Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information for

Smartly designed photoreactive silica nanoparticles and their reactivity.

by

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S2

Supporting information

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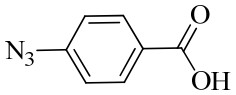
List of abbreviations:

AFM	atomic force microscopy
APTES	(3-aminopropyl)triethoxysilane
CDI	1,1'-carbonyldiimidazole
CP-MAS	cross polarization-magic angle spinning
DLS	dynamic light scattering
DMAP	para-dimethylaminopyridine
DMSO	dimethylsulfoxide
DSS	4,4-dimethyl-4-silapentane-1-sulfonic acid
EtOH	ethanol
FE	field emission
FIB	focused ion beam
FTIR	fourier transform infrared spectroscopy
HRMS	high resolution mass spectra
NMR	nuclear magnetic resonance
RT	room temperature
SEM	scanning electron microscope
ssNMR	solid state nuclear magnetic resonance
TEOS	tetraethyl orthosilicate
THF	tetrahydrofurane
TMS	tetramethylsilane
TEM	transmission electron spectroscopy
UV	ultra violet
XPS	X-ray photoelectron spectroscopy

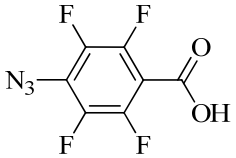
Literature compounds:

4-azidobenzoic acid



The 4-azidobenzoic acid was prepared according to a literature procedure.[1]

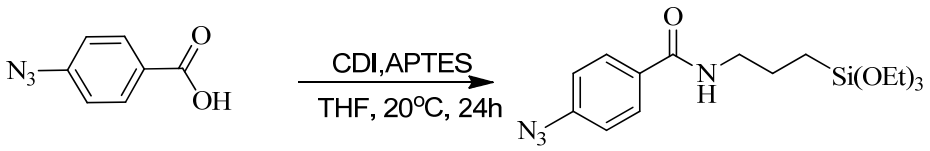
4-azido-2,3,5,6-tetrafluorobenzoic acid



The 4-azido-2,3,5,6-tetrafluorobenzoic acid was prepared according to a literature procedure.[2]

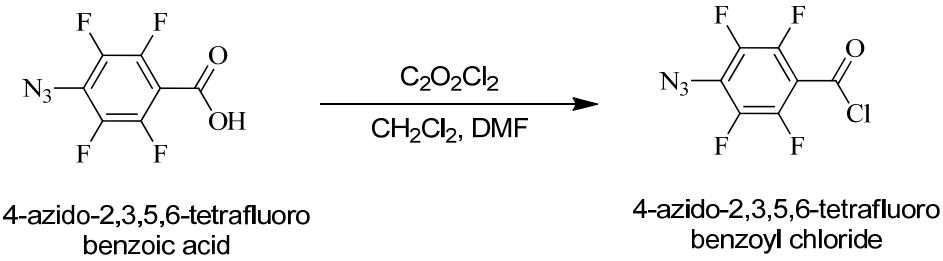
Experimental Procedures:

Synthesis of 4-azido-N-(3-(triethoxysilyl)propyl)benzamide **1 (PATES)**



Yellow oil; TLC, R_f = 0.24 (eluent: acetone /*n*-hexane: 85/15); ν_{max} (KBr easy diff)/cm^{-1} 3322 (NH), 2973 and 2885 (CH stretching), 2927 (CH_2 stretching), 2124 (azide), 1639 (C=O amide), 1549 and 1287 (C=C), 1287 (C-O), 1445 and 765 (CH_2 bending), 1390 (Si-OCH_2CH_3), 1100 (Si-O),956 (C-O); δ_H ^{1}H NMR (300 MHz; DMSO-d_6) 8.48 (1H, br t, NH), 7.91 (2H, d, J = 8.7 Hz, Ar-H), 7.17 (2H, d, J = 8.7 Hz, Ar-H), 3.74 (6H, q, J = 6.9 Hz, O-$\underline{CH_2}$-CH_3), 3.27-3.21 (2H, m, NH-$\underline{CH_2}$-CH_2), 1.64-1.54 (2H, m, CH_2-$\underline{CH_2}$-CH_2), 1.13 (9H, t, J = 6.9 Hz, O-CH_2-$\underline{CH_3}$), 0.61-0.56 (2H, m, $\underline{CH_2}$-Si); δ_C ^{13}C NMR (75 MHz, [D6] DMSO, TMS) 165.1 (C), 142.0 (C), 131.3 (C), 129.0 (CH), 118.7 (CH), 57.7 (CH_2), 42.0 (CH_2), 22.7 (CH_2), 18.1 (CH_3), 7.4 (CH_2); UV/Vis λ_{max} (EtOH)/nm (270); HRMS (DCI+ CH4) *m/z* calcd for $C_{16}H_{26}N_4O_4Si$ $(MH)^+$ 366.4875 found 366.1723.

Synthesis of 4-azido-2,3,5,6-tetrafluorobenzoyl chloride



The 4-azido-2,3,5,6-tetrafluoroenzoic acid (2.20 g, 9.36 mmol) was dissolved in dry CH_2Cl_2 (10 mL). In order to dissolve 4-azido-2,3,5,6-tetrafluoroenzoic acid completely dry DMF (0.3 mL) was added to a reaction mixture. Thus oxalyl chloride (3.6 mL, 42.12 mmol) was added and reaction was stirred at RT for 2h during with time gas evolution was observed. After reaction completion the solvents were evaporated to give 4-azido-2,3,5,6-tetrafluorobenzoyl chloride as yellow oil which was directly used in the next step without further purification.

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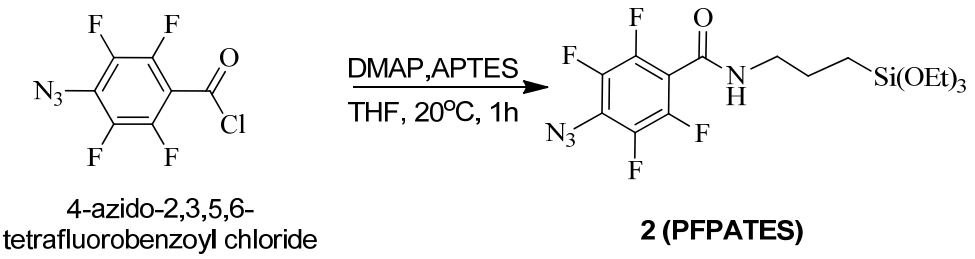
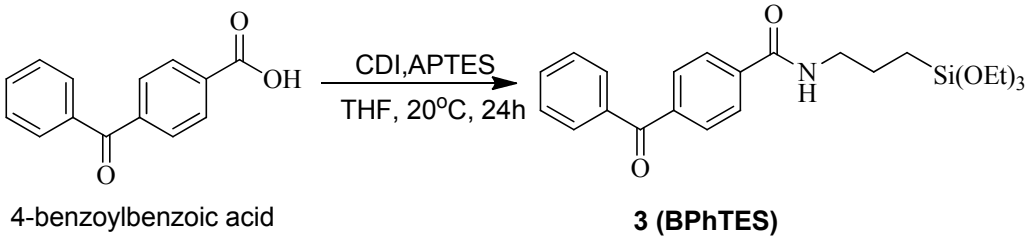
Synthesis of 4-azido-2,3,5,6-tetrafluoro-N-(3-(triethoxysilyl)propyl)benzamide **2 (PFPATES)**



Yellow oil; TLC, Rf = 0.37 (eluent: ether/n-hexane: 60/40); ν_{max} (KBr easy diff)/cm^{-1} 3280 (NH), 3080 and 2884 (CH stretching), 2930 (CH_2 stretching), 2133 (azide), 1650 (C=O amide), 1392 (Si-OCH_2CH_3), 1100 (Si-O), 958 (C-O), 777 (CH_2 bending); δ_H ^{1}H NMR (300 MHz, $CDCl_3$) 6.42 (1H, br t, NH), 3.81 (6H, q, J = 6.9 Hz, O-$\underline{CH_2}$-CH_2), 3.51-3.44 (2H, m, NH-$\underline{CH_2}$-CH_2), 1.81-1.71 (2H, m, CH_2-$\underline{CH_2}$-CH_2), 1.21 (9H, t, J = 6.9 Hz, O-CH_2-$\underline{CH_3}$), 0.73-0.66 (2H, m, $\underline{CH_2}$-Si); δ_C ^{13}C NMR (75 MHz; $CDCl_3$) 157.4 (C), 145.7 (C), 142.1 (C), 138.7 (C), 112.1 (C), 58.5 (CH_2), 42.4 (CH_2), 22.5 (CH_2), 18.2 (CH_3), 7.6 (CH_2); δ_F ^{19}F NMR (188 MHz; $CDCl_3$) 141.3-141.5 (m, 2F), 150.9-151.1 (m, 2F); UV/Vis λ_{max} (EtOH)/nm (260); HRMS (DCI+ CH_4) *m/z* calcd for $C_{16}H_{22}F_4N_4O_4Si$ $(MH\text{-}EtOH)^+$ 393.3810 found 393.1006.

