Supplementary Information (SI) for Nanoscale.

Hydrogen bonds driven supramolecular assemblies during hybrid mesoporous silica films structuration

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Supporting Information

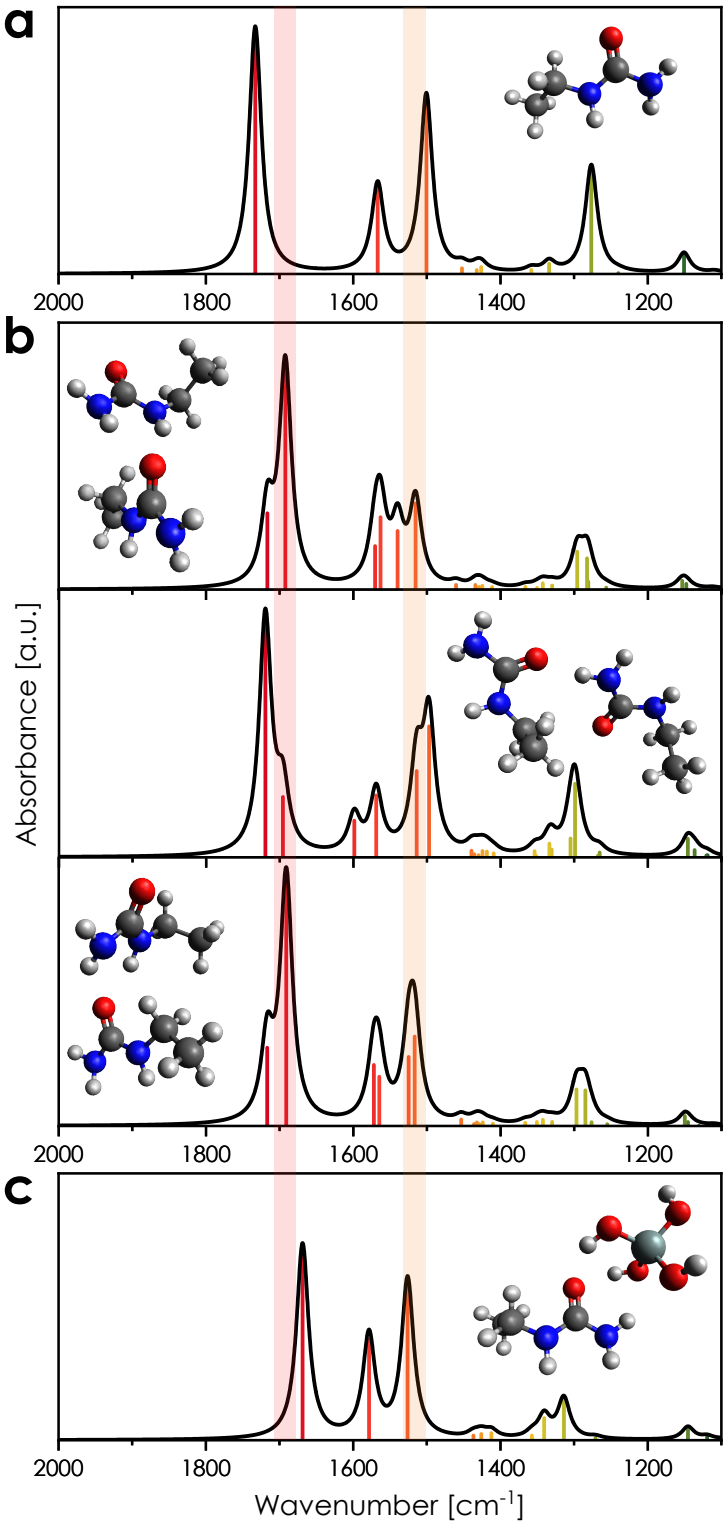


Figure S1: Spectra simulated by convoluting DFT computed harmonic frequencies with a Gaussian functions having an FWHM of 5 cm^{-1}: (a) Free ureido moiety; (b) Ureido-ureido dimers; (c) Ureido-silanol hydrogen bond. Red and orange lines correspond to the amide I and amide II bands in the spectrum of the H-bonded ureido moiety forming the dimer.

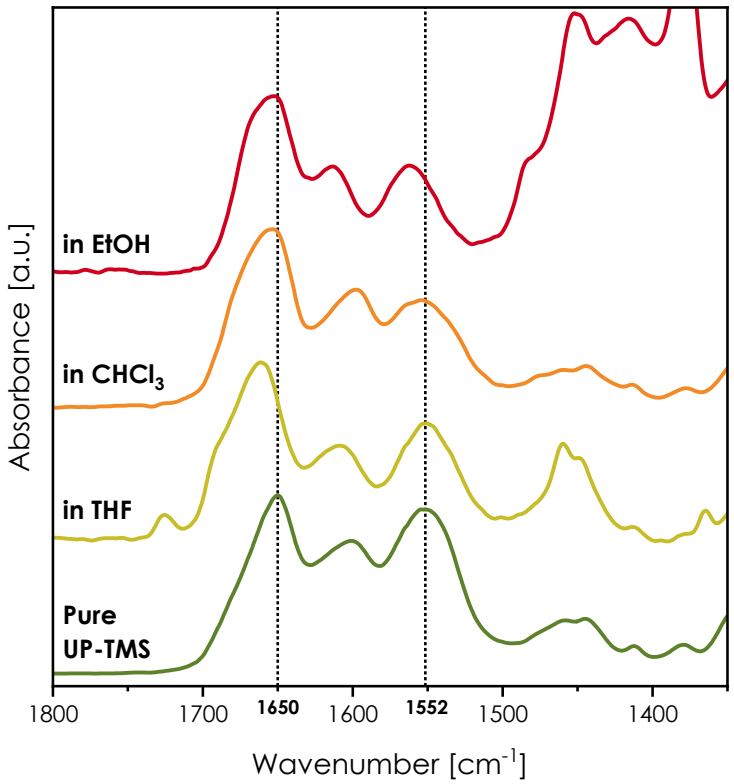


Figure S2: Evolution of IR spectra within amide I and II regions for UP-TMS after dilution in EtOH, $CHCl_3$, and THF compared with the spectrum of the pure precursor. Dashed lines at 1650 and 1552 cm^{-1} correspond to the amide I and II bands for pure UP-TMS precursor.

