

Hollow polymer nanocapsules with ferrocenyl copolymer shell

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Section 1

Materials

Tetraethylorthosilicate (TEOS, 99%), (3-aminopropyl) triethoxysilane (APTES, 99%), 3-mercaptopropionic acid (99%), benzylbromide (98%), sodium hydride (NaH, 90%), 4-dimethylamino pyridine (DMAP) and 1,3-dicyclohexyl carbodiimide (DCC) were purchased from Sigma-Aldrich and used as received without any further purification. Ferrocene mono carboxylic acid (FcCOOH) was purchased from Nanjing Finetech Chemical, China and used as received. 4-vinylbenzyl chloride (90%), propargyl alcohol (99%) and 2-hydroxyethyl methacrylate (99%) were purchased from Sigma-Aldrich and used after purification using standard procedures. 2, 2-azobis-isobutyronitrile (AIBN, 98%) was purchased from Sigma-Aldrich was recrystallized from methanol before use. Ammonium hydroxide, ethyl alcohol, sodium carbonate, sodium sulphate, dry tetrahydrofuran (AR grade), dichloromethane (AR grade), cyclohexane (AR grade), ether (AR grade), N-Hydroxysuccinimide (NHS, 99.8%), dry dimethylformamide (DMF, AR grade) and HPLC water were purchased from Finar chemicals Ltd, India. Tetrabutylammonium bromide (98%) was purchased from TCI, India. Tetrabutyl ammonium perchlorate (TBAP) was purchased from Across, India and used as received. Hydrofluoric acid (HF, 48%) was purchased from Fischer chemicals, India.

Section 2

Synthesis of chain transfer agent (CTA), 3-Benzylsulfanylthiocarbonylsufanyl-Propionic Acid (BSPA)

In a 250 ml RB flask, 3-Mercaptopropionic acid (5 mL, 5.75 mmol) was added to a stirred solution of potassium hydroxide solution (6.5 g, 11.5 mmol) in water (60 mL). Carbon disulfide (7.5 mL) was then added drop wise to the reaction solution which turned into an orange colour solution. This was further allowed to stir for 5h at room temperature. After that benzylbromide (9.9 g, 5.75 mmol) was added into the reaction mixture and heated for another

12 h at 80 °C. Then, after cooling down to room temperature, chloroform was added and the reaction mixture was acidified with 6(N) hydrochloric acid until the organic layer became yellow. After that, the water phase was extracted with chloroform several times. The obtained organic phase was dried over anhydrous Na₂SO₄ and solvent was evaporated in rotary evaporator. The product was purified by chromatography with a 3:1 hexane/ethyl acetate mixture as an eluent and separated as a yellow powder. ¹H-NMR (CDCl₃): 2.84 (t, 2H), 3.62 (t, 2H), 4.61 (s, 2H), 7.27 (m, 5H), 10.1 (b, 1H, OH). ¹³C-NMR (CDCl₃): 30.7, 32.8, 41.4, 127.7, 128.6, 129.1, 134.6, 177.9, 222.5. ESI-MS (m/z) [M + Na]⁺ calcd for C₁₁H₁₂O₂S₃Na: 295.0, Found: 295.0. Yield: 90%

Synthesis of silica nanoparticles (SiNP)

Silica nanoparticles (SiNP) were synthesized by the well-known Stöber process. To a 1000 mL round bottomed flask, ethanol (400 mL) was added followed by 10 mL of ammonium hydroxide at room temperature. After 10 minutes, HPLC water (10 mL) was added slowly. Then after another 10 minutes, tetraethylorthosilicate (TEOS, 10 mL) was added drop by drop very carefully under vigorous stirring and the reaction solution was continued to stir at constant rate for next 16 hours at room temperature. Just after completion of 16 hours, the formed colloidal solution of silica nanoparticles were collected using centrifugation at 10,000 rpm for 30 min. The particles were re-dispersed in ethanol and washed with HPLC water at least 3 times to wash out the unreacted ammonium hydroxide by centrifugation at 10,000 rpm for 30 min. The pure silica nanoparticles were finally dried at 80 °C for 48 h.

Synthesis of amine modified silica nanoparticles (SiNP-NH₂)

The synthesized SiNP (3 g) were dispersed in dry THF (50 mL) by using ultrasonication for 30 min and then 75 μL of (3-Aminopropyl) triethoxysilane (APTES, 0.3 mmol) was added drop wise under constant stirring and refluxed for next 16 hours at 85 °C. The reaction mixture was then precipitated in hexane and the amine modified SiNP (SiNP-NH₂) were isolated by

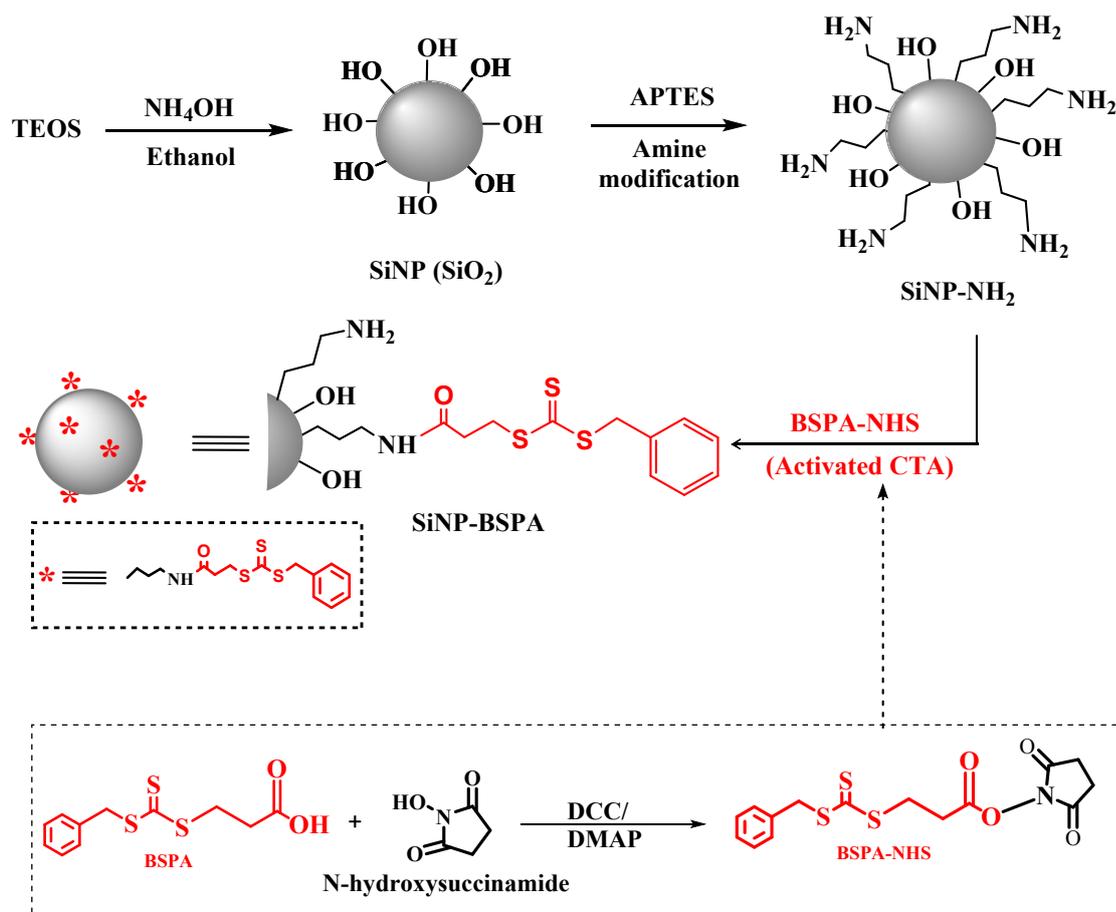
centrifugation at 7000 rpm for 15 min. The particles were re-dispersed in THF and centrifuged at 7000 rpm for 15 min. This process was repeated for three times. The obtained amine modified silica nanoparticles (SiNP-NH₂) were dried under vacuum at 60 °C for 24 h.

Synthesis of activated CTA (BSPA-NHS)

BSPA (0.6 g, 2.2 mmol) was dissolved in dry dichloromethane (30 mL) in presence of N₂ at 0 °C. Catalytic amount of DMAP and 0.664 g of DCC (3.22 mmol) was added and stirred for this process. After 15 minutes of stirring, N-hydroxysuccinamide (NHS) (0.322g, 2.78 mmol) was added and the stirring was continued for next 16 hours at room temperature under nitrogen atmosphere in the dark condition. The volume of the solution was reduced by evaporating to some extent and insoluble product was filtered. The remaining solution was concentrated and was purified by using silica column chromatography in hexane/ethyl acetate using as an eluent. This activated CTA (BSPA) is abbreviated as BSPA-NHS. ¹H NMR (CDCl₃): 2.82 (s, 4H), 3.08 (t, 2H), 3.67 (t, 2H), 4.59 (s, 2H), 7.28 (m, 5H). ¹³C NMR (CDCl₃): 25.5, 30.3, 41.5, 127.8, 128.6, 129.2, 134.5, 166.8, 168.8, 222.2. Yield: 53%

Synthesis of CTA anchored silica nanoparticles (SiNP-BSPA)

SiNP-NH₂ (2 g) were dispersed in dry THF (50 mL) in presence of nitrogen atmosphere. Activated BSPA (BSPA-NHS, 0.3 g, 1.1mmol) in 1 mL of dry THF was added drop wise into the solution while stirring and the reaction mixture was stirred for next 16 h at room temperature in dark condition under inert atmosphere. Finally, the yellow colour reaction mixture was precipitated from a mixture of cyclohexane and diethyl ether 4:1 v/v) and collected by using centrifugation at 3000 rpm for 10 min. This purification cycle was repeated three times and the collected CTA functionalized silica nanoparticles (designated as SiNP-BSPA) was dried under vacuum at room temperature for 24 h. The whole process of synthesizing of SiNP-BSPA is shown in the Scheme S1.