Synthesis of 4-benzoyl-N-(3-(triethoxysilyl)propyl)benzamide **3 (BPhTES)**



^{1}HNMR was identical to previously reported. [3]

White solid; TLC, R_f = 0.68 (eluent: acetone /*n*-hexane: 85/15); m.p. 90-91°C; ν_{max} (KBr easy diff)/cm^{-1} 3326 (NH), 2975 and 2885 (CH stretching), 2928 (CH_2 stretching), 1663 (C=O ketone), 1631 (C=O amide), 1553 (C=C), 1445 and 790 (CH_2 bending), 1390 (Si-OCH_2CH_3), 1300 (C-H bending), 1278 and 1108 (C-O), 1167 (C-N), 1080 (Si-O) cm^{-1}; δ_H ^{1}H NMR (300 MHz, [D_6] DMSO, TMS) 8.68 (1H, br t, NH), 8.02-7.98 (2H, m, Ar-H), 7.78-7.68 (5H, m, Ar-H),

7.61-7.56 (2H, m, Ar-H), 3.77 (6H, q, J = 9.6 Hz, O-$\underline{CH_2}$-CH_3), 3.35-3.25 (2H, m, NH-$\underline{CH_2}$-CH_2), 1.67-1.57 (2H, m, CH_2-$\underline{CH_2}$-CH_2), 1.15 (9H, t, J = 9.6 Hz, O-CH_2-$\underline{CH_3}$), 0.65-0.59 (2H, m, $\underline{CH_2}$-Si); δ_C ^{13}C NMR (75 MHz, [D_6] DMSO, TMS) 195.4 (C), 165.3 (C), 139.0 (C), 138.0 (C), 136.7 (C), 133.0 (CH), 129.7 (CH), 129.5 (CH), 128.7 (CH), 127.3 (CH), 57.7 (CH_2), 42.1 (CH_2), 22.7 (CH_2), 18.2 (CH_3), 7.5 (CH_2); UV/Vis λ_{max} (EtOH)/nm (260); HRMS (DCI+ CH_4) m/z calcd for $C_{23}H_{31}NO_5Si$ $(MH)^+$ 429.5814 found 430.248.

^{1}H- and ^{13}C- NMR Spectra:

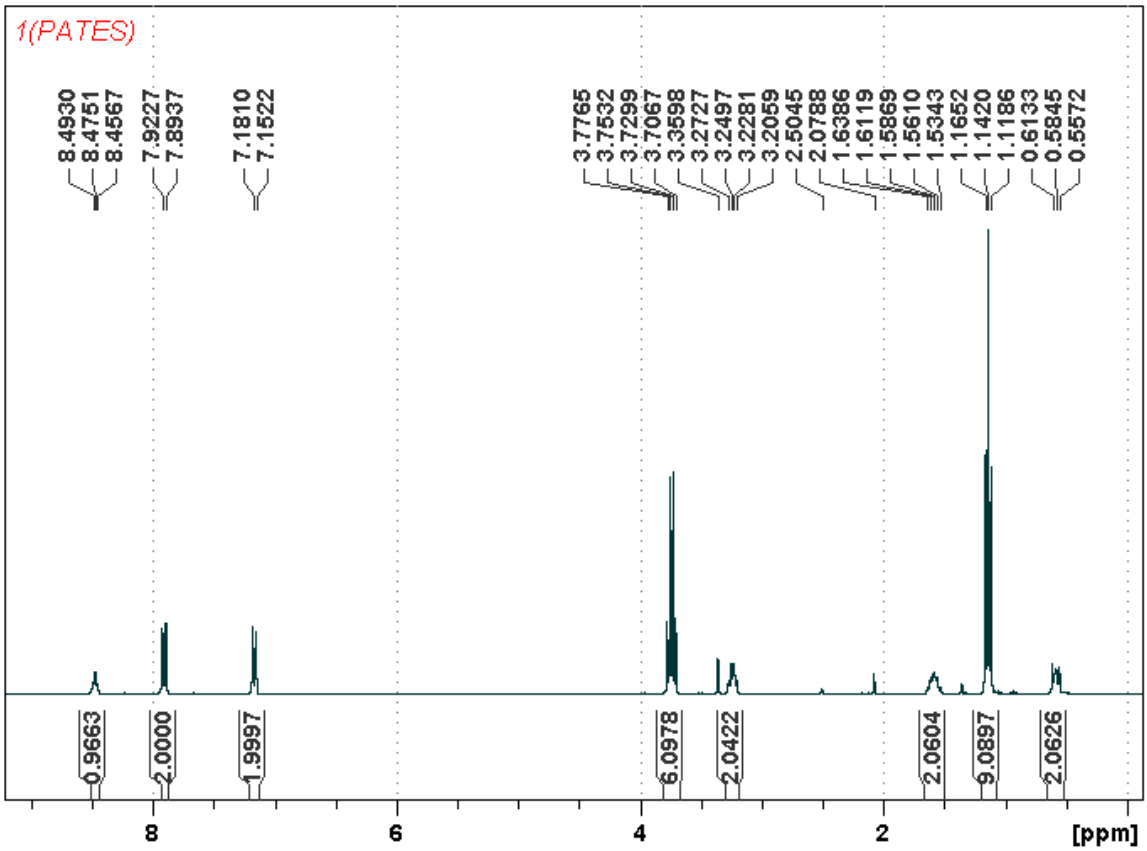


Figure 1. ^{1}H NMR spectrum of **1** (PATES)

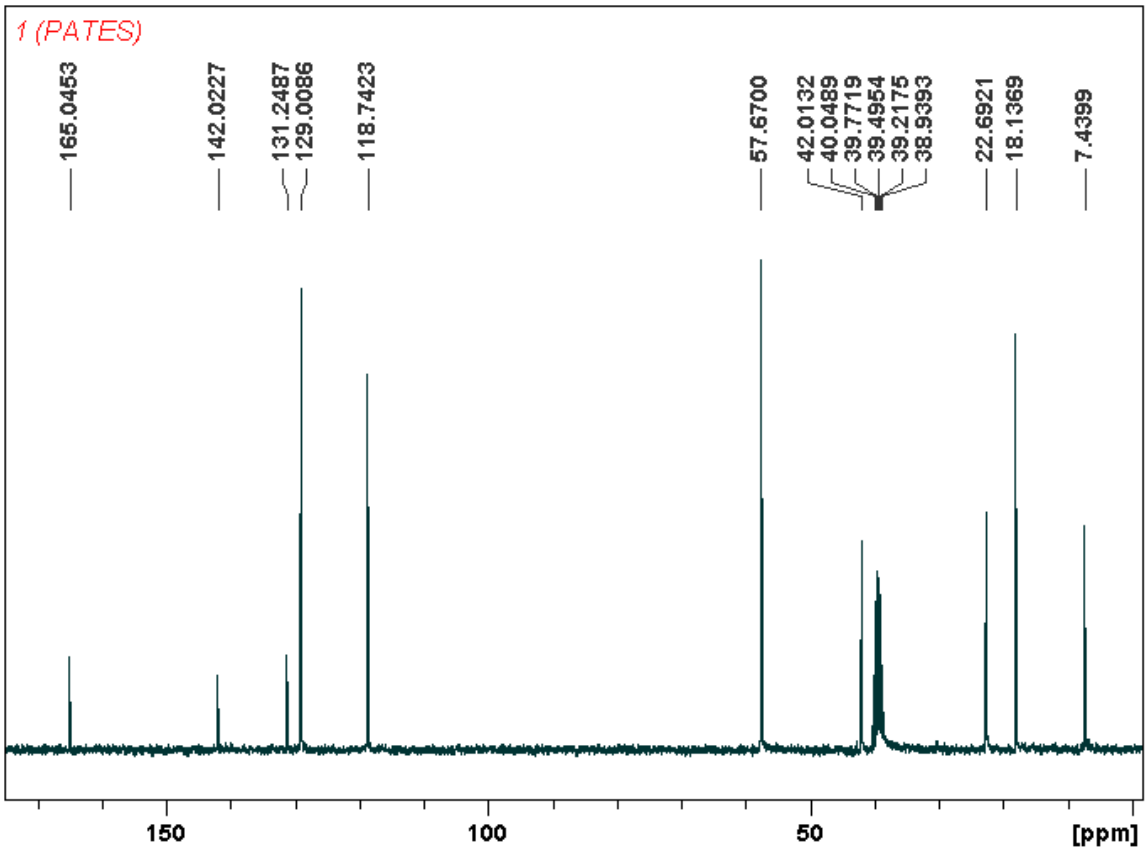


Figure 2. ^{13}C NMR spectrum of **1** (PATES)

