Supporting Information

Mechanically-Driven Vase–Kite Conformational Switch in Cavitand Cross-Linked Polyurethanes

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1. General information

All commercial reagents were used as received. Unless otherwise stated, reactions were conducted in flame-dried glassware under an atmosphere of argon using anhydrous solvents (either freshly distilled or passed through activated molecular sieves). Silica column chromatography was performed using silica gel 60 (Fluka 230-400 mesh ASTM) or silica gel 60 (Merck 70-230 mesh).

$^1$H NMR spectra were obtained using a Bruker AVANCE 300 (300 MHz) or a Bruker AVANCE 400 (400 MHz) spectrometer at 25 °C. All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from the incomplete deuteration of the NMR solvents. $^{13}$C NMR spectra were obtained using a Bruker AVANCE 300 (75 MHz) or a Bruker AVANCE 400 (100 MHz) spectrometer. All chemical shifts (δ) were reported in ppm relative to the carbon resonances of the NMR solvents.

MALDI was performed on an AB SCIEX MALDI TOF-TOF 4800 Plus (matrix: α-cyano-4-hydroxycinnamic acid).

Differential scanning calorimetry (DSC) was performed using a DSC Q100 from TA Instruments. Measurements were carried out at a heating and cooling rate of 10 °C/min from -70 °C to 70 °C.

Elongation tests setup: polymer specimens were uniaxially stretched by means of a handcrafted device, whose small size and geometry allowed the spectroscopic characterization of the samples under load. The simultaneous translation of two metallic clamps in opposite directions within a screw-driven rail table keeps the centre of mass of the sample stationary. Specimens were loaded at a rate of 0.5 mm s$^{-1}$.

UV-Vis spectra were collected using a Thermo Scientific Evolution 260 Bio spectrophotometer; for measurements in solution, matched quartz cells of 1 cm path length were used in the two beam paths. For measurements on films, air was taken as the reference.

Fully corrected steady-state emission spectra were obtained with a Fluoromax-3 Horiba Jobin-Yvon fluorometer equipped with a Xenon lamp as the excitation source. In order to minimize inner-filter effects, diluted samples were analysed (optical density < 0.1). For liquid samples, standard 1cm×1cm quartz cells were used. Films were placed in front-face excitation position, with an orientation of
about 30° or 60° with respect to the direction of the excitation beam, to minimize reflection and stray light.
2. Experimental procedures

Scheme S1 General synthetic scheme for cavitands involved in this work.
The synthetic procedures for quinoxaline 1 and QxCav C2A have been already reported.\textsuperscript{1} Literature references for 3QxCav,\textsuperscript{2} 2QxCav,\textsuperscript{2} Res[\text{C}_6\text{H}_{13}, \text{H}],\textsuperscript{3} Res[\text{C}_6\text{H}_{13}, \text{CH}_3],\textsuperscript{4} QxCav C\textsubscript{V},\textsuperscript{5} QxCav C\textsubscript{k}\textsuperscript{4}.

**Mono-ω-decene functionalized tetraquinoxaline cavitand (C1A)**

Triquinoxaline cavitand 3QxCav (0.260 g, 0.22 mmol) and K\textsubscript{2}CO\textsubscript{3} (0.039 g, 0.28 mmol) were suspended in 5 mL of DMSO. After the addition of dichloroquinoxaline 1 (0.091 g, 0.24 mmol) the mixture was heated at 70 °C under microwave irradiation for 30 min. The reaction was quenched with water (100 mL) and the precipitate was filtered, washed with water and dried. Flash column chromatography (hexane/AcOEt 9:1) afforded pure cavitand C1A as a white solid (0.215 g, 0.14 mmol, 46%).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) (ppm) = 8.65 (s, 1H, \text{H}_a), 8.19 (m, 4H, \text{H}_g), 8.09 (d, 1H, \text{J}=8.7 Hz, \text{H}_b), 7.87-7.73 (m, 7H, \text{H}_c + \text{H}_a), 7.52 (m, 4H, \text{H}_e), 7.42 (t, 1H, \text{J}=7.5 Hz, \text{H}_f), 7.33 (t, 1H, \text{J}=7.5 Hz, \text{H}_f), 7.24 (m, 4H, \text{H}_i), 5.82 (m, 1H, \text{CH}=\text{CH}_2), 5.60 (m, 4H, \text{CHCH}_2), 4.98 (m, 2H, \text{CH}=\text{CH}_2), 4.48 (m, 2H, \text{OCH}_2\text{CH}_2), 2.29 (m, 8H, \text{CHCH}_2), 2.06 (m, 2H, \text{CH}_2\text{CH}=\text{CH}_2), 1.92 (quint, 2H, \text{J}=6.9 Hz, \text{OCH}_2\text{CH}_2), 1.60-1.26 (m, 42H, -\text{CH}_2-), 0.95 (t, 12H, \text{J}=6.4 Hz, \text{CH}_2\text{CH}_3).