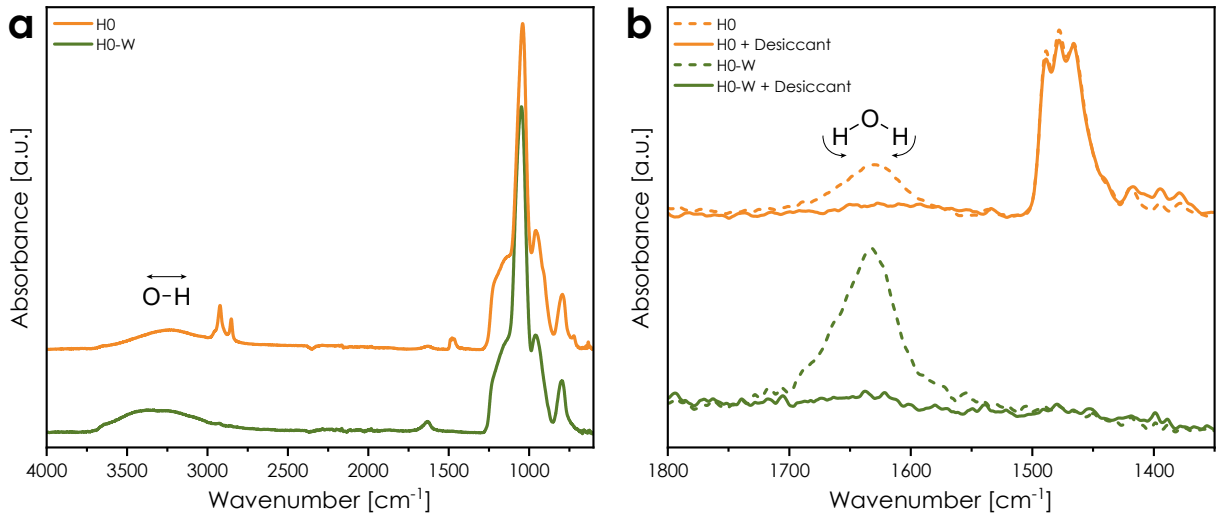


Figure S3: The template removal leads to two important changes in the IR spectrum: an increase of the broad band between 3700 and 3000 cm^{-1} (hydroxyl group stretching modes from adsorbed water and Si−OH species) and growth of δ(H−O−H) bending band at 1635 cm^{-1}.[1,2] The latter vibration, coming from physically adsorbed water, overlaps with the amide I band, introducing ambiguity in the analysis. Additionally, physisorbed water may compete with other species in forming hydrogen bonds with ureido groups. To eliminate this interference, all spectra of hybrid films were recorded by placing the samples on the ATR prism and covering them with a small cell filled with desiccant (drierite). This approach was demonstrated to be very efficient for immediate water desorption and suppression of δ(H−O−H) band, ensuring no overlap within the amide I region.

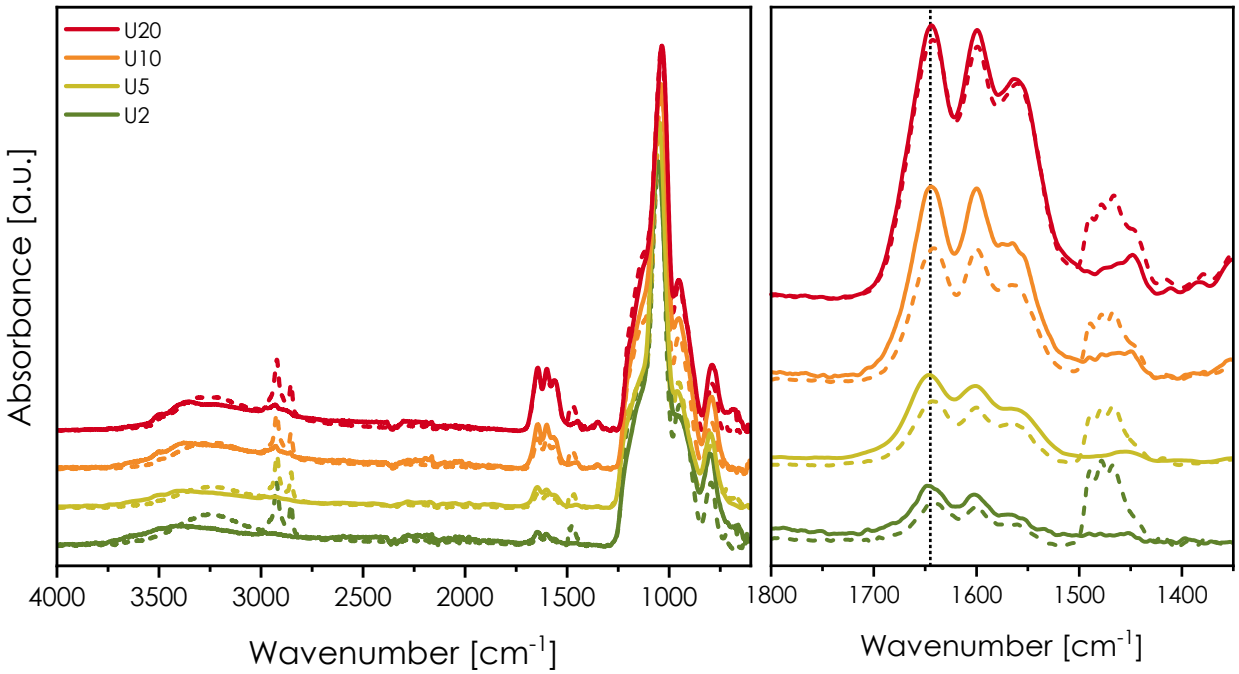


Figure S4: Full spectra of raw (dashed line) and washed (solid line) U2-U20 films normalized to (Si-O-Si) vibrational band. Dotted vertical line corresponds to the peak of the amide I band for the U20-W sample