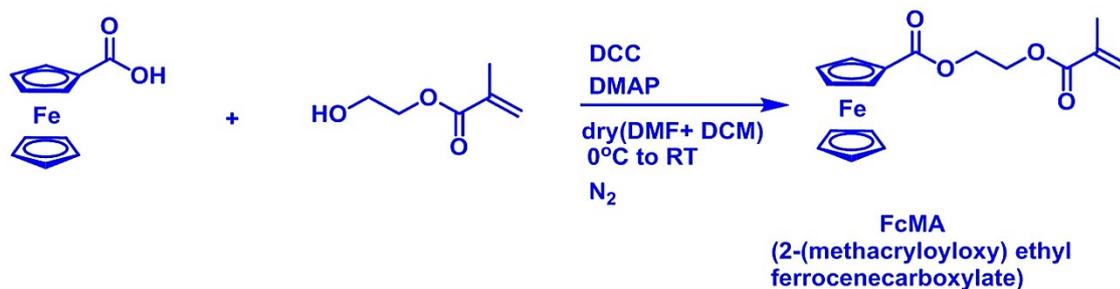


Scheme S1: Synthesis of BSPA functionalized SiNP (SiNP-BSPA)

Synthesis of FcMA

In a two-neck round bottom flask, 1g (4.35 mmol) of ferrocene carboxylic acid (FCA) was added in 15 mL of dry DMF and DCM mixture (1:2) in inert atmosphere. After complete dissolution, catalytic amount of DMAP was added to the stirred solution of FCA at 0°C followed by the addition of 1.345g (6.52mmol) of DCC in three slots. After stirring half an hour, the solution of HEMA (0.68g, 5.216mmol) in dry DCM was added drop-wise and stirred for 24 hours. The progress of reaction is monitored by TLC. After completion of reaction, the reaction mixture was extracted from ether with brine solution. This ether layer was collected & passed through anhydrous sodium sulphate. The crude product was obtained by solvent evaporation & dried. Column chromatography (hexane/ethyl acetate) was done to get the pure product. ¹H NMR (500 MHz, CDCl₃): δ 2.00 (dd, 3H), 4.2 (s, 5H), 4.4 (d, 2H), 4.5 (m, 4H),

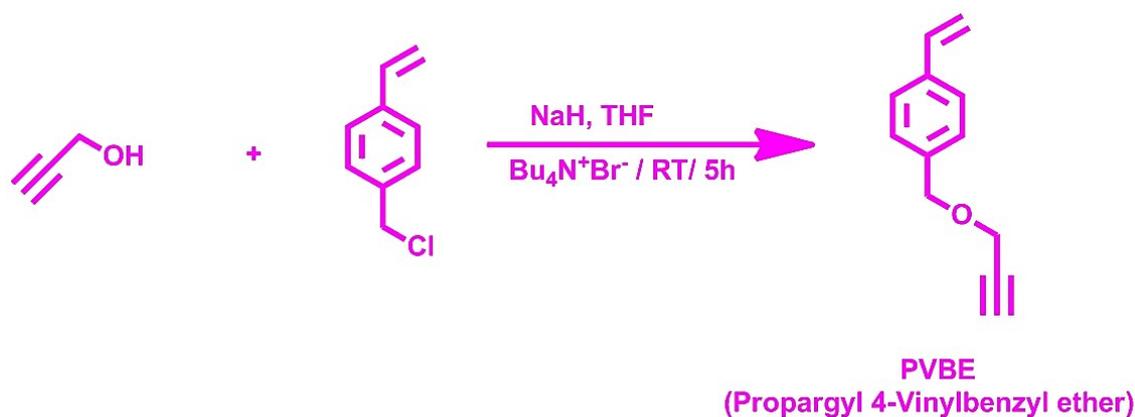
4.8 (d, 2H), 5.65 (dd, 1H), 6.15 (dd, 1H). HRMS-ESI $[M+H]^+$: calculated for $C_{17}H_{18}FeO_4$: 342.0547, found, 342.0546. Yield: 50%



Scheme S2: Synthesis of 2-(methacryloyloxy)ethyl ferrocenecarboxylate (FcMA)

Synthesis of PVBE

To a solution of propargyl alcohol (0.2 g, 3.56 mmol) in dry THF (5 mL) in inert atmosphere, sodium hydride (0.134 g, 5.56 mmol) was added at 0°C and the mixture was stirred for 15 min. After that, the reaction mixture was allowed to come to room temperature and 4-vinylbenzyl chloride (0.544 g, 3.56 mmol) was added followed by the addition of tetrabutylammonium bromide (0.69 g, 2.14 mmol) and after that the reaction was continued to stir at room temperature for next 24 h. After 24h, methanol was added to quench the excess of sodium hydride followed by dichloromethane. The whole mixture was washed with water several times, and the organic phase was dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate). 1H NMR (500 MHz, $CDCl_3$): δ 7.5–7.2 (m, 4H), 6.63 (dd, 1H), 5.78 (d, 1H), 5.30 (d, 1H), 4.65 (s, 2H), 4.20 (s, 2H), 2.51 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 137.5, 137.1 (C–Ar), 136.7, 128.6, 126.5, 114.2, 79.8, 74.9, 71.5, 57.2. HRMS (ESI): calcd for: m/z $C_{12}H_{12}ONa$ $[M + Na]^+$, 195.0786; found, 195.0781. Yield: 59%



Scheme S3: Synthesis of Propargyl 4-vinylbenzyl Ether (PVBE)

Cleaving of the copolymer chains from the silica surface for the molecular weight measurement

The copolymer grafted particles (20 mg) were dispersed in 2 mL of DCM and DMF mixture (3:1) in a 15 ml of Teflon vial. A catalytic amount of phase transfer catalyst tetrabutylammonium bromide was added to the stirred solution followed by the addition of 0.5 mL of 48% HF. The reaction mixture was allowed to proceed for 6 hours at room temperature. The polymer solution was extracted with saturated sodium bicarbonate solution and then finally precipitated with ether. The obtained copolymer was dried under vacuum for 24 hours at room temperature.

Section 3

Characterization techniques

^1H and ^{13}C NMR spectra were recorded on Bruker AV 500 and 400 MHz NMR spectrometer by using CDCl_3 as solvent and TMS as internal standard. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of all samples were recorded using a Nicolet iS5 ATR-FTIR (Thermo scientific, S-3, India) spectrometer. Transmission electron microscopy (TEM) images were captured using FEI (Technai Model No. 2083) TEM machine at an accelerating voltage of 200 kV. The samples were prepared by dispersing polymer samples in DMF

followed by drop casting on carbon coated copper (200 mesh) grids. The hydrodynamic radius of each particle was measured using a Zetasizer Nano S90 (Malvern Instruments, Germany) operating at 4mW He-Ne laser with 633nm wavelength at room temperature. Molecular weights (M. W.) and polydispersity index (PDI) of synthesized block copolymers were analysed by Gel permeation chromatography (GPC) using polystyrene standards and eluted in DMF at flow rate of 0.4 mL/min at 25 °C on a GPC (Waters 515 HPLC) fitted with Waters 2414 refractive index detector and using Styragel HR 2 DMF column. Thermo gravimetric analysis (TGA) of all polymer samples were performed using TGA (TGA Q500, TA instruments, USA) from 30 to 700°C with a heating rate of 10 °C/min under constant nitrogen flow. Cyclic voltammetry (CV) experiments were conducted using a Zahner Zanium electrochemical workstation operated with Thales software, by using a conventional three-electrode system consisting of a Pt working electrode, a Pt wire auxiliary electrode and a Ag wire as reference electrode. CV experiments were carried out after complete dissolution of the polymers in dry DCM in presence of electrolyte TBAP. DVS measurements were analysed by using a Q5000SA vapor sorption analyzer (TA Instruments, Delaware, and USA) at 40 °C. BET experiments were conducted in Autosorb iQ (quantachrome, ADIQC000-4) using nitrogen as adsorbing gas. The powder X-Ray diffraction (PXRD) of the powdered polymer samples were collected from an X-ray instrument (model: Xpert 3 powder) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) source at voltage 40 kV and 45 mA current at a scanning rate of 0.167°/minute in the 2θ range 5°- 85°. The morphology of the dye treated polymer samples were captured using Leica model ZEISS LSM 880 confocal laser scanning microscope (CLSM) with an Ar/Ar-Kr laser as the excitation (488 nm) source. The samples were stained by rhodamine dye for imaging. Coumarin dye treated samples were subjected to fluorescence lifetime imaging microscopic study by using PicoQuant Microtime 200 Time-resolved Confocal Fluorescence Microscope.

Section 4

Table S1: Monomer feed ratio, samples abbreviations and various parameters obtained from GPC analysis for different copolymers *grafted* over SiNP surface

(FcMa:PVBE) (wt %)	Sample name ^a	\bar{M}_n targeted ^b	\bar{M}_n achieved ^c	\bar{D} ^d
1:1	P ₁ Q ₁	10K10K	18,851	1.27
1:1	Q ₁ P ₁	10K10K	17,647	1.3
1:1	rP ₁ Q ₁	10K10K	21,496	1.4
1:3	P ₁ Q ₃	10K30K	32,304	1.35
1:3	Q ₃ P ₁	30K10K	28,326	1.3
1:3	rP ₁ Q ₃	10K30K	42,394	1.44
3:1	P ₃ Q ₁	10K3K	10,455	1.34
3:3:13.1	Q ₁ P ₃	3K10K	10,461	1.24
3:1	rP ₃ Q ₁	10K3K	13,038	1.31

^aP corresponds to FcMA block and Q is PVBE block. The detailed of the sample abbreviations are discussed in the experimental section ^b Targeted number average molecular weight (\bar{M}_n) calculated based on the equation often used in RAFT polymerization and K indicates thousands. ^c \bar{M}_n and ^d dispersity (\bar{D}) are

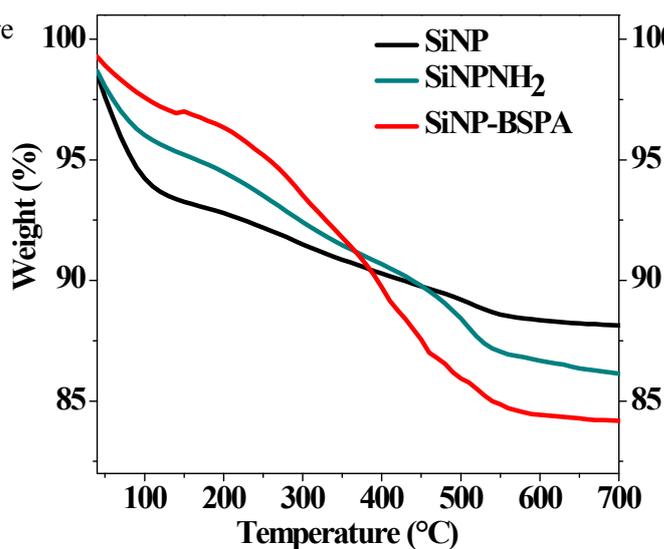


Figure S1: TGA plots of SiNP, SiNP-NH₂ and SiNP-BSPA.

