Supporting Information for

Coating of polydopamine on polyurethane open cell foams to design soft structured support for molecular catalysts

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1. Materials and methods

Commercial compounds were used as received. Polyurethane open cells foams (20 PPI) were purchased from FoamPartner. Dopamine hydrochloride (008896) was purchased from Fluorochem. Tris base (99.9+ % - T1503), 4-methoxybenzyl alcohol (98% - 136905), allyl alcohol (99%- 240532), cinnamyl alcohol (97% - 96330), phenol (99% - 77612) and benzaldehyde (≥ 99.5% - 418099) were purchased from Sigma-Aldrich. Benzyl alcohol (99+% - 41218), 4-aminobenzyl alcohol (98% - A14130), cyclohexanol (99% - A17576), furfuryl alcohol (98% - A10968), 4-(chloromethyl)phenyltrimethoxysilane (90% - L16432), diphenylsilane (97% - A10884) were purchased from Alfa Aesar. 4-Fluorobenzyl alcohol (97% - PC3660) was purchased from Apollo Scientific. 18.2 MΩ deionized water (TOC < 1 ppb), supplied by a Q20 Millipore system, was used for the preparation of aqueous solutions and washing procedures with water. All reactions involving DMAP-TES and nickel complexes were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon. 4-\{N-[3-(Triethoxysilyl)propyl]-N-methyl-amino\}pyridine (DMAP-TES)\textsuperscript{1} and 1-mesityl-1H-imidazole\textsuperscript{2} were prepared according to the published methods.

Scanning electron microscopy (SEM) measurements were recorded with a Hitachi SU8010 FE-SEM microscope at 1 kV at room temperature. No metallization of the samples was done, but their borders were covered with a metallic tape to evacuate the excess of charge.

Elemental mapping by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) was investigated with a Zeiss Gemini SEM 500 FEG EDAX Octane Elite EDX detector. The X-rays emitted upon electron irradiation were acquired in the range 0–20 keV. Quantification was done using the standard-less ZAF correction method in the Team EDS software from EDAX.

Compression tests were carried out on an Instron E3000 ElectroPuls system equipped with a 100 N load cell.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements were performed by the Plateforme Analytique of the Institut Pluridisciplinaire Hubert Curien (UMR CNRS 7178), Strasbourg, France.

Solution NMR spectra were recorded at 298 K on Bruker Avance I 300 MHz, Bruker Avance III HD 400 MHz or Bruker Avance III 600 MHz spectrometers operating at 300.13, 400.13 or 600.13 MHz for \textsuperscript{1}H and at 75.47, 100.61 or 150.89 MHz for \textsuperscript{13}C\{\textsuperscript{1}H\}. The chemical shifts are referenced to the residual deuterated or \textsuperscript{13}C solvent peaks. Chemical shifts (δ) and
coupling constants \( (J) \) are expressed in ppm and Hz respectively.

For solid-state NMR spectra, the foam samples were frozen into \( \text{N}_2(\text{l}) \) and grinded. The grinded foams were then packed in 4 mm \( \text{ZrO}_2 \) rotors under air. The \( ^{29}\text{Si} \) CP-MAS experiments spectra were recorded at 298 K on a Bruker Solid State DSX 300 MHz NMR spectrometer operating at 69.66 MHz, and equipped with a Bruker 4 mm \( ^1\text{H}/\text{X} \) CP-MAS probe. A shaped Cross-Polarization pulse sequence with tangential modulation on both channels was used with the following parameters: the spinning speed was set to 10 kHz, the spectral width to 30 kHz, the contact time was in the range of 1 ms, the proton RF field was around 55 kHz for decoupling (using SPINAL 64 sequence) and 40 kHz for contact, with a recycle delay of 5s. The spectra were calibrated with respect an external PDMS sample (\(-35.1\) ppm).

High-resolution mass spectra were recorded on a Bruker micrOTOF or Bruker micrOTOF-Q mass spectrometer by the Laboratoire de Spectrométrie de Masse BioOrganique, of the Institut Pluridisciplinaire Hubert Curien (UMR CNRS 7178), Strasbourg, France.

