Endgroups of Functionalized Siloxane Oligomers Direct Block Copolymeric or Liquid Crystalline Self-Assembly Behavior

R. Helen Zha,[†] Bas de Waal,[†] Martin Lutz,[‡] Abraham J. P. Teunissen,[†] E. W. Meijer[†]*

†Institute for Complex Molecular Systems and Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

‡Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, 3584 CH Utrecht, The Netherlands

Supporting Information

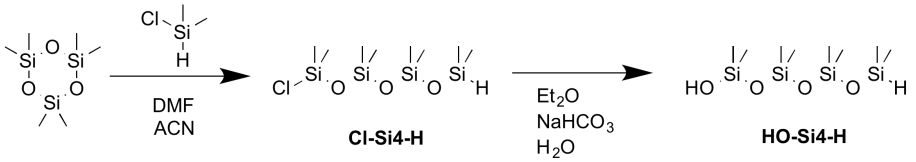
Materials. Bulk solvents were purchased from Biosolve Chimie and used as received unless otherwise specified. When necessary, solvents were dried using 4 Å molecular sieves. Hexamethylcyclotrisiloxane (98% purity), chlorodimethylsilane (99.5% purity), and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane were purchased from ABCR. Palladium on carbon (Pd/C, 10%) was purchased from Merck. 2-Amino-6-methylpyrimidin-4(1H)-one was purchased from Santa Cruz Biotechnology. Allylamine (>99% purity), benzyl bromide (98% purity), and 1,1'-carbonyldiimidazole was purchased from Sigma Aldrich.

Methods. Flash chromatography for siloxane oligomers was performed using a Grace Reveleris instrument equipped with an evaporative light scattering detector. Flash chromatography for UV-active compounds was performed on a Biotage Isolera One system. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 400 MHz or 500 MHz Varian Unit Inova NMRs at room temperature. Gel permeation chromatography (GPC) was performed using Shimadzu Prominence LC-2030C, and solutions were dissolved at 2 mg/mL and filtered through 0.2 μm Whatman Anatop 10 filters before injection. Matrix-assisted laser desorption/ionization mass spectra (MALDI) were obtained on a Bruker Autoflex Speed spectrometer using a-cyano-4-hydroxycinnamic acid (CHCA) and 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrices. Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-2000 equipped with a GSMS-QP2010+ detector using a Phenomenex Zebron ZB-5 MS column. IR spectra were recorded on a Perkin Elmer UATR Two FTIR spectrometer. X-ray diffraction was used to determine the structure of O-benzylated UPy (methods and results described at the end of this Supporting Information document).

All UZSi*N* and USi*N* samples were annealed for 3 days at 45 ^{o}C in a vacuum oven prior to polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small angle X-ray scattering (SAXS). Thermal transitions were determined using a TA Q2000 DSC with 10 ^{o}C/min heating and cooling. Mixtures of UZSi*N* or USi*N* were made by combining solutions of molecules separately dissolved in $CHCl_3$, allowing samples to dry overnight, and annealing samples for 3 days at 45 ^{o}C in a vacuum oven. POM samples were placed on glass slides and imaged using a Nikon Xfinity1 Lumenera microscope with 5X magnification at room temperature. Samples for SAXS were mounted on V1 grade mica sheets 5-7 μm thick and measured using a SAXSLAB GANESHA system equipped with a GeniX-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of 1 x 108 phs^{-1}. Scattering patterns were collected using a Pilatus 300K silicon pixel detector and the beam center and the *q* range were calibrated using the diffraction peaks of silver behenate. Conversion of 2D images into 1D spectra was accomplished with Saxsgui software. Domain spacings (L_0) were calculated for various morphologies using primary scattering peak positions (q*) and interplanar spacings ($d^* = 2\pi/q^*$). Volume fractions of UZSi*N* and USi*N* were calculated using the molecular weight of subunits, the density of polydimethylsiloxane from literature,[1] the density of UPy from literature,[2] and the density of O-benzylated UPy from crystallographic data (presented at the end of this Supporting Information document).

Synthesis of Dimethylsiloxane Oligomers.

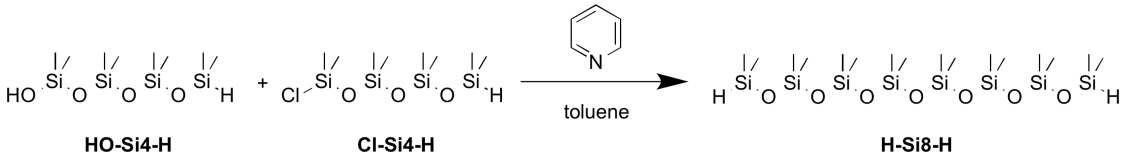
The synthetic strategy of monodisperse dimethylsiloxane oligomers in various lengths will be further reported in subsequent publications. The synthesis and characterization of oligomers used in the current work is as follows:



Scheme S1. Synthesis of chlorosilane and silanol building blocks.

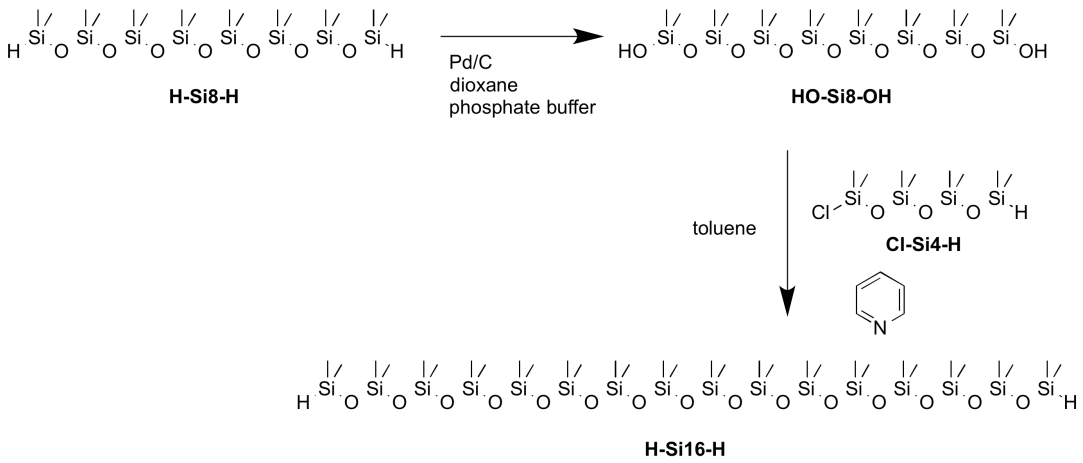
1-chloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxanen (Cl-Si4-H). Ring opening of hexamethylcyclotrisiloxane was conducted as described by Brown and coworkers.[3] Hexamethylcyclotrisiloxane (99.13 g; 445.6 mmol), chlorodimethylsilane (44.38 g; 469.0 mmol), and 22 mL acetonitrile were stirred together. After 25 mins, 1.14 ml DMF was added and the reaction was stirred at ambient temperature for 5 days. The reaction mixture was vacuum distilled at 55 – 56 ^{o}C and 2.5 torr to yield 91.8 g (65%) product. ^{1}H-NMR (400MHz, $CDCl_3$) δ 4.70 (m, 1H, H-Si, J_{HSICH} = 2.8 Hz), 0.45 (s, 6H, Cl-Si-CH), 0.198 (d, 6H, H-Si-CH, J_{HSICH} = 2.8 Hz), 0.132 (s, 6H), 0.085 (s, 6H) ppm. ^{13}C-NMR (100MHz, $CDCl_3$) δ 4.02, 0.85, 0.77, 0.64 ppm. GC/MS: standard program 50-300 °C; RT = 3.075 min. MALDI-TOF: m/z calc. for $C_8H_{25}ClO_3Si_4$: 316.05; found 301 ($[M-15]^+$).

