 mL of 1% florescein sodium salt solution (in distilled water) was added and put under 10 minutes sonication. After fluorescein sodium salt solution treatment, the surfaces colour was turned to reddish (except BC and BCC surfaces). After that the surfaces were washed with more amount of distilled water until the colourless solution was obtained. Then the bounded fluorescent counterions was desorbed from the QP4VP and QPVPP polymer grafted surfaces by immersing (under 15 minutes sonicating) with 5 mL 0.5 % of freshly prepared hexadecyltrimethyl ammonium chloride solution and this procedure was repeated for 5 times with total 25 mL of solution. Every 5 mL solution was collected in one standard measuring flask and pH of the solution was adjusted at 9 by using saturated sodium bicarbonate solution. The absorbance of final solution (Figure S13) was measured at 501 nm to calculate the density of quaternary ammonium groups present in per area by using Beer-Lambert law (reference 3).

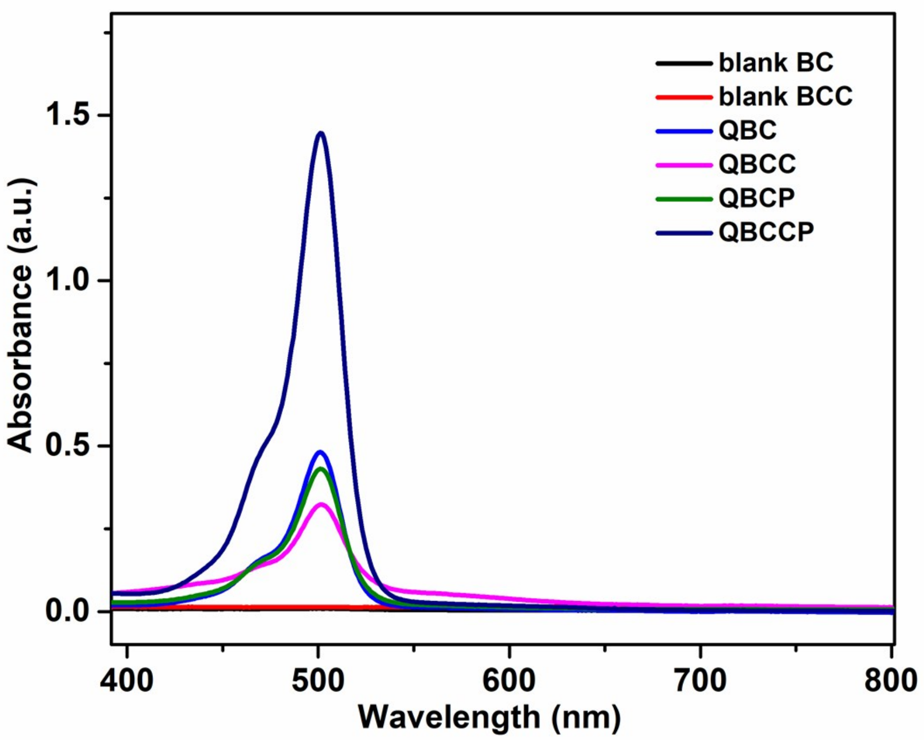


Figure S14. Uvvis spectra of cetyl ammonium bromide solution after fluorescent ion exchanges from functionlized (fluorescent ion treated) surfaces.

Table S2: Density of quaternary ammonium group present on blank surfaces and polymer (P4VP and QP4VP-PBz) functionalized BC and BCC surfaces.

Surfaces	**Density of N^+/ cm^2**	**Surfaces**	**Density of N^+/ cm^2**
BC	0	BCC	0
QBC	0.050×10^{15}	QBCC	0.035×10^{15}
QBCP	0.047×10^{15}	QBCCP	0.16×10^{15}