S9

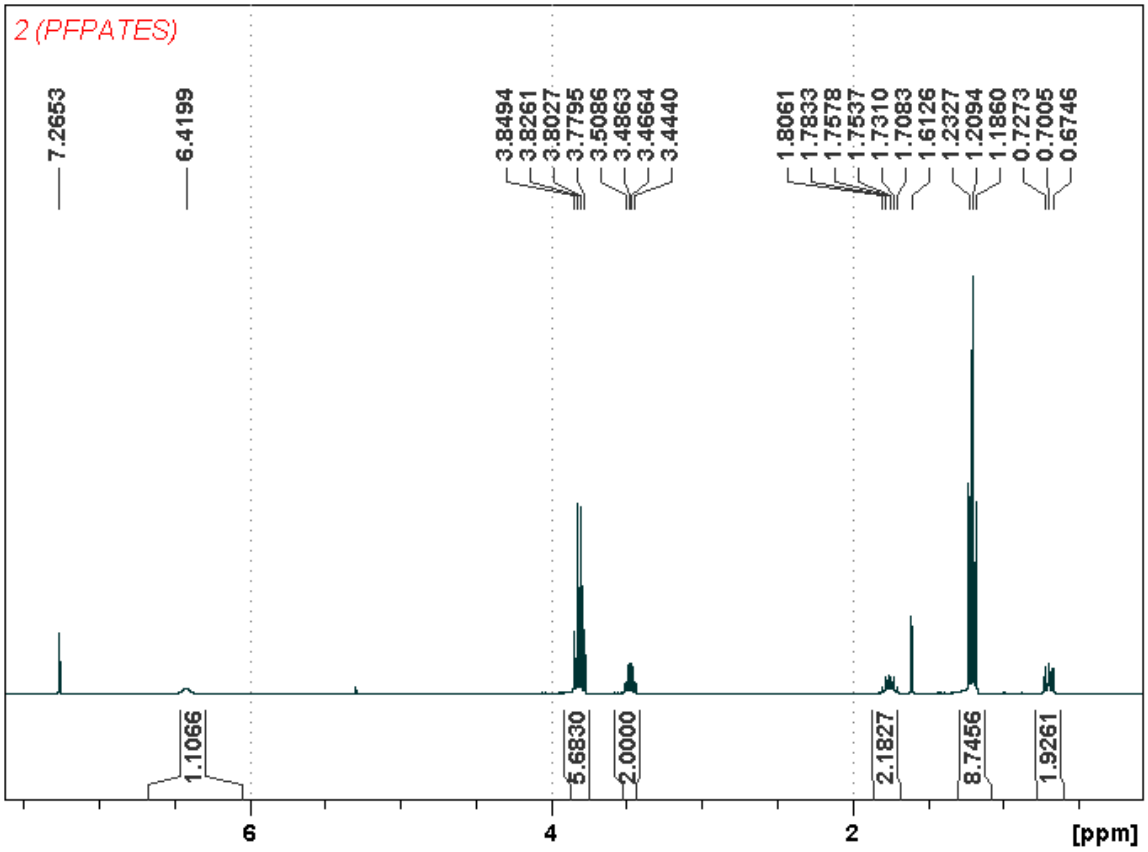


Figure 3. ^{1}H NMR spectrum of **2** (PFPATES)

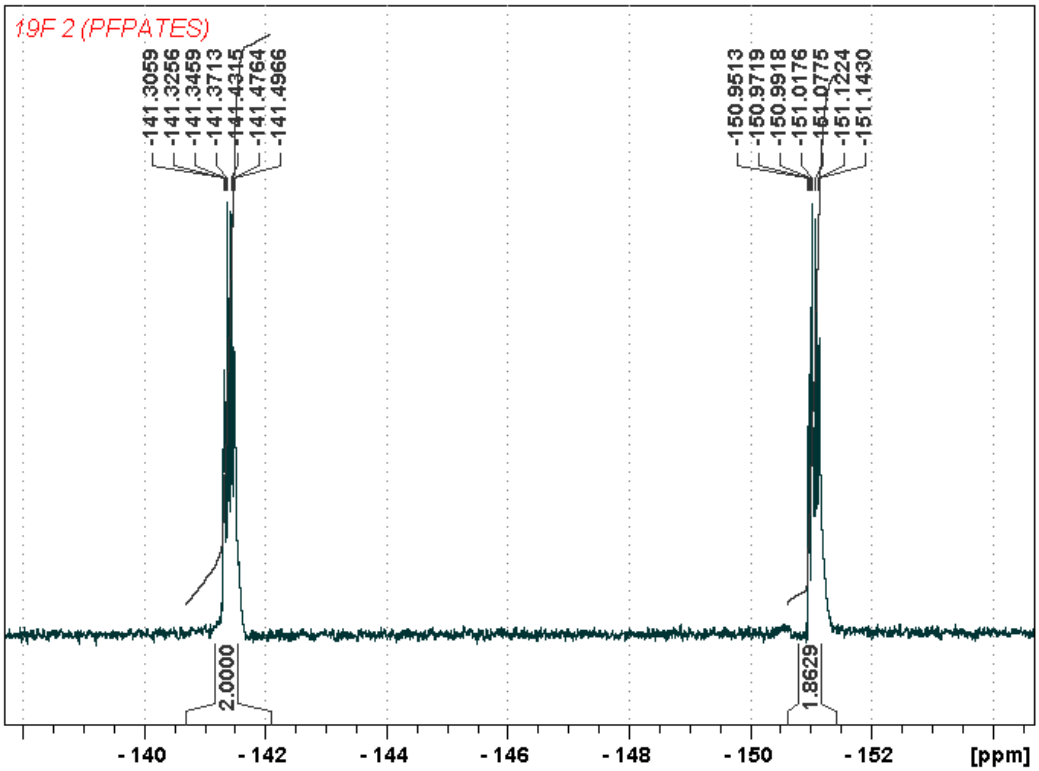


Figure 4. ^{19}F NMR spectrum of **2** (PFPATES)

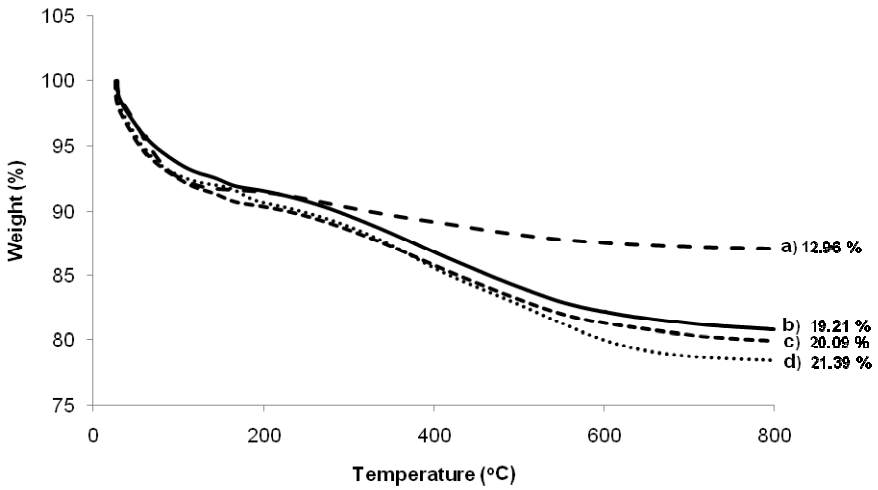


Figure 5. TGA of a) SiO_2, b) SiO_2@BPh, c) SiO_2@PFPA, d) SiO_2@PA NPs. TGA was performed in air at a heating rate of 10 ºC/min

Solid state ^{13}C and ^{29}Si CP-MAS NMR spectra:

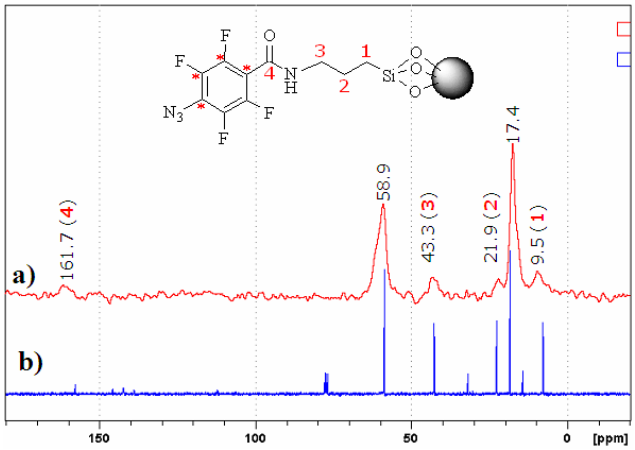


Figure 6. a) ^{13}C CP/MAS NMR spectrum of the SiO_2@PFPA NPs; b) ^{13}C NMR (75 MHz; $CDCl_3$) spectrum of **2** (PFPATES)

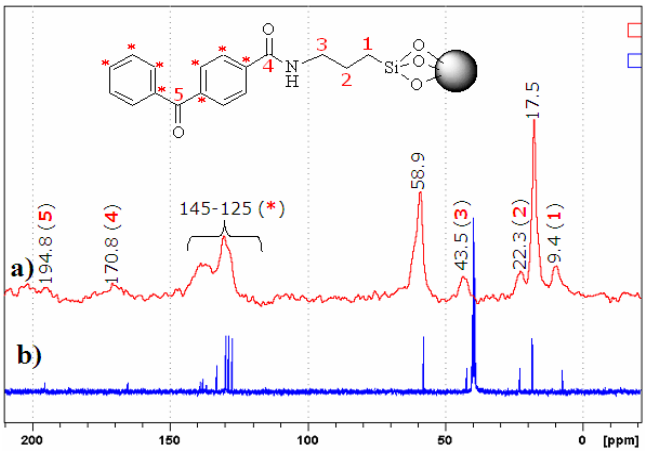


Figure 7. a) ^{13}C CP/MAS NMR spectrum of the SiO_2@BPh NPs; b) ^{13}C NMR (75 MHz; [D_6] DMSO) spectrum of **3** (BPhTES)

UV absorbance spectra:

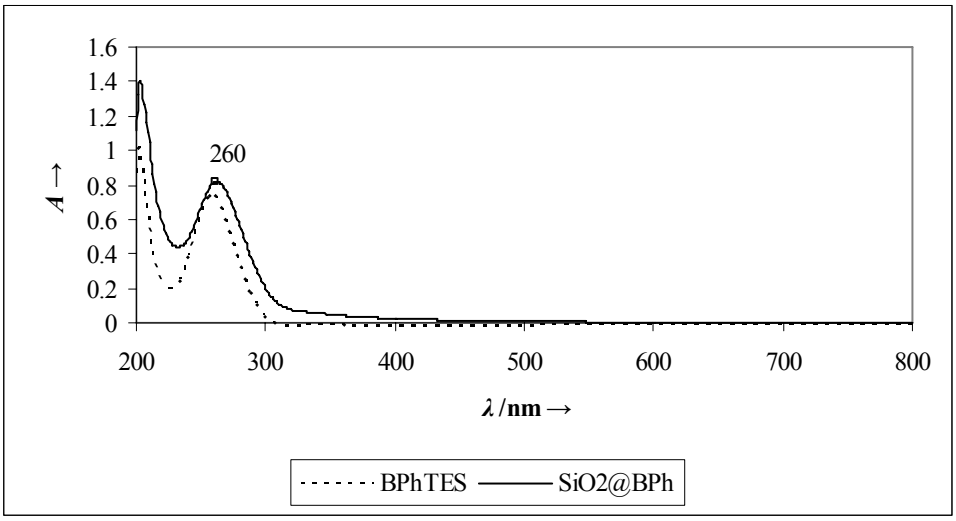


Figure 8. UV/Vis spectra of the **3** (BPhTES) and SiO_2@BPh NPs

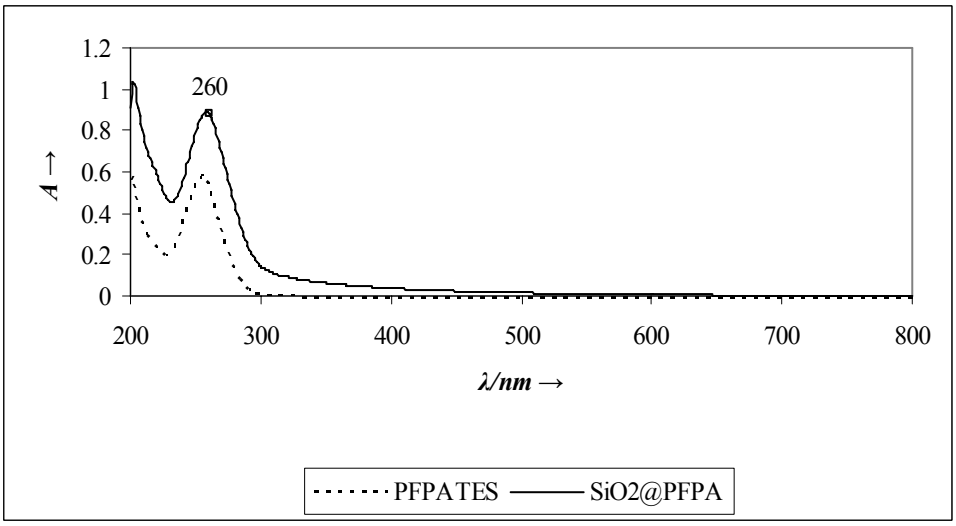


Figure 9. UV/Vis spectra of the **2** (PFPATES) and SiO_2@PFPA NPs

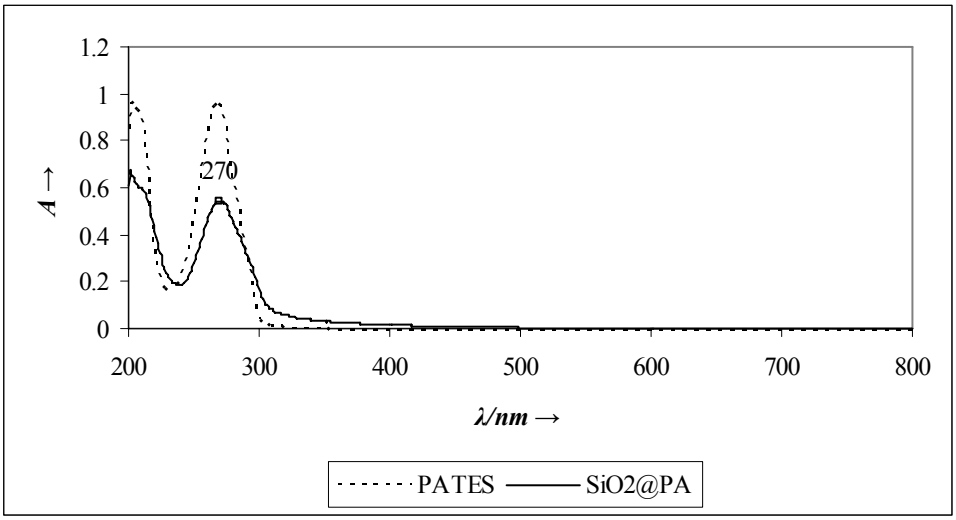


Figure 10. UV/Vis spectra of the **1** (PATES) and SiO_2@PA NPs

FT-IR spectra:

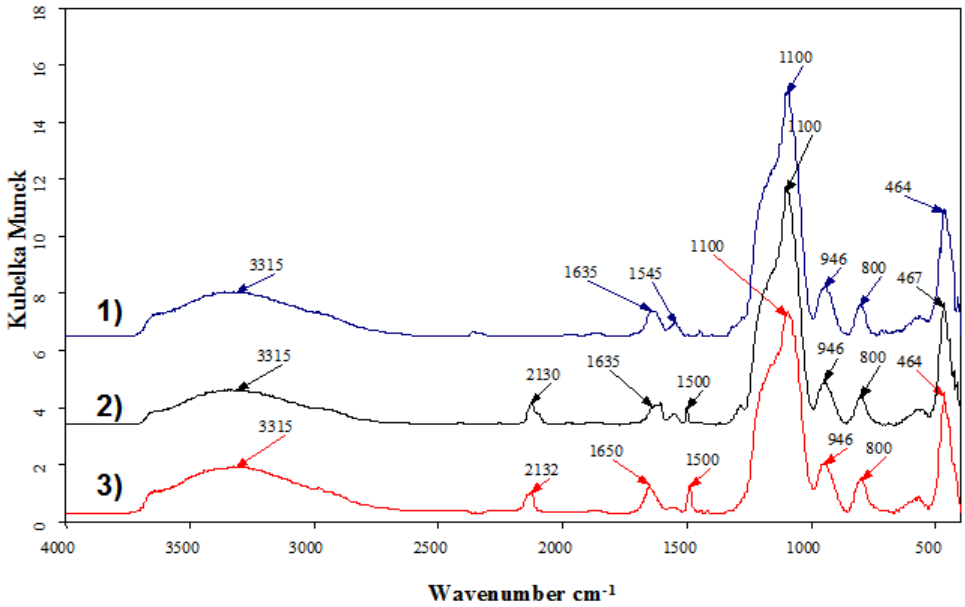


Figure 11. FTIR spectra of 1) SiO_2@BPh, 2) SiO_2@PA, and 3)SiO_2@PFPA NPs

Size distribution graphs (according to TEM):