1,1,3,3,5,5,7,7-octamethyltetrasiloxan-1-ol (HO-Si4-H). A solution of sodium bicarbonate (4.40 g; 52.37 mmol) in 80 mL water and 300 mL diethylether was stirred together with ice bath cooling. A solution of 16 mL **Cl-Si4-H** (15.09 g; 47.74 mmol) in 200 mL dry diethylether was dropwise added over 85 mins. After another 45 mins, the ice bath was removed and the reaction mixture was stirred for an additional 1.5 hrs. The mixture was then washed with 200 mL water, followed by 200 mL brine. After concentrating by rotary evaporation, the mixture was co-evaporated with 50 mL toluene, which yielded 14.11 g product (99 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 1H, HO-Si-$(CH_3)_2$), 0.20 (s, 6H, HO-Si-$(CH_3)_2$)), 0.15 (s, 6H, CH_3), 0.10 (s, 6H, CH_3), 0.08 (s, 6H, CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 0.97, 0.84, 0.65, 0.31 ppm. IR (ATR): ν = 3306, 2963, 2905, 2126, 1414, 1258, 1033, 905, 792 cm^{-1}. GC/MS: standard program 50-300 °C; RT = 3.191 min. MALDI-TOF: m/z calc. for $C_8H_{26}O_4Si_4$: 298.09; found 281 ($[M-17]^+$).



Scheme S2. Synthesis of silyl hydride oligomer with 8 repeat units.

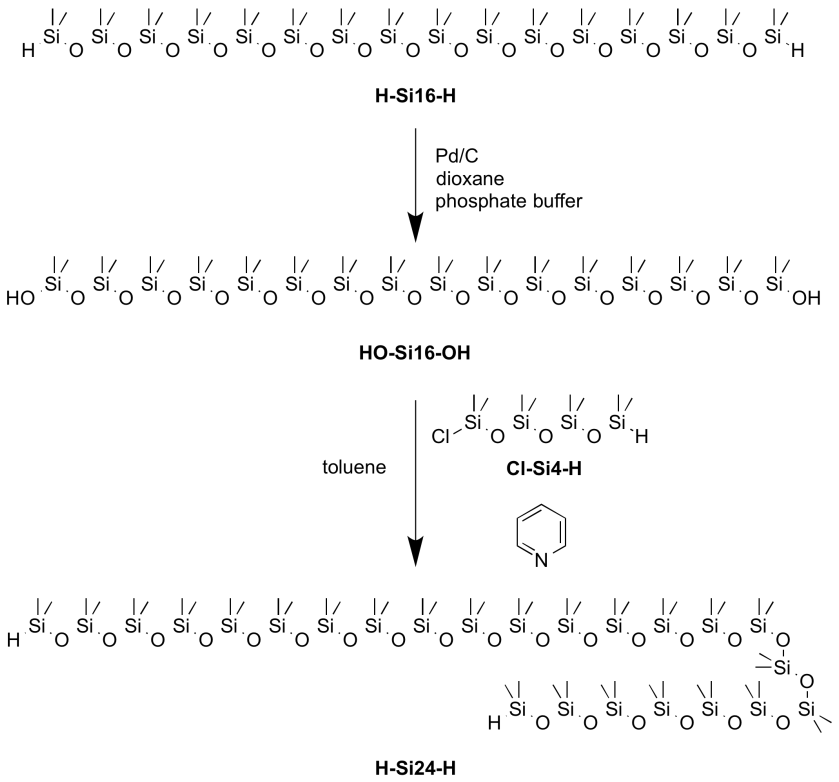
1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyloctasiloxane (H-Si8-H). To an ice bath-cooled reaction flask containing **Cl-Si4-H** (14.71 g; 46.4 mmol) in 50 mL toluene, pyridine (4.3 mL; 52.8 mmol) was dropwise added over 5 mins. A solution of **HO-Si4-H** (13.64 g; 45.7 mmol) in 50 mL toluene was then added dropwise using a dropping funnel over 40 mins. After 2.5 hrs, the ice bath was removed and the reaction was left to stir for 1 hr at room temperature. The white, turbid reaction mixture was then mixed with 150 mL toluene and washed with water (3 times, 150 mL each). The organic layer was concentrated by rotary evaporation and then co-evaporated with toluene (2 times, 30 mL each). Low molecular weight siloxanes were removed by high vacuum (0.30 torr, 70 °C water bath) to yield 21.80 g product (82%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.70 (sept, ^{3}J = 2.8 Hz, 2H, H-Si-$(CH_3)_2$), 0.20 (d, ^{3}J = 2.8 Hz, 12H, H-Si-$(CH_3)_2$)), 0.10 –0.08 ppm (m, 36H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 1.04, 1.02, 0.85, 0.69 ppm. IR (ATR): ν = 2963, 2905, 2127, 1413, 1258, 1017, 907, 788 cm^{-1}. GC/MS: standard program 50-300 °C. RT = 5.45 min. MALDI-TOF: m/z calc. for $C_{16}H_{50}O_7Si_8$: 578.17; found: 601.22 ($[M+Na]^+$). GPC ($CHCl_3$, RI detector): M_w/M_n = 1.030.



Scheme S3. Synthesis of silyl hydride oligomer with 16 repeat units.

1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyloctasiloxane-1,15-diol (HO-Si8-OH). A mixture of 65 mL dioxane and 34 mL of 1 M phosphate buffer (pH = 7.0) was stirred together and bubbled with nitrogen gas. Pd/C (480 mg) was then added and the reaction flask was cooled in an ice bath while **H-Si8-H** (11.23 g; 19.39 mmol) was added dropwise over 10 mins. After 3.5 hrs, the ice bath was removed and the reaction was stirred for another 1 hr. The mixture was filtered, 400 mL toluene was added, and the mixture was washed with water (3 times, 300 mL each). The organic layer was concentrated by rotary evaporation and the product was co-evaporated with toluene (2 times, 10 mL each) at 50 °C to yield 11.14 g (94%) of a clear viscous oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 2H, HO-Si), 0.14 (s, 12H, HO-Si-(CH_3)$_2$)), 0.12 –0.05 ppm (m, 36H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 1.06, 1.00, 0.31 ppm. IR (ATR): ν = 3304, 2963, 2906, 1412, 1258, 1017, 891, 858, 787 cm^{-1}. MALDI-TOF: m/z calc. for $C_{16}H_{50}O_9Si_8$: 610.16; found: 633.24 ([M+Na]$^+$).

