Supporting Information

Chain stretching in brushes favors sequence recognition for nucleobase-functionalized flexible precise oligomers

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S1. General considerations and instrumentation

Reagents were obtained from commercial sources and used without further purification. All reactions were carried out under argon. Flash column chromatography was carried out using Silica gel 230-400 mesh (Sigma-Aldrich) as the stationary phase. Milli-Q water (resistivity 18.2 MΩ.cm) was obtained from a Millipore system.

NMR spectra were recorded on Bruker-300 and Bruker-500 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to residual solvent. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: br= broad, s= singlet, d= doublet, t= triplet, q= quartet, quint= quintet, m= multiplet.

High-resolution mass spectra (HRMS) were measured on a Q-Exactive (Orbitrap) from ThermoFisher using an atmospheric pressure chemical ionization (APCI) source. Electrospray ionisation mass spectrometry (ESI-MS) and ESI-MS/MS were performed on an SYNAPT G2-Si high definition mass spectrometer (Waters) equipped with a NanoLockSpray dual electrospray ion source (Waters). Precut fused silica PicoTipR Emitters (outer diameters: 360 µm; inner diameter: 20 µm; 10 µm tip; 2.5" length (Waters)) were used to carry samples for nanoelectrospray-injecting the test solution.

LC-QTOF-MS/MS Analysis were performed on an SYNAPT G2-Si high definition mass spectrometer (Waters) equipped with a NanoLockSpray dual electrospray ion source (Waters). Samples were diluted 2 to 10 times in 50% (v/v) acetonitrile, 0.1% formic acid or in 50% (v/v) methanol depending on the quality and the intensity of the signal. Coated fused silica PicoTip™ Econo12 Emitters for nanoelectrospray, outer diameters: 1 µm Tip (New Objective, USA) were filled with 5 µL of samples and placed on the Universal NanoFlow™ Sprayer (Waters). The eluent was sprayed at a spray voltage of 2.8 kV. The source temperature was set to 100°C. The cone gas flow was 20 liter/h with a nano flow gas pressure of 0.3 bar. MS spectra were acquired and processed with MassLynx software (Waters). Full scan MS and MS2 spectra (*m/z* 50 to 2000) were in resolution mode (20,000 resolution FWHM at *m/z* 400) with a scan time of 0.1 sec. Tandem mass spectra of the precursor were generated in the trapping region of the ion mobility cell by using a collision energy ramp from 10 V to 70 V. Charged ions are selected to be submitted to the MS/MS fragmentation over the *m/z* range from 50 to 2000 with a scan time of 0.25 sec. For the post-acquisition lock mass correction of the data in the MS method, the doubly charged monoisotopic ion of [Glu^1]-fibrinopeptide B was used at 100 fmol/µL using the reference sprayer of the nanoESI source with a frequency of 30 s at 0.5 µL/min into the mass spectrometer.

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed on VersaProbe III photoelectron spectrometer from Physical Electronics (USA) equipped with a monochromatized micro focused Al X-ray source (powered at 50 W). The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyser lens was 45°. High-resolution scans of the C 1s, O 1s and N 1s photoelectron peaks were recorded from a spot diameter of 200 µm using a pass energy of 55 eV and a step size of 0.1 eV. Charge stabilization was achieved thanks to a combination of Argon and electron guns. The C-C component of the C1s peak of carbon was fixed to 284.8 eV to set the binding energy scale. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK). Some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non-linear baseline. Molar fractions were calculated using peak areas normalised based on acquisition parameters and sensitivity factors provided by the manufacturer.

X-ray Reflectometry (XRR). XRR measurements were carried out with a modified Siemens D5000 2-circle goniometer (0.002° positioning accuracy). X-rays of 0.15418 nm wavelength (Cu Kα) were obtained from a Rigaku rotating anode operated at 40 kV and 300 mA, fitted with a collimating mirror (Osmic, Japan) delivering a close-to-parallel beam of ~0.0085° vertical angular divergence. The beam size was defined by a 40-µm-wide slit placed 17.5 cm away from the focal spot. The sample was placed within 2 µm of the center of the goniometer, and the reflected beam was collected through a 200-µm-wide detector slit. Soller slits in the incident and reflected beam limited the axial divergence to 0.02°. The data were corrected for spill over and normalized to unit incident intensity; they are reported as a function of k_{z0}, the vertical component of the photon wavevector in a vacuum.

The XRR data were analysed by procedure described elsewhere.[1] Thus, an estimation of the average thickness of the monolayer, d_x, and grafting densities σ_g from the electron density profiles $\rho(z)$ were obtained.

Water contact angle. The water contact angles were measured at ambient temperature using the sessile drop method and image analysis of the drop profile. A contact angle goniometer from OCA DataPhysics (Germany) was used. The Milli-Q water droplet volume was 0.5 µL, and the contact angle was measured 5 s after the drop was deposited on the sample. For each sample, the reported value is the average of the results obtained on at least five droplets.

In situ ellipsometry. Ellipsometry measurements were performed on Jobin-Yvon UVisel spectroscopic ellipsometer at an incidence angle of *ca*. 65°. Spectroscopic scans were recorded for wavelengths ranging from 400 to 700 nm. Kinetic measurements were performed at *ca*. 65° incidence angle and at a wavelength of 400 nm. All measurements were recorded at room temperature. An Accurion temperature-controlled liquid cell (volume 0.7 mL) was fixed on a homemade multi-axis sample stage attached to the ellipsometer. The solvent flow rate of the solvent was set to *ca*. 0.09 mL/min, with two pumps (peristaltic and syringe) used to inject the solvent and the oligomer solution, respectively. The scheme of the setup is in Fig.3 of the article.

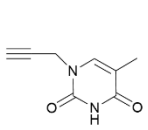
Cleaning of Silicon Wafers. One-side-polished (100) silicon wafers with their *ca*. 1.3 nm thick native oxide layer were purchased from Wacker (Germany) and cut in squares of 1.5 cm side. The wafers were cleaned by dipping into a freshly-prepared piranha solution (H_2SO_4 (98%)/H_2O_2 (30%) v/v 3:1 – *caution: piranha solution is an extremely strong oxidant and should only be handled with proper equipment*). The substrates were then rinsed 3 times with Milli-Q water and dried under a flow of nitrogen. The silicon wafers were immediately used to prevent surface contamination.

Deposition of the Silane self-assembled monolayers (AzUTMS SAMs). The 11-azidoundecyltrimethoxysilane (AzUTMS) layer was formed by gas-phase silanation in a Schlenk tube at 100 °C as described previously.[2] After reaction, the samples were washed twice with acetone and methanol. After a subsequent rinse, these were dried with nitrogen.

Grafting of the oligomers by CuAAC. Sequence-controlled oligomers were immobilized on the AzUTMS SAMs by Cu-Catalyzed Azide-Alkyne Cycloaddition Reactions (CuAAC), in mixtures of DMF and DMSO. Substrates with the AzUTMS SAM layer were placed in Schlenk tubes containing 13.25 mL of a DMF:DMSO mixture, 0.75 mL of a copper(I) iodide solution in the same solvent (160 mM), 1 mL of oligomer dissolved in pure DMSO (3 mM) and 95 µL of Et_3N. After overnight stirring at 80°C under argon, the substrates were rinsed with DMSO, methanol, 1M HCl, MilliQ water, MeOH, Et3N/DCM (v/v 5%) and dichloromethane before being dried with nitrogen.

S2. Synthesis of the stereo-controlled and sequenced-defined tetramers.