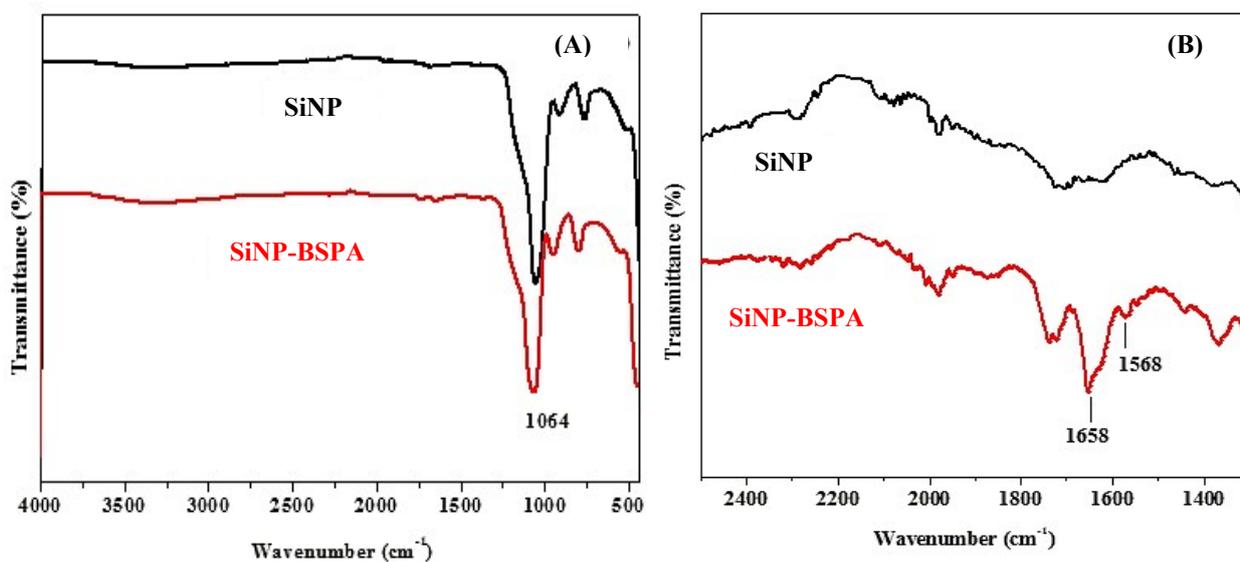


Figure S2: FTIR spectra (A) of SiNP and SiNP-BSPA and zoomed portion (B) to show the BSPA functional group peaks.

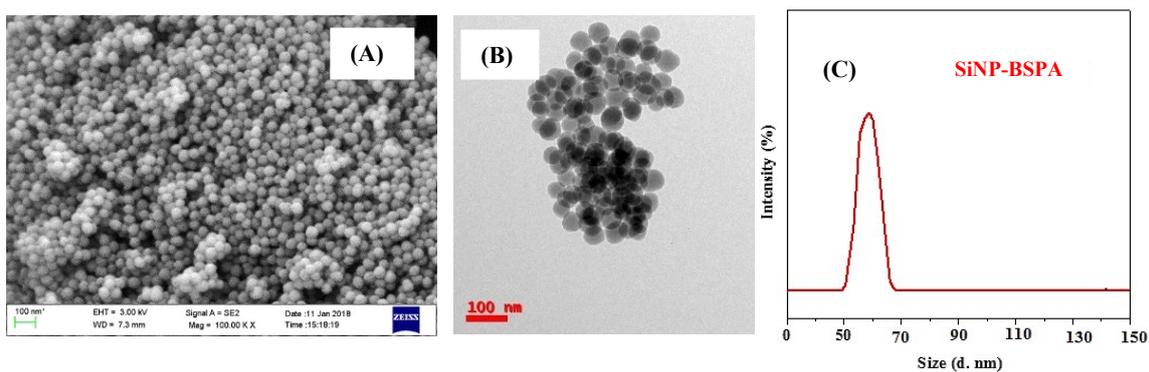


Figure S3: (A) FESEM, (B) TEM images and (C) DLS plot of SiNP-BSPA.

Section 5

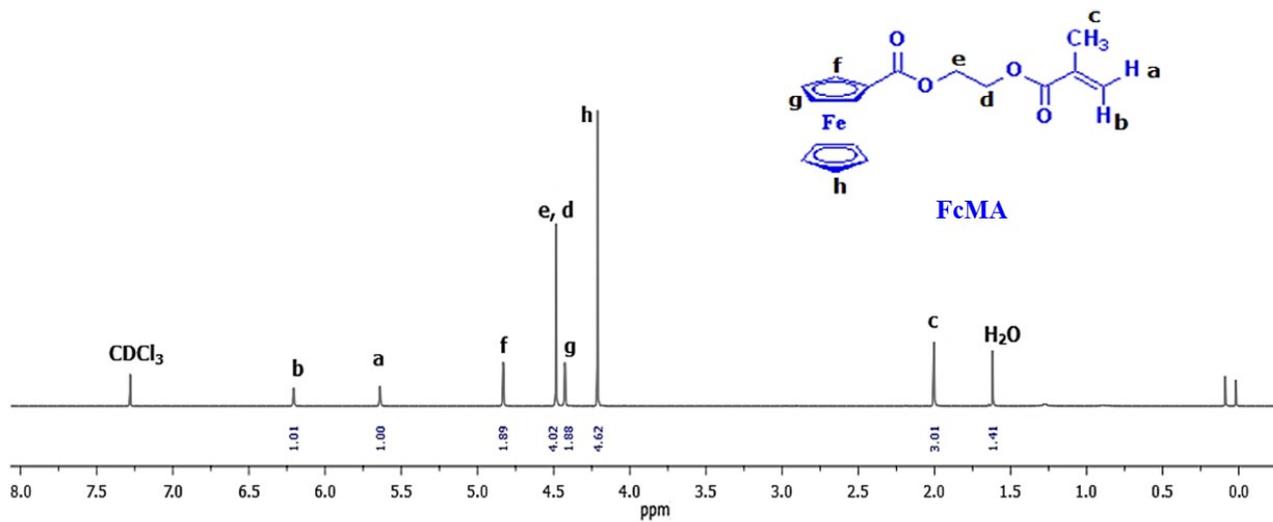


Figure S4: ¹H-NMR spectra of 2-(methacryloyloxy)ethyl ferrocenecarboxylate (FcMA)

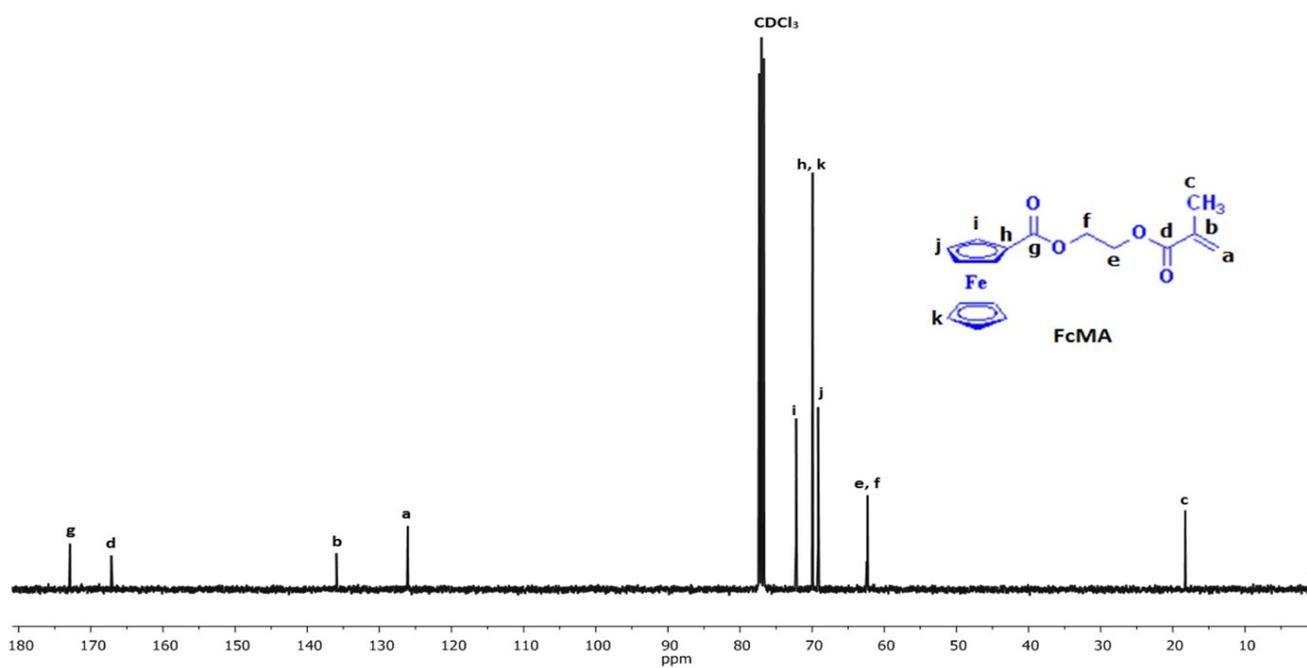


Figure S5: ¹³C-NMR spectra of FcMA

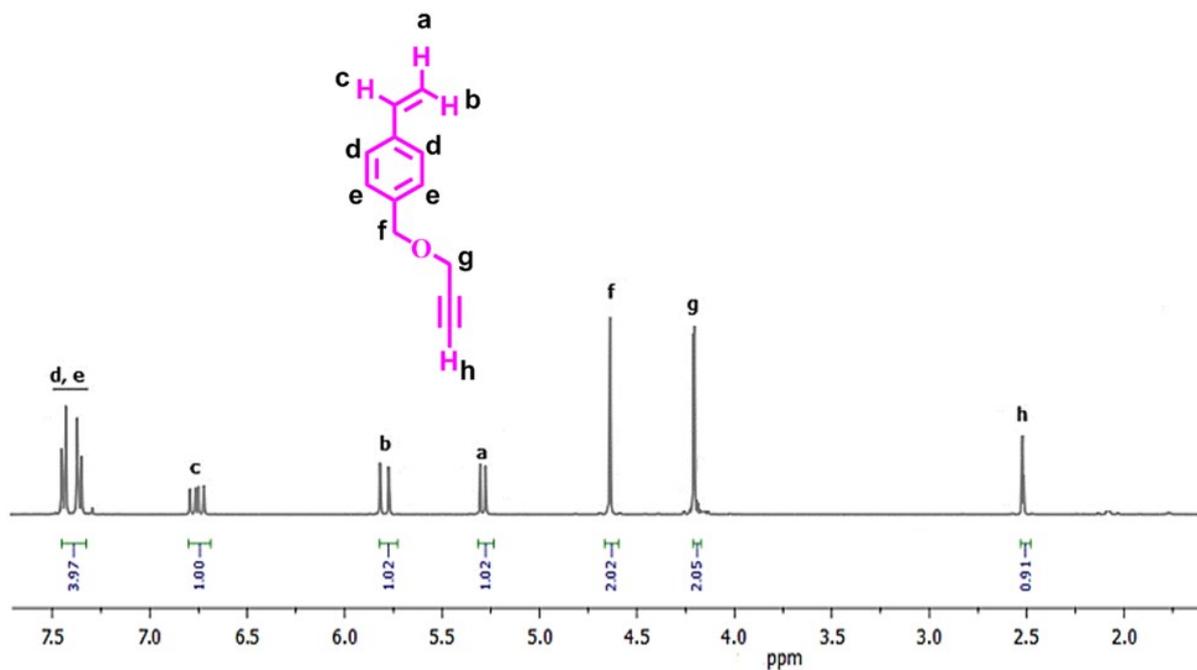


Figure S6: ¹H-NMR spectra of Propargyl 4-vinylbenzyl ether (PVBE)