1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31-dotriacontamethylhexadecasiloxane (H-Si16-H). A solution of **Cl-Si4-H** (13.20 g; 41.64 mmol) in 35 ml toluene was cooled on an ice bath and 3.95 mL pyridine was added dropwise over 1 min. **HO-Si8-OH** (11.03 g; 18.04 mmol) dissolved in 10 mL toluene was added dropwise over 10 mins. After 15 mins of stirring, 20 mL toluene was added to the viscous reaction mixture. After 1.5 hrs, the ice bath was removed and stirring continued for an additional 1.5 hrs at room temperature. The reaction mixture was combined with 200 mL toluene and washed with water (2 times, 200 mL each). The organic phase was then concentrated by rotary evaporation and washed with acetonitrile (4 times, 40 mL each), yielding 18.72 g of a clear liquid. Purification was further performed using flash chromatography with a heptane/chloroform gradient from 100/0% to 88/12%, yielding 9.85 g (47%) product.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.70 (sept, ^{3}J = 2.8 Hz, 2H, H-Si-(CH_3)$_2$), 0.19 (d, ^{3}J = 2.8 Hz, 12H, H-Si-(CH_3)$_2$)), 0.08–0.06 ppm (m, 36H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 1.06, 1.05, 1.04, 1.02, 0.85, 0.69 ppm. IR (ATR): ν = 2963, 2906, 2127, 1413, 1258, 1013, 910, 788 cm^{-1}. MALDI-TOF: m/z calc. for $C_{32}H_{98}O_{15}Si_{16}$: 1170.32; found: 1193.35 ([M+Na]$^+$). GPC ($CHCl_3$; RI detector): M_w/M_n=1.026.

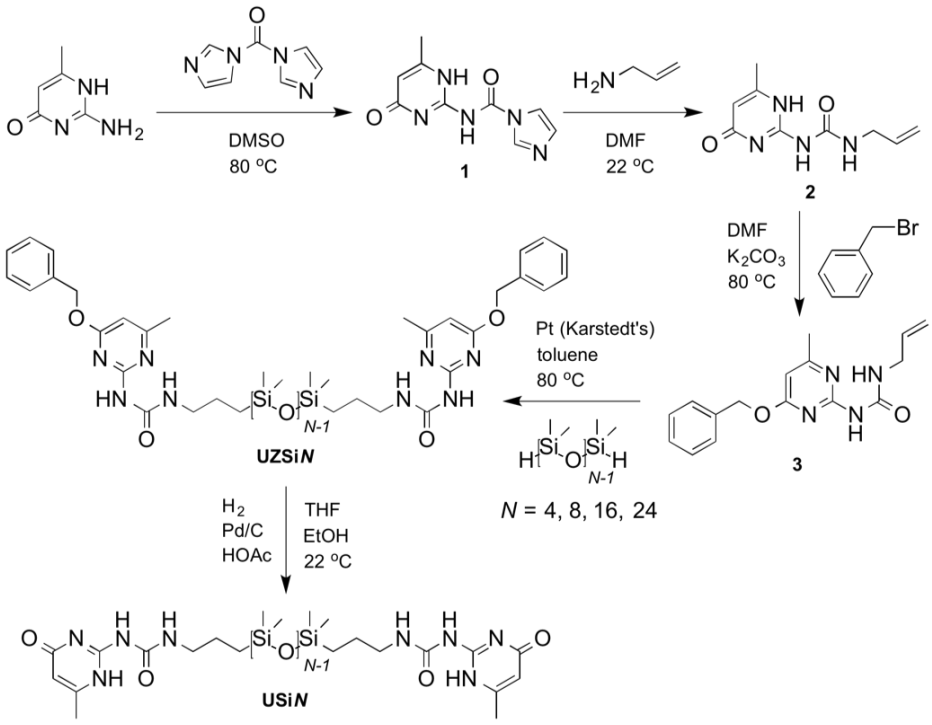


Scheme S4. Synthesis of silyl hydride oligomer with 24 repeat units.

1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31-dotriacontamethylhexadecasiloxane-1,31-diol (HO-Si16-OH). Nitrogen gas was bubbled through a solution of 100 mL dioxane and 31 mL 1 M phosphate buffer (pH = 7.3). Pd/C (340 mg) was added and the mixture was cooled by an ice bath. A solution of **H-Si16-H** (8.05 g; 6.87 mmol) in 10 mL dioxane was added dropwise over 10 mins. After 15 mins, the ice bath was removed and the reaction was stirred for another 23 hrs at room temperature. The reaction was mixed with 250 mL toluene and washed with water (2 times, 200 mL each). The organic phase was concentrated by rotary evaporation and further co-evaporated with toluene (2 times, 20 mL each), yielding 6.74 g (82 %) product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.27, (s, 1H, O<u>H</u>), 0.14 (s, 12H, HO-Si-(C<u>H</u>$_3$)$_2$), 0.10-0.06 (m, 84H, C<u>H</u>$_3$) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 1.02, 0.97, 0.29 ppm. IR (ATR): ν = 3305, 2963, 2906, 1412, 1258, 1017, 891, 787 cm^{-1}. MALDI-TOF: calc. for $C_{32}H_{98}O_{17}Si_{16}$: 1202.31; found 1225.44 ($[M+Na]^+$).

1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31,33,33,35,35,37,37,39,39,41,41,43,43,45,45,47,47-octatetracontamethyltetracosasiloxane (H-Si24-H). To an ice bath-cooled solution of **Cl-Si4-H** (4.37 g; 13.8 mmol) in 30 mL toluene, 1.5 mL pyridine was added dropwise. A solution of **HO-Si16-OH** (6.62; 5.48 mmol) in 10 ml toluene was dropwise added over 10 mins. Formation of a white, turbid mixture was immediately observed. After 2 hrs, the ice bath was removed and the solution was stirred for another 2 hrs at room temperature. The reaction mixture was then mixed with 150 mL toluene and washed with water (3 times, 150 mL each). After concentration by rotary evaporation, the product was co-evaporated with toluene (2 times, 20 mL each). The crude was further washed with acetonitrile (4 times, 30 mL each), yielding 9.15 g (94%) of the product as a clear colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.70 (sept, ^{3}J = 2.8 Hz, 2H, H-Si-(C<u>H</u>$_3$)$_2$), 0.19 (d, ^{3}J = 2.8 Hz, 12H, H-Si-(C<u>H</u>$_3$)$_2$)), 0.08–0.06 ppm (m, 132H, C<u>H</u>$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 1.40, 1.03, 0.84, 0.68 ppm. IR (ATR): ν = 2963, 2906, 2127, 1403, 1258, 1013, 910, 788 cm^{-1}. MALDI-TOF: m/z calc. for $C_{48}H_{146}O_{23}Si_{24}$: 1762.47; found: 1785.46 ($[M+Na]^+$). GPC ($CHCl_3$, RI detector): M_w/M_n = 1.024.

Synthesis of Functionalized Dimethylsiloxane Oligomers.



Scheme S5. Synthesis of dimethylsiloxane oligomers functionalized with UPy or O-benzylated UPy.