**MALDI-TOF:** calculated for C\textsubscript{95}H\textsubscript{99}N\textsubscript{8}O\textsubscript{10} [M+H]\textsuperscript{+} \(m/z = 1511.748\), found \(m/z = 1511.745\).
Tetra-ω-decene functionalized tetraquinoxaline cavitand (C4A)

K₂CO₃ (0.044 g, 0.26 mmol) was added to a solution of Res[C₉H₁₇, H] (0.051 g, 0.06 mmol) in 2 mL of DMSO, followed by dichloroquinoxaline 1 (0.085 g, 0.26 mmol). The reaction mixture was heated at 70 °C under microwave irradiation for 2 h. Water (100 mL) was added and the precipitate was filtered, washed with water and dried. The crude was purified by flash column chromatography (CH₂Cl₂/AcOEt 98:2) affording cavitand C4A as a white solid (0.019 g, 0.01 mmol, 17%).

¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 8.60 (s, 4H, ArH), 8.02 (d, 4H, ArHup), 8.12 (d, 4H, J=8.7 Hz, ArH), 7.86 (d, 4H, J=8.7 Hz, ArH), 7.26 (s, 4H, ArHdown), 5.85 (m, 4H, CH=CH₂), 5.57 (t, 4H, J=8.0 Hz, CHCH₂), 5.00 (m, 8H, CH=CH₂), 4.48 (m, 8H, J=6.6 Hz, OCH₂CH₂), 2.37-2.13 (m, 16H, CHC₆H₄ + OCH₂CH₂), 1.92 (m, 8H, CH₂CH=CH₂), 1.74-1.19 (m, 40H, J=1.9 Hz, CH₂CH₃).

MALDI-TOF: calculated for C₁₁₂H₁₂₁N₈O₁₂ [M+H]⁺ m/z: 1835.897, found m/z: 1835.852; calculated for C₁₁₂H₁₂₀N₈O₁₂Na [M+Na]⁺ m/z: 1856.875, found m/z: 1856.823; calculated for C₁₁₂H₁₂₀N₈O₁₂K [M+K]⁺ m/z: 1872.849, found m/z: 1872.824.

Resorcinarene [C₅H₁₇, H]

A 37% solution of HCl (2 mL, 6.6 mmol) was slowly added to an ice-cold solution of resorcinol (0.428 g, 3.89 mmol) in 2 mL of MeOH. At the same temperature 9-decenal (0.6 g, 3.89 mmol) in 4 mL of EtOH was added drop-wise over 20 min. The mixture was stirred at 100 °C for 5 min under microwave irradiation. Water (250 mL) was added and the precipitate was filtered, washed with water and dried. The crude was purified by recrystallization from CH₃CN affording Res[C₅H₁₇, H] as a white solid (1.38 g, 1.4 mmol, 36%).
1H NMR (Acetone-d6, 300 MHz): δ (ppm) = 8.46 (s, 8H, OH), 7.56 (s, 4H, ArH_up), 6.25 (s, 4H, ArH_down), 5.81 (m, 4H, CH=CH2), 4.98 (m, 8H, CH=CH2), 4.31 (t, 4H, J=8.1 Hz, CHCH2), 2.30 (q, 8H, J=8.1 Hz, CHCH2) 1.39-1.25 (m, 48H, -C_H2-).

ESI-MS: m/z = 986 [M+H]+, 1008 [M+Na]+.

Dec-9-en-1-yl-footed tetraquinoxaline cavitand (C4AL)

K2CO3 (0.152 g, 1.10 mmol) was added to a solution of Res[C9H17,H] (0.25 g, 0.245 mmol) in 10 mL of dry DMSO, followed by 2,3-dichloroquinoxaline (0.219 g, 1.10 mmol). The reaction mixture was heated at 70 °C under microwave irradiation for 30 min. Water (200 mL) was added and the precipitate was filtered, washed with water and dried. The crude was purified by recrystallization from acetone affording cavitand C4AL as a white solid (0.167 g, 0.11 mmol, 44%).