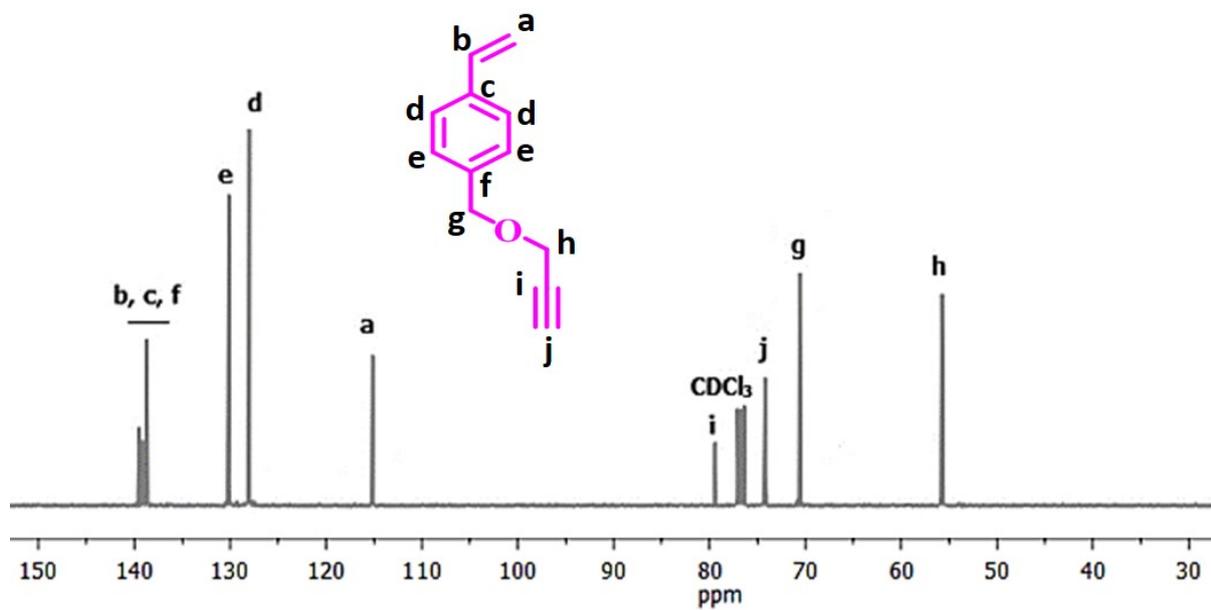


Figure S7: ¹³C-NMR spectra of PVBE

Section 6

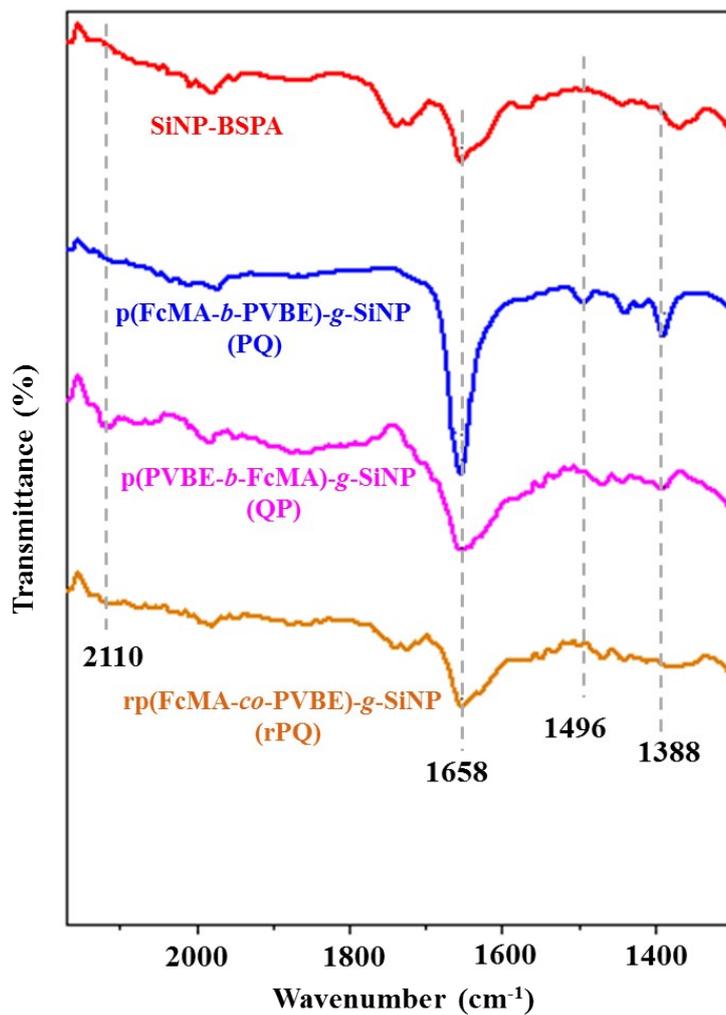


Figure S8: A comparison of FT-IR spectra of copolymers *grafted* on SiNP surface along with CTA anchored SiNP.

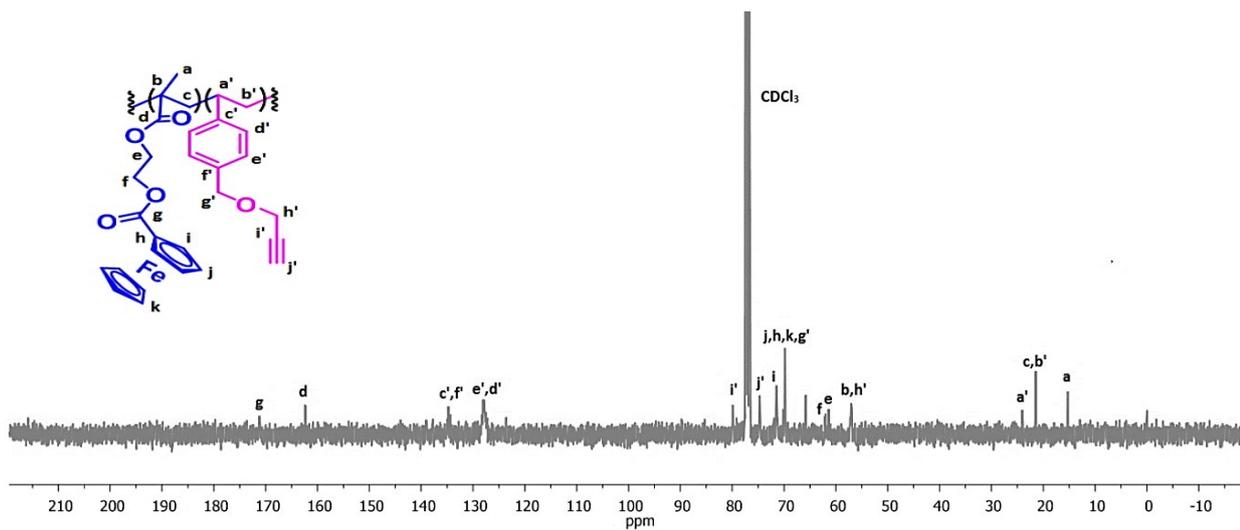


Figure S9: ^{13}C -NMR spectrum of random copolymer *grafted* on SiNP surface. All the peak position are assigned as indicated in the structure and the spectrum

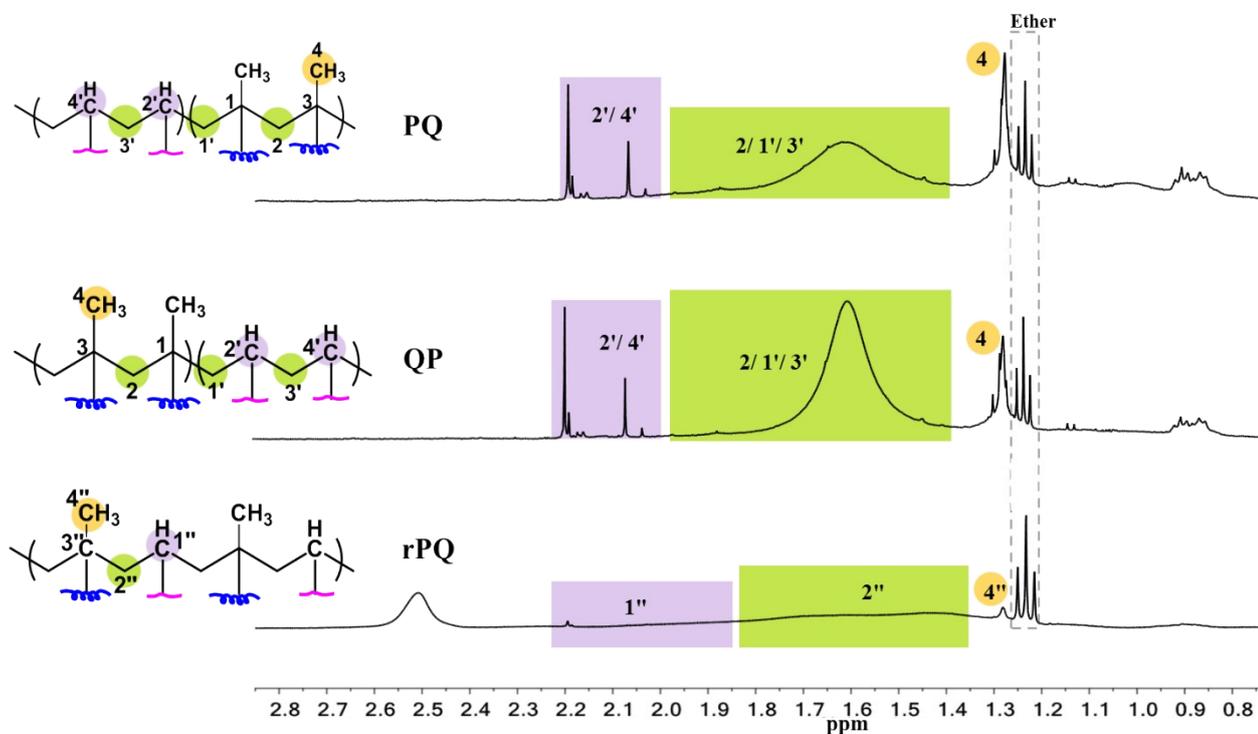


Figure S10: Comparative analysis of ^1H -NMR spectra of copolymers to differentiate structurally a block and a random copolymer. All the peak intensities in all the spectra are normalized with respect to solvent peak.