N-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)-1H-imidazole-1-carboxamide (1). Synthesis and characterization of (1) was conducted as described by Teunissen and coworkers.[4] 2-Amino-6-methylpyrimidin-4(1H)-one (1.0 g; 7.99 mmol) was dissolved in 10 mL DMSO. Di(1H-imidazol-1-yl)methanone (1.68 g; 10.36 mmol) was added and the mixture was stirred for 24 hrs at 80 °C. The solution was cooled to room temperature and acetone was added to precipitate the product. The precipitate collected by filtration and washed with acetone. The product was dried under vacuum to yield 1.59 g (91%) product as a white powder. Due to extremely low solubility in most solvents, characterization of this compound is difficult. IR (ATR): ν = 3175, 3075, 2648 (bs), 1701, 1645, 1601, 1509, 1479, 1375, 1334, 1320, 1276, 1233, 1224, 1190, 1169, 1090, 1065, 1026, 983 cm^{-1}.

1-allyl-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (2). Compound **1** (4.0 g; 18.26mmol) was dissolved in 80mL dry DMF. Allylamine (1.57 g; 27.5 mmol) was added dropwise and the reaction was stirred under argon for 12 hrs. The solution was then precipitated into 850 mL acetone and the white powder was collected by filtration. The powder was further washed with acetone and dried under vacuum to yield 3.45 g product (91%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 13.05 (s, 1H, N-H), 11.97 (s, 1H, N-H), 10.42 (s, 1H, N-H), 5.91 (ddt, *J* = 16.7; 10.8; 5.6 Hz, 1H, -C<u>H</u>=CH_2), 5.83 (s, 1H, pyrimidyl), 5.27 (dd, *J* = 17.2; 1.1 Hz, 1H, -CH-C<u>H_2</u>), 5.16 (dd, *J* = 10.2; 1.1 Hz, 1H, -CH-C<u>H_2</u>), 3.89 (t, *J* = 5.3 Hz, 2H, NH-C<u>H_2</u>-CH), 2.22 (s, 3H, Ar-CH_3). ^{13}C-NMR (126 MHz; $CDCl_3$): δ = 173.22, 156.80, 154.79, 148.45, 134.40, 115.99, 106.96, 42.38, 19.10 ppm. IR (ATR): ν = 3211, 3146, 2953, 1696, 1665, 1575, 1517, 1255 cm^{-1}. MALDI-TOF: m/z calc. for $C_9H_{12}N_4O_2$: 208.10; found: 209.3 ($[M+H]^+$).

1-allyl-3-(4-(benzyloxy)-6-methylpyrimidin-2-yl)urea (3). To a suspension of K_2CO_3 (4.84 g; 35 mmol) in 40 mL dry DMF, compound **2** (2.09 g; 10 mmol) was added. Benzyl bromide (6 g; 35 mmol) was added dropwise over 2 mins and the reaction was stirred at 80 °C under argon for 24 hrs. The reaction mixture was stirred with 50 mL acetone and filtered in order to remove K_2CO_3. Rotary evaporation was then used to remove acetone from the filtrate, which was subsequently mixed with 400 mL water to produce chunky off-white precipitate. The solids were collected by filtration and recrystallized twice in ethanol to yield 1.55 g (60%) product as

white crystals. Note that most shifts seen in ^{1}H-NMR are further split due to conformational effects of the benzyl group. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.32 (s, 1H, N-H), 7.40-7.32 (m, 5H, Ph-H), 7.11 (s, 1H, N-H), 6.22 (d, *J* = 0.5 Hz, 1H, pyrimidyl), 5.96 (ddt, *J* = 16.8; 10.8; 5.6 Hz, 1H, -C<u>H</u>=CH_2), 5.32 (s, 2H, Ph-CH_2), 5.28 (dq, *J* = 17.2; 1.5 Hz, 1H, -CH=C<u>H</u>$_2$), 5.16 (dq, *J* = 10.3; 1.5 Hz, 1H, -CH=C<u>H</u>$_2$), 4.01 (tt, *J* = 5.3; 1.6 Hz, 2H, NH-C<u>H</u>$_2$-CH), 2.34 (d, *J* = 0.5 Hz, 3H, Ar-C<u>H</u>$_3$). ^{13}C-NMR (126 MHz; $CDCl_3$): δ = 170.10, 167.47, 157.44, 154.46, 136.05, 134.88, 128.68, 128.36, 128.18, 115.36, 100.65, 68.23, 42.36, 23.78 ppm. IR (ATR): ν = 3209, 3068, 3002, 2957, 1676, 1594, 1547, 1335, 1279 cm^{-1}. MALDI-TOF: m/z calc. for $C_{16}H_{18}N_4O_2$: 298.14; found: 299.3 ($[M+H]^+$).

UZSi*N*. Oligomeric dimethylsiloxanes (N = 4, 8, 16, 24) were functionalized with O-benzylated UPy (**3**) using the same general procedure for all lengths. UZSi4 was synthesized using 1,1,3,3,5,5,7,7-octamethyltetrasiloxane purchased from ABCR, while UZSi8, UZSi16, and UZSi24 were synthesized using oligomers synthesized as described above. Siloxane oligomer (0.5 mmol) and benzylated UPy (**3**) (1.15 mmol) were dissolved in 4 mL dry toluene and heated up to 80 ^{o}C. Karstedt's catalyst in xylene (3 drops from Pasteur pipette) was then added and the reaction was stirred for 18 hrs under argon. The solvent was removed by rotary evaporation and the crude was purified by flash chromatography with a heptane/ethyl acetate gradient from 80/20% to 65/35%. The solvent was removed again by rotary evaporation, and the product was further purified by an isocratic flash chromatography column at 50% heptane/50% ethyl acetate in order to remove unreacted benzylated UPy. The product was dried under vacuum and was then washed with acetonitrile (20 mL) to yield ~0.3 mmol (~60%) of pure material. Characterizations for each molecule are as follows:

1,1'-((1,1,3,3,5,5,7,7-octamethyltetrasiloxane-1,7-diyl)bis(propane-3,1-diyl))bis(3-(4-(benzyloxy)-6-methylpyrimidin-2-yl)urea) (UZSi4). ^{1}H-NMR (500 MHz; $CDCl_3$): δ = 9.26 (s, 2H, N-H), 7.40-7.32 (m, 10H, Ph-H), 7.08 (s, 2H, N-H), 6.22 (s, 2H, pyrimidyl), 5.32 (s, 4H, Ph-CH_2), 3.34 (q, *J* = 6.3 Hz, 4H, NH-C<u>H</u>$_2$-CH_2), 2.33 (s, 6H, Ar-CH_3), 1.63-1.57 (m, 4H, NH-CH_2-C<u>H</u>$_2$), 0.63-0.60 (m, 4H, Si-C<u>H</u>$_2$), 0.09-0.04 (m, 12H, CH_3-Si), 0.03-0.02 (m, 12H, CH_3-Si). ^{13}C-NMR (126 MHz; $CDCl_3$): δ = 170.19, 167.21, 157.48, 154.42, 136.11, 128.72, 128.42, 128.26, 100.63, 68.23, 43.00, 23.81, 15.71, 1.33 ppm. IR (ATR): ν = 3216, 3148, 3006, 2959, 1675, 1600, 1552, 1337, 1256, 1079, 1028, 786 cm^{-1}. MALDI-TOF: m/z calc. for $C_{40}H_{62}N_8O_7Si_4$: 878.38; found: 901.4 ($[M+Na]^+$). GPC (THF, PDA detector): M_w/M_n = 1.009.