The compounds (*R*)/(*S*)-1, (*R*)/(*S*)-2 and (*R*)/(*S*)-3 (Scheme 1 of the article) were prepared according to the literature and our previous works. [1-4] The synthesis of bases and monomers in the scheme below were reported in our previous work.[3]



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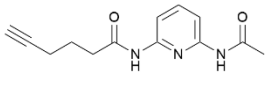

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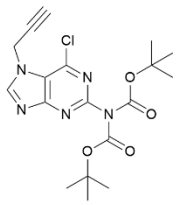

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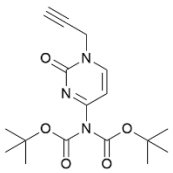

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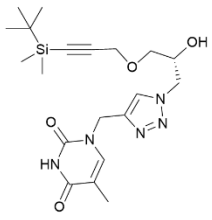

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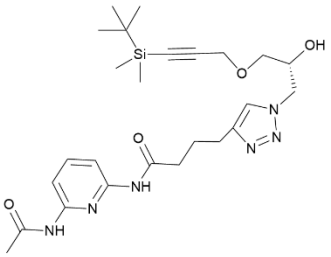

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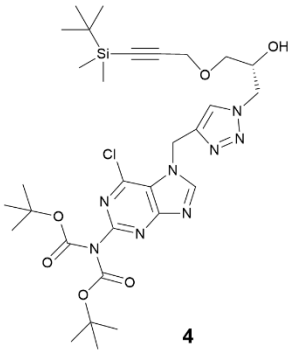

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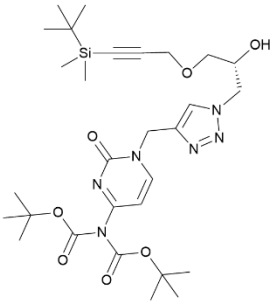

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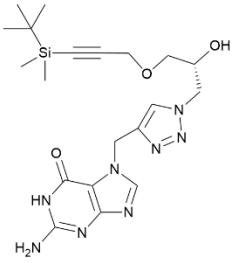

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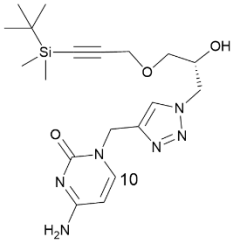

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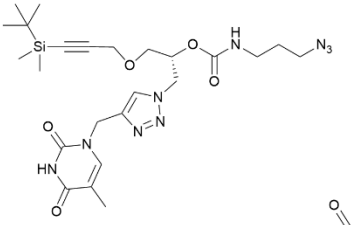

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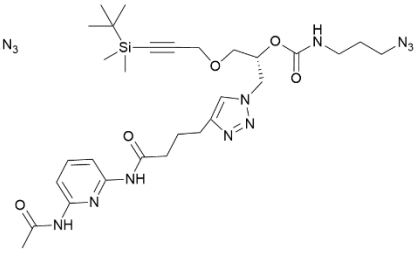
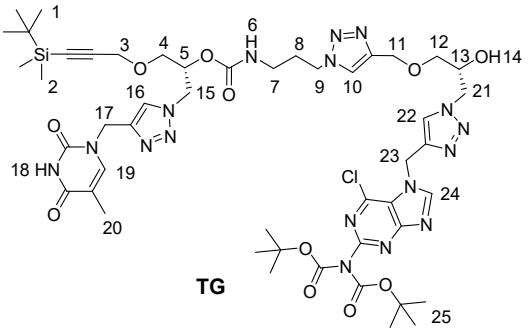


7

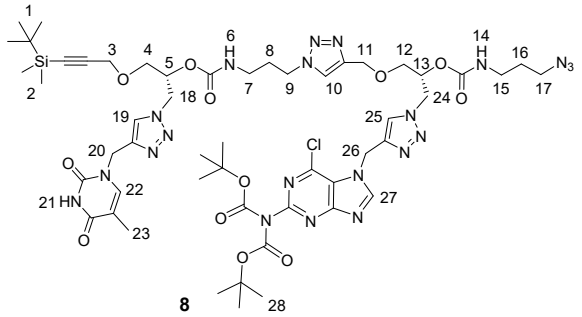
2.1. Synthesis of all-*R* tetramer TGCT



TG

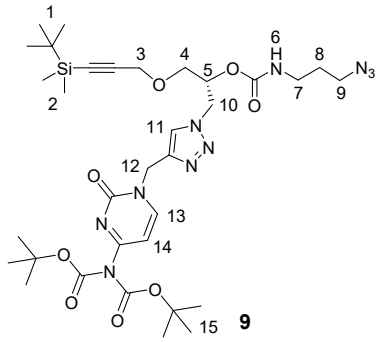
Compound **4** (0.88 g, 1.3 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (1.95 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **6** (0.728 g, 1 equiv.)) was added into the residue followed by EtOH (9.1 mL) with stirring. Milli-Q water (3.9 mL), sodium ascorbate solution (52 mg in 2 mL water, 0.2 equiv.) and $CuSO_4$ solution (20.8 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The

residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product **TG** as foamy white solid (1.314 g, 90%). **TG**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.69 (s, 1H, H_{18}), 8.38 (s, 1H, H_{24}), 7.95 (s, 1H, H_{16}), 7.78 (s, 1H, H_{22}), 7.69 (s, 1H, H_{10}), 7.30 (d, J = 1.5 Hz, 1H, H_{19}), 5.62 (t, J = 6.2 Hz, 1H, H_6), 5.55 (s, 2H, H_{23}), 5.18 (dd, J = 7.2, 4.0 Hz, 1H, H_5), 4.94 – 4.82 (m, 2H, H_{17}), 4.69 – 4.59 (m, 4H, H_{11} and H_{15}), 4.51 (dd, J = 14.0, 3.7 Hz, 1H, H_{21}), 4.32– 4.41 (m, 3H, H_9 and H_{21}), 4.25 – 4.16 (m, 2H, H_3 and H_{13}), 3.70 – 3.57 (m, 3H, H_4 and H_{12}), 3.51 – 3.46 (m, 1H, H_{12}), 3.08 (q, J = 6.3 Hz, 2H, H_7), 2.08 – 1.99 (m, 2H, H_8), 1.85 (d, J = 1.2 Hz, 3H, H_{20}), 1.46 (s, 18H, H_{25}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.49, 155.41, 152.55, 151.96, 151.31, 151.15, 150.98, 146.32, 144.54, 142.26, 141.09, 140.56, 130.09, 125.26, 125.10, 123.53, 111.28, 101.17, 90.97, 84.03, 71.60, 71.19, 69.15, 68.22, 64.64, 59.64, 53.19, 50.90, 47.39, 43.35, 39.41, 37.70, 28.48, 28.05, 26.16, 16.57, -4.57. **HRMS** *m/z*= 1122.4815 (calcd. for $C_{48}H_{68}ClN_{17}O_{11}Si$ 1122.4815 $[M+H]^+$).