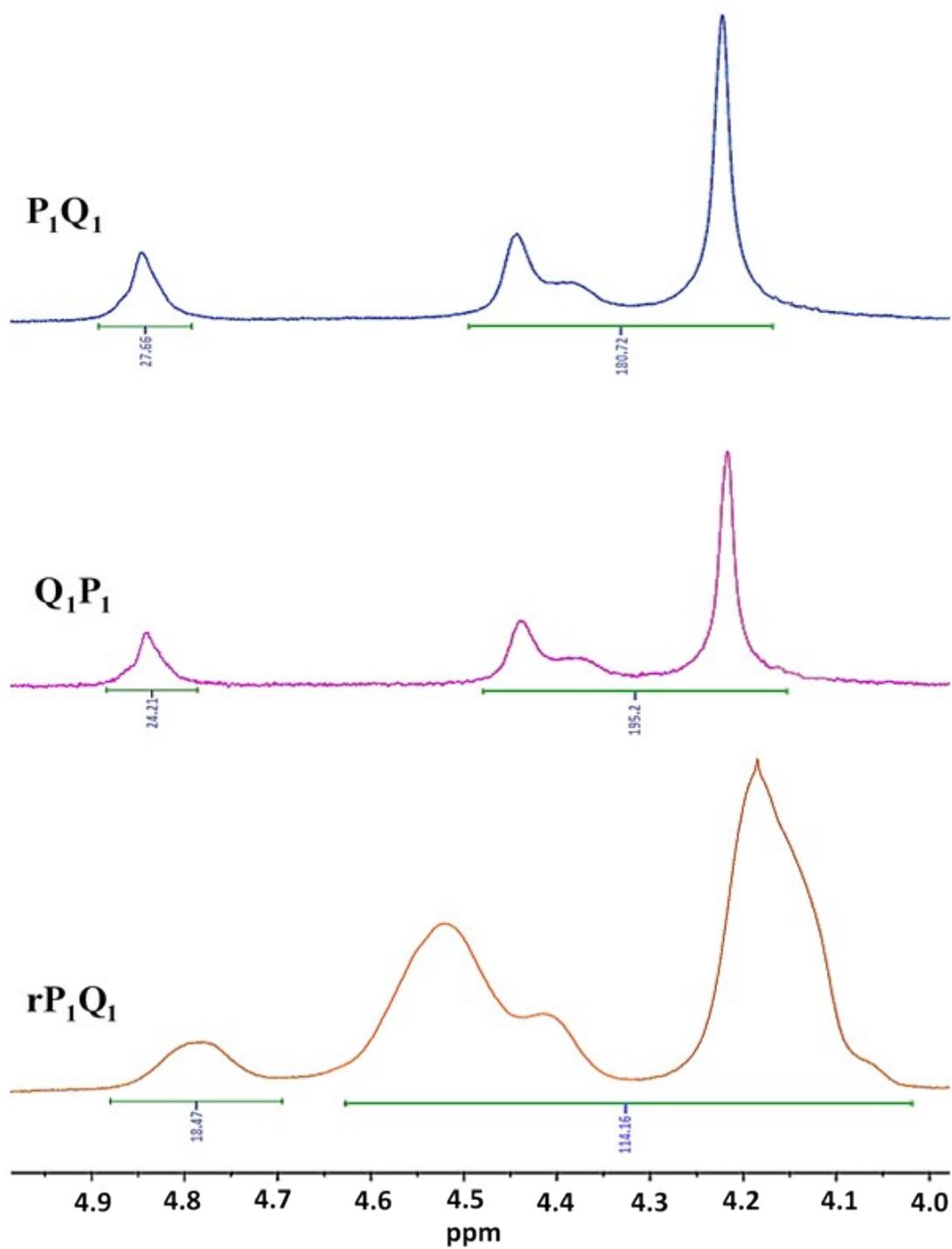


Figure S11: Peak integrals of $^1\text{H-NMR}$ spectra of copolymers for calculating the molecular weight, degree of polymerization and % of monomer conversion.

Section 7

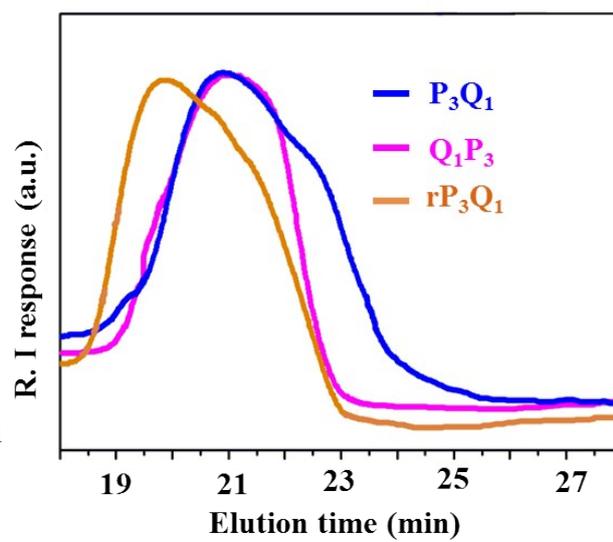
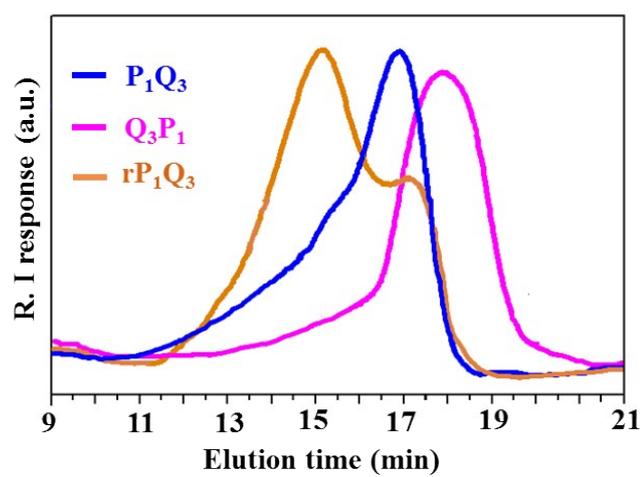


Figure S12: GPC chromatograms of copolymers (with monomers ratio of 1:3 and 3:1) *grafted* on the particle surface

Section 8

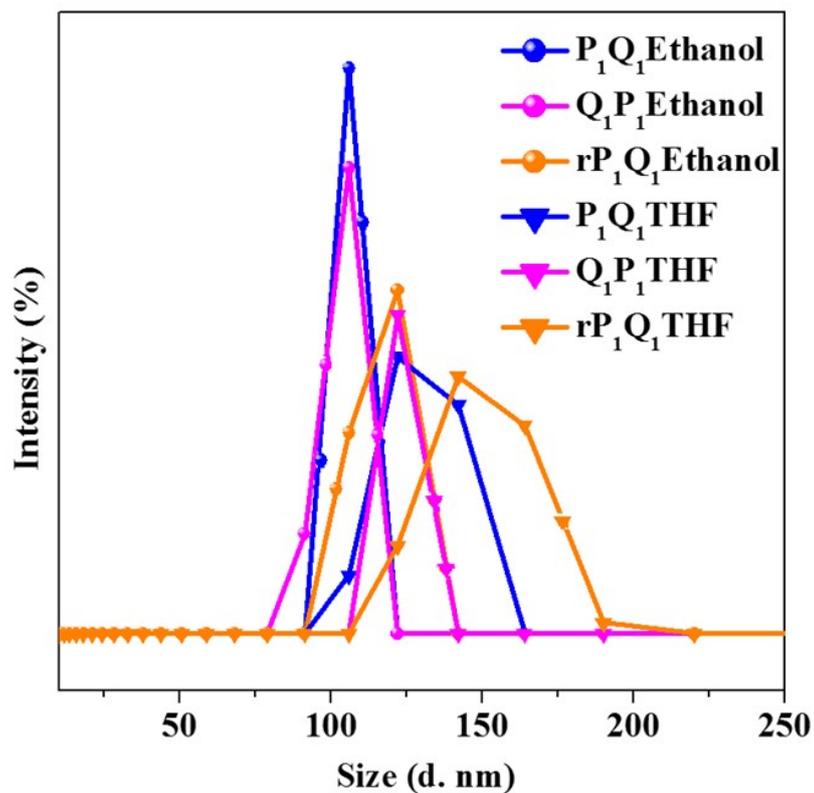


Figure S13: DLS plots of copolymers grafted SiNP in THF and ethanol

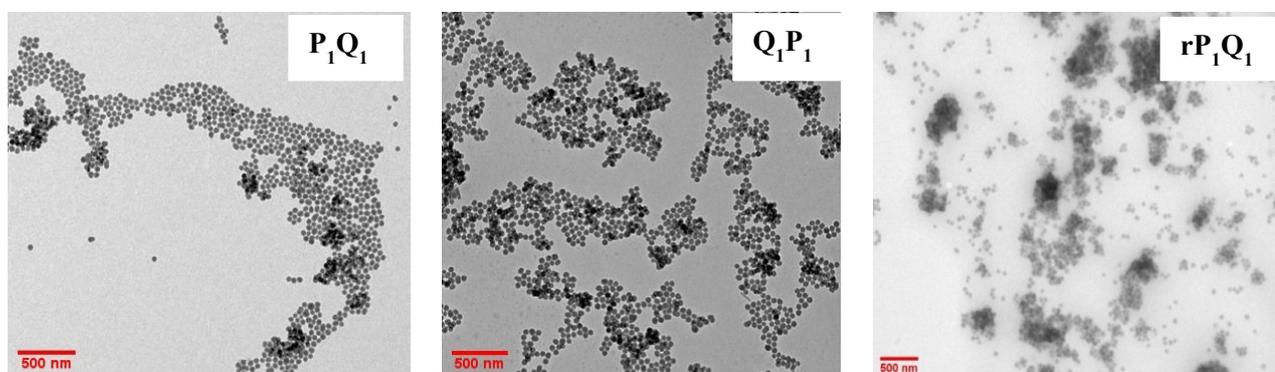


Figure S14: TEM images (lower magnifications in comparison to Figure 3 of the manuscript) of copolymer grafted SiNP to see the self-assembled/ aggregated features of copolymers brush tethered particles.

Section 9

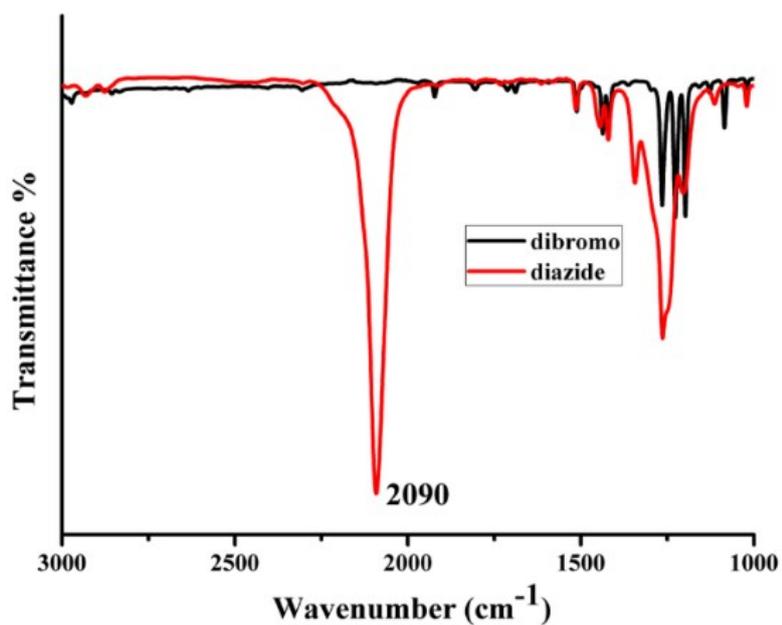


Figure S15: IR spectra of 1,4-bis(azidomethyl)benzene.