1,1'-((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyloctasiloxane-1,15-diyl)bis(propane-3,1-diyl))bis(3-(4-(benzyloxy)-6-methylpyrimidin-2-yl)urea) (UZSi8). ^{1}H-NMR (500 MHz; $CDCl_3$): δ = 9.26 (s, 2H, N-H), 7.40-7.32 (m, 10H, Ph-H), 7.08 (s, 2H, N-H), 6.22 (s, 2H, pyrimidyl), 5.32 (s, 4H, Ph-CH_2), 3.34 (q, *J* = 6.3 Hz, 4H, NH-C<u>H</u>$_2$-CH_2), 2.33 (s, 6H, Ar-CH_3), 1.63-1.57 (m, 4H, NH-CH_2-C<u>H</u>$_2$), 0.63-0.60 (m, 4H, Si-C<u>H</u>$_2$), 0.09-0.02 (m, 48H, CH_3-Si). ^{13}C-NMR (126 MHz; $CDCl_3$): δ = 170.15, 166.82, 157.23, 154.15, 135.87, 128.47, 128.17, 128.01, 100.38, 67.99, 42.76, 23.63, 15.48, 0.97 ppm. IR (ATR): ν = 3216, 3148, 3006, 2961, 1675, 1602, 1552, 1339, 1258, 1079, 1017, 787 cm^{-1}. MALDI-TOF: m/z calc. for $C_{48}H_{86}N_8O_{11}Si_8$: 1174.46; found: 1197.5 ($[M+Na]^+$). GPC (THF, PDA detector): M_w/M_n = 1.011.

1,1'-((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31-dotriacontamethylhexadecasiloxane-1,31-diyl)bis(propane-3,1-diyl))bis(3-(4-(benzyloxy)-6-methylpyrimidin-2-yl)urea) (UZSi16). ^{1}H-NMR (500 MHz; $CDCl_3$): δ = 9.26 (s, 2H, N-H), 7.40-7.32 (m, 10H, Ph-H), 7.08 (s, 2H, N-H), 6.22 (s, 2H, pyrimidyl), 5.32 (s, 4H, Ph-CH_2), 3.34 (q, *J* = 6.3 Hz, 4H, NH-C<u>H</u>$_2$-CH_2), 2.33 (s, 6H, Ar-CH_3), 1.63-1.57 (m, 4H, NH-CH_2-C<u>H</u>$_2$), 0.63-0.60 (m, 4H, Si-C<u>H</u>$_2$), 0.09-0.02 (m, 96H, CH_3-Si). ^{13}C-NMR (126 MHz; $CDCl_3$): δ = 170.20, 167.21, 157.30, 154.41, 136.11, 128.72, 128.41, 127.92, 100.62, 68.24, 43.04, 23.88, 15.77, 1.22 ppm. IR (ATR): ν = 3216, 3148, 3006, 2962, 1676, 1604, 1555, 1340, 1258, 1079, 1013, 787 cm^{-1}. MALDI-TOF: m/z calc. for $C_{64}H_{134}N_8O_{19}Si_{16}$: 1766.61; found: 1789.6 ($[M+Na]^+$). GPC (THF, PDA detector): M_w/M_n = 1.016.

1,1'-((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31,33,33,35,35,37,37,39,39,41,41,43,43,45,45,47,47-octatetracontamethyltetracosasiloxane-1,47-diyl)bis(propane-3,1-diyl))bis(3-(4-(benzyloxy)-6-methylpyrimidin-2-yl)urea) (UZSi24). ^{1}H-NMR (500 MHz; $CDCl_3$): δ = 9.26 (s, 2H, N-H), 7.40-7.32 (m, 10H, Ph-H), 7.08 (s, 2H, N-H), 6.22 (s, 2H, pyrimidyl), 5.32 (s, 4H, Ph-CH_2), 3.34 (q, *J* = 6.3

Hz, 4H, NH-C$\underline{H}_2$-CH$_2$), 2.33 (s, 6H, Ar-CH$_3$), 1.63-1.57 (m, 4H, NH-CH$_2$-C$\underline{H}_2$), 0.63-0.60 (m, 4H, Si-C$\underline{H}_2$), 0.09-0.04 (m, 144H, CH$_3$-Si). ^{13}C-NMR (126 MHz; CDCl$_3$): δ = 170.24, 167.21, 157.49, 154.41, 136.13, 128.73, 128.43, 128.29, 100.64, 68.25, 43.03, 23.89, 15.76, 1.22 ppm. IR (ATR): ν = 3216, 3148, 3006, 2962, 1676, 1604, 1555, 1340, 1258, 1079, 1013, 787 cm^{-1}. MALDI-TOF: m/z calc. for $C_{80}H_{182}N_8O_{27}Si_{24}$: 2358.76; found: 2381.9 ([M+Na]$^+$). GPC (THF, PDA detector): M_w/M_n = 1.017.

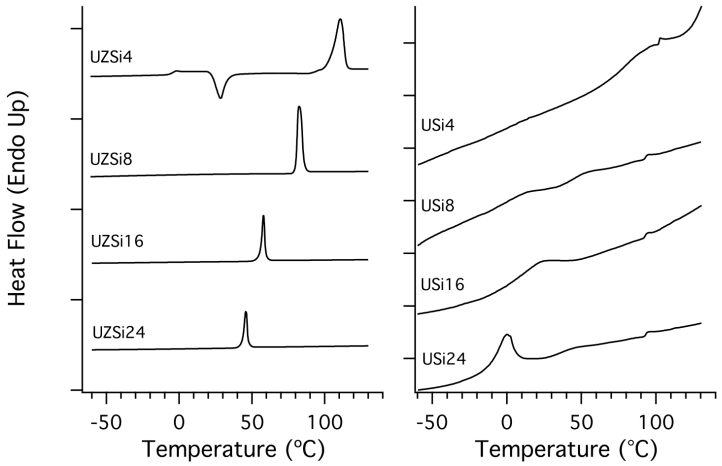
USi*N*. Oligomeric dimethylsiloxanes (N = 4, 8, 16, 24) functionalized with UPy were synthesized using the same general procedure for all lengths. UZSi*N* (0.5 mmol) was dissolved in 20 mL THF with 10 mL ethanol and 33 μL acetic acid. Nitrogen gas was bubbled through the solution for 10 mins and 100 mg Pd/C was added. The reaction was carried out in a Parr reactor at 40 psi for 22 hrs. The solution was then filtered through celite and the solvent was removed by rotary evaporation. The product was purified by an isocratic flash chromatography column with 5% methanol/95% CHCl$_3$ and dried under vacuum. Finally, the product was washed with 20 mL acetonitrile to yield 0.43 mmol (85%). Characterizations for each molecule are given below. It should be noted that some chemical shifts undergo additional splitting in ^{1}H-NMR at low concentrations due to supramolecular cyclization and that GPC traces show tailing due to supramolecular interactions.