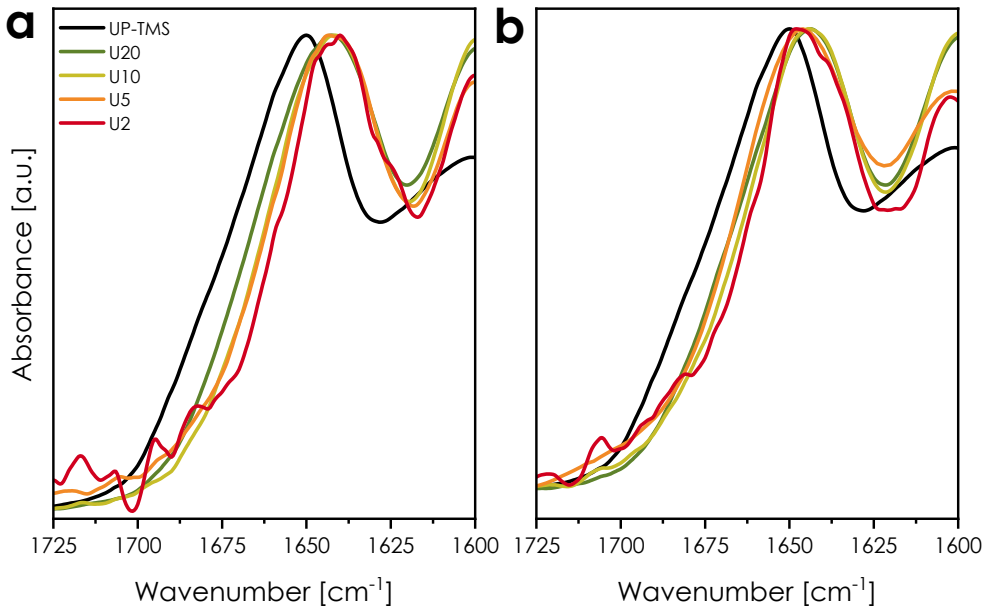


Figure S5: Zoom into amide I band of films with increasing UP-TMS concentration: (a) As-made films; (b) Films after the template removal.

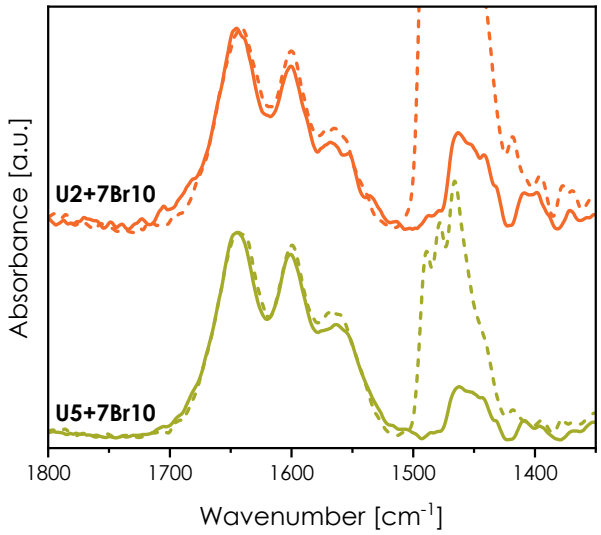


Figure S6: Comparison of ternary films derived from UP-TMS and 7Br-TMS precursors before (dashed lines) and after the template removal (solid lines).

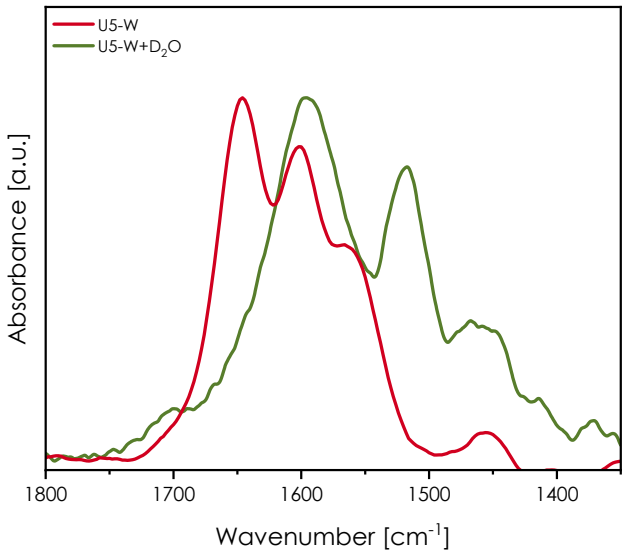


Figure S7: Deuteration of hydroxyl groups on the silica surface can be easily achieved by placing the sample in a closed container with D_2O vapors. While this method can be helpful to analyse hydrogen bonds, it cannot be used for UP-TMS hybrid films due to additional and immediate exchange of amid protons, which is observed in this IR spectrum.

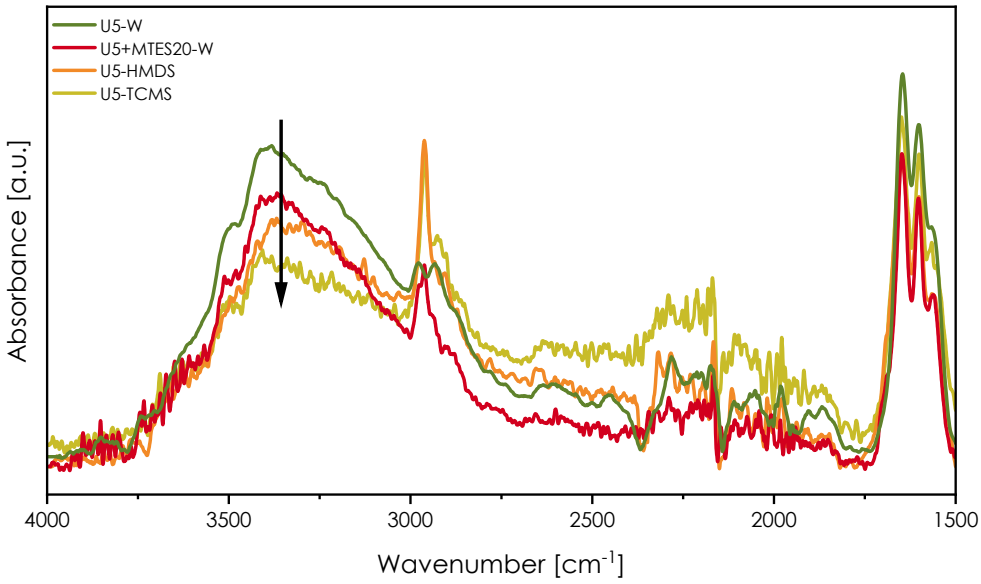


Figure S8: Decrease of the intensity of the broad band associated with OH stretching observed when hydroxyl groups on the silica surface are replaced through post-functionalization with TCMS or HMDS.