1H NMR (CDCl3, 300 MHz): 8.18 (s, 4H, ArH_up), 7.82 (m, 8H, ArH), 7.49 (m, 8H, ArH), 7.23 (s, 4H, ArH_down), 5.84 (m, 4H, CH=CH2), 5.65 (t, 4H, J=7.9 Hz, CHCH2), 4.98 (m, 8H, CH=CH2), 2.29 (q, 8H, J=7.9 Hz, CHCH2), 1.39-1.25 (m, 48H, -C_H2-).

MALDI-TOF: calculated for C96H97N8O8 [M+H]+ m/z: 1490.746, found m/z: 1490.734; calculated for C96H96N8O8Na [M+Na]+ m/z: 1512.728, found m/z: 1512.715.

6-[(tert-butyldimethylsilyl)oxy]hexyl 2,3-dichloroquinoxaline-6-carboxylate (2)

2,3-dichloroquinoxaline-6-acyl chloride, obtained by reaction of 2,3-dihydroxyquinoxaline-6-carboxylic acid (0.22 g, 1.11 mmol) with Vilsmeier reagent, was isolated under inert atmosphere and immediately reacted with 6-[(tert-butyldimethylsilyl)oxy]hexan-1-ol (0.258 g, 1.11 mmol) in CH2Cl2 in the presence of Et3N (0.154 mL, 1.11 mmol). The solution was stirred at room temperature for 12
h. The crude was diluted with CH$_2$Cl$_2$ and washed with a saturated solution of NaHCO$_3$, HCl 1 N and brine. The solvent was removed under reduced pressure and the crude was purified by flash column chromatography (hexane/AcOEt 95:5) affording compound 2 (0.386 g, 0.84 mmol, 76%) as a colourless oil.

$^1$H NMR (CDCl$_3$, 300 MHz): δ (ppm) = 8.57 (s, 1H, ArH); 8.36 (dd, 1H, $J_\alpha$=8.8 Hz, $J_m$=1.9 Hz, ArH); 8.21 (d, 1H, $J_\alpha$=8.7 Hz, ArH); 4.37 (t, 2H, $J$=6.6 Hz, (CO)OC$_2$H$_5$); 3.59 (t, 2H, $J$=6.4 Hz, CH$_2$OSi); 1.5 (m, 8H, -C$_2$H$_4$-); 0.91 (s, 9H, Si$^t$Bu); 0.07 (s, 6H, SiCH$_3$).

**Mono-TBDMSO-hexyl functionalized tetraquinoxaline cavitand (3)**

Cavitand 3QxCav (0.100 g, 0.083 mmol) and K$_2$CO$_3$ (0.015 g, 0.11 mmol) were suspended in 3 mL of dry DMSO. After the addition of dichloroquinoxaline 2 (0.042 g, 0.081 mmol) the mixture was heated at 70 °C under microwave irradiation for 30 min. The reaction was quenched with water (100 mL) and the precipitate was filtered, washed with water and dried. Flash column chromatography (hexane/AcOEt 95:5) afforded pure cavitand 3 (0.065 g, 0.041 mmol, 49%) as a white solid.

$^1$H NMR (CDCl$_3$, 300 MHz): δ (ppm) = 8.66 (s, 1H, H$_a$), 8.19 (m, 4H, H$_g$), 8.09 (dd, 1H, $J_\alpha$=8.7 Hz, $J_m$=1.4 Hz, H$_b$), 7.84-7.76 (m, 7H, H$_c$ + H$_d$), 7.52 (m, 4H, H$_e$), 7.42 (t, 1H, $J$=7.4 Hz, H$_f$), 7.34 (t, 1H, $J$=7.4 Hz, H$_i$), 7.24 (m, 4H, H$_i$), 5.61 (m, 4H, CHCH$_2$), 4.48 (m, 2H, (CO)OCH$_2$), 3.67 (m, 2H, CH$_2$OSi), 2.29 (m, 8H, CHCH$_2$), 1.93 (m, 2H, (CO)OCH$_2$CH$_2$), 1.60-1.26 (m, 30H, -CH$_2$-), 0.95 (t, 12H, $J$=6.4 Hz, CH$_2$CH$_3$), 0.92 (s, 9H, Si$^t$Bu), 0.07 (s, 6H, SiCH$_3$).
MALDI-TOF: calculated for C_{97}H_{107}N_{8}O_{11}Si [M+H]^+ m/z: 1587.775, found m/z: 1587.549; calculated for C_{97}H_{107}N_{8}O_{11}SiNa [M+Na]^+ m/z: 1611.002, found m/z: 1611.455.