1,1'-((1,1,3,3,5,5,7,7-octamethyltetrasiloxane-1,7-diyl)bis(propane-3,1-diyl))bis(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea) (USi4). ^{1}H-NMR (500 MHz; CDCl$_3$): δ = 13.14 (s, 2H, N-H), 11.87 (s, 2H, N-H), 10.21 (s, 2H, N-H), 5.79 (s, 2H, pyrimidyl), 3.19 (q, *J* = 6.4 Hz, 4H, NH-C$\underline{H}_2$-CH$_2$), 2.22 (s, 6H, Ar-CH$_3$), 1.62-1.56 (m, 4H, NH-CH$_2$-C$\underline{H}_2$), 0.58-0.54 (m, 4H, Si-C$\underline{H}_2$), 0.09-0.02 (m, 24H, CH$_3$-Si). ^{13}C-NMR (126 MHz; CDCl$_3$): δ = 172.82, 156.69, 154.88, 148.25, 106.75, 43.24, 23.63, 19.06, 15.63, 1.34 ppm. IR (ATR): ν = 3216, 2957, 1698, 1664, 1585, 1522, 1250, 1070, 1028, 790 cm^{-1}. MALDI-TOF: m/z calc. for $C_{26}H_{50}N_8O_7Si_4$: 698.29; found: 699.3 ([M+H]$^+$). GPC (THF, PDA detector): M_w/M_n = 1.040.

1,1'-((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyloctasiloxane-1,15-diyl)bis(propane-3,1-diyl))bis(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea) (USi8). ^{1}H-NMR (500 MHz; CDCl$_3$): δ = 13.14 (s, 2H, N-H), 11.87 (s, 2H, N-H), 10.21 (s, 2H, N-H), 5.79 (s, 2H, pyrimidyl), 3.20 (q, *J* = 6.3 Hz, 4H, NH-C$\underline{H}_2$-CH$_2$), 2.22 (s, 6H, Ar-CH$_3$), 1.62-1.56 (m, 4H, NH-CH$_2$-C$\underline{H}_2$), 0.58-0.54 (m, 4H, Si-C$\underline{H}_2$), 0.09-0.02 (m, 48H, CH$_3$-Si). ^{13}C-NMR (126 MHz; CDCl$_3$): δ = 173.10, 156.73, 154.87, 148.21, 106.76, 43.22, 23.68, 19.04, 15.62, 1.23 ppm. IR (ATR): ν = 3213, 2960, 1700, 1666, 1592, 1527, 1255, 1079, 1017, 787 cm^{-1}. MALDI-TOF: m/z calc. for $C_{34}H_{74}N_8O_{11}Si_8$: 994.36; found: 995.41 ([M+H]$^+$). GPC (THF, PDA detector): M_w/M_n = 1.013.

1,1'-((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31-dotriacontamethylhexadecasiloxane-1,31-diyl)bis(propane-3,1-diyl))bis(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea) (USi16). ^{1}H-NMR (500 MHz; CDCl$_3$): δ = 13.14 (s, 2H, N-H), 11.87 (s, 2H, N-H), 10.21 (s, 2H, N-H), 5.79 (s, 2H, pyrimidyl), 3.23 (q, *J* = 6.3 Hz, NH-C$\underline{H}_2$-CH$_2$), 2.22 (s, 6H, Ar-CH$_3$), 1.62-1.56 (m, 4H, NH-CH$_2$-C$\underline{H}_2$), 0.58-0.54 (m, 4H, Si-C$\underline{H}_2$), 0.09-0.02 (m, 96H, CH$_3$-Si). ^{13}C-NMR (126 MHz; CDCl$_3$): δ = 173.13, 156.74, 154.90, 148.26, 106.79, 43.24, 23.65, 19.05, 15.62, 1.31 ppm. IR (ATR): ν = 3216, 2962, 1700, 1666, 1593, 1527, 1257, 1079, 1013, 787 cm^{-1}. MALDI-TOF: m/z calc. for $C_{50}H_{122}N_8O_{19}Si_{16}$: 1586.51; found: 1587.54 ([M+H]$^+$). GPC (THF, PDA detector): M_w/M_n = 1.021.

1,1'-((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31,33,33,35,35,37,37,39,39,41,41,43,43,45,45,47,47-octatetracontamethyltetracosasiloxane-1,47-diyl)bis(propane-3,1-diyl))bis(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea) (USi24). ^{1}H-NMR (500 MHz; CDCl$_3$): δ = 13.14 (s, 2H, N-H), 11.87 (s, 2H, N-H), 10.21 (s, 2H, N-H), 5.79 (s, 2H, pyrimidyl), 3.23 (q, *J* = 6.5 Hz, 4H, NH-C$\underline{H}_2$-CH$_2$), 2.22 (s, 6H, Ar-CH$_3$), 1.62-1.56 (m, 4H, NH-CH$_2$-C$\underline{H}_2$), 0.58-0.54 (m, 4H, Si-C$\underline{H}_2$), 0.09-0.02 (m, 144H, CH$_3$-Si). ^{13}C-NMR (126 MHz; CDCl$_3$): δ = 173.13, 156.76, 154.91, 148.26, 106.80, 43.25, 23.66, 19.06, 15.62, 1.20 ppm. IR (ATR): ν = 3216, 2962, 1701, 1666, 1595, 1526, 1257, 1079, 1010, 788 cm^{-1}. MALDI-TOF: m/z calc. for $C_{66}H_{170}N_8O_{27}Si_{24}$: 2178.66; found: 2179.7 ([M+H]$^+$). GPC (THF, PDA detector): M_w/M_n = 1.027.



	T_g (°C)	T_{ODT} (°C)	ΔH_{ODT} (J/g)
UZSi4	-3.7	110.7	62.0
UZSi8	-	82.4	42.6
UZSi16	-	58.0	23.4
UZSi24	-	45.8	17.2
USi4	63.7	-	-
USi8	35.5	-	-
USi16	-11.4	-	-
USi24	-13.8	-	-

Figure S1. Differential scanning calorimetry of annealed UZSi*N* and USi*N* materials. The second heating scan is shown. UZSi*N* molecules exhibit a single sharp transition from ordered solid to isotropic liquid upon heating. UZSi4 additionally exhibits glass transition and cold crystallization in the second and subsequent heating scans. USi*N* materials exhibit glass transitions only.