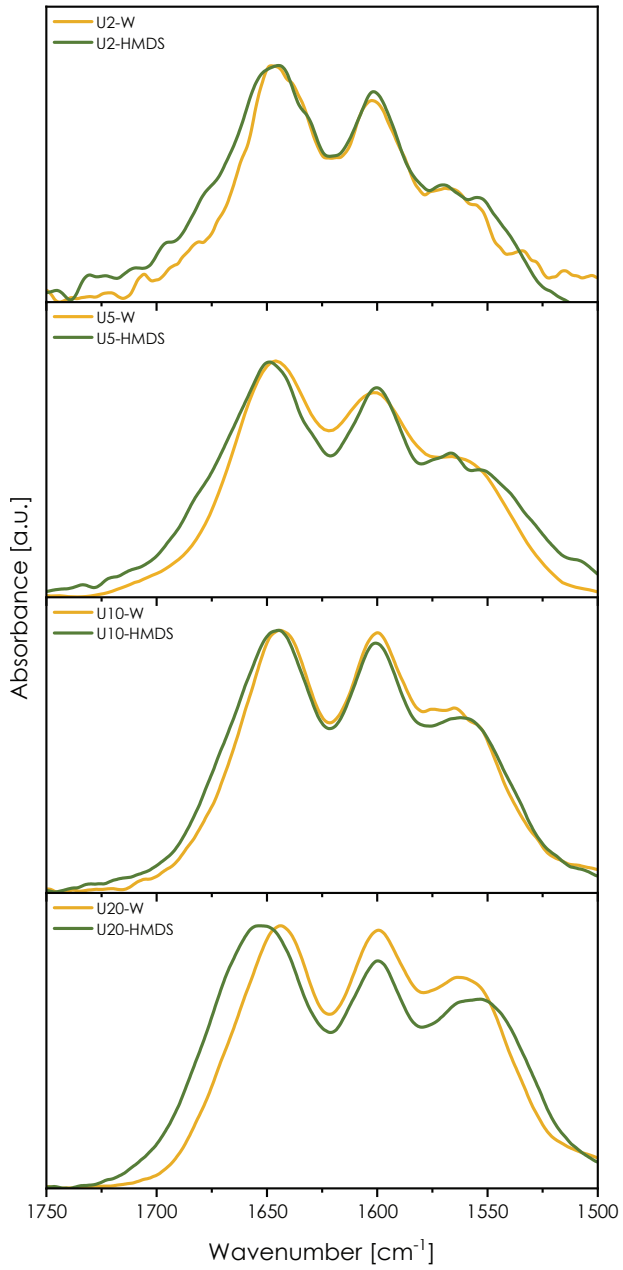


Figure S9: Spectra of samples before and after HMDS treatment with increasing concentration of UP-HMDS: U2-HMDS, U5-HMDS, U10-HMDS, and U20-HMDS.

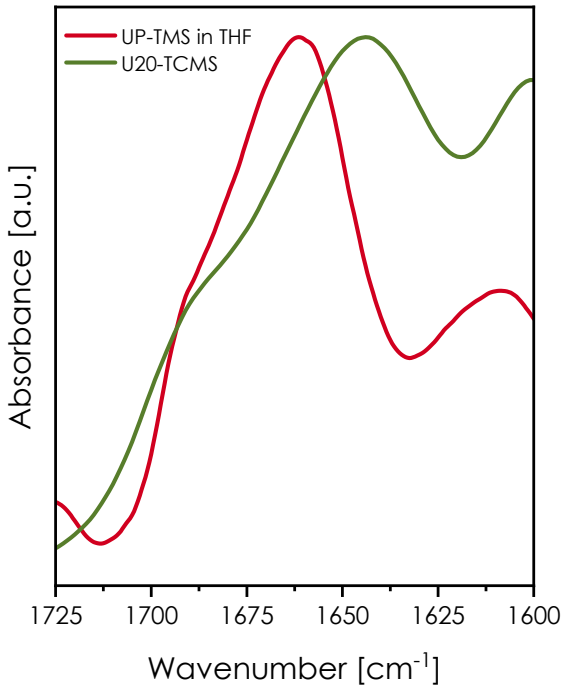


Figure S10: Comparison of IR spectra of U20-HMDS film and UP-TMS diluted in THF. A bulge below 1700 cm^{-1} suggest the presence of free ureido groups in functionalized silica U20-HMDS.

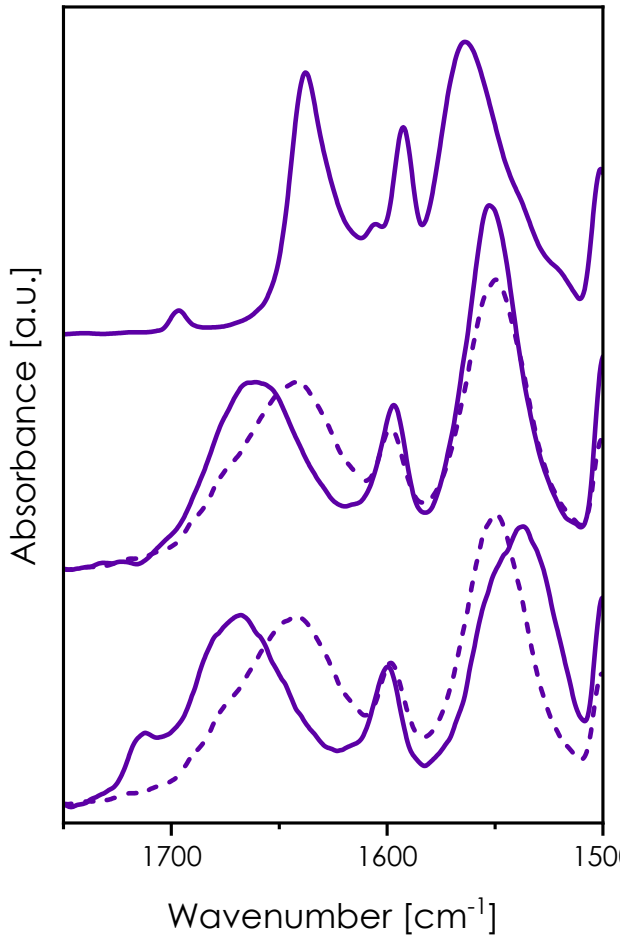


Figure S11: Evolution of the amide I band in films containing 5 mol% of PhU-TES precursor. Top: pure PhU-TES; middle: hybrid film before (solid lines) and after the template removal (dashed lines); bottom: thin films before (dashed lines) and after (solid lines) the HMDS post-functionalization.