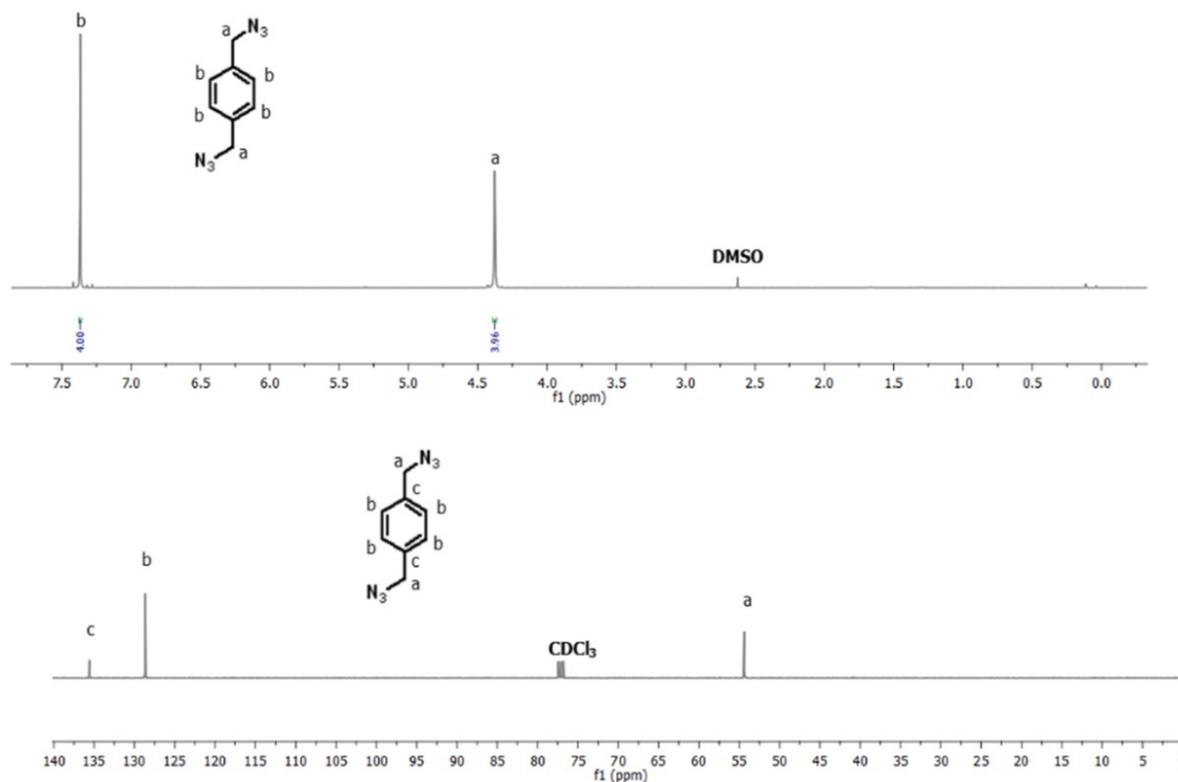


Figure S16: ^1H -NMR and ^{13}C -NMR spectra of 1,4-bis(azidomethyl)benzene.

Section 10

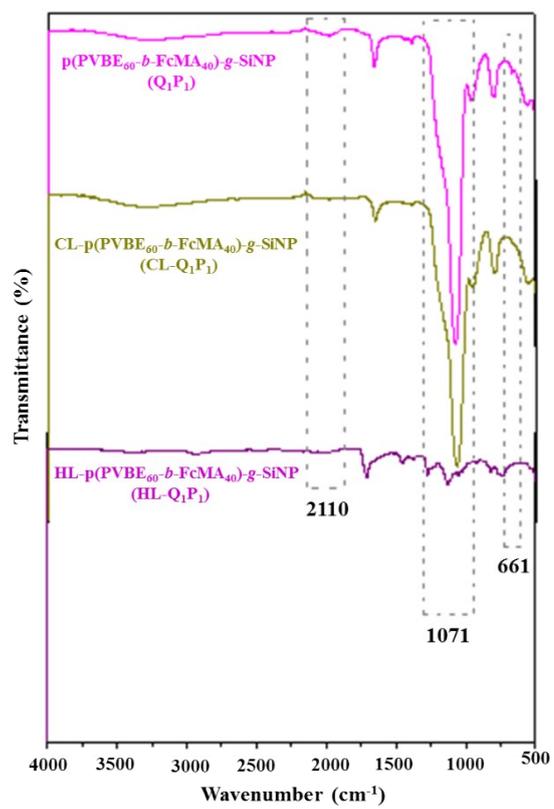


Figure S17: IR spectra of p(PVBE₆₀-*b*-FcMA₄₀)-*g*-SiNP (Q₁P₁), cross-linked p(PVBE₆₀-*b*-FcMA₄₀)-*g*-SiNP (CL-Q₁P₁) and hollow p(PVBE₆₀-*b*-FcMA₄₀)-*g*-SiNP (HL-Q₁P₁)

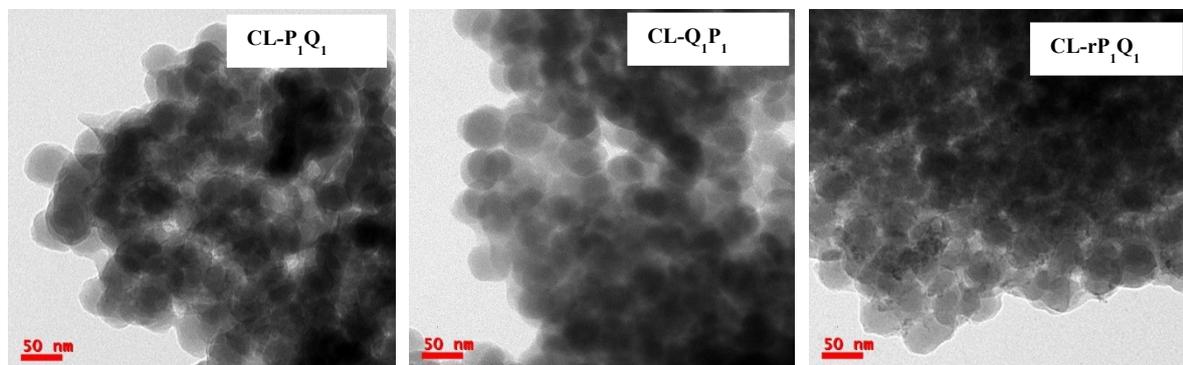


Figure S18: TEM images of cross-linked copolymer *grafted* SiNP

Section 11

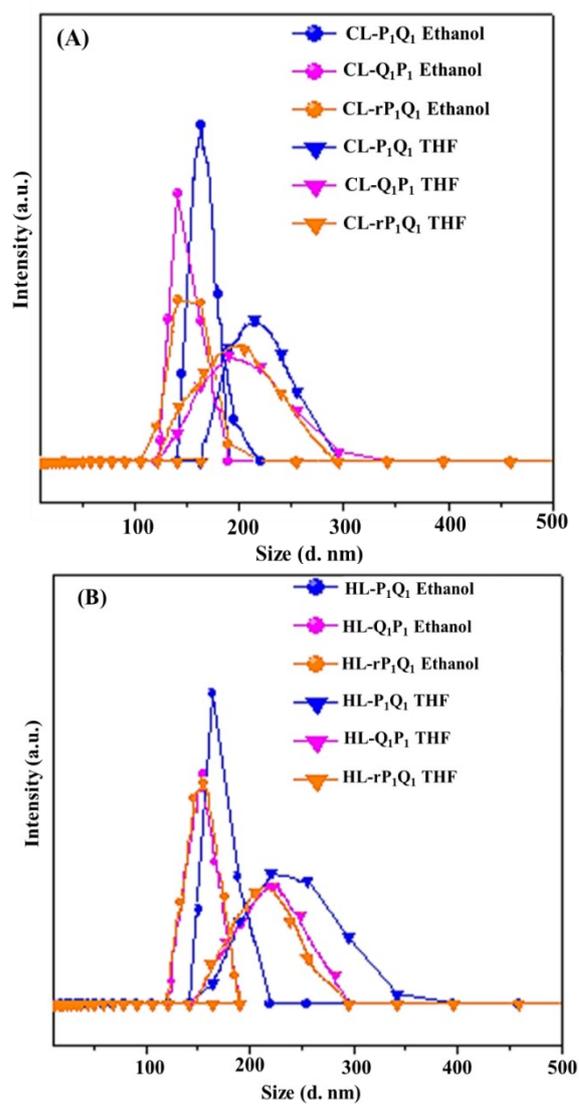


Figure S19: DLS plots of (A) cross-linked and (B) hollow particles dispersed in THF and ethanol.