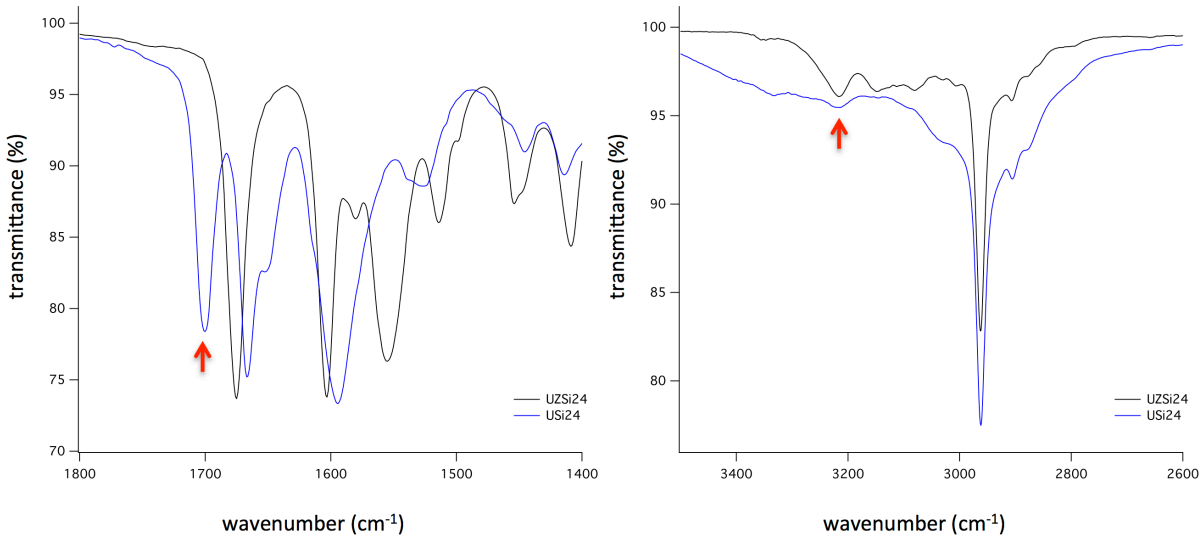


Figure S2. FTIR spectra of UZSi24 and USi24. An IR band at 1700 cm^{-1} in USi24 is characteristic of the pyrimidinone carbonyl stretch, indicating that UPy endgroups exist in the strongly dimerizing keto form (left). IR bands at 3216 cm^{-1} indicate hydrogen bonding of UPy and O-benzylated UPy endgroups to form supramolecular polymers (right).

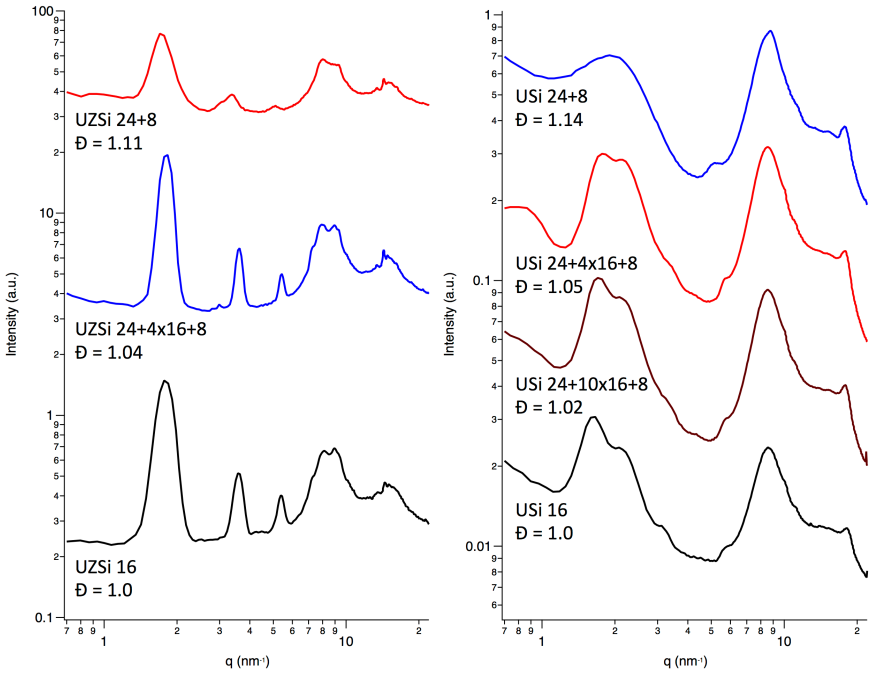


Figure S3. SAXS spectra of mixed UZSi*N* and USi*N* samples. In both cases, molecules were mixed in the proportions indicated to give an artificial dispersity with an average length of 16 dimethylsiloxane repeat units. Mixed UZSi*N* maintained lamellar morphology with identical D* to monodisperse UZSi16, though long-range ordering became worse with higher dispersity as indicated by diminished peak intensity and increase peak broadness. Mixed USi*N* became disordered upon increase in dispersity past 1.14, as evidenced by the disappearance of higher order reflections and the appearance of broad, low intensity correlation hole scattering.

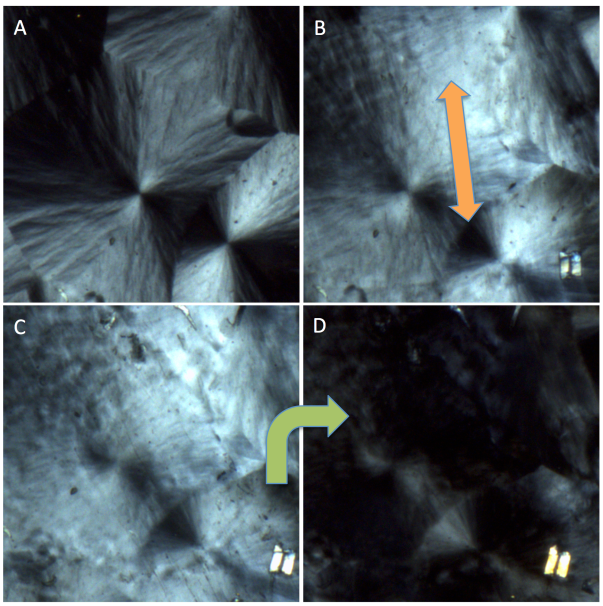


Figure S4. POM imaging of UZSi24 as it undergoes shear applied by directional rubbing. Since UZSi24 is a waxy liquid crystalline material (A), it can be aligned by manually applying shear force in the direction indicated by the orange arrow, which results in increasingly brighter birefringence along the rubbed direction (B and C). Rotating the polarizer by 90^{O} shows the alignment of this area (D).

X-ray crystallography of O-benzylated UPy (compound 3, Scheme S5)

The crystal structure of O-benzylated UPy was determined on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å). 13184 Reflections were measured at a temperature of 100(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The intensities were integrated with the Eval15 software.[5] Multiscan absorption correction and scaling was performed with SADABS[6] (correction range 0.72-0.75). 3545 Reflections were unique (R_{int} = 0.014), of which 3215 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.[7] Least-squares refinement was performed with SHELXL-2014[8] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. N-H hydrogen atoms were refined freely with isotropic displacement parameters, C-H hydrogen atoms were refined with a riding model. The methyl group at C16 was refined with a disorder model of two conformations related by a 60° rotation. 209 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0347 / 0.0889. R1/wR2 [all refl.]: 0.0382 / 0.0914. S = 1.051. Residual electron was density between -0.22 and 0.29 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[9]

$C_{16}H_{18}N_4O_2$, Fw = 298.34, colorless needle, 0.39 × 0.19 × 0.12 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 7.7614(4), b = 7.9275(4), c = 12.9954(6) Å, α = 88.676(2), β = 77.819(2), γ = 80.925(2) °, V = 771.76(6) Å^3, Z = 2, D_x = 1.284 g/cm^3, μ = 0.09 mm^{-1}