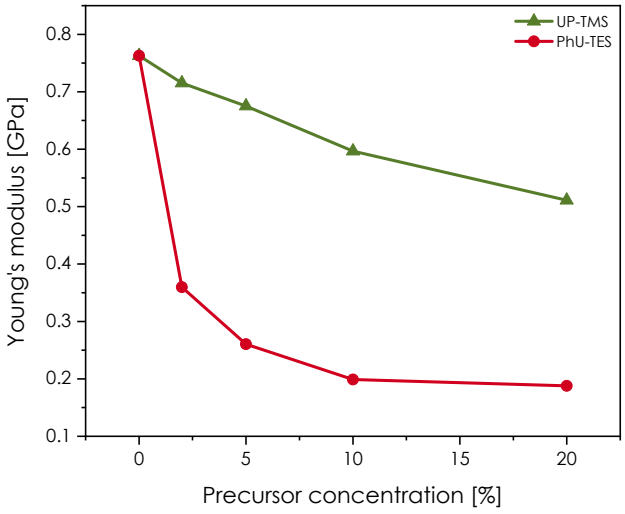


Figure S12: Evolution of the Young's modulus with precursor concentration for UP-TMS and PhU-TES films.

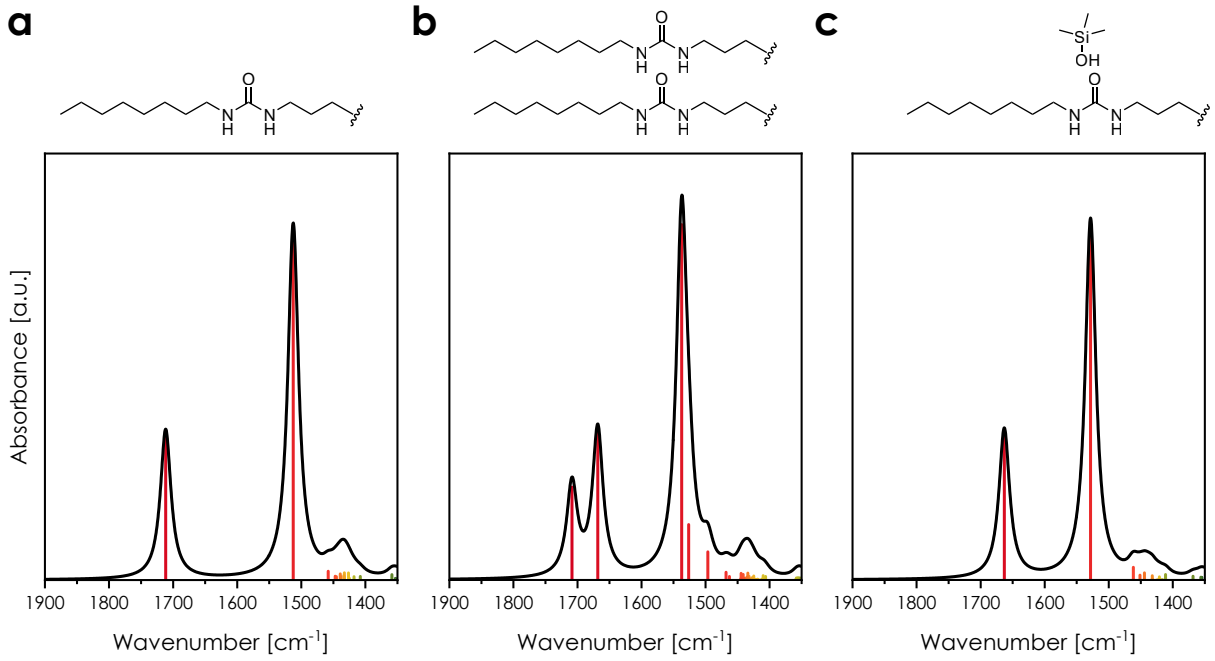


Figure S13: Spectra simulated by convoluting DFT computed harmonic frequencies with a Gaussian functions having an FWHM of 5 cm^{-1}: (a) Free C_8U molecule; (b) C_8U dimers; (c) C_8U bonding with silanol.

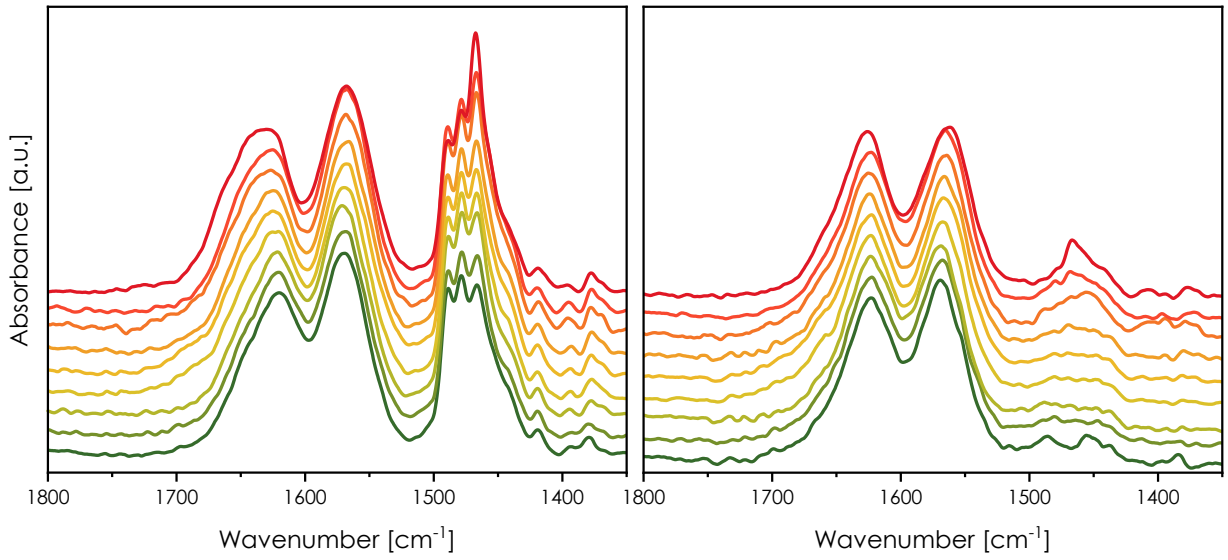


Figure S14: IR spectra of raw (left) and washed (left) samples containing 5 mol% of C_nU-TES precursors. Chain length decreases from top to bottom.

