SUPPORTING INFORMATION

Surface Functionalisation of Alumina Ceramic Foams with Organic Ligands

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SUMMARY

Synthesis of the organic linkers

General. Commercial reagents (Fluka, Aldrich) were used without further purification. Anhydrous solvents were obtained by filtration. TLC for reaction monitoring: Merck silica gel 60 F254 plates; detection by UV light, KMnO4 or ninhydrine. IR spectra: Perkin-Elmer-1420 spectrometer. ^{1}H NMR spectra: Bruker-ARX-400 spectrometer (400 MHz); δ (H) in ppm relative to the solvent's residual ^{1}H signal $CHCl_3$, δ (H) 7.27 as internal reference; ^{13}C NMR spectra: same instrument as above (100.6 MHz); δ (C) in ppm relative to solvent's C-signal $CDCl_3$, δ (C) 77.1 as internal reference. ^{19}F NMR spectra: same instrument as above (376 MHz); δ (F) in ppm relative to $CFCl_3$ = 0 ppm. MS: Nermag R-10-10C, chemical ionization (NH_3) mode m/z (amu) [% relative base peak (100%)]. Semi-preparative HPLC: XTerra Prep RP C18 (19 x 150).

1-{1-[4-(trifluoromethyl)benzyl]-1H-1,2,3-triazol-4-yl}-2,5,8,11-tetraoxatridecan-13-amine (**6**). 3,6,9,12-tetraoxapentadec-14-yn-1-amine (**4**) (100 mg, 0.432 mmol, 1.0 equiv), 1-(azidomethyl)-4-(trifluoromethyl)benzene (**5**) (87 mg, 0.432 mmol, 1.0 equiv), $CuSO_4.5H_2O$ (2 mg, 0.008 mmol, 0.02 equiv), sodium ascorbate (3 mg, 0.016 mmol, 0.04 equiv), acetic acid (5 μL, 0.086 mmol, 0.2 equiv) were dissolved in a mixture *tert*-butanol/water 1:2 (200 μL) and the reaction mixture was stirred at rt for 2 h. EtOAc (50 mL) was added followed by water (10 mL) and brine (4 mL). The organic layer was separated, dried over anhy. Na_2SO_4, filtered and concentrated to give **6** as a yellow oil (166 mg, 89% crude yield). The product was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 3H), 7.38 (d, J = 7.9 Hz, 2H), 5.58 (s, 2H), 4.66 (s, 2H), 3.70-3.50 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 138.7, 130.9 (q, J_{FC} = 32 Hz), 128.3, 126.1 (q, J_{FC} = 11 Hz), 123.8 (q, J_{FC} = 272 Hz), 123.0, 70.6, 70.4, 70.2, 64.6, 53.4; IR (neat): 1320, 1106, 1063, 1014 cm^{-1}; HRMS (ESI): (*m*/*z*): calcd for $C_{19}H_{27}F_3N_4O_4$+H: 433.2063, found: 433.2057.

General procedure for the synthesis of amides **3**, **10** and **11**. The corresponding carboxylic acid (0.128 mmol, 1.1 equiv) was dissolved in dry CH_2Cl_2 (2 mL) under argon atmosphere and DMF (1 drop) was added. The reaction mixture was cooled down to 0 °C and oxalyl chloride (12 μL, 0.139 mmol, 1.2 equiv) was added dropwise. After 15 min, volatiles were evaporated under vacuum and the resulting residue was dissolved in dry CH_2Cl_2. A solution of **6** (50 mg, 0.116 mmol, 1.0 equiv) in dry CH_2Cl_2 (1 mL) was added followed by *i*-Pr_2NEt (40 μL, 0.231 mmol, 2.0 equiv). After 1h, EtOAc (50 mL) was added and the organic phase was sequentially washed with 1% $NaHCO_3$ (5 mL), sat. NH_4Cl (2 x 5 mL), dried over anhy. Na_2SO_4, filtered and concentrated to give the desired amide.

N-(1-{1-[4-(trifluoromethyl)benzyl]-1H-1,2,3-triazol-4-yl}-2,5,8,11-tetraoxatridecan-13-yl)-benzamide (**3**): From benzoic acid (**9**) (16 mg, 0.128 mmol, 1.1 equiv), amide **3** was obtained as a yellow oil (58 mg, 94% crude yield). For the functionalisation experiments, **3** was purified by reverse phase HPLC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.51 (s, 1H), 7.50-7.35 (m, 5H), 6.93 (s, 1H), 5.57 (s, 2H), 4.66 (s, 2H), 3.70-3.55 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 162.7, 138.5, 134.4, 131.5, 131.1 (q, J_{FC} = 32.8 Hz), 128.6, 128.5, 127.2, 126.1 (q, J_{FC}= 4.0 Hz), 123.8 (q, J_{FC} = 272.2 Hz), 70.5, 70.4, 70.2, 69.9, 69.8, 64.5, 53.6, 40.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ 63.2 (s); IR (neat): 1782, 1320, 1176, 1040 cm^{-1}; HRMS (ESI): (*m*/*z*): calcd for $C_{26}H_{31}F_3N_4O_5$+H: 537.2325, found: 537.2336.