8

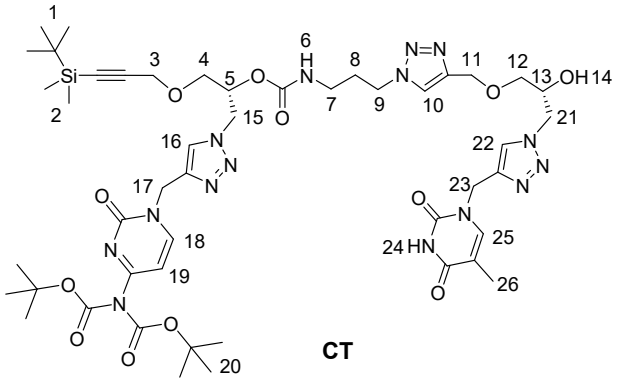
Compound **TC** (1.123 g, 1 mmol) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.503 g, 2.5 equiv.) and pyridine (202 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.3 g, 3 eq.) and Et_3N (0.697 mL, 5 eq.). The mixture was stirred for 2 h at room temperature, then DCM (50 mL) and water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **8** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 6/94) as a foamy-yellow solid (0.937 g, 75%). **8**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.55 (s, 1H, H_{21}), 8.40 (s, 1H, H_{27}), 7.86 (s, 1H, H_{19}), 7.78 (s, 1H, H_{25}), 7.72 (s, 1H, H_{10}), 7.35 – 7.28 (m, 1H, H_{22}), 5.68 – 5.42 (m, 4H, H_6, H_{14} and H_{23}), 5.19 (s, 1H, H_5), 5.07 (s, 1H, H_{13}), 4.98 – 4.82 (m, 2H, H_{20}), 4.72 – 4.51 (m, 6H, H_{11}, H_{18} and H_{24}), 4.40 (t, J = 6.7 Hz, 2H, H_9), 4.27 – 4.14 (m, 2H, H_3), 3.73 – 3.42 (m, 4H, H_4 and H_{12}), 3.31 – 3.22 (m, 2H, H_{17}), 3.18 – 2.98 (m, 4H, H_7 and H_{15}), 2.06 – 1.96 (m, 2H, H_8), 1.87 (d, J = 1.1 Hz, 3H, H_{23}), 1.66 – 1.59 (m, 2H, H_{16}), 1.49 (s, 18H, H_{28}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.43, 155.38, 155.20, 152.59, 151.87, 151.39, 151.26, 151.14, 146.43, 144.45, 142.30, 140.46, 130.22, 125.21, 125.08, 123.56, 111.28, 101.19, 90.93, 84.28, 71.13, 70.95, 68.43, 68.18, 64.84, 59.62, 50.88, 49.01, 47.39, 43.30, 39.54, 38.49, 37.78, 30.27, 28.94, 28.47, 28.04, 26.15, 16.56, 12.43, -4.58. **HRMS** *m/z*= 1248.5367 (calcd. for $C_{57}H_{83}ClN_{19}O_{13}Si$ 1248.5356 $[M+Na]^+$).



9

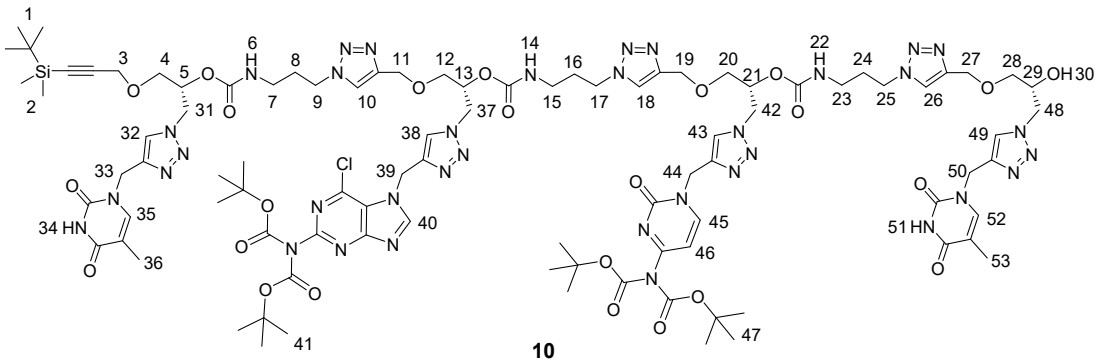
Compound **5** (1 g, 1.62 mmol) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.49 g, 1.5 equiv.) and pyridine (200 µL, 1.5 equiv.). The mixture was stirred for 1 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.324 g, 2 eq.) and Et_3N (0.68 mL, 3 eq.). The mixture was stirred for 1 h at room temperature, then DCM (50 mL) and Milli-Q water (50 mL) were added to the mixture. The organic phase was washed with Milli-Q water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **9**

was obtained after passing the residue through a chromatography column (EtOAc /n-hexane = 5/5 to 10/0) as a foamy-yellow solid (1.207 g, 100%). **10**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.84 (t, J = 3.7 Hz, 2H, H_{11} and H_{13}), 7.05 (d, J = 7.4 Hz, 1H, H_{14}), 5.25 – 5.10 (m, 2H, H_5 and H_6), 5.07 (d, J = 5.2 Hz, 2H, H_{12}), 4.71 – 4.55 (m, 2H, H_{10}), 4.20 (d, J = 4.0 Hz, 2H, H_3), 3.60 (d, J = 4.2 Hz, 2H, H_4), 3.43 – 3.32 (m, 4H, H_7 and H_9), 1.83 – 1.73 (m, 2H, H_8), 1.54 (s, 18H, H_{15}), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.73, 158.39, 155.11, 149.58, 148.01, 141.70, 125.76, 101.23, 96.89, 90.83, 85.15, 71.00, 68.00, 59.59, 50.66, 49.08, 38.65, 37.98, 29.08, 27.80, 26.15, 16.55, -4.59. **HRMS** m/z= 745.3810 (calcd. for $C_{33}H_{52}N_{10}O_8Si$ 745.3812 $[M+H]^+$).



CT

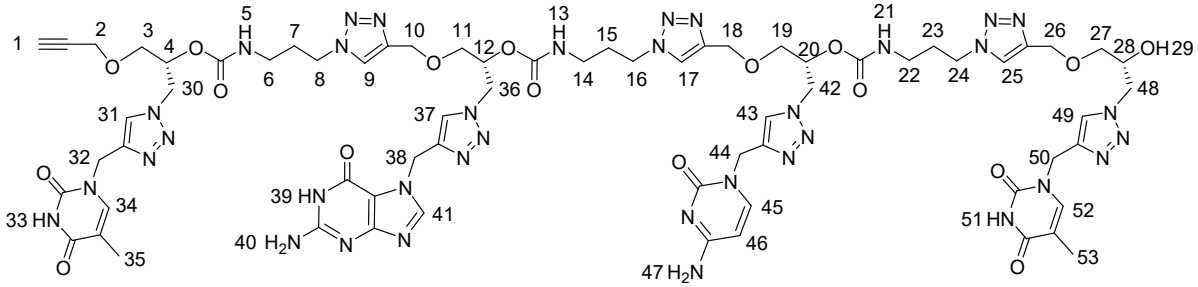
Compound **T** (0.88 g, 1.2 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (1.95 mL, 1.8 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **9** (0.728 g, 1 equiv.)) was added into the residue followed by EtOH (9.1 mL) with stirring. Water (3.9 mL), sodium ascorbate solution (52 mg in 2 mL Milli-Q water, 0.2 equiv.) and $CuSO_4$ solution (20.8 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product TG as foamy white solid (1.314 g, 96%).**CT**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.36 (s, 1H, H_{24}), 7.94 – 7.84 (m, 3H, H_{16}, H_{18} and H_{22}), 7.79 (s, 1H, H_{10}), 7.37 – 7.31 (m, 1H, H_{25}), 7.04 (d, J = 7.4 Hz, 1H, H_{19}), 5.59 (t, J = 6.1 Hz, 1H, H_6), 5.20 – 5.01 (m, 3H, H_5 and H_{23}), 4.93 (s, 2H, H_{17}), 4.70 – 4.49 (m, 5H, H_{11}, H_{15} and H_{21}), 4.47 – 4.34 (m, 3H, H_9 and H_{21}), 4.26 – 4.13 (m, 3H, H_3 and H_{13}), 3.71 – 3.60 (m, 2H, H_4), 3.58 – 3.45 (m, 2H, H_{12}), 3.21 – 2.92 (m, 2H, H_7), 2.05 (m, 2H, H_8), 1.88 (d, J = 1.2 Hz, 3H, H_{26}), 1.51 (s, 18H, H_{20}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.32, 162.74, 155.51, 155.27, 151.06, 149.60, 148.39, 144.50, 142.04, 141.68, 140.43, 126.10, 125.26, 123.72, 111.28, 101.25, 97.00, 90.88, 85.26, 71.49, 71.12, 69.25, 68.20, 64.78, 59.62, 53.11, 50.76, 47.45, 45.75, 43.15, 37.76, 30.33, 27.80, 26.16, 16.56, -4.57. **HRMS** m/z= 1064.5099 (calcd. for $C_{47}H_{69}N_{15}O_{12}Si$ 1064.5092 $[M+H]^+$).