Mono-ω-hydroxy functionalized tetraquinoxaline cavitand (C1H)

DMSO (2.7 mL) was added to a solution of cavitand 3 (0.062 g, 0.04 mmol) in 1.5 mL of purified THF, followed by H_{2}O (260 µL) and N-bromosuccinimide (0.016 g, 0.009 mmol). The reaction mixture was stirred at room temperature for 12 h in the dark. Volatiles were evaporated under reduced pressure and the crude was dissolved in CHCl_{3} and washed with water. Purification via flash column chromatography (CH_{2}Cl_{2}/MeOH 99:1) afforded cavitand C1H (0.047 g, 0.031 mmol, 79%) as a white solid.

^1H NMR (CDCl_{3}, 300 MHz): δ (ppm) = 8.66 (d, 1H, J_{m}=1.7 Hz, H_{a}), 8.19 (m, 4H, H_{g}), 8.09 (dd, 1H, J_{o}=8.7 Hz, J_{m}=1.7 Hz, H_{b}), 7.84-7.76 (m, 7H, H_{e} + H_{a}), 7.54-7.50 (m, 4H, H_{e}), 7.42 (t, 1H, J=7.4 Hz, H_{f}), 7.34 (t, 1H, J=7.4 Hz, H_{f}), 7.24 (m, 4H, H_{i}), 5.58 (m, 4H, CHCH_{2}), 4.49 (m, 2H, (CO)OCH_{2}), 3.71 (t, 2H, J=6.2 Hz, CH_{2}OH), 2.29 (m, 8H, CHCH_{2}), 1.93 (m, 2H, (CO)OCH_{2}CH_{2}), 1.60-1.26 (m, 30H, -CH_{2}-), 0.95 (t, 12H, J=6.4 Hz, CH_{2}CH_{3}).

MALDI-TOF: calculated for C_{91}H_{93}N_{8}O_{11} [M+H]^+ m/z: 1474.751, found m/z: 1474.449.
Bis-TBDMOS-hexyl functionalized tetraquinoxaline cavitand (4)

Dichloroquinoxaline 2 (0.094 g, 0.205 mmol) was added to a suspension of 2QxCav (0.100 g, 0.093 mmol) and K₂CO₃ (0.038 g, 0.28 mmol) in 4 mL of dry DMSO. The mixture was heated at 70 °C under microwave irradiation for 1 h. The reaction was quenched with water and the resulting precipitate was filtered, washed with water and dried. The crude was purified by flash column chromatography (hexane/AcOEt 95:5) affording cavitand 4 (0.070 g, 0.038 mmol, 41%) as a white solid.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.68 (s, 2H, Hₐ), 8.20 (m, 4H, H₀), 8.13 (dd, 2H, J₀=8.7 Hz, Jₐ=6.9 Hz, Hₐ), 7.85-7.75 (m, 6H, Hₑ+Hₐ), 7.56 (m, 1H, Hₑ), 7.45 (m, 1H, Hₑ), 7.37 (m, 1H, Hₑ), 7.29-7.22 (m, 5H, Hₑ+Hₑ), 5.60 (m, 4H, CHCH₂), 4.49 (m, 4H, (CO)OCH₂), 3.66 (m, 4H, CH₂OSi), 2.29 (m, 8H, CHCH₂), 1.93 (m, 4H, (CO)OCH₂CH₂), 1.61-1.37 (m, 36H, -CH₂-), 0.96 (t, 12H, J=7 Hz, CH₂CH₃), 0.92 (d, 18H, Si²Bu), 0.07 (d, 12H, SiCH₃).

MALDI-TOF: calculated for C₁₁₀H₁₃₃N₈O₁₄Si₂ [M+H]⁺ m/z: 1847.441, found m/z: 1847.458; calculated for C₁₁₀H₁₃₃N₈O₁₄Si₂Na [M+Na]⁺ m/z: 1869.431, found m/z: 1869.488.
Bis-ω-hydroxy functionalized tetraquinoxaline cavitand (C2H)

DMSO (2 mL) was added to a solution of cavitand 4 (0.040 g, 0.022 mmol) in 1 mL of THF purified via alumina percolation, followed by H2O (160 µL) and N-bromosuccinimide (0.008 g, 0.048 mmol). The reaction mixture was stirred at room temperature for 12 h in the dark. Volatiles were evaporated under reduced pressure and the crude was dissolved in CHCl3 and washed with water. Purification via flash column chromatography (CH2Cl2/MeOH 97:3) afforded cavitand C2H (0.026 g, 0.016 mmol, 73%) as a white solid.