2. **Open cell polyurethane foam (OCPF) coating with polydopamine (PDA)**

Adapted from our published procedure.\(^3\) Dopamine hydrochloride (2 mg/mL) was dissolved in an aqueous solution of Tris base (10 mM) buffered to pH 8.5 with aqueous HCl (1 M) (500 mL). Four cubic samples of OCPF (1.5 × 1.5 × 1.5 cm) were immersed in the stirred solution for 16 h at RT. The solution slowly turned black. The resulting PDA-coated foams (OCPF@PDA) were then taken out of the solution and dried in an oven at 80 °C. They were later washed in vigorously stirred water (3 × 10 min) and dried again in an oven at 80 °C.

OCPF and OCPF@PDA were characterized by SEM (Fig. S1 and S2).

3. **Functionalization of OCPF@PDA with DMAP-TES**

OCPF@PDA was washed for a few minutes in vigorously stirred toluene (3 × 30 mL) and dried under vacuum prior to the reaction.

A cubic sample of OCPF@PDA (1.5 × 1.5 × 1.5 cm) was introduced in a Schlenk tube under argon. A solution of DMAP-TES (10 mg/mL) in toluene (30 mL) was added, and the solution was stirred for 24 h at 70 °C. The resulting DMAP-functionalized foam, OCPF@PDA@DMAP, was then removed from the reaction medium, washed for a few minutes in vigorously stirred toluene (3 × 30 mL), and then dried under vacuum.
OCPUF@PDA@DMAP was characterized by SEM (Fig. 2), $^{29}\text{Si}$ CP-MAS NMR (Fig. S3), SEM-EDX (Fig. S4 and S5), and ICP-AES (mean Si content of 4.44 g ± 0.59 g/kg).

4. Acylation of alcohols

4.1. Acylation of benzyl alcohol catalyzed by DMAP or DMAP-TES under homogeneous conditions

Benzyl alcohol (6.3 mmol), acetic anhydride (8.7 mmol) and DMAP or DMAP-TES (0.6 mol%) were stirred in $n$-hexane or $n$-hexane/acetic acid (1:1) (25 mL) at 30 °C. After 3 h, $^1\text{H}$ NMR conversions were determined by removing an aliquot with a syringe, drying it under high vacuum, extracting the residue with CDCl$_3$ and filtering it in an NMR tube.

4.2. Acylation of alcohols catalyzed by OCPUF@PDA@DMAP under heterogeneous conditions

OCPUF@PDA@DMAP was washed in vigorously stirred $n$-hexane/acetic acid (1:1) (3 × 10 min in 30 mL) and dried under vacuum prior to the reaction.

An alcohol (6.3 mmol), acetic anhydride (8.7 mmol) and a cubic sample of OCPUF@PDA@DMAP whose mass was adjusted to have 0.6 mol% of immobilized DMAP-TES based on the Si content (i.e. 239 mg of OCPUF@PDA@DMAP for 4.44 g Si/kg) were stirred (600 rpm) in $n$-hexane/acetic acid (1:1) (25 mL) at 30 °C for 3-24 h. $^1\text{H}$ NMR conversions were determined by removing an aliquot with a syringe, drying it under high vacuum, extracting the residue with CDCl$_3$ and filtering the solution in an NMR tube.

4.3. Reusability procedure

After each run, the piece of OCPUF@PDA@DMAP was removed from the reaction medium, washed for a few minutes in vigorously stirred $n$-hexane/acetic acid (1:1) (3 × 30 mL), dried under vacuum, possibly submitted to a compression test, and re-used (up to 10 times) as described in Section 4.2.

4.4. Stop-and-go experiment

OCPUF@PDA@DMAP was washed in vigorously stirred $n$-hexane/acetic acid (1:1) (3 × 10 min in 30 mL) and dried under vacuum prior to the reaction.
Benzyl alcohol (6.3 mmol), acetic anhydride (8.7 mmol) and a cubic sample of OCPUF@PDA@DMAP whose mass was adjusted to have 0.6 mol% of immobilized DMAP-TES based on the Si content were stirred (600 rpm) in n-hexane/acetone (1:1) (25 mL) at 30 °C. After 2 h, OCPUF@PDA@DMAP was removed from the reaction medium, which was let under stirring for 2 h in the absence of catalyst before OCPUF@PDA@DMAP was re-immersed in the solution. Aliquots were removed at T = 1, 2, 3, 4, and 5 h, dried under high vacuum, extracted with CDCl₃ and filtered in an NMR tube to follow the conversion by ¹H NMR spectroscopy (Fig. S6).