10

Compound **CT** (0.341 g, 0.32 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.64 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with

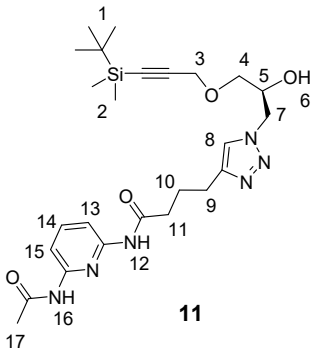
Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **9** (0.400 g, 1 equiv.) was added into the residue followed by EtOH (2.24 mL) with stirring. Milli-Q water (0.96 mL), sodium ascorbate solution (12.8 mg in 0.5 mL water, 0.2 equiv.) and $CuSO_4$ solution (5.1 mg in 0.3 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 12/88) to give the final product **10** as foamy white solid (0.457 g, 65%). **10**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.27 – 9.98 (m, 2H, H_{34} and H_{51}), 8.43 (s, 1H, H_{40}), 7.98 – 7.68 (m, 8H, H_{10}, H_{18}, H_{26}, H_{32}, H_{38}, H_{43}, H_{45} and H_{49}), 7.36 – 7.28 (m, 2H, H_{35} and H_{52}), 7.02 (d, *J* = 7.3 Hz, 1H, H_{46}), 6.31 – 5.94 (b, 3H, H_6, H_{14}, H_{22}), 5.61 – 5.34 (s, 2H, H_{39}), 5.23 – 4.80 (m, 9H, H_5, H_{13}, H_{21}, H_{33}, H_{44} and H_{50}), 4.58 (m, *J* = 26.1, 17.4, 7.5 Hz, 13H, H_{11}, H_{19}, H_{27}, H_{31}, H_{37}, H_{42} and H_{48}), 4.44 – 4.27 (m, 7H, H_9, H_{17}, H_{25} and H_{48}), 4.25 – 4.09 (m, 3H, H_3 and H_{29}), 3.74 – 3.41 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.16– 2.90 (m, 5H, H_7, H_{15} and H_{23}), 2.09 – 1.89 (m, 6H, H_8, H_{16} and H_{24}), 1.86 – 1.77 (m, 6H, H_{36} and H_{53}), 1.56 – 1.40 (m, 36H, H_{41} and H_{47}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.68, 162.68, 155.61, 155.49, 155.22, 152.64, 151.27, 151.14, 149.60, 148.60, 146.72, 144.53, 144.27, 144.18, 143.31, 142.30, 142.03, 141.69, 141.38, 140.64, 140.53, 126.03, 125.27, 125.14, 123.85, 111.09, 101.26, 96.90, 90.84, 85.21, 84.17, 71.57, 71.14, 69.17, 68.74, 68.33, 64.73, 59.59, 53.25, 50.97, 50.52, 47.49, 45.60, 43.16, 39.46, 37.83, 30.23, 29.82, 28.47, 28.03, 27.78, 26.15, 16.55, 12.40, -4.57. **TOF MS ES +** *m/z*= 2197.0074 (calcd. for $C_{93}H_{129}ClN_{36}O_{24}Si$ 2197.9511 $[M+H]^+$).



TGCT

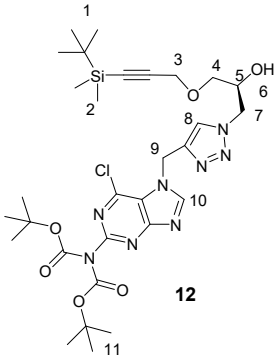
Compound **10** (0.41 g, 0.19 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.57 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The residue was obtained and followed by adding TFA (3 mL) and Milli-Q water (1 mL) stirring at room temperature for 48 h. The crude product was precipitated from the solution with the neutralization of saturated $NaHCO_3$. Then, the solid product was wash with brine, water, acetone and Et_2O, respectively. The final product was dried under vacuum to give the final product **TGCT** as foamy yellow solid (0.22 g, 71%). **TGCT**, **^{1}H NMR (500 MHz, DMSO)** δ 11.30 (s, 2H, H_{33} and H_{51}), 11.06 (s, 1H, H_{39}), 8.19 – 7.85 (m, 7H, H_9, H_{17}, H_{25}, H_{31}, H_{37}, H_{41} and H_{49}), 7.78 – 7.48 (m, 3H, H_{34}, H_{43} and H_{52}), 7.46 – 7.32 (m, 2H, H_{45} and H_{47}), 7.11 (d, *J* = 124.8 Hz, 1H, H_{46}), 6.68 (s, 2H, H_{40}), 5.31 (d, *J* = 5.6 Hz, 1H, H_{21}), 5.21 (s, 2H, H_{38}), 5.09 (s, 3H, H_4, H_{12} and H_{20}), 4.88 (d, *J* = 4.2 Hz, 6H, H_{32}, H_{44} and H_{50}), 4.64 – 4.46 (m, 12H, H_{10}, H_{18}, H_{26}, H_{30}, H_{36} and H_{42}), 4.42 (dd, *J* = 13.9, 3.5 Hz, 1H, H_{48}), 4.36 – 4.20 (m, 7H, H_8, H_{16}, H_{24} and H_{48}), 4.17 (d, *J* = 2.4 Hz, 2H, H_2), 3.96 (s, 1H, H_{28}), 3.62 – 3.39 (m, 8H, H_3, H_{11}, H_{19} and H_{27}), 2.98 – 2.79 (m, 6H, H_6, H_{14} and H_{22}), 2.46 (t, *J* = 4.0, 2.0 Hz, 1H, H_1), 1.95 – 1.80 (m, 6H, H_7, H_{15} and H_{23}), 1.78 – 1.68 (m, 6H, H_{35} and H_{53}). **^{13}C NMR (126 MHz, DMSO)** δ 166.10, 166.01, 164.33, 155.60, 155.20, 151.23, 150.77, 145.90, 145.74, 143.67, 143.40, 142.96, 142.41, 142.13, 141.15, 141.01, 124.53, 124.45, 124.28, 124.13, 108.84, 93.62, 79.82, 77.68, 71.62, 70.43, 68.67, 68.21, 63.87, 57.92, 54.93, 52.90, 50.06, 48.61, 46.96, 42.15, 37.41, 29.95, 26.24, 11.98 **HRMS** *m/z*= 1665,6914 (calcd. for $C_{67}H_{84}N_{36}O_{17}$ 1665,6888 $[M+H]^+$).