1H NMR (CDCl3, 400 MHz): δ (ppm) = 8.69 (s, 2H, H_a), 8.19 (m, 4H, H_f), 8.11 (dd, 2H, J_o=8.7 Hz, J_m=1.6 Hz, H_b), 7.85-7.75 (m, 6H, H_c + H_a), 7.55 (m, 1H, H_c), 7.45 (m, 1H, H_c), 7.36 (m, 1H, H_e), 7.24 (m, 5H, H_g + H_e), 5.60 (m, 4H, CHCH2), 4.50 (m, 4H, (CO)OCH2), 3.69 (t, 4H, J=6.3 Hz, CH2OH), 2.29 (m, 8H, CHCH2), 1.93 (m, 4H, (CO)OCH2CH2), 1.61-1.37 (m, 36H, -CH2-), 0.96 (t, 12H, J=7 Hz, CH2CH3).

MALDI-TOF: calculated for C98H105N8O14 [M+H]^+ m/z: 1618.919, found m/z: 1618.892.

Tetra-TBDMSO-hexyl functionalized tetraquinoxaline cavitand (5)

K2CO3 (0.159 g, 1.15 mmol) was added to a solution of Res[C6H13, H] (0.158 g, 0.19 mmol) in 5 mL of dry DMSO, followed by dichloroquinoxaline 2 (0.386 g, 0.84 mmol). The reaction mixture was
heated at 70 °C under microwave irradiation for 2 h. Water (100 mL) was added and the precipitate was filtered, washed with water and dried. The crude was purified by flash column chromatography (CH₂Cl₂/MeOH 98:2) affording cavitand 5 (0.054 g, 0.023 mmol, 12%) as a white solid.

¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 8.61 (d, 4H, J=1.6 Hz, ArHₐ), 8.18 (s, 4H, ArHₐup), 8.03 (dd, 4H, J₀=8.7 Hz, Jₘ=1.8 Hz, ArHₐ), 7.85 (d, 4H, J=8.7 Hz, ArHₑ), 7.23 (s, 4H, ArHdown), 5.55 (t, 4H, J=7.8 Hz, CHCH₂), 4.48 (t, 8H, J=6.7 Hz, (CO)OCH₂), 3.64 (t, 8H, J=6.4 Hz, CH₂OSi), 2.29 (m, 8H, CHC₂H₂), 1.92 (m, 8H, (CO)OCH₂CH₂), 1.58-1.28 (m, 56H, -C₆H₂-), 0.94 (m, 12H, CH₂CH₃), 0.90 (s, 36H, Si₃Bu), 0.09 (s, 24H, SiC₆H₃).

MALDI-TOF: calculated for C₁₃₆H₁₈₂N₈O₂₀Si₄ [M+H]⁺ m/z: 2364.299, found m/z: 2364.428.

dashed hydroxy functionalized tetraquinoxaline cavitand (C₄H)

Tetra-ω-hydroxy functionalized tetraquinoxaline cavitand (C₄H)

DMSO (1 mL) was added to a solution of cavitand 5 (0.054 g, 0.023 mmol) in 0.5 mL of purified THF, followed by H₂O (100 µL) and N-bromosuccinimide (0.027 g, 0.23 mmol). The reaction mixture was stirred at room temperature for 12 h in the dark. Volatiles were evaporated under reduced pressure and the crude was dissolved in CHCl₃ and washed with water. Purification via flash column chromatography (CH₂Cl₂/MeOH 95:5) afforded cavitand C₄H (0.024 g, 0.013 mmol, 55%) as a white solid.

¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 8.61 (d, 4H, J=1.6 Hz, ArHₐ), 8.21 (s, 4H, ArHₐup), 8.01 (dd, 4H, J₀=8.7 Hz, Jₘ=1.7 Hz, ArHₐ), 7.85 (d, 4H, J=8.7 Hz, ArHₑ), 7.25 (s, 4H, ArHdown), 5.61 (t, 4H, J=7.7 Hz, CHCH₂), 4.48 (t, 8H, J=6.7 Hz, (CO)OCH₂), 3.71 (t, 8H, J=6.1 Hz, CH₂OH), 2.29 (m, 8H, CHCH₂), 1.92 (m, 8H, (CO)OCH₂CH₂), 1.59-1.36 (m, 56H, -CH₂-), 0.92 (m, 12H, CH₂CH₃).

MALDI-TOF: calculated for C₁₁₂H₁₂₉N₈O₂₀Na [M+Na]⁺ m/z: 1929.246, found m/z: 1929.367; calculated for C₁₁₂H₁₂₉N₈O₂₀K [M+K]⁺ m/z: 1945.355, found m/z: 1945.886.
Tetra-TBDMSO-hexyl functionalized tetraquinoxaline kite cavitand (6)

K₂CO₃ (0.093 g, 0.67 mmol) was added to a solution of Res[C₆H₁₃, CH₃] (0.098 g, 0.11 mmol) in 4 mL of dry DMSO, followed by dichloroquinoxaline 2 (0.225 g, 0.49 mmol). The reaction mixture was heated at 70 °C under microwave irradiation for 1 h. Water (100 mL) was added and the precipitate was filtered, washed with water and dried. The crude was purified by flash column chromatography (CH₂Cl₂/AcOEt 96:4) affording cavitand 6 (0.135 g, 0.056 mmol, 51%) as a white solid.