4-[(1-{1-[4-(trifluoromethyl)benzyl]-1H-1,2,3-triazol-4-yl}-2,5,8,11-tetraoxatridecan-13-yl)-carbamoyl]benzene-1,2-diyl diacetate (**10**): From 3,4-diacetoxybenzoic acid (**7**) (30 mg, 0.128 mmol, 1.1 equiv), amide **10** was obtained as a yellow oil (62 mg, 83% crude yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.70 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.49 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.27-7.20 (m, 2H), 5.54 (s, 2H), 4.64 (s, 2H), 3.72-3.58 (m, 16H), 2.31 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 167.9, 165.7, 145.5, 142.0, 138.7, 133.3, 128.3, 126.0 (q, J_{FC} = 4.0 Hz), 125.4, 123.4, 123.0, 122.8, 70.48, 70.47, 70.4, 70.2, 69.82, 69.79, 64.6, 53.3, 40.0, 20.7, 20.6; IR (neat): 1767, 1321, 1201, 1164, 1101 cm^{-1}; HRMS (ESI): (*m*/*z*): calcd for $C_{30}H_{35}F_3N_4O_9$+H: 653.2436, found: 653.2444

5-[(1-{1-[4-(trifluoromethyl)benzyl]-1H-1,2,3-triazol-4-yl}-2,5,8,11-tetraoxatridecan-13-yl)-carbamoyl]benzene-1,2,3-triyl triacetate (**11**): From 3,4,5-triacetoxybenzoic acid (**8**) (38 mg, 0.128 mmol, 1.1 equiv), amide **11** was obtained as a yellow oil (72 mg, 88% crude yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.47 (s, 1H), 7.36 (d, J = 8.2 Hz, 2H), 5.53 (s, 2H), 4.63 (s, 2H), 3.70-3.55 (m, 16H), 2.31 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.6, 165.0, 145.6, 143.3, 137.1, 132.8, 130.2 (q, J_{FC} = 32.8 Hz), 128.3, 126.0 (q, J_{FC} = 3.8 Hz), 123.8, (q, J_{FC} = 274.0 Hz), 123.0, 122.9, 120.1, 70.5, 70.4, 70.2, 69.8, 69.7, 64.5, 53.3, 40.1, 20.6, 20.2; IR (neat): 1776, 1322, 1178, 1045 cm^{-1}; HRMS (ESI): (*m*/*z*): calcd for $C_{32}H_{37}F_3N_4O_{11}$+H: 711.2489, found: 711.2500.

General procedure for the synthesis of phenols **1** and **2**. The corresponding acetoxy derivative was dissolved in EtOH (2 mL) under argon atmosphere and hydrazine monohydrate was added. After 15 min, volatiles were evaporated under vacuum to give the desired phenol.

3,4-dihydroxy-N-(1-{1-[4-(trifluoromethyl)benzyl]-1H-1,2,3-triazol-4-yl}-2,5,8,11-tetraoxa-tridecan-13-yl)benzamide (**1**): From **10** (50 mg, 0.077 mmol, 1.0 equiv) and hydrazine monohydrate (8 μL, 0.154 mmol, 2.0 equiv), ligand **1** was obtained as a yellow oil (34 mg, 78% crude yield). For the

functionalisation experiments, **1** was purified by reverse phase HPLC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.45-7.40 (m, 2H), 7.35-7.28 (m, 3H), 7.11 (s, 1H), 6.89 (d, J = 8.1 Hz, 1H), 5.51 (s, 2H), 4.59 (s, 2H), 3.72-3.54 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 148.3,144.2, 144.1, 138.4, 131.0 (q, J_{FC} = 32.7 Hz), 128.4, 126.1 (q, J_{FC} = 3.7 Hz), 123.7 (q, J_{FC} = 272.0 Hz), 120.4, 115.0, 114.3, 70.3, 70.26, 70.24, 70.18, 70.0, 69.8, 69.7, 64.1, 53.5, 39.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ 63.3 (s); IR (neat): 1635, 1593, 1509, 1324, 1120 cm^{-1}; HRMS (ESI): (*m*/*z*): calcd for $C_{26}H_{31}F_3N_4O_7$+H: 569.2223, found: 569.2217