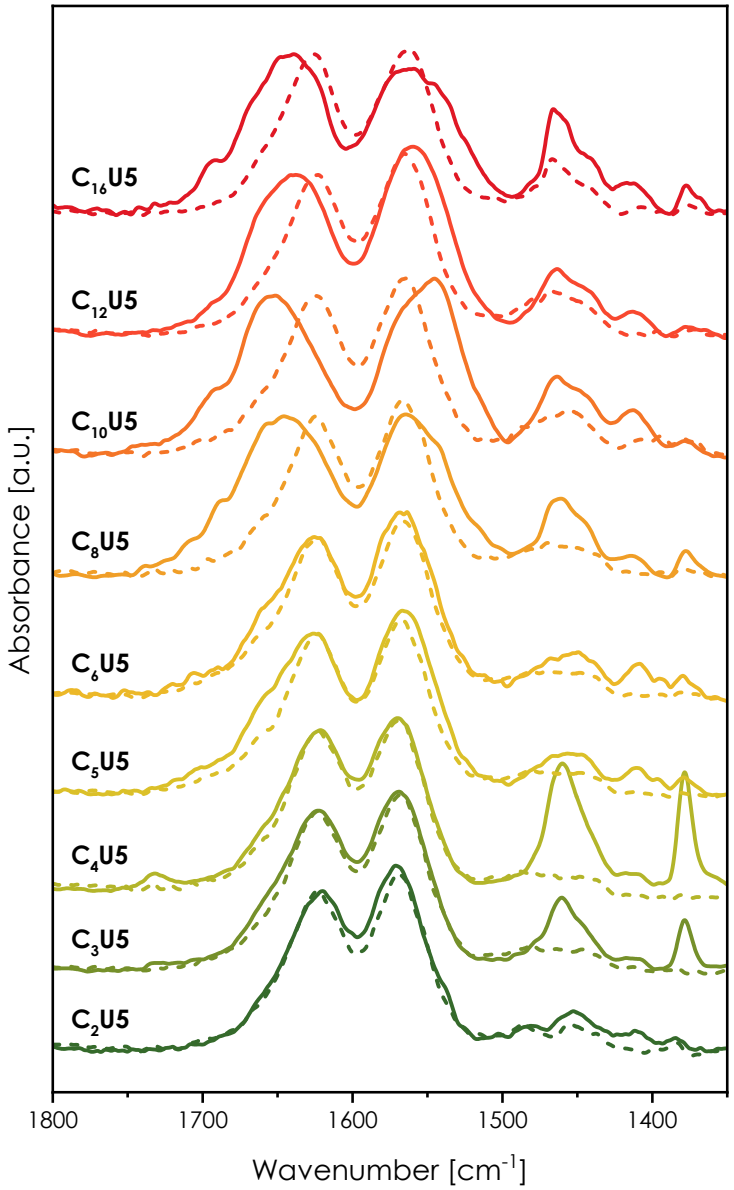


Figure S15: IR spectra samples containing 5 mol% of C_nU-TES precursors before (dashed lines) and after (solid lines) the functionalization with HMDS.

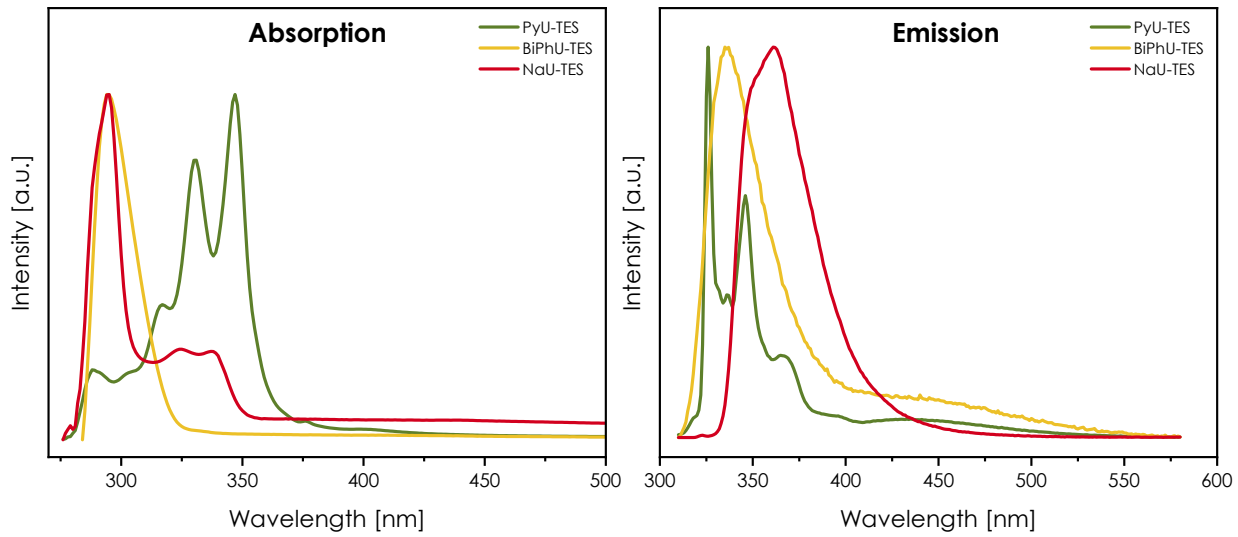


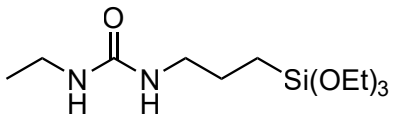
Figure S16: UV-Vis absorption and fluorescence emission spectra for dual-functionality probes UMePy-TES, BiPhU-TES, and UNa-TES.