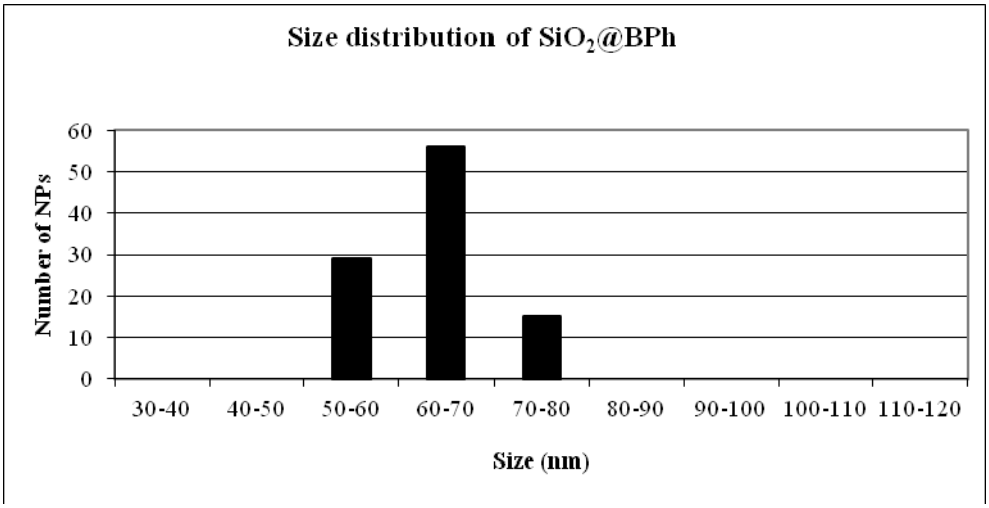


Figure 12. Size distribution of the SiO_2@BPh NPs

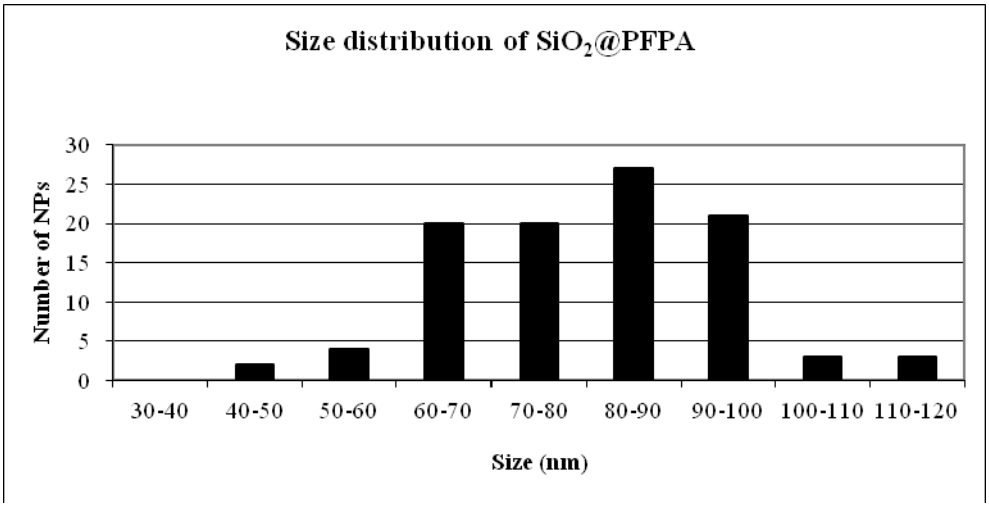


Figure 13. Size distribution of the SiO_2@PFPA NPs

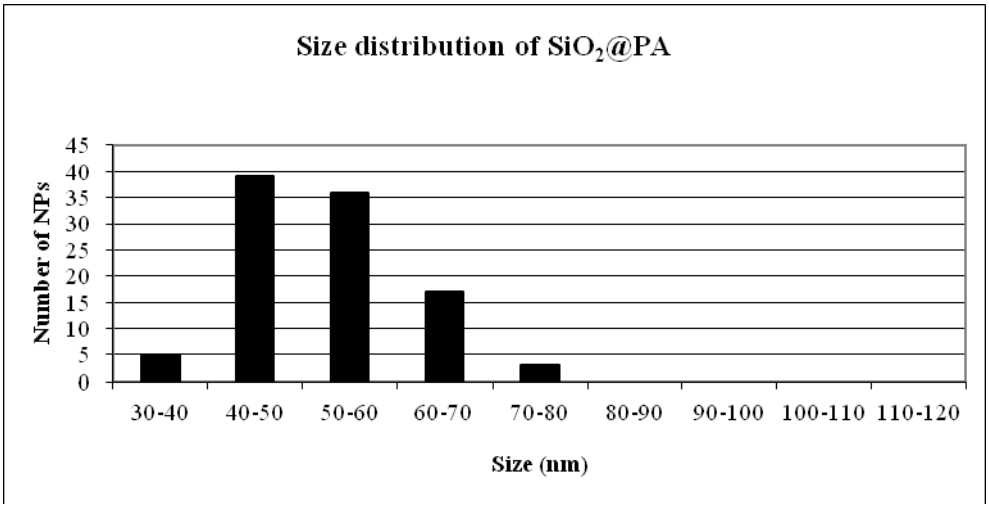


Figure 14. Size distribution of the SiO_2@PFPA NPs

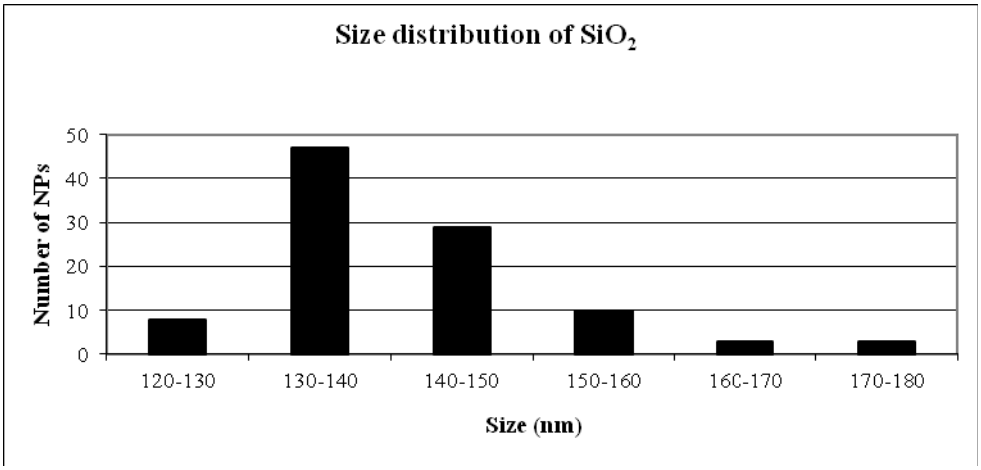


Figure 15. Size distribution of the SiO_2 NPs

SEM tilt images:

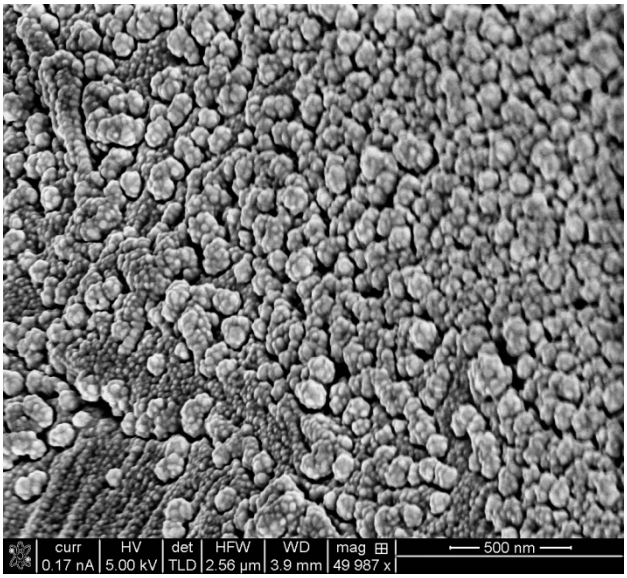


Figure 16. SEM tilt image of PC-SiO_2@PA film

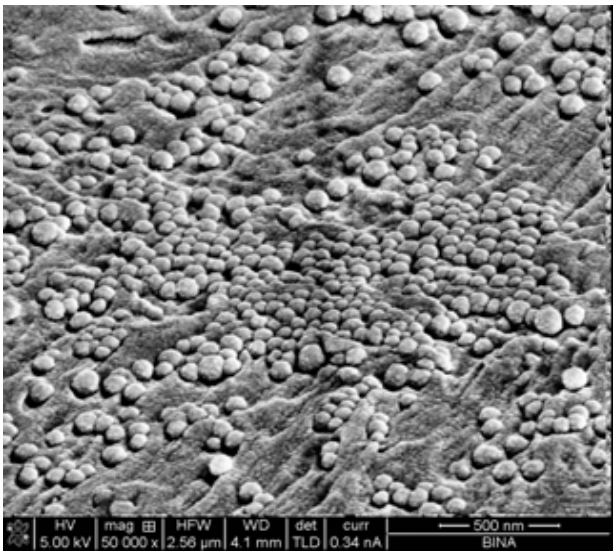


Figure 17. SEM tilt image of PC-SiO_2@PFPA film

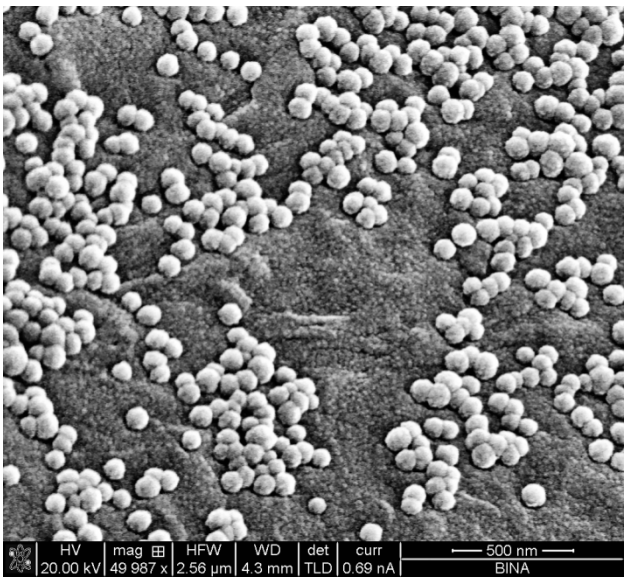


Figure 18. SEM tilt image of PC-SiO_2@BPh film

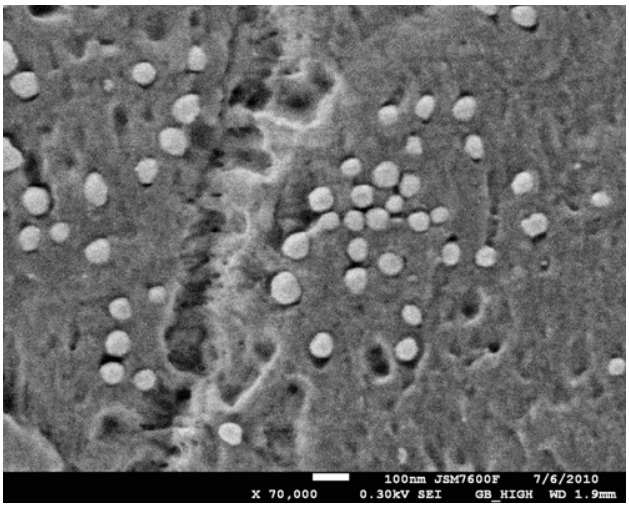


Figure 19. FE-SEM image of PC-SiO_2@PFPA modified film (the analysis was performed without gold conducting coating)

AFM images:

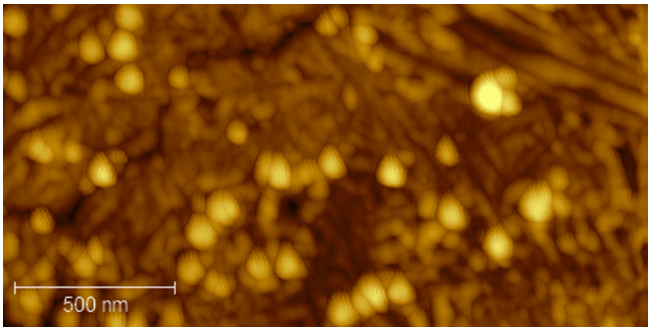


Figure 20. AFM image of PC-SiO_2@PA film

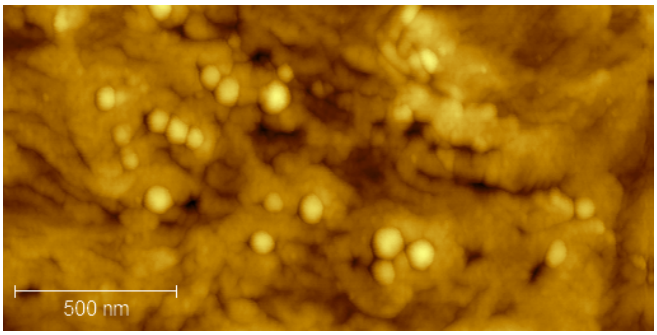


Figure 21. AFM image of PC-SiO_2@PFPA film

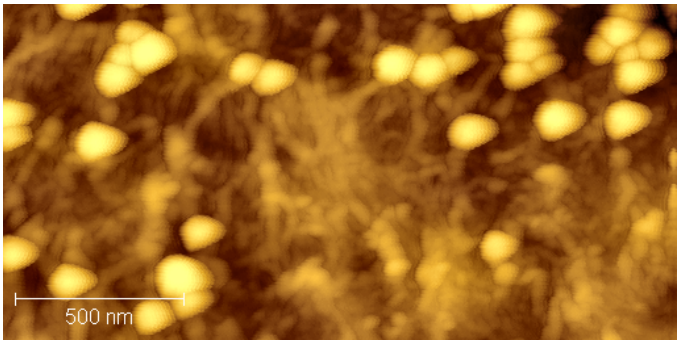


Figure 22. AFM image of PC-SiO_2@BPh film

AFM NP manipulation images:

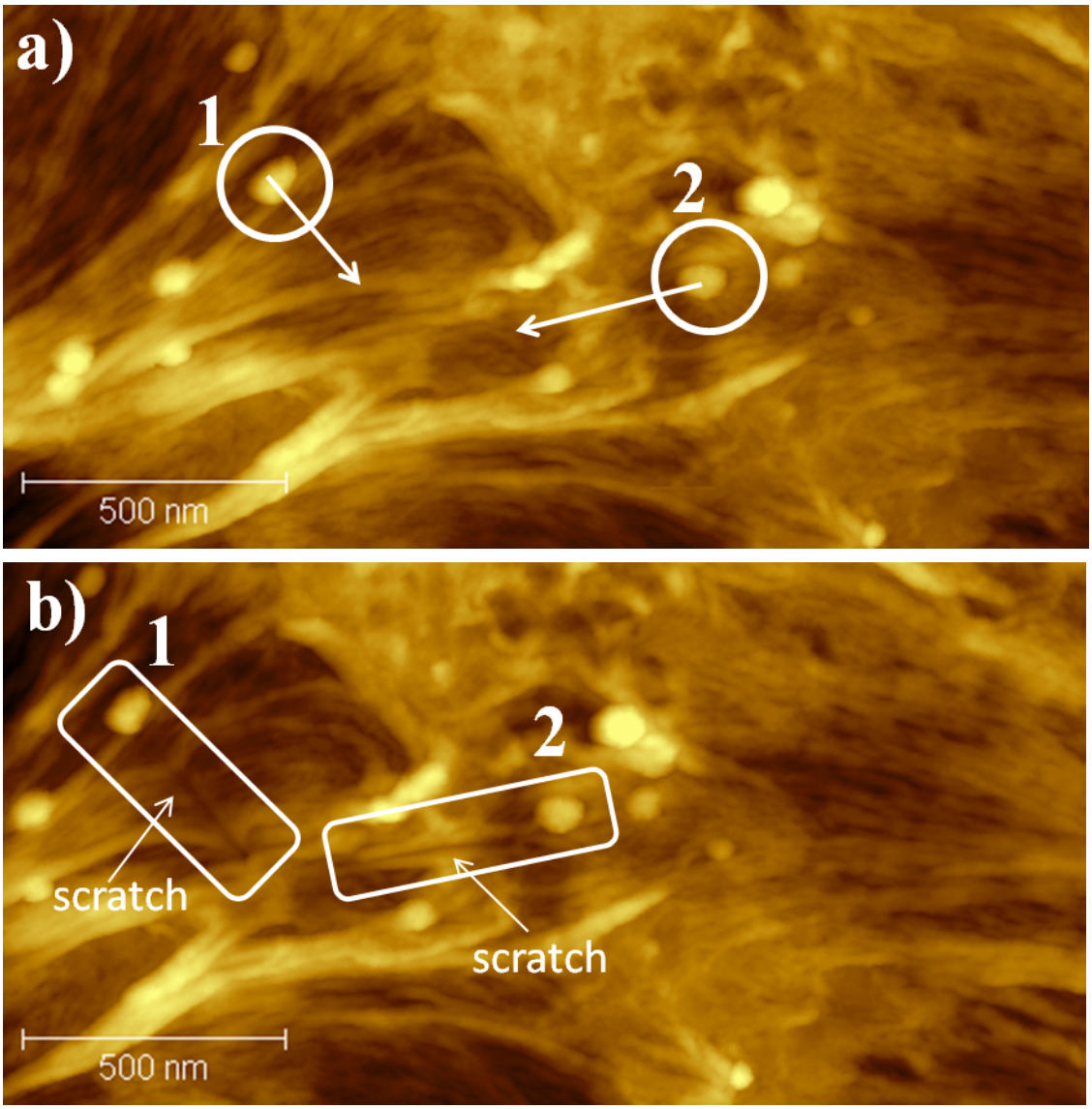


Figure 23. AFM image of PC-SiO_2@PA film : a) before and b) after NP manipulations. Particle **1** was moved with vertical tip depth of Z = -40nm and particle **2** with Z = -30nm both particles did not moved and scratches can be seen for both cases.

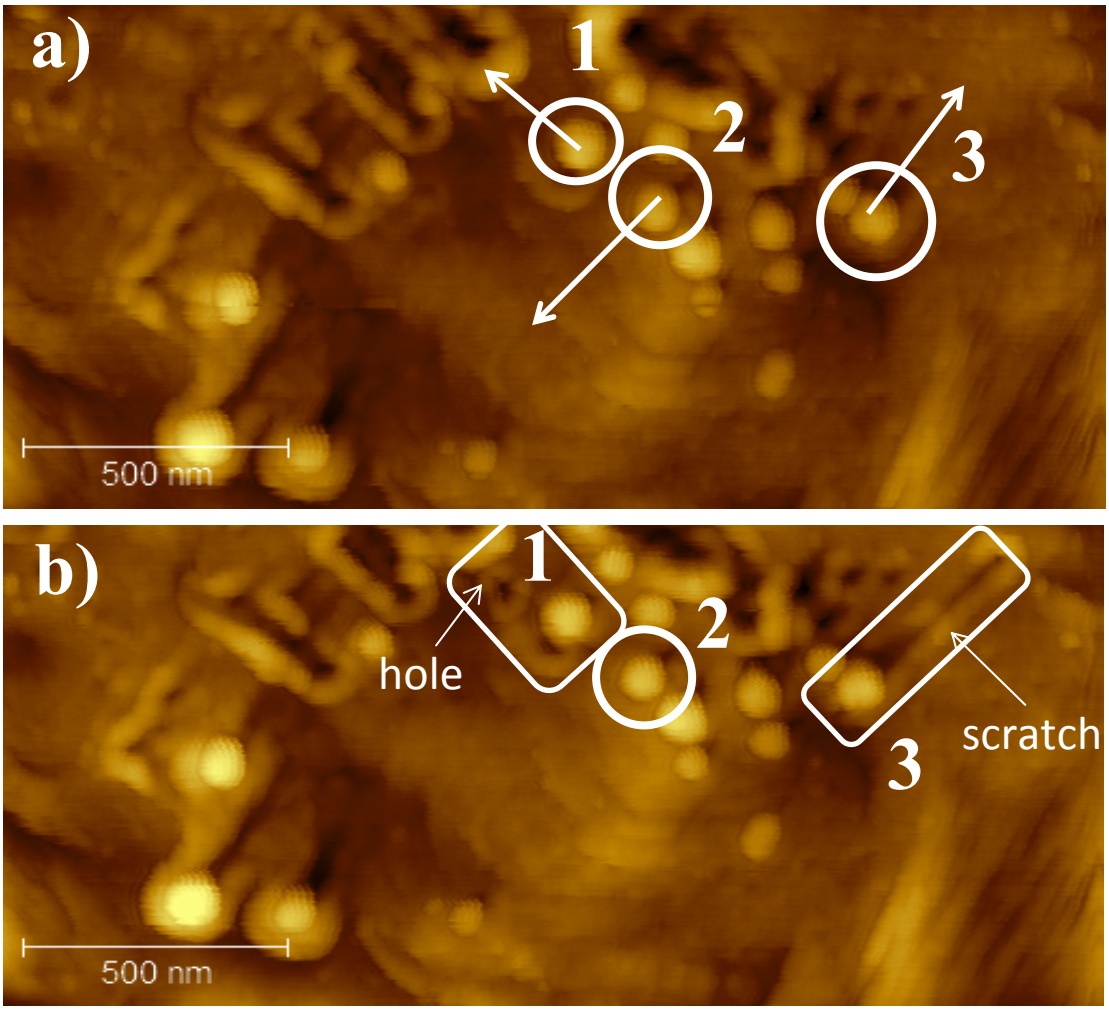


Figure 24. AFM image of PC-SiO_2@PFPA film : a) before and b) after NP manipulations. Particle **1** was moved with vertical tip depth of Z = -20nm and Z = -30, particle **2** with Z = -30nm and particle **3** with Z = -40nm all three particles did not moved and a dip scratch can be seen for **3** and a hole in the place where the tip stopped for **2**.