2.2. Synthesis of all-*R* and all-*S* tetramer DCGD



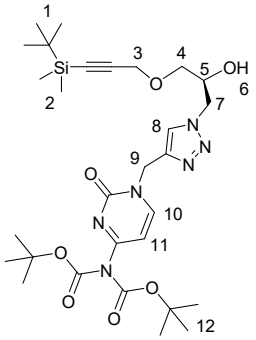
11

Compound **(*S*)-3** (0.808 g, 3 mmol) and **base D** (0.735 g, 1 equiv.) were added into a flask followed by EtOH (21 mL) with stirring. Water (9 mL), sodium ascorbate solution (120 mg in 4 mL water, 0.2 equiv.) and $CuSO_4$ solution (48 mg in 3 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, EtOAc (100 mL) and Na_2EDTA (0.05 M, 100 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (100 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was crystallized from cold EtOAc, the final product **11** was obtained as a yellow solid (1.544 g, 100%) after removing the solvent. **11**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.55 (s, 1H, H_{12}), 8.34 (s, 1H, H_{16}), 7.78 – 7.55 (m, 2H, H_{13} and H_{15}), 7.67 (t, J = 8.0 Hz, 1H, H_{14}), 7.49 (s, 1H, H_8), 4.59 – 4.34 (m, 2H, H_7), 4.30 – 4.18 (m, 3H, H_3 and H_5), 3.67 – 3.52 (m, 2H, H_4), 2.80 (t, J = 6.9 Hz, 2H, H_9), 2.43 (t, J = 7.1 Hz, 2H, H_{11}), 2.21 (s, 3H, H_{17}), 2.08 (t, J = 7.0 Hz, 2H, H_{10}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.95, 169.20, 149.57, 149.41, 146.90, 141.11, 123.09, 109.50, 101.31, 90.97, 70.94, 69.32, 59.69, 53.21, 36.38, 26.14, 25.18, 24.83, 24.22, 16.56, -4.59. **HRMS** *m/z*= 537.2637 (calcd. for $C_{25}H_{38}N_6O_4Si$ 537.2640 $[M+Na]^+$).



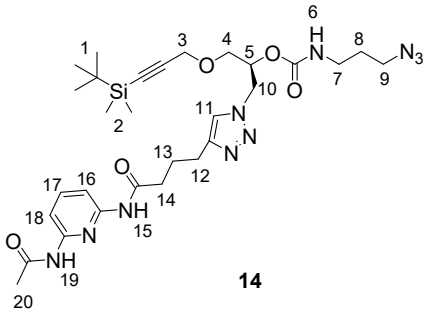
12

Compound **(*S*)-3** (0.404 g, 1.5 mmol) and **base G** (0.612 g, 1 equiv.) were added into a flask followed by EtOH (10.5 mL) with stirring. Water (4.5 mL), sodium ascorbate solution (60 mg in 2 mL water, 0.2 equiv.) and $CuSO_4$ solution (24 mg in 1.5 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, EtOAc (60 mL) and Na_2EDTA (0.05 M, 60 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (60 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc /n-hexane = 5/5 to 0/10) to give the final product **12** as foamy white solid (0.944 g, 93%). **12, ^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.32 (s, 1H, H_{10}), 7.92 (s, 1H, H_8), 5.53 (s, 2H, H_9), 4.59 – 4.29 (m, 2H, H_7), 4.23 – 4.14 (m, 3H, H_3 and H_5), 3.61 (dd, J = 9.7, 4.5 Hz, 1H, H_4), 3.49 (dd, J = 9.7, 5.6 Hz, 1H, H_4), 1.48 (s, 18H, H_{11}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 152.47, 152.01, 151.49, 151.01, 145.94, 141.18, 130.15, 125.11, 101.27, 90.99, 84.03, 70.70, 69.19, 59.64, 53.36, 39.54, 28.07, 26.15, 16.56, -4.58. **HRMS** *m/z*= 677.2990 (calcd. for $C_{30}H_{45}ClN_8O_6Si$ 677.2993 $[M+H]^+$).



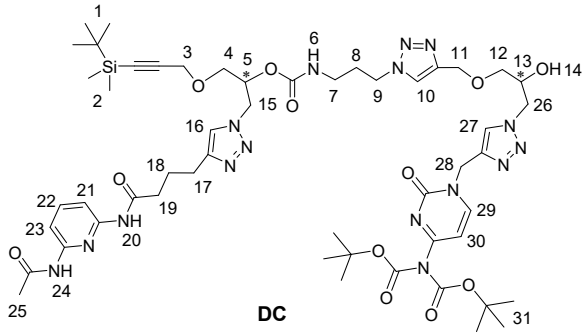
13

Compound **(*S*)-3** (0.539 g, 2 mmol) and **base C** (0.699 g, 1 equiv.) were added into a flask followed by EtOH (14 mL) with stirring. Water (6 mL), sodium ascorbate solution (80 mg in 6 mL water, 0.2 equiv.) and $CuSO_4$ solution (32 mg in 4 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, EtOAc (60 mL) and Na_2EDTA (0.05 M, 60 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with EtOAc (60 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc /n-hexane = 5/5 to 0/10) to give the final product **13** as foamy light-yellow solid (0.998 g, 81%). **13**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.93 (s, 1H, H_8), 7.85 (d, J = 7.4 Hz, 1H, H_{10}), 7.03 (d, J = 7.3 Hz, 1H, H_{11}), 5.09 (s, 2H, H_9), 4.30 – 4.57 (m, 2H, H_7), 4.27 – 4.13 (m, 3H, H_3 and H_5), 3.66 – 3.43 (m, 2H, H_4), 1.54 (s, 18H, H_{12}), 0.93 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.74, 155.05, 149.64, 147.96, 141.75, 125.84, 101.42, 96.83, 90.83, 85.11, 70.66, 69.24, 59.63, 53.28, 45.51, 27.84, 26.17, 16.57, -4.57. **HRMS** *m/z*= 619.3270 (calcd. for $C_{29}H_{46}N_6O_7Si$ 619.3270 $[M+H]^+$).



14

Compound **11** (0.566 g, 1.1 mmol) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.333 g, 1.5 equiv.) and pyridine (138 µL, 1.5 equiv.). The mixture was stirred for 1 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.22 g, 2 eq.) and Et_3N (0.46 mL, 3 eq.). The mixture was stirred for 1 h at room temperature, then DCM (50 mL) and Milli-Q water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **14** was obtained after passing the residue through a chromatography column (MeOH/DCM= 0/100 to 5/95) as a foamy-white solid (0.705 g, 100%). **14**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.60 (s, 1H, H_{15}), 8.17 (s, 1H, H_{19}), 7.91 – 7.77 (m, 2H, H_{16} and H_{18}), 7.68 (t, J = 8.0 Hz, 1H, H_{17}), 7.39 (s, 1H, H_{11}), 5.37 – 5.12 (m, 2H, H_5 and H_6), 4.59 (d, J = 5.6 Hz, 2H, H_{10}), 4.22 (s, 2H, H_3), 3.65 (d, J = 4.9 Hz, 2H, H_4), 3.33 (t, J = 6.5 Hz, 2H, H_9), 3.21 (q, J = 6.5 Hz, 2H, H_7), 2.90 – 2.71 (m, 2H, H_{12}), 2.39 (t, J = 8.0 Hz, 2H, H_{14}), 2.19 (s, 3H, H_{20}), 2.09 (q, J = 7.0 Hz, 2H, H_{13}), 1.73 (p, J = 6.5 Hz, 2H, H_8), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.96, 169.08, 161.28, 155.34, 149.62, 147.20, 140.93, 122.46, 109.47, 101.07, 91.08, 71.38, 68.35, 59.72, 50.75, 49.09, 38.72, 36.06, 28.98, 26.13, 25.19, 24.79, 24.09, 16.56, -4.59. **HRMS** *m/z*= 641.3338 (calcd. for $C_{29}H_{44}N_{10}O_5Si$ 641.3316 $[M+H]^+$).