¹H NMR (CDCl₃, 400 MHz): 8.69 (m, 4H, ArHₐ), 8.28 (m, 4H, ArHₐ), 7.80 (m, 4H, ArHₐ), 6.91 (s, 2H, ArHₐ), 6.18 (s, 2H, ArHₐ), 4.50 (m, 4H, CHCH₂), 4.39 (m, 8H, (CO)OC₂H₂), 3.64 (m, 12H, CH₂C₂H₂ + C₂H₂OSi), 3.15 (s, 6H, ArCH₃), 2.23 (s, 6H, ArCH₃), 1.84 (m, 8H, CHCH₂), 1.60-1.22 (m, 56H, -CH₂-), 0.93 (s, 12H, CH₂C₂H₃), 0.89 (s, 36H, SiBu³), 0.03 (s, 24H, SiC₂H₃).

MALDI-TOF: calculated for C₁₄₀H₁₉₃N₈O₂₀Si₄ [M+H]⁺ m/z: 2419.406, found m/z: 2419.529; calculated for C₁₄₀H₁₹₂N₈O₂₀Si₄Na [M+Na]⁺ m/z: 2442.396, found m/z: 2442.246.

Tetra-ω-hydroxy functionalized tetraquinoxaline kite cavitand (C₄K4H)

DMSO (2 mL) was added to a solution of cavitand 6 (0.100 g, 0.041 mmol) in 1 mL of destabilized THF, followed by H₂O (200 µL) and N-bromosuccinimide (0.054 g, 0.46 mmol). The reaction mixture was stirred at room temperature for 12 h in the dark. Volatiles were evaporated under reduced pressure and the crude was dissolved in CHCl₃ and washed with water. Purification via flash column chromatography (CH₂Cl₂/MeOH 94:6) afforded cavitand C₄K4H (0.040 g, 0.02 mmol, 49%) as a white solid.

¹H NMR (CDCl₃, 400 MHz): 8.52 (m, 2H, ArH), 8.29 (m, 4H, ArH), 8.13 (m, 2H, ArH), 7.83 (m, 4H, ArH), 6.93 (s, 2H, ArH), 6.21 (s, 2H, ArH), 4.54 (m, 4H, CHCH₂), 4.37 (m, 8H,
(CO)OCH₂, 3.78 (m, 12H, CHCH₂ + CH₂OH), 3.19 (s, 6H, ArCH₃), 2.25 (s, 6H, ArCH₃), 1.83 (m, 8H, CHCH₂), 1.69-1.16 (m, 56H, -CH₂), 0.92 (s, 12H, CH₂CH₃).

MALDI-TOF: calculated for C₁₁₆H₁₃₇N₈O₂₀ [M+H]⁺ m/z: 1962.363, found m/z: 1962.914; calculated for C₁₄₀H₁₉₂N₈O₂₀Si₄Na [M+Na]⁺ m/z: 1985.353, found m/z: 1985.591.
3. X-ray data collection and crystal structure determination

The crystal structure of QxCav C4A was determined by X-ray diffraction on single crystals. Crystal data and experimental details for data collection and structure refinement are reported in Table S1. Intensity data and cell parameters were recorded at 100(2) K at the ELETTRA Synchrotron Light Source (CNR Trieste, strada statale 14, Area Science Park, 34149, Basovizza, Trieste, Italy). The raw frame data were processed using the program package CrysAlisPro 1.171.38.41.7 The structure was solved by Direct Methods using the SIR97 program8 and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-2014/79 program in the WinGX suite v.2014.1.10 All non-hydrogen atoms were refined with anisotropic atomic displacements, except when disorder was present (one of the two orientation of cyclohexane, two carbon atoms of one alkyl chain at the lower rim, and the second orientation of the ester moieties at the upper rim). The carbon-bound and the nitrogen-bound H atoms were placed in calculated positions and refined isotropically using a riding model with C-H ranging from 0.95 to 1.00 Å and Uiso(H) set to 1.2–1.5Ueq(C). The weighting schemes used in the last cycle of refinement was w = 1/[σ^2F_o^2 + (0.4500P)^2] where P = (F_o^2 + 2F_c^2)/3. The crystallographic data for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1913582 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**Figure S1** X-ray molecular structure of QxCav C4A; crystals grown from CHCl3/CyHex. H atoms have been omitted for clarity
Table S1 Crystal data and structure refinement information for QxCav C4A.