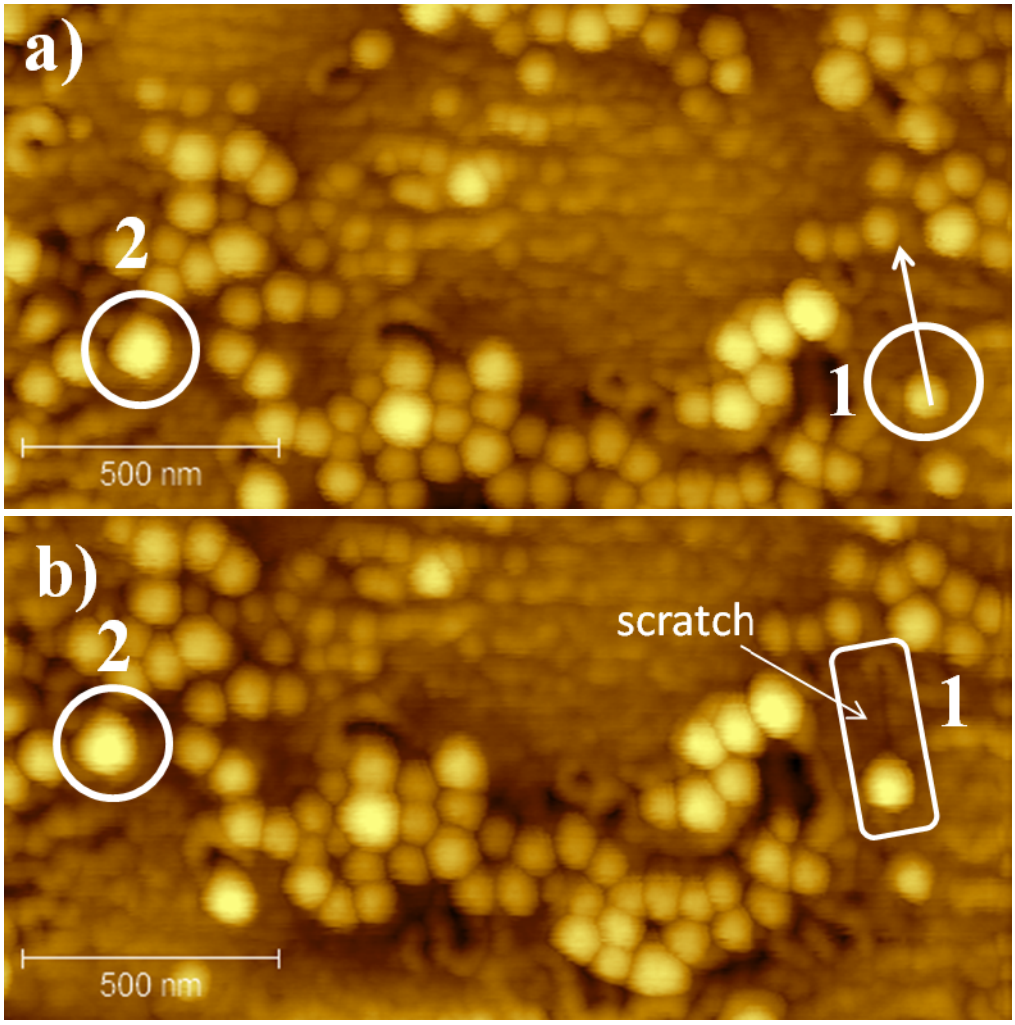


Figure 25. AFM image of PC-SiO_2@BPh film: a) before and b) after NP manipulations. Particle **1** was moved with vertical tip depth of Z = -30 and Z = -40nm and particle **2** with Z = -40nm, Z = -50nm and Z = -60nm both particles did not moved and scratch can be seen for **1**.

Neat PC film

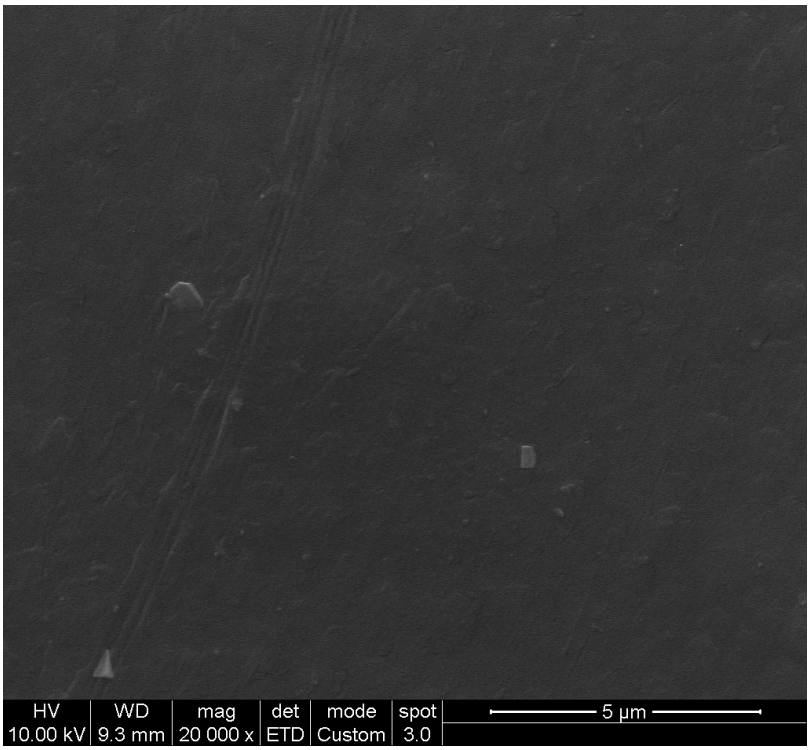


Figure 26. SEM image of neat PC film

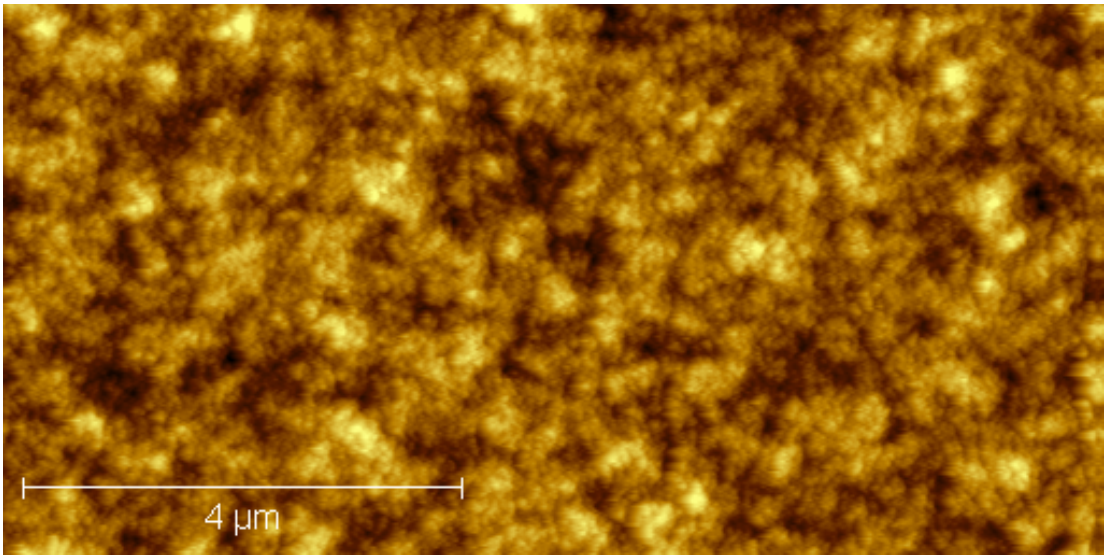


Figure 27. AFM image of neat PC film

XPS spectra:

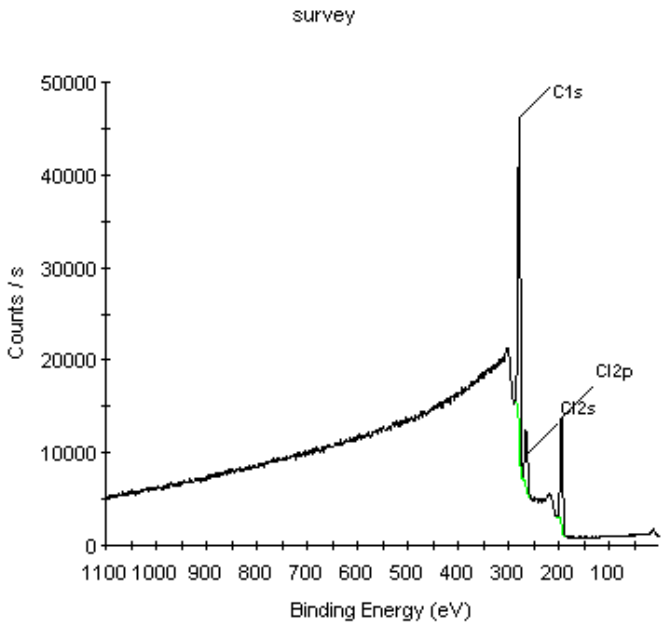


Figure 28. XPS spectra of neat PC film

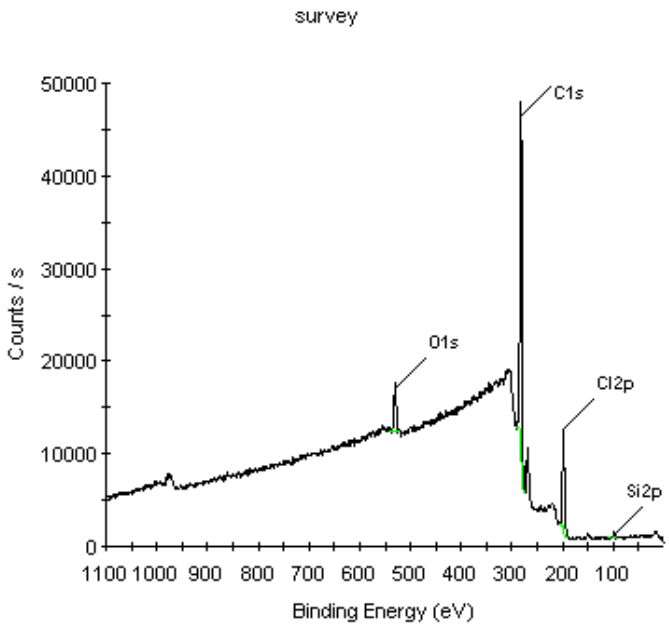


Figure 29. XPS spectra of PC-SiO_2 film

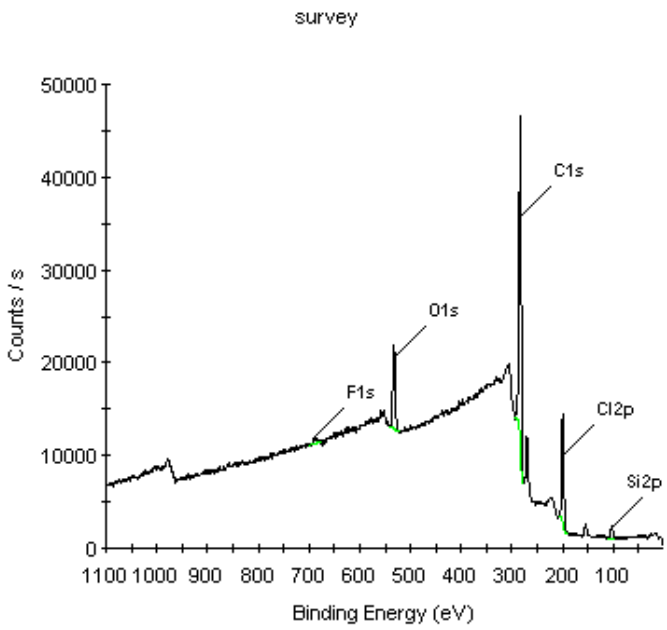


Figure 30. XPS spectra of PC-SiO_2@PFPA film

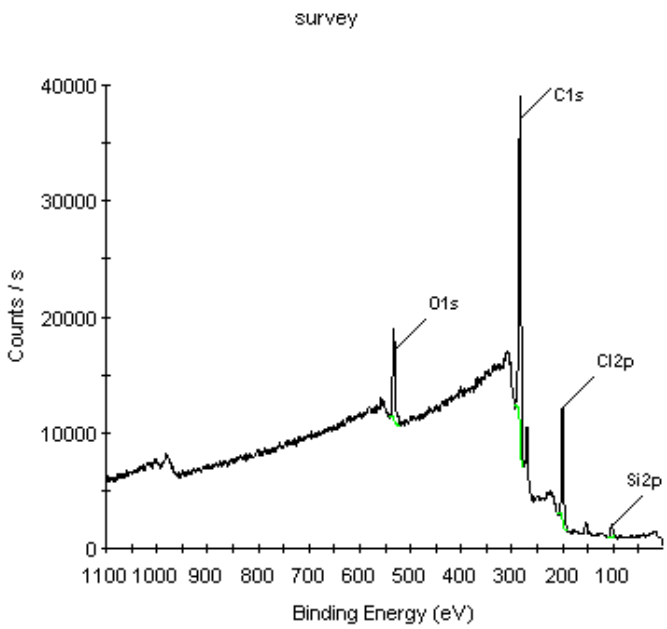


Figure 31. XPS spectra of PC-SiO_2@BPh film

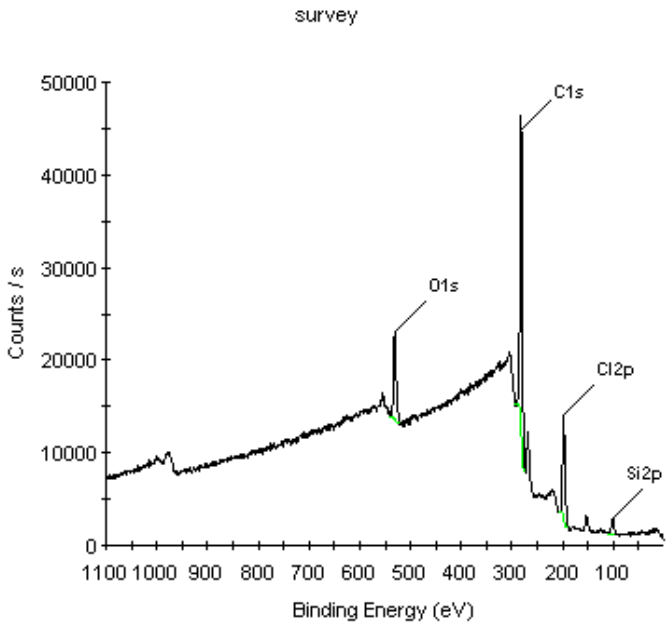


Figure 32. XPS spectra of PC-SiO_2@PA film

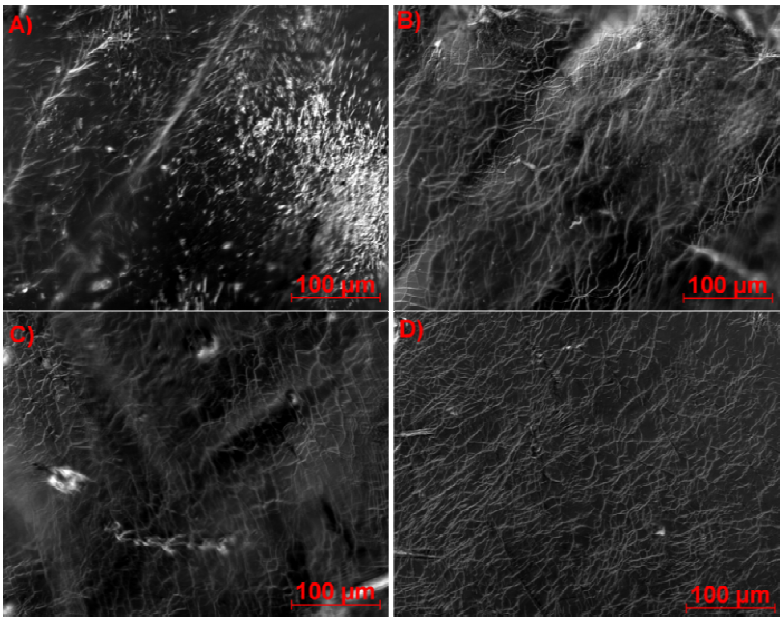


Figure 33. DIC filter images of A) PC-SiO_2@PA ; B) PC-SiO_2@PFPA; C) PC-SiO_2@BPh, and D) PC-SiO_2 films

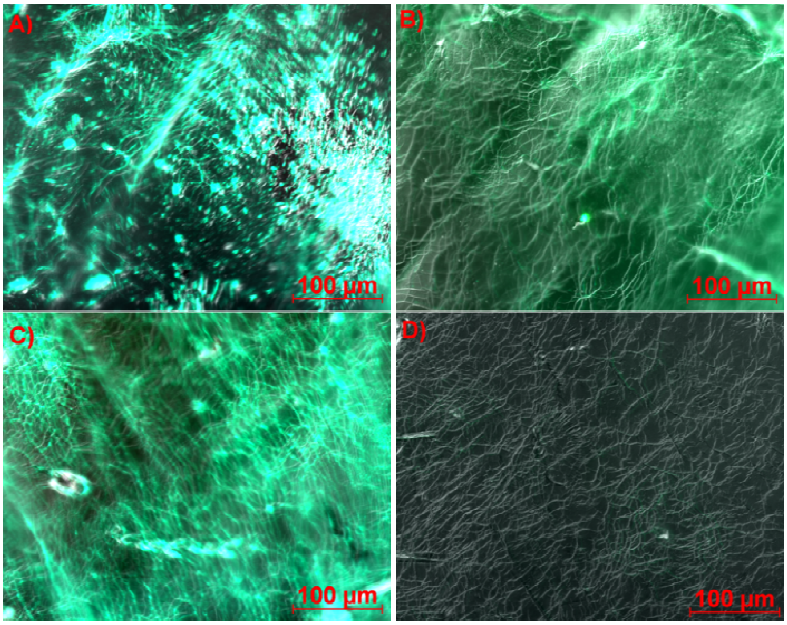


Figure 34. merged GFP, CFP, and DIC filters fluoresence images of A) PC-SiO_2@PA ; B) PC-SiO_2@PFPA; C) PC-SiO_2@BPh, and D) PC-SiO_2 films

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