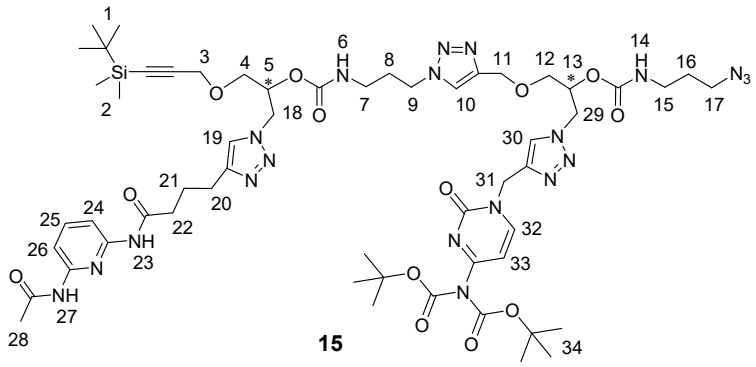


DC

Compound **5** (1.134 g, 1.8 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (2.7 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (60 mL) and washed with brine (3 × 60 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **7** (1.152 g, 1 equiv.) was added into the residue followed by EtOH (12.6 mL) with stirring. Milli-Q water (5.4 mL), sodium ascorbate solution (72 mg in 3 mL water, 0.2 equiv.) and $CuSO_4$ solution (28.8 mg in 2 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (60 mL) and Na_2EDTA (0.05 M, 60 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (60 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product (*R*, *R*)-**DC** as foamy white solid (1.443 g, 70%). The products (*S*, *S*)-**DC** (0.659 g, 72%) was prepared following the same protocol.

(*R*, *R*)-**DC**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.81 (s, 1H, H_{20}), 8.55 (s, 1H, H_{24}), 8.00 – 7.58 (m, 6H, H_{10}, H_{21}, H_{22}, H_{23}, H_{27} and H_{29}), 7.46 (d, *J* = 7.0 Hz, 1H, H_{16}), 7.04 (d, *J* = 7.3 Hz, 1H, H_{30}), 5.64 (b, 1H, H_6), 5.26 (d, *J* = 5.9 Hz, 1H, H_5), 5.10 (s, 2H, H_{28}), 4.70 – 4.31 (m, 8H, H_9, H_{11}, H_{15}, H_{26}), 4.29 – 4.08 (m, 3H, H_3 and H_{13}), 3.77 – 3.60 (m, 2H, H_4), 3.57 – 3.42 (m, 2H, H_{12}), 3.22 – 2.94 (m, 2H, H_7), 2.80 – 2.64 (m, 2H, H_{17}), 2.39 (s, 2H, H_{19}), 2.20 (s, 3H, H_{25}), 2.09 – 1.93 (m, 4H, H_8 and H_{18}), 1.51 (s, 18H, H_{31}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.08, 169.25, 162.70, 155.59, 155.19, 149.67, 148.28, 147.31, 144.91, 144.67, 144.18, 141.69, 140.75, 125.73, 123.69, 122.63, 109.53, 101.19, 96.85, 90.98, 85.28, 71.43, 71.24, 69.17, 68.50, 64.81, 59.70, 53.10, 50.90, 47.45, 45.68, 37.83, 36.17, 30.27, 27.80, 26.15, 25.15, 24.72, 24.41, 16.57, -4.56. **HRMS** *m/z*= 1145.5678 (calcd. for $C_{52}H_{76}N_{16}O_{12}Si$ 1145.5671 $[M+H]^+$).

(*S*, *S*)-**DC**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.07 – 8.43 (m, 2H, H_{20} and H_{24}), 7.94 – 7.59 (m, 6H, H_{10}, H_{21}, H_{22}, H_{23}, H_{27} and H_{29}), 7.52 – 7.40 (m, 1H, H_{16}), 7.05 (d, *J* = 7.4 Hz, 1H, H_{30}), 5.77 (b, 1H, H_6), 5.37 – 5.21 (m, 1H, H_5), 5.10 (s, 2H, H_{28}), 4.67 – 4.29 (m, 8H, H_9, H_{11}, H_{15}, H_{26}), 4.28 – 4.10 (m, 3H, H_3 and H_{13}), 3.77 – 3.58 (m, 2H, H_4), 3.57 – 3.40 (m, 2H, H_{12}), 3.25 – 2.93 (m, 2H, H_7), 2.85 – 2.66 (m, 2H, H_{17}), 2.40 (s, 2H, H_{19}), 2.20 (s, 3H, H_{25}), 2.10 – 1.89 (m, 4H, H_8 and H_{18}), 1.51 (s, 18H, H_{31}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.99, 169.21, 162.71, 155.61, 155.25, 149.66, 148.33, 147.29, 144.82, 144.64, 144.29, 141.64, 140.79, 125.72, 123.69, 122.67, 109.49, 101.21, 96.90, 90.95, 85.29, 71.47, 71.21, 69.15, 68.48, 64.78, 59.68, 53.12, 50.90, 47.47, 45.68, 37.83, 36.17, 30.26, 27.79, 26.15, 25.10, 24.69, 24.43, 16.57, -4.57. **HRMS** *m/z*= 1145.5672 (calcd. for $C_{52}H_{76}N_{16}O_{12}Si$ 1145.5671 $[M+H]^+$).



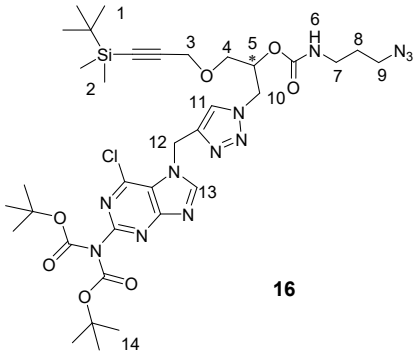
15

Compound (*R*, *R*)-**DC** (0.573 g, 0.5 mmol) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.252 g, 2.5 equiv.) and pyridine (101 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed

by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.15 g, 3 eq.) and Et_3N (0.348 mL, 5 eq.). The mixture was stirred for 2 h at room temperature, then DCM (50 mL) and Milli-Q water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product (*R*, *R*)-**15** was obtained after passing the residue through a chromatography column (MeOH/DCM= 3/97 to 8/92) as a foamy-white solid (0.636 g, 100%). The products (*S*, *S*)-**15** (0.425 g, 88%) was prepared following the same protocol.

(*R*, *R*)-**15**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.92 – 8.38 (m, 2H, H_{23} and H_{27}), 7.97 – 7.64 (m, 6H, H_{10}, H_{24}, H_{25}, H_{26}, H_{30} and H_{24}), 7.44 (s, 1H, H_{19}), 7.07 (d, *J* = 7.3 Hz, 1H, H_{33}), 5.92 – 5.54 (b, 2H, H_6 and H_{14}), 5.26 (d, *J* = 6.2 Hz, 1H, H_5), 5.17 – 5.05 (m, 3H, H_{13} and H_{31}), 4.68 – 4.51 (m, 6H, H_{11}, H_{18} and H_{29}), 4.39 (t, *J* = 6.6 Hz, 2H, H_9), 4.22 (d, *J* = 2.3 Hz, 2H, H_3), 3.80 – 3.58 (m, 2H, H_4), 3.54 – 3.39 (m, 2H, H_{12}), 3.33 (t, *J* = 6.6 Hz, 2H, H_{17}), 3.25 – 3.10 (m, 3H, H_7 and H_{15}), 3.08 – 2.96 (m, 1H, H_{15}), 2.88 – 2.67 (m, 2H, H_{20}), 2.38 (s, 2H, H_{22}), 2.20 (s, 3H, H_{28}), 2.13 – 1.96 (m, 6H, H_8 and H_{21}), 1.78 – 1.70 (m, 2H, H_{16}), 1.52 (s, 18H, H_{34}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.27, 169.45, 162.75, 155.56, 155.33, 155.25, 149.92, 149.66, 148.34, 148.17, 147.28, 144.44, 141.73, 140.72, 125.92, 123.74, 122.61, 109.51, 101.17, 96.93, 91.00, 85.28, 71.23, 70.64, 68.47, 68.13, 64.88, 59.69, 50.86, 49.05, 47.42, 45.77, 38.57, 37.84, 36.08, 30.20, 29.05, 27.79, 26.14, 25.23, 24.72, 24.31, 16.56, -4.58. **HRMS** *m/z*= 1271.6209 (calcd. for $C_{56}H_{82}N_{20}O_{13}Si$ 1271.6212 $[M+H]^+$).