Synthesis of the organosilane precursors

(3-Isocyanatopropyl)triethoxysilane (95%), Ethylamine (in THF, 2M), Pentylamine (99%), Decylamine (95%), Hexadecylamine (99%), 1-Pyrenemethylamine hydrochloride (95%), 4-Aminobiphenyl were purchased from Sigma-Aldrich. Propylamine (99%) and Heptylamine (99%) were bought from Acros, Hexylamine (99%) and Cyclohexylamine (99%) from TCI, Octylamine (99%) from Thermo Fisher, 11-Aminoundecyltriethoxysilane from Gelest, and 2-Naphtylamine (95%) from Enamine. All chemicals were used without any supplementary purification.

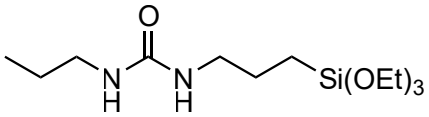
All the compounds (except PyMeU-TES) were prepared in the same conditions according to the protocol published by Pichon *et al.*[3] Under an argon atmosphere, 3-isocyanatopropyl-triethoxysilane (2 mmol) was added to a solution of amine (2 mmol) in dry THF (4 mL). An exothermic effect was observed while mixing the reagents. The mixture was heated for two hours at 60°C. The solvent was removed under a vacuum, and the crude product was taken in pentane (5 mL). After the filtration, products were obtained quantitatively.

1-Ethyl-3-(3-(triethoxysilyl)propyl)urea (C_2U-TES)



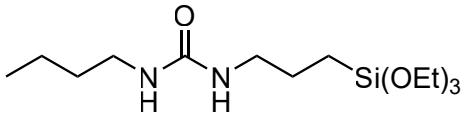
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8 Hz, 2H), 1.12 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7 Hz, 9H), 1.60 (p, J = 7.54 Hz, 2H), 3.15 (q, J = 7.2 Hz, 2H), 3.20 (q, J = 7.0 Hz, 2H), 3.80 (q, J = 7.0 Hz, 6H), 4.18 (s, 1H), 4.39 (s, 1H)

1-Propyl-3-(3-(triethoxysilyl)propyl)urea (C_3U-TES)



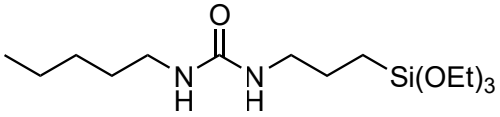
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H)1.20 (t, J = 7.0 Hz, 9H), 1.49 (q, J = 7.2 Hz, 2H), 1.60 (m, 2H), 3.12 (m, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.26 (s, 1H), 4.42 (s, 1H)

1-Butyl-3-(3-(triethoxysilyl)propyl)urea (C_4U-TES)



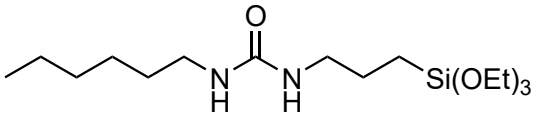
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.90 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.0 Hz, 9H), 1.33 (m, 2H), 1.46 (m, 2H), 1.60 (m, 2H), 3.14 (m, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.22 (s, 1H), 4.41 (s, 1H).

1-Pentyl-3-(3-(triethoxysilyl)propyl)urea (C_5U-TES)



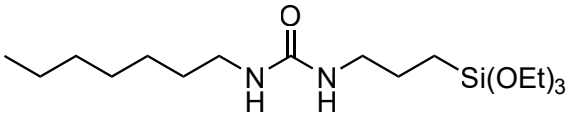
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.87 (t, J = 6.8 Hz, 3H), 1.21 (t, J = 7.0 Hz, 9H), 1.29 (m, 4H), 1.48 (m, 2H), 1.61 (m, 2H), 3.16 (p, J = 6.4 Hz, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.19 (s, 1H), 4.38 (s, 1H).

N-Hexyl-*N*'-[3-(triethoxysilyl)propyl]urea (C_6U-TES)



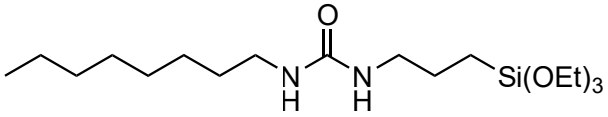
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.86 (t, J = 6.7 Hz, 3H), 1.21 (t, J = 7.0 Hz, 9H), 1.28 (m, 6H), 1.47 (m, 2H), 1.60 (m, 2H), 3.14 (p, J = 6.4 Hz, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.19 (s, 1H), 4.38 (s, 1H).

N-Heptyl-*N*'-[3-(triethoxysilyl)propyl]urea (C_7U-TES)



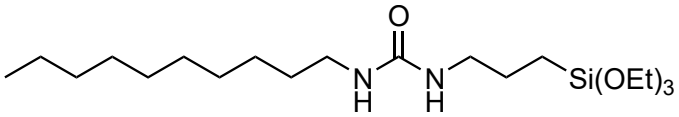
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.86 (t, J = 6.7 Hz, 3H), 1.21 (t, J = 7.0 Hz, 9H), 1.26 (m, 8H), 1.47 (m, 2H), 1.61 (m, 2H), 3.13 (p, J = 6.5 Hz, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.20 (s, 1H), 4.39 (s, 1H).

N-Octyl-*N*'-[3-(triethoxysilyl)propyl]urea (C_8U-TES)



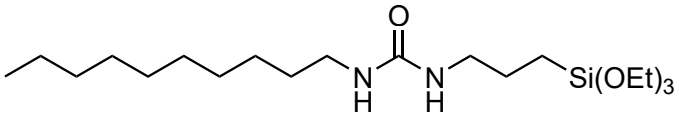
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.85 (t, J = 6.6 Hz, 3H), 1.20 (t, J = 7 Hz, 9H), 1.25 (m, 10H), 1.46 (m, 2H), 1.60 (m, 2H), 3.13 (p, J = 6.5 Hz, 4H), 3.80 (q, J = 7 Hz, 6H), 4.25 (s, 1H), 4.43 (s, 1H).

N-Decyl-*N*'-[3-(triethoxysilyl)propyl]urea ($C_{10}U-TES$)



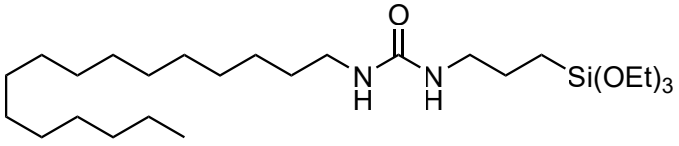
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.86 (t, J = 6.7 Hz, 3H), 1.21 (t, J = 7 Hz, 9H), 1.25 (m, 14H), 1.47 (m, 2H), 1.60 (m, 2H), 3.13 (p, J = 6.6 Hz, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.19 (s, 1H), 4.38 (s, 1H).