5. Compression tests

5.1. Compressive stress/strain response tests

Compression tests were performed at room temperature on cubic samples of OCPUF, OCPUF@PDA, and OCPUF@PDA@DMAP (as-synthesized, and after run 1 and 5; see Section 4.3.), by compressing it at 22 ± 2 °C between two cylindrical platens at a rate of 1% deformation/min to a strain of ca. 30% (Fig. S6), and recording the stress/strain response (see Fig. 3A and 3C).

5.2. Fatigue test

A fatigue test was performed at 22 ± 2 °C on a cubic sample of OCPUF@PDA@DMAP that had been used for 5 runs of 24 h (see Section 4.3.) by compressing it 5000 times between two cylindrical platens to a strain of ca. 30% through sinusoidal cycles of 1 Hz (Fig. S6). The stress/strain response (Fig. 3C) was then recorded according to the procedure detailed in Section 5.1.

6. Synthesis of [Ni(η⁵-C₅H₅)Cl(Mes-NHC-CH₂-C₆H₄-Si(OMe)₃)] (1) (Fig. S12)

6.1. Synthesis of 1-[3-(trimethoxysilyl)propyl]-3-(mesityl)imidazolium chloride

1-Mesityl-1H-imidazole (2.00 g, 11.6 mmol) and (4-chloromethyl)phenyltrimethoxysilane (2.31 mL, 10.5 mmol) (25 mL) were heated in toluene at 110 °C for 60 h. The solvent was then evaporated under vacuum, and the residue triturated with n-pentane (3 × 15 mL) and diethyl ether (3 × 15 mL) to afford a beige powder (4.05 g, 9.35 mmol, 89%). Anal. Calcd for C₂₂H₂₉N₂O₃SiCl: C, 61.02; H, 6.75; N, 6.47. Found: C, 60.63; H, 6.72; N, 6.44. HR-MS (ESI): m/z [M]+ calcd for C₂₂H₂₉N₂O₃Si 397.1947, found 397.1981. ¹H NMR (CDCl₃, 400 MHz): δ
10.89 (s, 1H, NCHN), 7.66 (s, 1H, NCH), 7.65 (d, J = 8.0, 2H, C₆H₄), 7.57 (d, J = 8.0, 2H, C₆H₄), 7.11 (s, 1H, NCH), 6.94 (s, 2H, m-HMes), 5.95 (s, 2H, CH₂), 3.59 (s, 9H, OCH₃), 2.29 (s, 3H, p-CH₃), 2.01 (s, 6H, o-CH₃) [Fig. S13]. ¹³C{¹H} NMR (CDCl₃, 106.61 MHz): δ 141.2 (NCHN), 138.4 (ipso-CMes), 136.4 (p-CMes), 135.8 (m-CMes), 134.2 (o-CMes), 131.1 and 130.9 (ipso- and p-C₆H₄), 129.9 and 128.6 (o- and m-C₆H₄), 123.6 (NCH), 123.3 (NCH), 53.2 (CH₂), 51.0 (OCH₃), 21.2 (p-CH₃), 17.7 (o-CH₃) [Fig. S14].

6.2. Synthesis of complex 1

Nickelocene (217 mg, 1.15 mmol) and 1-[3-(trimethoxysilyl)propyl]-3-(mesityl)imidazolium chloride (500 mg, 1.15 mmol) were refluxed in THF (20 mL) for 2 days. The reaction mixture was cooled to room temperature, concentrated under vacuum, and then extracted with hot toluene (15 mL). The solution was filtered through a Celite pad that was washed with toluene until the solvent went colorless. The solvent was removed under vacuum, and the solid residue washed with n-pentane (3 × 5 mL). The product was obtained as red solid (626 mg, 1.13 mmol, 98%). Anal. Caled for C₂₇H₃₃N₂O₃SiNiCl: C, 58.35; H, 5.99; N, 5.04. Found: C, 58.38; H, 6.02; N, 5.12. HR-MS (ESI): m/z [M]⁺ calcd for C₂₇H₃₃N₂O₃SiNi 519.1614, found 519.1592. ¹H NMR (CDCl₃, 400 MHz): δ 7.71 (d, J = 7.8, 2H, C₆H₄), 7.34 (d, J = 7.8, 2H, C₆H₄), 7.10 (s, 2H, m-HMes), 7.07 (s, 1H, NCH), 6.86 (s, 1H, NCH), 6.29 (s, 2H, CH₂), 4.62 (s, 5H, C₅H₅), 3.65 (s, 9H, OCH₃), 2.43 (s, 3H, p-CH₃), 2.16 (br. s, 6H, o-CH₃) [Fig. S15]. ¹³C{¹H} NMR (CDCl₃, 106.61 MHz): δ 164.9 (NCN), 140.1, 139.4 and 136.8 (ipso-, o-, p-CMes), 135.5 (m-CMes), 135.3 (ipso- or p-C₆H₄), 129.4 and 127.4 (o- and m-C₆H₄), 124.0 (NCH), 123.6 (NCH), 91.8 (C₃H₃), 55.7 (CH₂), 51.1 (OCH₃), 21.4 (p-CH₃), 18.6 (o-CH₃) [Fig. S16].