3,4,5-trihydroxy-N-(1-{1-[4-(trifluoromethyl)benzyl]-1H-1,2,3-triazol-4-yl}-2,5,8,11-tetraoxa-tridecan-13-yl)benzamide (**2**): From **11** (65 mg, 0.092 mmol, 1.0 equiv) and hydrazine monohydrate (13 μL, 0.275 mmol, 3.0 equiv), ligand **2** was obtained as a yellow oil (46 mg, 86% crude yield). For the functionalisation experiments, **2** was purified by reverse phase HPLC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.8 Hz, 2H), 7.49 (s, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.22 (s, 1H), 6.99 (s, 2H), 5.49 (s, 2H), 4.56 (s, 2H), 3.65-3.45 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.0, 138.6, 136.1, 130.7 (q, J_{FC} = 32.5 Hz), 128.4, 126.0 (q, J_{FC} = 3.8 Hz), 125.3, 123.8 (q, J_{FC} = 272.2 Hz), 123.5, 107.4, 70.22, 70.17, 70.07, 70.0, 69.6, 64.1, 53.4, 39.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ 63.2 (s); IR (neat): 1591, 1514, 1320, 1120, 905 cm^{-1}; HRMS (ESI): (*m*/*z*): calcd for $C_{26}H_{31}F_3N_4O_8$+H: 585.2172, found: 585.2197

Functionalisation of ceramic foams S1-S3

A small fragment of ceramic foam (ca. 0.1 cm^3) was incubated in a 1 mM aqueous solution of the corresponding linker (**1**, **2** or **3**, 1 mL), at rt for 16 h in darkness. The ceramic foam was drained on a piece of absorbent paper before being soaked in fresh water (1.5 mL) for 5 min to remove the non-attached linker. This procedure was repeated 3 times and the sample was then dried under vacuum for 24 h and subsequently analysed by XPS. The samples were named as follows:

ceramic	linker	Sample
S1	ø	A-S1
S2	ø	A-S2
S3	ø	A-S3
S1	**3**	B-S1
S2	**3**	B-S2
S3	**3**	B-S3
S1	**1**	C-S1
S2	**1**	C-S2
S3	**1**	C-S3
S1	**2**	D-S1
S2	**2**	D-S2
S3	**2**	D-S3

XPS analysis

X-ray Photoelectron Spectroscopy (XPS) data were collected by an Axis Ultra instrument (Kratos analytical, Manchester, UK) under ultra-high vacuum condition ($<10^{-8}$ Torr) and using a monochromatic Al K_α X-ray source (1486.6 eV), in the Surface Analysis Facility of the Interdisciplinary Centre for Electron Microscopy at EPFL. The source power was maintained at 150 W and the emitted photoelectrons were sampled from a 750μm×300μm area. The analyzer pass energy was 80 eV for survey spectra and 40 eV for high-resolution spectra. The adventitious carbon 1s peak was calibrated at 285 eV and used as an internal standard to compensate for any charging effects. Both curve fitting of the spectra and quantification were performed with the CasaXPS software, using relative sensitivity factors given by Kratos.

XPS data

Sample	Element	%At Conc.	SD
A-S1	O 1s	51.7	0.4
	Ca 2p	3.8	0.1
	C 1s	17.4	0.6
	Al 2p	27.1	0.6
B-S1	O 1s	51.6	0.4
	Ca 2p	4.3	0.1
	C 1s	21.0	0.6
	Al 2p	23.1	0.6
C-S1	O 1s	35.2	0.4
	N 1s	5.2	0.2
	Ca 2p	1.9	0.1
	C 1s	36.3	0.6
	Al 2p	15.0	0.6
	F 1s	6.4	0.2
D-S1	O 1s	24.2	0.4
	N 1s	7.5	0.2
	Ca 2p	1.0	0.1
	C 1s	52.5	0.6
	Al 2p	7.4	0.6
	F 1s	7.4	0.2

Table 3. XPS calculated atomic concentrations corresponding to Figure 2.

Functionalisation of alumina with 3,4,5-trihydorxybenzamide

Aluminium oxide powder (<50 nm) was incubated in a 1 mM aqueous solution of the 3,4,5-trihydroxybenzamide (1 mL), at rt for 16 h in darkness. The powder of aluminium oxide was transferred in an eppendorf and centrifuged for 5 min at 13 000 rpm. The supernatant was removed and the powder was resuspended in water and centrifuged under the same conditions. This procedure was repeated three times to remove the non-attached 3,4,5-trihydroxybenzamide and the sample was then dried under vacuum for 24 h and subsequently analysed by DNP-MAS-NMR.

DNP-MAS-^{13}C NMR analyses

Sample preparation was performed based on the procedure published elsewhere.[18]

Spectrum 1 (pure 3,4,5-trihydroxybenzamide) was measured at rt. Spectra 2 (alumina functionalized with 3,4,5-trihydroxybenzamide) and 3 (untreated alumina) were registered in the same conditions (ca. 100 K, soaked with a H_2O/D_2O 20/80 solution containing 5 mM of TOTAPOL using 5 W of microwave irradiation). All measurements were done on a 400 MHz wide-bore Bruker Avance NMR using a LT-MAS-NMR probe. The 5 W microwave irradiation was generated by a 263 GHz Bruker gyrotron. The small chemical shift between 1 and 2 can be explained by the temperature difference.