N-Dodecyl-*N*'-[3-(triethoxysilyl)propyl]urea ($C_{12}U-TES$)



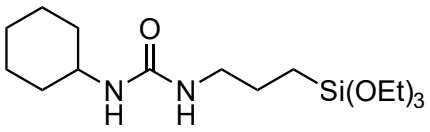
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.86 (t, J = 6.7 Hz, 3H), 1.21 (t, J = 7 Hz, 9H), 1.25 (m, 18H), 1.47 (m, 2H), 1.60 (m, 2H), 3.13 (p, J = 6.6 Hz, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.19 (s, 1H), 4.38 (s, 1H).

N-Hexadecyl-*N*'-[3-(triethoxysilyl)propyl]urea ($C_{16}U-TES$)



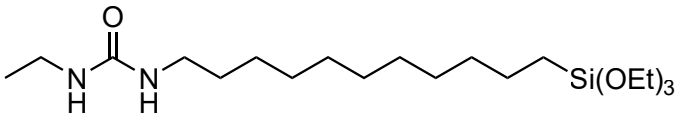
^1HNMR (300 MHz, $CDCl_3$) δ = 0.62 (t, J = 8.1 Hz, 2H), 0.86 (t, J = 6.7 Hz, 3H), 1.21 (t, J = 7 Hz, 9H), 1.25 (m, 26H), 1.46 (m, 2H), 1.60 (m, 2H), 3.13 (p, J = 6.6 Hz, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.18 (s, 1H), 4.39 (s, 1H).

N-Cyclohexyl-*N*'-[3-(triethoxysilyl)propyl]urea (CyU-TES)



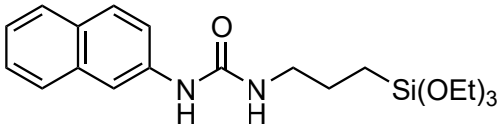
^1HNMR (300 MHz, $CDCl_3$) $\delta = 0.62$ (t, J = 8.1 Hz, 2H), 0.98-1.43 (m, 5H), 1.21 (t, J = 7 Hz, 9H), 1.63 (m, 5H), 1.92 (m, 2H), 3.14 (q, J = 6.6 Hz, 2H), 3.48 (m, 1H), 3.80 (q, J = 7.0 Hz, 6H), 4.07 (s, 1H), 4.33 (s, 1H).

N-Ethyl-*N*'-[11-(triethoxysilyl)undecyl]urea ($UC_{11}-TES$)



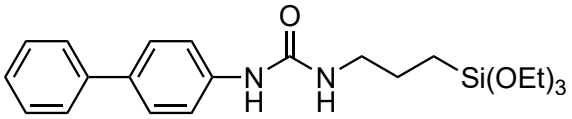
^1HNMR (300 MHz, $CDCl_3$) $\delta = 0.61$ (t, J = 8.0 Hz, 2H), 1.12 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7 Hz, 9H), 1.25 (m, 18H), 3.16 (m, 4H), 3.80 (q, J = 7.0 Hz, 6H), 4.11 (s, 2H).

N-2-Naphthalenyl-*N*'-[3-(triethoxysilyl)propyl]urea ($NaU-TES$)



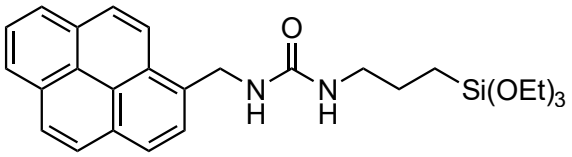
^1HNMR (300 MHz, $CDCl_3$) $\delta = 0.65$ (t, J = 8 Hz, 2H), 1.19 (t, J = 7 Hz, 9H), 1.66 (m, 2H), 3.28 (q, J = 6.6 Hz, 2H), 3.79 (q, J = 7 Hz, 6H), 4.96 (s, 1H), 6.33 (s, 1H), 7.38 (m, 3H), 7.77 (m, 4H).

N-[1,1'-Biphenyl]-4-yl-*N'*-[3-(triethoxysilyl)propyl]urea (BiPhU-TES)



^1HNMR (300 MHz, $CDCl_3$) δ = 0.65 (t, J = 8.0 Hz, 2H), 1.20 (t, J = 7.0 Hz, 9H), 1.66 (m, 2H), 3.24 (q, J = 6.5 Hz, 2H), 3.80 (q, J = 7.0 Hz, 6H), 4.90 (t, 1H), 6.20 (s, 1H), 7.37 (m, 5H), 7.54 (m, 4H).

N-(1-Pyrenylmethyl)-*N'*-[3-(triethoxysilyl)propyl]urea (PyMeU-TES)



The compound was synthesized following the protocol presented by Ramapzzo *et al.*[4] Triethoxy(3-isocyanatopropyl)silane (3.30 mL, 13.3 mmol) and triethylamine (0.20 mL, 1.43 mmol) were added to a solution of 1-methylaminopyrene hydrochloride (0.238 g, 0.89 mmol) in dry dimethylformamide (4.0 mL). The mixture was stirred at RT for five hours, followed by the addition of a few drops of DCM. The precipitation was induced by adding petroleum ether (100 mL). A white solid containing the product was filtered and washed with petroleum ether. The crude was taken in THF and filtered again. The solvent was removed under a vacuum, and petroleum ether (100 mL) was slowly added to the concentrated product. After filtration, *N*-(1-pyrenylmethyl)-*N'*-[3-(triethoxysilyl)propyl]urea was obtained as a yellowish solid (0.29 g, yield: 76%). ^1HNMR (300 MHz, $CDCl_3$) δ = 0.60 (t, J = 8.1 Hz, 2H), 1.14 (t, J = 7.0 Hz, 9H), 1.61 (m, 2H), 3.02 (q, J = 7.2 Hz, 2H), 3.72 (q, J = 7.0 Hz, 6H), 4.82 (s, 1H), 5.01 (s, 1H), 5.08 (d, J = 5.3 Hz, 2H), 7.99 (m, 4H), 8.13 (m, 4H), 8.32 (d, J = 9.2 Hz, 1H)

References

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