Section 12

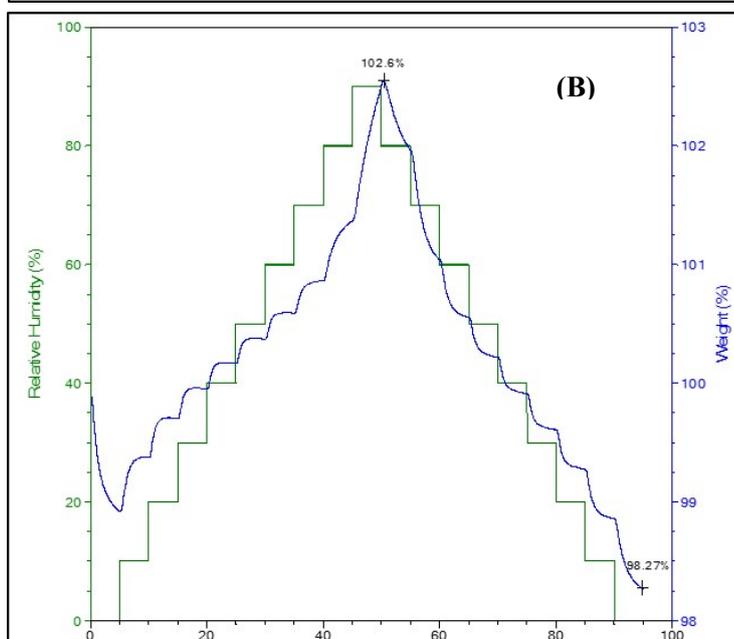
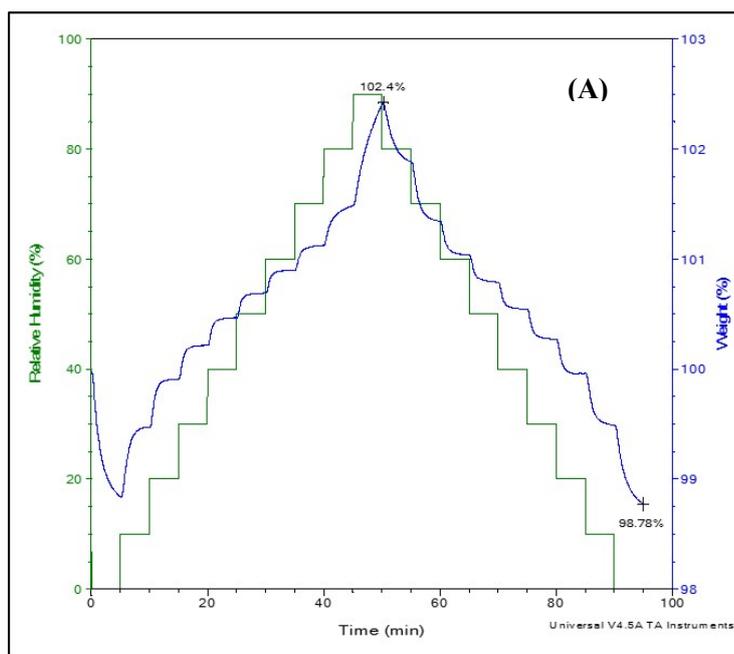


Figure S20: DVS plots of (A) p(FcMA₅₇-*b*-PVBE₄₃)-*g*-SiNP (P₁Q₁) and (B) CL-P₁Q₁ samples.

The absorbed water for P₁Q₁ and CL-P₁Q₁ are 0.9 and 1.25 wt%, respectively in the RH range 70-92% which means the net increment in water adsorption upon cross-linking is 0.35 wt%.

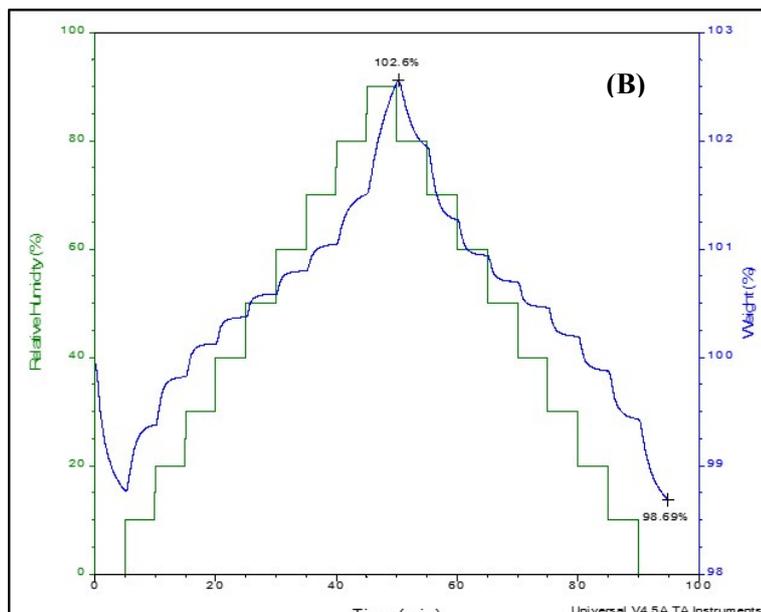
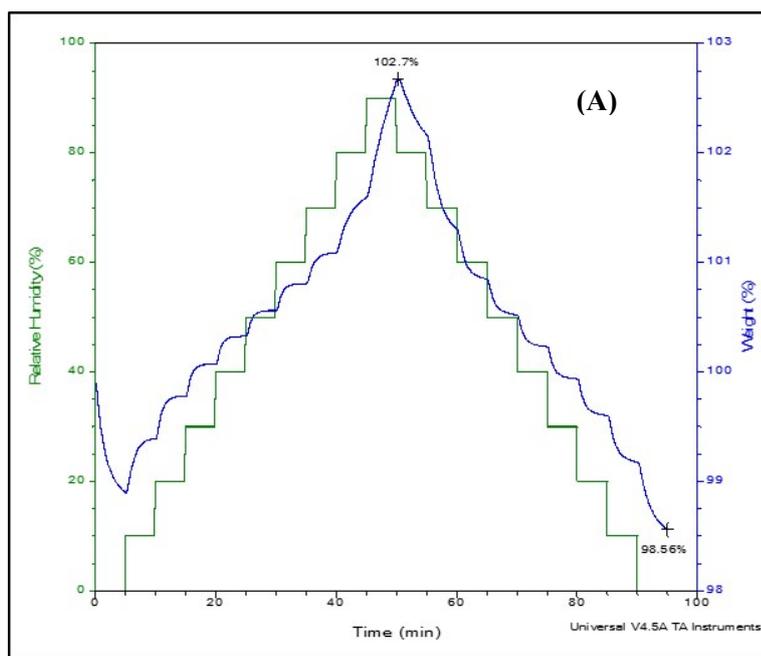


Figure S21: DVS plots of (A) p(PVBE₆₀-*b*-FcMA₄₀)-*g*-SiNP (Q₁P₁) and (B) CL-Q₁P₁ samples. The adsorbed water for Q₁P₁ and CL-Q₁P₁ are 1.07 and 1.1 wt%, respectively in the RH range 70-92% which means the net increment in water adsorption upon cross-linking is 0.03 wt%.

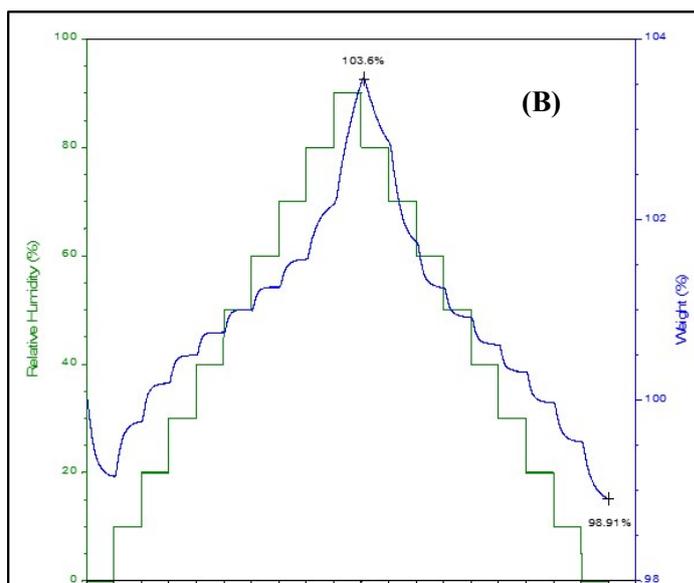
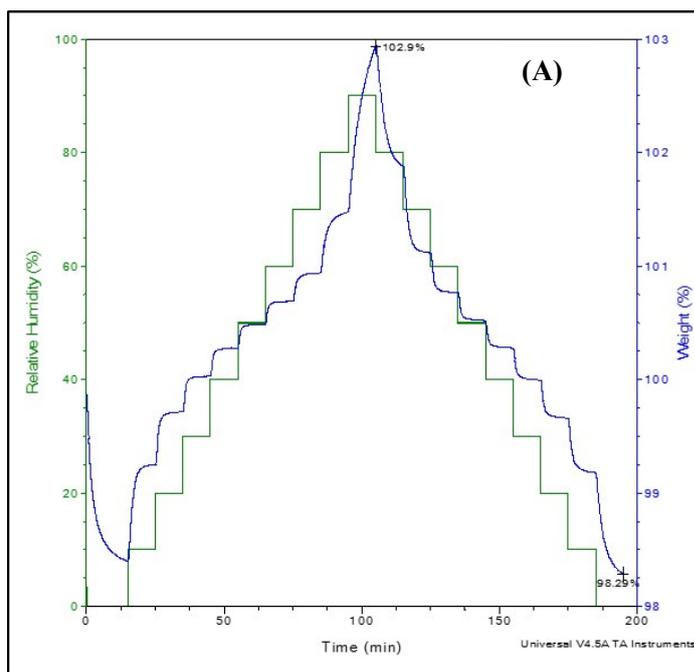
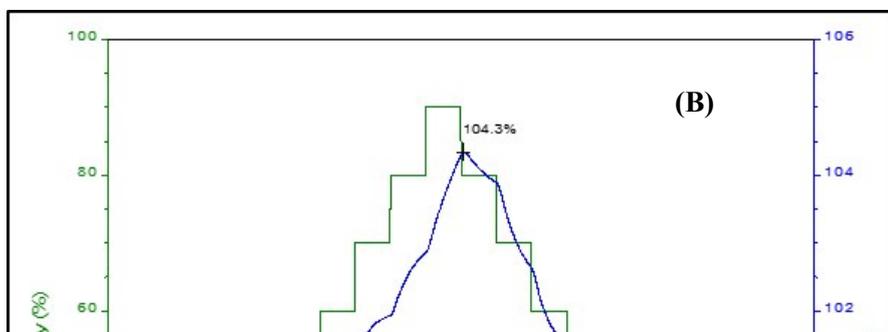
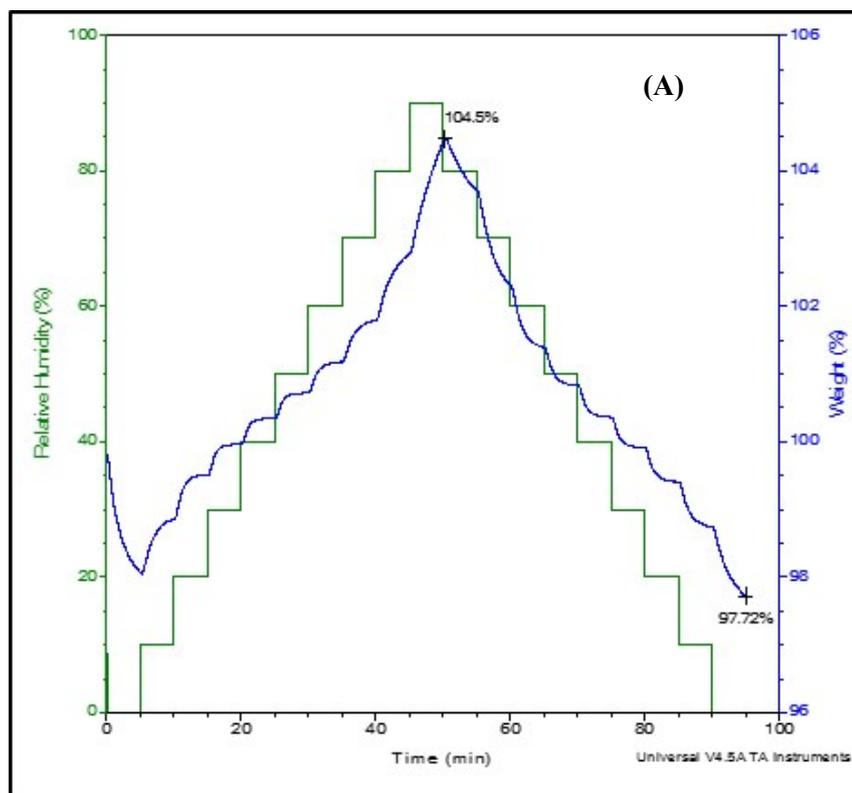


Figure S22: DVS plots of (A) $\text{rp}(\text{FcMA}_{63}\text{-}b\text{-PVBE}_{37})\text{-g-SiNP}$ (rP_1Q_1) and (B) $\text{CL-rP}_1\text{Q}_1$ samples. The adsorbed water for rP_1Q_1 and $\text{CL-rP}_1\text{Q}_1$ are 1.44 and 1.49 wt%, respectively in the RH range 70-92% which means the net increment in water adsorption upon cross-linking is 0.05 wt%.