S4. 4. AFM analysis of BC fiber

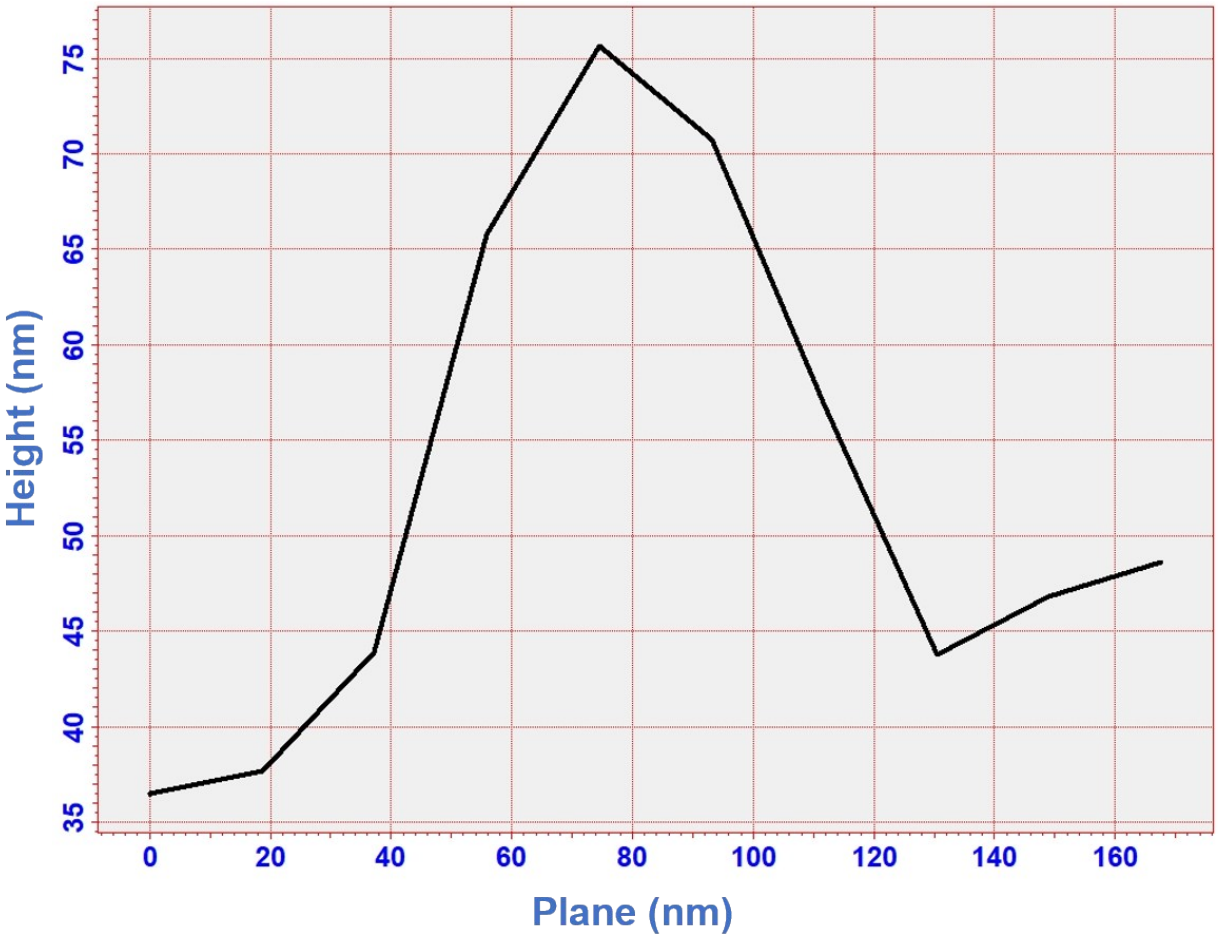


Figure S15. AFM height profile spectra of BC single fiber

S4.5. SAXS analysis procedure

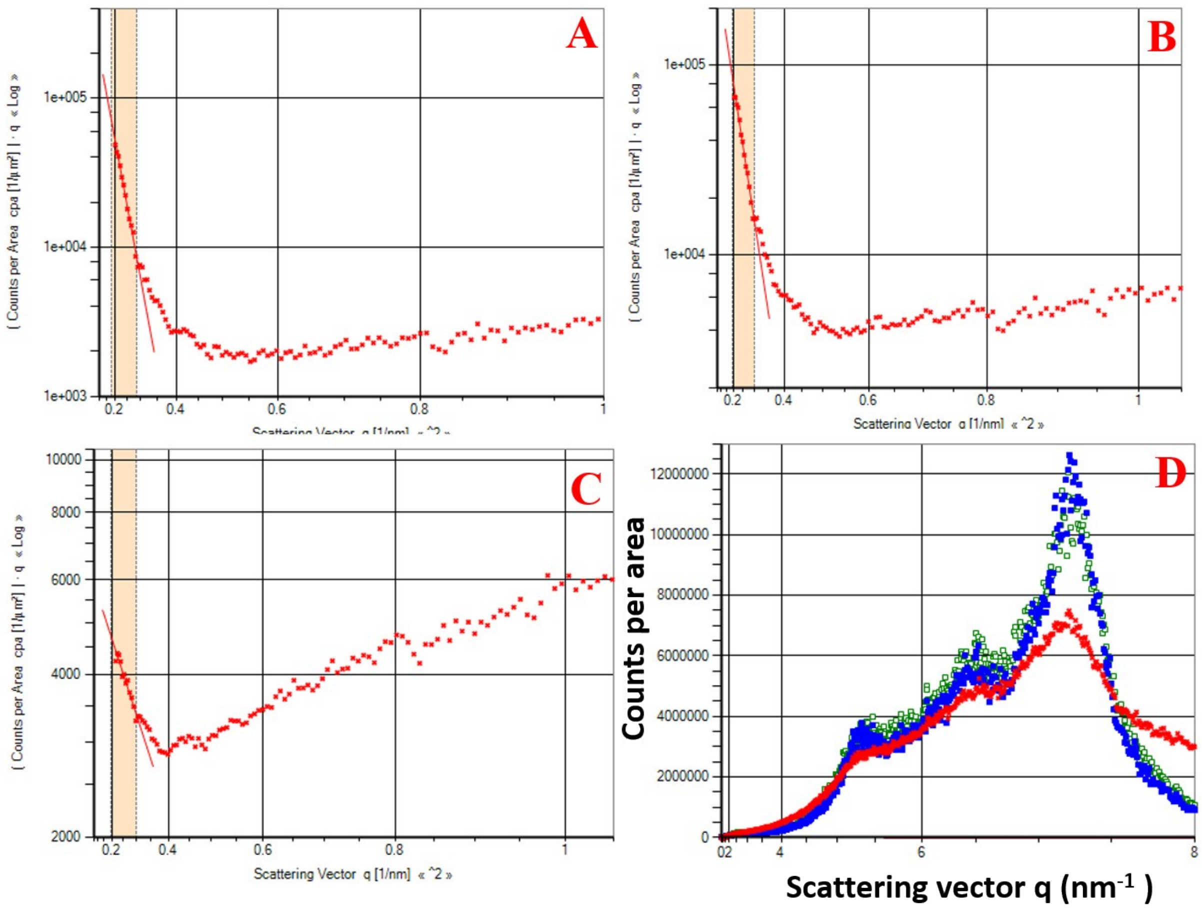


Figure S16. SAXS analysis: Guinier plot of (A)BC, (B)BCTMS, and (C)QBC and (D)their combinedporodplots ofBC (blue curve), BCTMS (green curve) and QBC (red curve)

S4.6. Mechanical strength study of BC and QBC surfaces

Table S3. Mechanical strength data of BC and QBC film surfaces