7. Functionalization of OCPUF@PDA with 1

OCPUF@PDA was washed in vigorously stirred toluene (3 × 10 min in 30 mL) and dried under vacuum prior to the reaction.

A cubic sample of OCPUF@PDA (1.5 × 1.5 × 1.5 cm) was introduced in a Schlenk tube under argon. A solution of 1 (10 mg/mL) in toluene (30 mL) was added, and the solution was stirred for 24 h at 70 °C. The resulting functionalized foam, OCPUF@PDA@Ni-NHC, was then removed from the reaction medium, washed for a few minutes in vigorously stirred toluene (3 × 30 mL), and then dried under vacuum.
OCPUF@PDA@Ni-NHC was characterized by SEM (Fig. S17), $^{29}$Si CP-MAS NMR (Fig. S18), and ICP-AES (mean Ni content of 4.24 g ± 0.49 g/kg).

8. **Hydrosilylation of benzaldehyde**

8.1. *Hydrosilylation of benzaldehyde catalyzed by 1 under homogeneous conditions*

An oven dried Schlenk tube containing a stirring bar was loaded with 1 (5.6 mg, 0.01 mmol) and 25 mL of THF. To the resulting red solution was added benzaldehyde (102 µL, 1.00 mmol) and PhSiH$_3$ (148 µL, 1.20 mmol), in this order, and the reaction mixture was stirred at 25 °C for 22 h. $^1$H NMR conversion was then determined by removing an aliquot with a syringe, drying it under high vacuum, extracting the residue with CDCl$_3$ and filtering it in an NMR tube.

8.2. *Hydrosilylation of benzaldehyde catalyzed by OCPUF@PDA@Ni-NHC under heterogeneous conditions*

OCPUF@PDA@Ni-NHC was washed in vigorously stirred $n$-hexane/acetone (1:1) (3 × 10 min in 30 mL) and dried under vacuum prior to the reaction.

An oven dried Schlenk tube containing a stirring bar was loaded with OCPUF@PDA@Ni-NHC, whose mass was adjusted to have 1.0 mol% of immobilized 1 based on the Ni content (*i.e.* 139 mg of OCPUF@PDA@Ni-NHC for 4.24 g Ni/kg), and 25 mL of THF. After addition of benzaldehyde (102 µL, 1.00 mmol) and PhSiH$_3$ (148 µL, 1.20 mmol), the reaction mixture was stirred at 25 °C for 22 h. $^1$H NMR conversion was then determined by removing an aliquot with a syringe, drying it under high vacuum, extracting the residue with CDCl$_3$ and filtering it in an NMR tube.

9. **Finite element simulation** (Figs. S8 and S9)

A finite element simulation method was developed and allowed determining the full stiffness tensor $C$ (inverse of it is the compliance tensor $D$) of 2D foam microstructure, regardless of its complexity. To this aim, the relationship between the stiffness and compliance tensor of the structure and the elastic strain energy $U$ per volume $V$ is used, as follow: $\frac{U}{V} = \frac{1}{2} \sigma^T \sigma = \frac{1}{2} \epsilon^T C \epsilon = \frac{1}{2} \sigma^T D \sigma$, where $\sigma$ is the stress and $\epsilon$ is the strain. Therefore, the 21 elements of $C$ can be computed by applying 21 specific deformations to the heterogeneous material and calculating the corresponding strain energy. Only six terms have to be determined in the case of 2D problem,
leading to six different loading conditions to be computed. For the present numerical calculus, periodic conditions were chosen so unit cell representative geometry was chosen. In respect to Plateau’s laws relevant to low-density open cell foams, regular hexagonal cell geometry was considered. For this representative cell, elastic constants are calculated varying the solid material distribution by using either flat cell edges, plateau border cell shape or corrugated edges with respect to experimental SEM observations of the samples. Post-processing numerical procedure allowed computing in any direction Young’s and shear modulus of the effective porosity (density).