| Compound                  | QxCav C4A       |
|---------------------------|-----------------|
| empirical formula         | C_{134}H_{164}N_{8}O_{16} |
| $M$                       | 2142.72         |
| crys syst                 | Triclinic       |
| space group               | $P-1$           |
| a/Å                       | 12.472(2)       |
| b/Å                       | 16.173(2)       |
| c/Å                       | 29.790(1)       |
| $\alpha/^{\circ}$        | 90.927(1)       |
| $\beta/^{\circ}$         | 93.632(3)       |
| $\gamma/^{\circ}$        | 95.386(2)       |
| $V/$Å$^3$                 | 9336.7(4)       |
| Z                         | 2               |
| $T$/K                     | 100(2)          |
| $\rho$ /g cm$^{-3}$       | 1.192           |
| $\mu$ /mm$^{-1}$          | 0.076           |
| $F$(000)                  | 2304            |
| total reflections         | 34742           |
| unique reflections (R$_{int}$) | 20813 (0.0579) |
| observed reflections [$F_o>4\sigma(F_o)$] | 12492 |
| GOF on F$^{2a}$           | 1.008           |
| $R_{indices}$ [$F_o>4\sigma(F_o)$]$^{b}R_1$, wR$_2$ | 0.1423, 0.4504 |
| largest diff. peak and hole (eÅ$^{-3}$) | 0.992, -0.792 |

$^a$Goodness-of-fit $S = [\Sigma w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$, where $n$ is the number of reflections and $p$ the number of parameters. $^bR_1 = \Sigma ||F_o|-|F_c||\Sigma|F_o|$, $wR_2 = [\Sigma [w(F_o^2-F_c^2)^2]/\Sigma [w(F_o^2)]^{1/2}$. 
4. PDMS samples

Table S2 PDMS specimens containing mono-functionalized QxCav C1A, bis-alkene functionalized QxCav C2A and tetrafunctionalized QxCav C4A and C4AL.

| Cavitand | Conc. (% w/w) |
|----------|---------------|
| I        | C2A 0.05      |
| II       | C2A 0.1       |
| III      | C2A 0.2       |
| IV       | C2A 0.3       |
| V        | C2A 0.5       |
| VI       | C2A 0.6       |
| VII      | C2A 0.7       |
| VIII     | C1A 0.1       |
| IX       | C4A 0.1       |
| X        | C4A 0.3       |
| XI       | C4A 0.5       |
| XII      | C4AL 0.7      |
| XIII     | C4AL 0.1      |

Table S3 Control PDMS specimens containing unfunctionalized QxCav Cv and Ck.

| Cavitand | Conc. (% w/w) |
|----------|---------------|
| I        | Cv 0.05       |
| II       | Cv 0.1        |
| III      | Cv 0.5        |
| IV       | Ck 0.05       |
| V        | Ck 0.1        |
Table S4 Optimization of the curing conditions for PDMS specimens with different concentrations of tetrafunctionalized cavitands C4A and C4AL as cross-linkers and different ratios between vinyl-terminated and H-terminated pre-polymers. Curing is indicated with (✓) while non-curing is indicated with (✗).

| Cavitand | Conc. (% w/w) | RTV 615 base/H-term. (w/w) | Curing |
|----------|---------------|----------------------------|--------|
| I        | C4A           | 1                          | 1/1    | ✓      |
| II       | C4A           | 1                          | 1/2    | ✓      |
| III      | C4A           | 1                          | 2/1    | ✓      |
| IV       | C4A           | 3                          | 1/2    | ✓      |
| V        | C4A           | 1                          | 1/5    | ✓      |
| VI       | C4A           | 1                          | 1/10   | ✓      |
| VII      | C4A           | 0.5                        | 1/10   | ✓      |
| VIII     | C4A           | 0.3                        | 1/10   | ✓      |
| IX       | C4AL          | 1                          | 1/10   | ✓      |
| X        | C4AL          | 0.5                        | 1/10   | ✓      |
| XI       | C4AL          | 0.3                        | 1/10   | ✓      |
5. Soxhlet extraction tests

In order to prove the effective participation of cavitand double bonds in the hydrosilylation reaction and thus validate the proposed method, Soxhlet extraction with CHCl$_3$ on two PDMS samples, one cured in the presence of bis-alkene functionalized cavitand C$_2$A (Table S2, Entry II) and the other with unfunctionalized QxCav C$_V$ (Table S3, Entry II) were performed. The extracted polymer and the organic phase were analysed by UV-Vis spectroscopy. Fig. S2 shows that the absorption pattern of the cavitand is retained for PDMS-C$_2$A in the polymeric specimen, while it is not present in the organic phase. Opposite result was obtained for PDMS-C$_V$. This experiment, although being crucial for proving the covalent incorporation of cavitands in the polysiloxane network, does not demonstrate the effective reaction of all their functionalities.