(*S*, *S*)-**15**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.13 – 8.20 (m, 2H, H_{23} and H_{27}), 7.97 – 7.59 (m, 6H, H_{10}, H_{24}, H_{25}, H_{26}, H_{30} and H_{24}), 7.46 (d, *J* = 6.8 Hz, 1H, H_{19}), 7.07 (t, *J* = 8.3 Hz, 1H, H_{33}), 5.93 – 5.55 (b, 2H, H_6 and H_{14}), 5.26 (d, *J* = 5.6 Hz, 1H, H_5), 5.18 – 4.99 (m, 3H, H_{13} and H_{31}), 4.68 – 4.50 (m, 6H, H_{11}, H_{18} and H_{29}), 4.40 (t, *J* = 6.6 Hz, 2H, H_9), 4.30 – 4.16 (m, 2H, H_3), 3.80 – 3.60 (m, 2H, H_4), 3.56 – 3.39 (m, 2H, H_{12}), 3.33 (t, *J* = 6.6 Hz, 2H, H_{17}), 3.25 – 3.11 (m, 3H, H_7 and H_{15}), 3.02 (dd, *J* = 14.0, 6.5 Hz, 1H, H_{15}), 2.85– 2.67 (m, 2H, H_{20}), 2.40 (s, 2H, H_{22}), 2.21 (s, 3H, H_{28}), 2.14 – 1.94 (m,, 4H, H_8 and H_{21}), 1.74 (p, *J* = 6.6 Hz, 2H, H_{16}), 1.52 (s, 18H, H_{34}), 0.92 (s, 9H, H_1), 0.11 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.29, 169.78, 162.54, 155.67, 155.63, 155.19, 150.28, 150.11, 149.64, 148.63, 146.48, 144.57, 141.82, 140.20, 126.32, 124.18, 123.55, 109.30, 101.32, 96.85, 90.62, 85.08, 71.42, 70.84, 69.04, 68.08, 64.76, 59.54, 53.00, 50.76, 47.43, 45.01, 37.65, 36.11, 35.97, 30.17, 28.08, 27.74, 26.11, 25.09, 24.67, 24.38, 16.50, -4.62. **HRMS** *m/z*= 1271.6187 (calcd. for $C_{56}H_{82}N_{20}O_{13}Si$ 1271.6212 $[M+H]^+$).



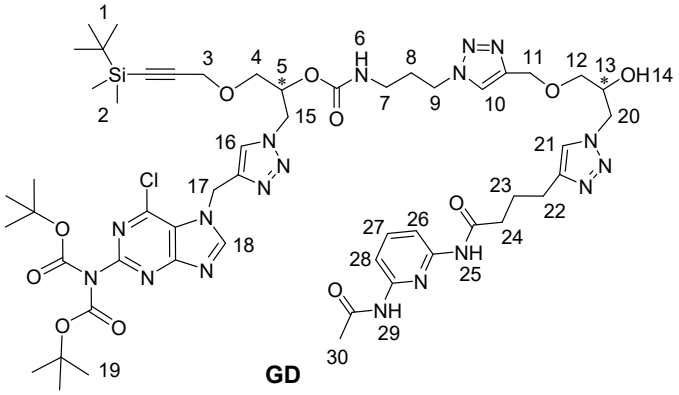
16

Compound **4** (1.3 g, 1.9 mmol) was added in a flask followed by DCM (10 mL), 4-nitrophenyl chloroformate (0.585 g, 1.5 equiv.) and pyridine (235 µL, 1.5 equiv.). The mixture was stirred for 1 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (10 mL) and added to a flask followed by 3-azido-1-propylamine (0.38 g, 2 eq.) and Et_3N (0.794 mL, 3 eq.). The mixture was stirred for 1 h at room temperature, then DCM (60 mL) and Milli-Q water (60 mL) were added to the mixture. The organic phase was washed with water (2 × 60 mL) and brine (2 × 60 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product (*R*)-**16** was obtained after passing the residue through a chromatography column (MeOH/DCM= 3/97 to 8/92) as a foamy-white solid (1.53 g, 100%). The products (*S*)-**17** (0.521 g, 88%) was prepared following the same protocol.

(*R*)-**16**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.30 (s, 1H, H_{13}), 7.81 (s, 1H, H_{11}), 5.53 (s, 2H, H_{12}), 5.28 (t, *J* = 6.0 Hz, 1H, H_6), 5.09 (dd, *J* = 8.4, 4.2 Hz, 1H, H_5), 4.69 – 4.41 (m, 2H, H_{10}), 4.18 (d, *J* = 3.6 Hz, 2H, H_3), 3.69 – 3.54 (m, 2H, H_4), 3.23 (t, *J* = 6.5 Hz, 2H, H_9), 3.13 – 2.89 (m, 2H, H_7), 1.62 – 1.54 (m, 2H, H_8), 1.51 (s, 18H, H_{14}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.09, 152.57, 151.93, 151.56, 151.31, 146.06, 141.39, 130.31, 125.02, 101.20, 90.84,

84.35, 71.18, 68.22, 59.63, 51.10, 49.04, 39.79, 38.49, 28.95, 28.07, 26.15, 16.55, -4.57. **HRMS** *m/z*= 803.3535 (calcd. for $C_{34}H_{51}ClN_{12}O_7Si$ 803.3534 $[M+H]^+$)

(*S*)-**16**, **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8 8.30 (s, 1H, H_{13}), 7.81 (s, 1H, H_{11}), 5.53 (s, 2H, H_{12}), 5.27 (t, *J* = 6.0 Hz, 1H, H_6), 5.09 (dd, *J* = 8.1, 4.0 Hz, 1H, H_5), 4.72 – 4.45 (m, 2H, H_{10}), 4.18 (d, *J* = 3.6 Hz, 2H, H_3), 3.63 (dd, *J* = 9.0, 4.6 Hz, 2H, H_4), 3.30 – 3.19 (m, 2H, H_9), 3.12 – 2.90 (m, 2H, H_7), 1.83 – 1.68 (m, 2H, H_8), 1.51 (s, 18H, H_{14}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.09, 152.57, 151.92, 151.56, 151.31, 146.06, 141.38, 130.32, 125.02, 101.19, 90.84, 84.35, 71.18, 68.22, 59.63, 51.10, 49.04, 39.79, 38.49, 28.95, 28.07, 26.15, 16.56, -4.57. **HRMS** *m/z*= 803.3534 (calcd. for $C_{34}H_{51}ClN_{12}O_7Si$ 803.3534 $[M+H]^+$)

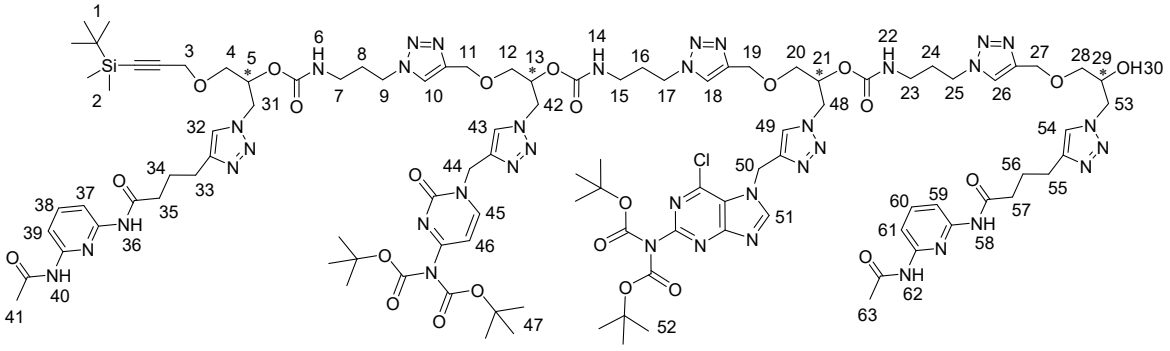


Compound (*R*)-**D** (0.309 g, 0.6 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.9 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound (*R*)-**16** (0.48 g, 1 equiv.) was added into the residue followed by EtOH (4.2 mL) with stirring. Milli-Q water (1.8 mL), sodium ascorbate solution (24 mg in 1 mL water, 0.2 equiv.) and $CuSO_4$ solution (9.6 mg in 0.5 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product (*R*, *R*)-**GD** as foamy yellow solid (0.65 g, 90%). The products (*S*, *S*)-**GD** (0.613 g, 79%) was prepared following the same protocol.