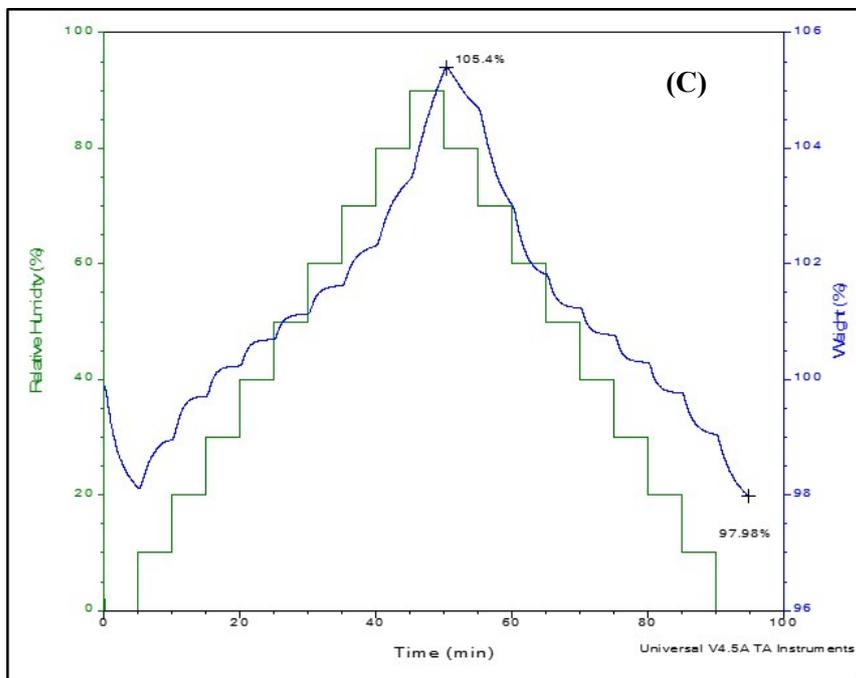


Figure S23: DVS plots of (A) HL-P₁Q₁ (B) HL-Q₁P₁ (C) HL-r P₁Q₁. The net increment in HL-P₁Q₁, HL-Q₁P₁ and HL-rP₁Q₁ water adsorption upon cross-linking are 0.48, 0.41 and 1.99 wt%, respectively in the RH range 70-92%.

Section 13

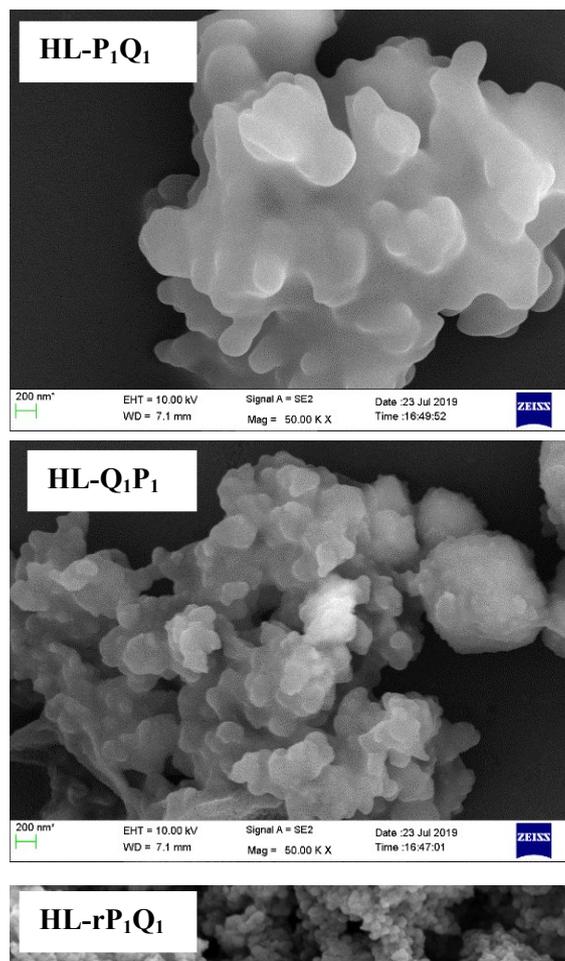


Figure S24: FESEM images of HL particles

Section 14

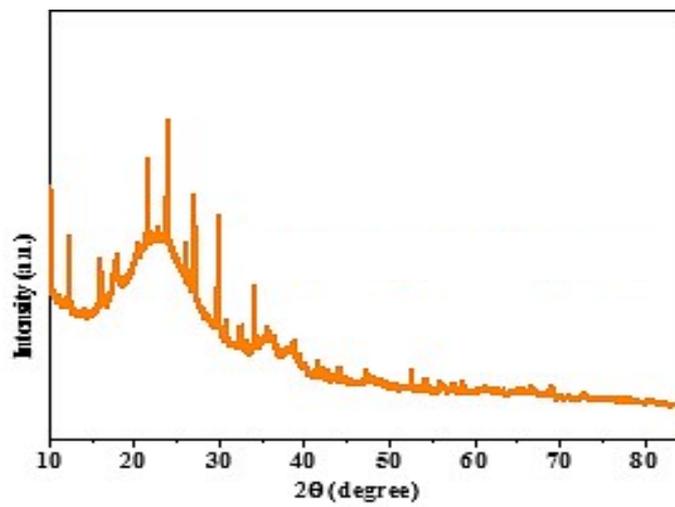


Figure S25: PXR D plot of Al-NP/ CL-rp(FcMA₆₃-co-PVBE₃₇) nanocomposite

Section 15

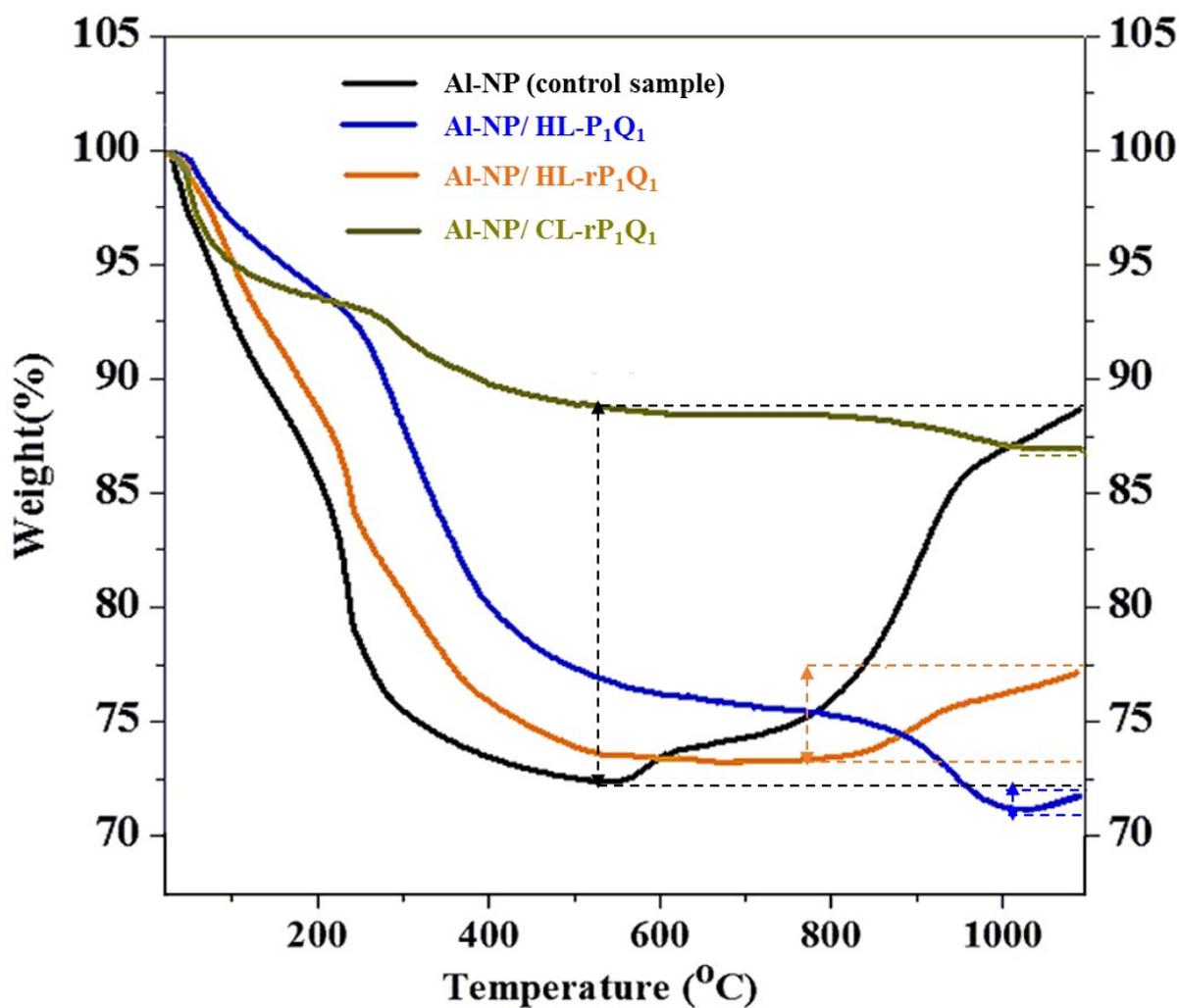


Figure S26: TGA plots of Al (control sample), Al-NP/ HL-p(FcMA₅₇-b-PVBE₄₃) nanocomposite, Al/ HL-rp(FcMA₆₃-co- PVBE₃₇) nanocomposite and Al/ CL-rp(FcMA₆₃-co- PVBE₃₇) nanocomposite. Weight gain is shown in the figure by dotted lines and double-sided arrow.