10. Figures

Figure S1. SEM images of OCPUF with different magnifications
Figure S2. SEM images of OCPUF@PDA with different magnifications

Figure S3. SEM images of OCPUF@PDA@DMAP with different magnifications
Figure S4. SEM-EDX Si mapping of OCPUF@PDA@DMAP.

Figure S5. EDX spectrum of OCPUF@PDA@DMAP
**Figure S6.** (a, b) Schematic representation of the stress/strain response compression test; (c) Schematic representation of the fatigue test; (d) Photograph of the Instron E3000 electrodynamic testing system.

**Figure S7.** Young’s modulus (in kPa) of OCPUF, OCPUF@PDA and OCPUF@PDA@DMAP (as-synthesized, after run 1, after run 5 and after the fatigue test)
**Figure S8.** Finite element models: 2D representative cell geometry with flat edges (left), rounded junction/plateau border (middle) and corrugated edges (right). Note that the porosity of the flat-edges and the rounded-junction models are similar (difference of only 0.4 %), whereas that of the corrugated-edges is 2.4% more important.

**Figure S9.** Young’s modulus direction dependency (normalized values) between flat edge cell geometry, with and without rounded-junction and corrugated-edge-cell geometry with induced porosity increase of 2.4%. A reduction of about 30% is obtained for the elastic limit with corrugated edge cells. An anisotropy effect appears when rounded shape junction is used for the model foam microstructure.
**Figure S10.** Acylation of benzyl alcohol catalyzed by OCPUF@PDA@DMAP vs. time during the stop-and-go experiment. Reaction conditions: benzyl alcohol (6.3 mmol), Ac₂O (8.7 mmol), catalyst (0.6 mol%) in n-hexane/acetone (1:1) (25 mL) at 30 °C for 5 h; stirring rate: 600 rpm; OCPUF@PDA@DMAP (0.145 g; Si content: 7.32 g/kg) was removed after 2 h of reaction and put back in after 4 h. Conversion followed by ¹H NMR.
Figure S11. Acylation of benzyl alcohol catalyzed by OCPUF@PDA@DMAP after 3 h reaction (blue line) and/or 19 h reaction (red histograms) for runs 1 to 10. Reaction conditions: benzyl alcohol (6.3 mmol), Ac₂O (8.7 mmol), catalyst (0.6 mol%) in n-hexane/acetone (1:1) (25 mL) at 30 °C for 3 to 19 h; stirring rate: 600 rpm; OCPUF@PDA@DMAP (0.220 g; Si content: 4.82 g/kg). Conversion followed by ¹H NMR.
Figure S12. SEM images of OCPUF@PDA@DMAP after 10 catalytic runs with different magnifications

Figure S13. Synthetic path for the preparation of \([\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{Mes-NHC-CH}_2\text{-C}_6\text{H}_4-\text{Si(OMe)}_3)]\) (I).
Figure S14. $^1$H NMR spectrum of 1-[3-(trimethoxysilyl)propyl]-3-(mesityl)imidazolium chloride.
Figure S15. $^{13}$C ($^1$H) NMR spectrum of 1-[3-(trimethoxysilyl)propyl]-3-(mesityl)imidazolium chloride
Figure S16. $^1$H NMR spectrum of [Ni($^5$-C$_5$H$_5$)Cl(Mes-NHC$_2$-CH$_2$-C$_6$H$_4$-Si(OMe)$_3$)] (1)
Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{Ni}(\eta^5\text{C}_5\text{H}_5)\text{Cl}(\text{Mes-NHC-CH}_2\text{-C}_6\text{H}_4\text{-Si(OMe)}_3)]$ (I)
Figure S18. SEM images of OCPUF@PDA@Ni-NHC with different magnifications

11. References