Surface	Maximum load (N)	Tensile strength (MPa)	Elongation at break (%)	Extension at maximum load (mm)	Thickness (mm)
BC	12.08	5.75	4.72	1.42	0.21
	12.61	5.48	7.45	2.23	0.23
	26.93	10.36	22.39	6.72	0.26

QBC	32.61	10.19	21.00	6.30	0.27

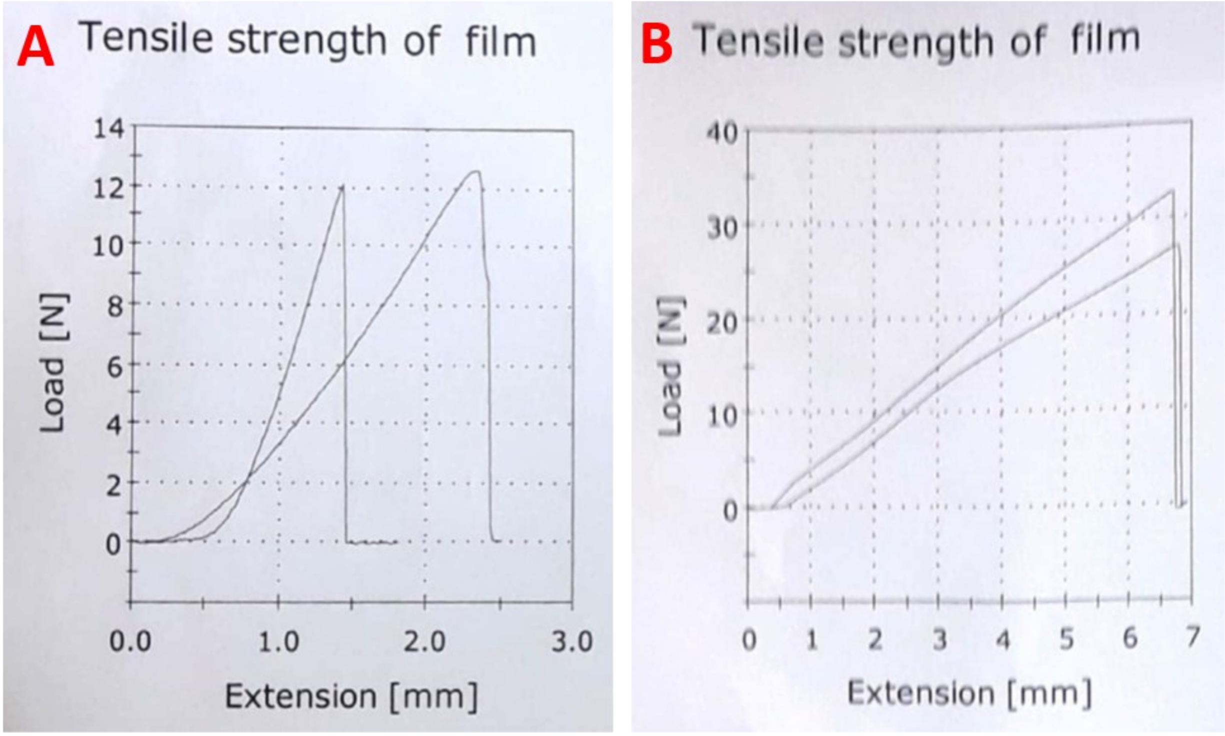


Figure S17. Tensile strength data of (A) BC and (B) QBC surfaces

S5. References:

1. C. Näther, I. Jess, P. Kuśb, and P. G. Jones, *CrysEngComm.,* 2016, **18**, 3142.
2. L. Zhang,Q. Tang, R. A. Weiss, and K. A. Cavicchi, *Polym. Chem.,* 2014, **5**, 5492.