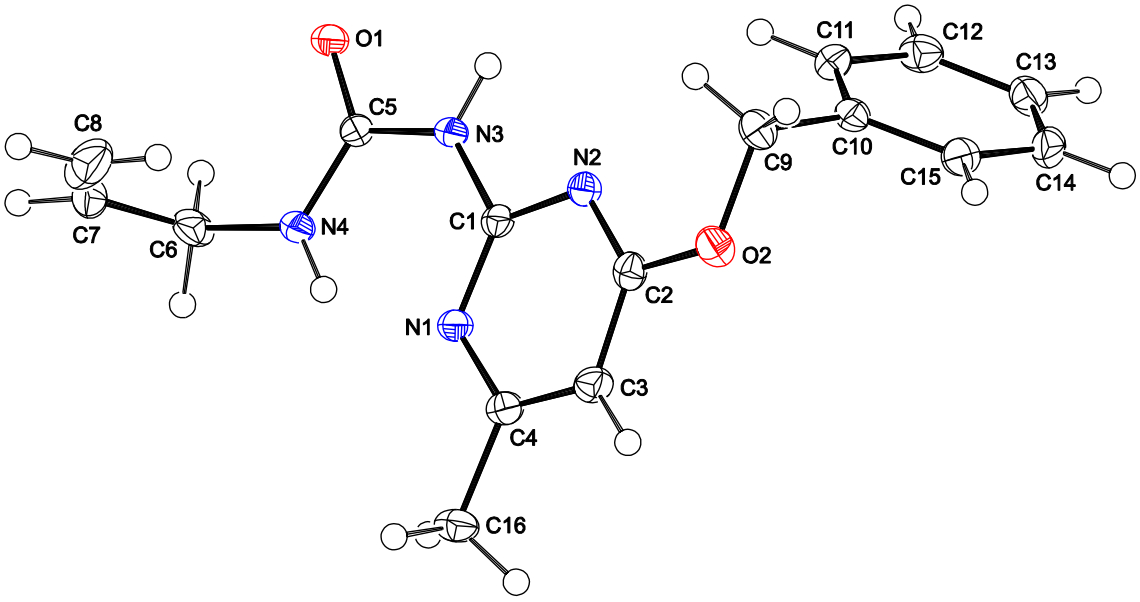


Figure S5. Displacement ellipsoid plot (50% probability level) of O-benzylated UPy (compound **3**) in the crystal. Only the major conformation of the orientationally disordered methyl group at C16 is shown.

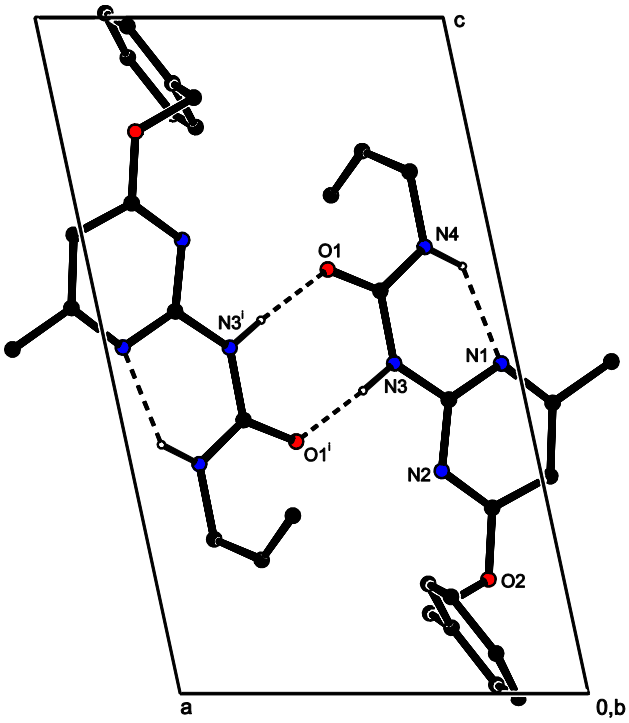


Figure S6. Hydrogen-bonded dimer in the crystal structure of compound **3** viewed along the b-axis. C-H hydrogen atoms are omitted for clarity. Symmetry code *i*: 1-x, 1-y, 1-z.

Table S1. Geometry of hydrogen bonds. Symmetry code *i*: -x, 1-y, 1-z.

	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [deg.]
N3-H3N...O1^{i}	0.896(15)	1.906(15)	2.7995(11)	174.1(13)
N4-H4N...N1	0.895(14)	1.979(14)	2.6921(12)	135.5(12)

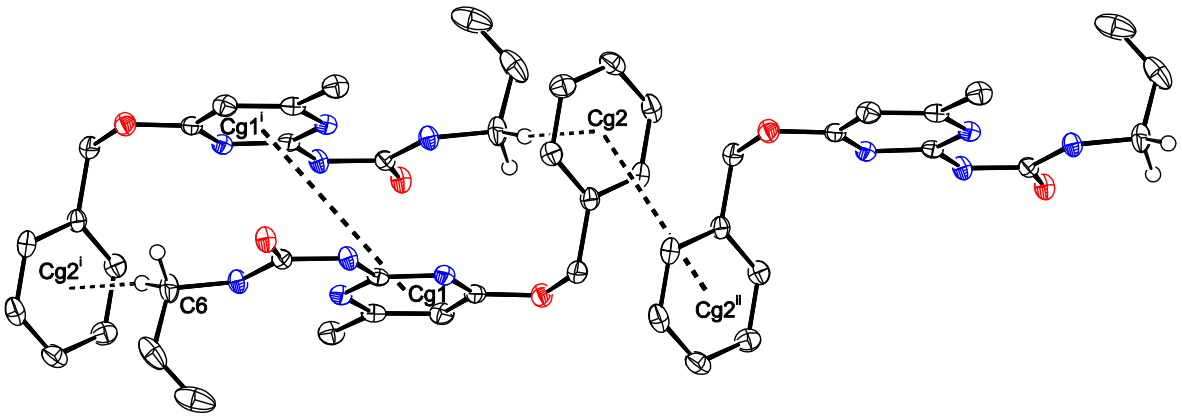


Figure S7. Intermolecular C-H...π and slipped π...π interactions in the crystal structure of compound **3**. Hydrogen atoms except at C6 are omitted for clarity. Symmetry codes *i*: -x, 1-y, 1-z; *ii*: 1-x, 1-y, -z.

Table S2. Geometry of intermolecular C-H...π contacts. Symmetry code *i*: -x, 1-y, 1-z.

	H...Cg [Å]	C....Cg [Å]	C-H...Cg [deg.]
C6-H6A...Cg2^{i}	2.46	3.4406(12)	170

Table S3. Geometry of intermolecular π...π contacts. Symmetry codes *i*: -x, 1-y, 1-z; *ii*: 1-x, 1-y, -z.

	Cg...Cg [Å]	Cg_perp [Å]	α [deg.]	Δ [Å]
Cg1...Cg1^{i}	4.6100(6)	3.1899(4)	0	3.328
Cg2...Cg2^{ii}	4.7117(7)	3.4385(4)	0	3.221

Cg_perp: perpendicular distance of Cg to ring
α: dihedral angle between planes
Δ: distance between Cg and the perpendicular projection of the other Cg on the ring (ring slippage)

Supporting Information References

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