![Figure S2](image)

**Figure S2** UV-Vis spectra of Soxhlet treated samples (solid line) and extracts (dashed line) from PDMS-C$_2$A (a) and PDMS-C$_V$ (b).
6. UV-Vis spectra of PDMS samples

Figure S3 UV-Vis spectra of QxCav $C_V$ (black) and $C_K$ (red) in CHCl$_3$ (solid lines) and in PDMS (dashed lines; 0.1% w/w, Table S3, entry II and V respectively).

Figure S4 Normalized UV-Vis spectra of PDMS-C4A$_L$ (0.7% w/w, Table S2 entry XII) upon progressive elongation.
Figure S5 Normalized UV-Vis spectra of QxCav C4A in CHCl₃ before (black) and after (magenta) the addition of TFA.
7. PU samples

**Table S5** Control PU specimens containing mono functionalized QxCav C1H, difunctionalized QxCav C2H and tetrafunctionalized QxCav C4H and Ck4H.

| Cavitand | Conc. (% w/w) |
|----------|--------------|
| I        | C2H          | 0.1          |
| II       | C2H          | 0.3          |
| III      | C1H          | 0.5          |
| IV       | C1H          | 0.3          |
| V        | C1H          | 0.1          |
| VI       | C4H          | 0.5          |
| VII      | C4H          | 0.3          |
| VIII     | C4H          | 0.2          |
| IX       | C4H          | 0.1          |
| X        | C4H          | 0.01         |
| XI       | C4H          | 0.02         |
| XII      | Ck4H         | 0.01         |

**Table S6** PU specimens containing unfunctionalized QxCav CV and CK.

| Cavitand | Conc. (% w/w) |
|----------|--------------|
| I        | CV           | 0.5          |
| II       | CV           | 0.3          |
| III      | CV           | 0.01         |
| IV       | CK           | 0.5          |
| V        | CK           | 0.3          |
| VI       | CK           | 0.01         |
8. DSC of PU-C4H

Figure S6 DSC traces of **PU-C4H** (0.2% w/w, Table S5, entry VIII), first (red) and second (blue) scans are reported.
9. UV-Vis spectra of PU samples

Figure S7 UV-Vis spectra of \( Q_xCav \) \( C_V \) (black) and \( C_K \) (red) in \( CHCl_3 \) (solid lines) and in \( PU-C_V \) and \( PU-C_K \) (dashed lines; 0.5% w/w, Table S6, entry I and IV respectively).

Figure S8 Ratio of adsorption values at 348 and 318 nm as function of the strain for \( PU-C4H \) (0.3% w/w, Table S5 entry VII) (black squares) and \( PU-C_V \) (0.3% w/w, Table S6 entry II) (red circles); initial values are subtracted for direct comparison of the two trends (black and red lines).
Figure S9 Normalized UV-Vis spectra of **PU-C1H** (0.3% w/w, Table S5 entry IV) upon progressive elongation.

Figure S10 Normalized UV-Vis spectra of **PU-C2H** (0.3% w/w, Table S5 entry II) upon progressive elongation.
10. Fluorescence measurements for PU samples

Figure S11 Normalized fluorescence emission spectra of QxCav Cᵥ and Cₖ in solvents of different polarity; vertical dashed lines are a guide to the eye to appreciate the shift.

Figure S12 Normalized fluorescence emission spectra of vase (black) and kite cavitand (red) physically dispersed (PU-Cᵥ and PU-Cₖ, dashed lines) and covalently linked (PU-C₄H and PU-Cₖ4H, solid lines) to the polymer backbone.
Figure S13 Normalized fluorescence emission spectra of vase $QxCav\; C_V$ (top) and kite $QxCav\; C_K$ (bottom) in $10^{-4}\text{M}$ (black) and $10^{-6}\text{M}$ (red) $\text{CHCl}_3$ solutions; vertical dashed lines are a guide to the eye.

Figure S14 Normalized emission spectra of $\text{PU-C}_V$ (0.01% w/w; Table S6 entry III) upon tensile elongation.
11. References

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