(*R*, *R*)-**GD**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ .95 – 8.42 (m, 2H, H_{25} and H_{29}), 8.38 (s, 1H, H_{18}), 7.90 – 7.74 (m, 3H, H_{10}, H_{16} and H_{26}), 7.70 – 7.62 (m, 2H, H_{27} and H_{28}), 7.50 (s, 1H, H_{21}), 5.76 (t, *J* = 6.0 Hz, 1H, H_6), 5.52 (d, *J* = 4.5 Hz, 2H, H_{17}), 5.15 (dd, *J* = 8.3, 4.1 Hz, 1H, H_5), 4.70 – 4.09 (m, 11H, H_3, H_9, H_{11}, H_{13}, H_{15} and H_{20}), 3.72 – 3.41 (m, 4H, H_4 and H_{12}), 2.97 – 2.86 (m, 2H, H_7), 2.74 (t, *J* = 7.0 Hz, 2H, H_{22}), 2.40 (t, *J* = 7.2 Hz, 2H, H_{24}), 2.20 (s, 3H, H_{30}), 2.04 (p, *J* = 7.0 Hz, 2H, H_{23}), 1.97 – 1.82 (m, 2H, H_8), 1.49 (s, 18H, H_{19}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.23, 169.35, 155.45, 152.59, 151.90, 151.34, 151.31, 149.77, 149.58, 146.82, 146.55, 144.53, 141.31, 140.90, 130.16, 125.19, 123.44, 123.18, 109.51, 109.48, 101.12, 90.95, 84.45, 71.37, 71.17, 69.27, 68.30, 64.70, 59.63, 52.96, 51.18, 47.45, 39.69, 37.76, 36.30, 30.17, 28.06, 26.14, 25.11, 24.77, 24.28, 16.55, -4.57. **HRMS** *m/z*= 1225.5204 (calcd. for $C_{53}H_{75}ClN_{18}O_{11}Si$ 1225.5213 $[M+Na]^+$)

(*S, S*)-**GD**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ δ 9.13 – 8.47 (m, 2H, H_{25} and H_{29}), 8.39 (s, 1H, H_{18}), 7.94 – 7.73 (m, 3H, H_{26}, H_{27} and H_{14}), 7.69 – 7.62 (m, 2H, H_{10} and H_{16}), 7.51 (s, 1H, H_{21}), 5.85 – 5.74 (t, *J* = 6.0 Hz, 1H, H_6), 5.53 (d, *J* = 3.4 Hz, 2H, H_{17}), 5.15 (dd, *J* = 7.9, 3.9 Hz, 1H, H_5), 4.74 – 4.06 (m, 11H, H_3, H_9, H_{11}, H_{13}, H_{15} and H_{20}), 3.71 – 3.43 (m, 4H, H_4 and H_{12}), 2.99 – 2.86 (m, 2H, H_7), 2.74 (t, *J* = 6.9 Hz, 2H, H_{22}),), 2.40 (t, *J* = 7.2 Hz, 2H, H_{24}), 2.20 (s, 3H, H_{30}), 2.04 (q, *J* = 7.2 Hz, 2H, H_{23}), 1.89 (p, *J* = 27.5, 6.8 Hz, 2H, H_8), 1.49 (s, 18H, H_{19}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.14, 169.55, 155.45, 152.58, 151.87, 151.33, 151.29, 149.69, 149.48, 146.79, 146.59, 144.50, 141.30, 141.01, 130.14, 125.21, 123.47, 123.22, 109.48, 109.44, 101.11, 90.93, 84.46, 71.40, 71.15, 69.24, 68.28,

64.67, 59.63, 52.98, 51.17, 47.45, 39.67, 37.74, 36.26, 30.16, 28.05, 26.13, 25.07, 24.75, 24.27, 16.54, -4.58. **HRMS** *m/z*= 1203.5392 (calcd. for $C_{53}H_{75}ClN_{18}O_{11}Si$ 1203.5393 $[M+H]^+$)

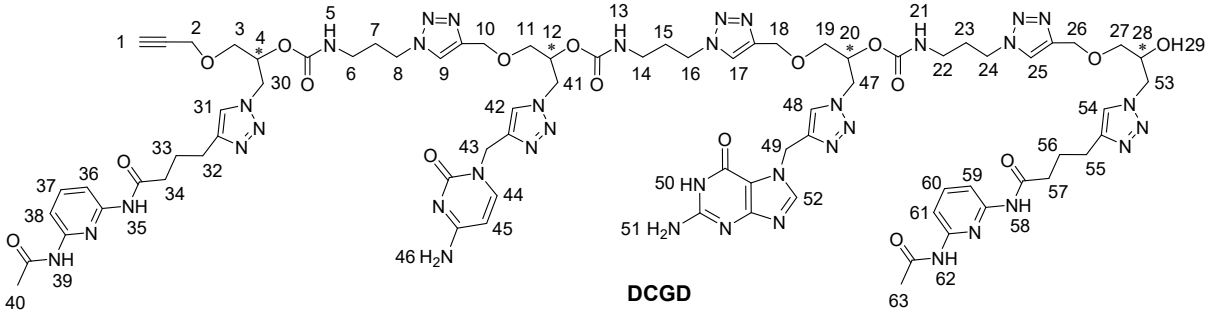


17

Compound (*R*, *R*)-**GD** (0.309 g, 0.6 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.9 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound (*R*, *R*)-**16** (0.48 g, 1 equiv.) was added into the residue followed by EtOH (4.2 mL) with stirring. Milli-Q water (1.8 mL), sodium ascorbate solution (24 mg in 1 mL water, 0.2 equiv.) and $CuSO_4$ solution (9.6 mg in 0.5 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 8/92) to give the final product all-*R* **17** as foamy yellow solid (0.766 g, 87%). The products all-*S* 19 (0.623 g, 88%) was prepared following the same protocol.

(*R, R, R, R*)-**17**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.48 – 8.48 (m, 4H, H_{36}, H_{40}, H_{58} and H_{62}), 8.41 (s, 1H, H_{51}), 8.01 – 7.57 (m, 12H, H_{10}, H_{18}, H_{26}, H_{37}, H_{38}, H_{39}, H_{43}, H_{45}, H_{49}, H_{59}, H_{60} and H_{61}), 7.51 (s, 1H, H_{54}), 7.44 (s, 1H, H_{32}), 7.08 – 6.99 (m, 1H, H_{46}), 6.38 – 5.91 (b, 3H, H_6, H_{14} and H_{22}), 5.61 – 4.91 (m, 7H, H_5, H_{13}, H_{21}, H_{44} and H_{50}), 4.87 – 4.02 (m, 25H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{29}, H_{31}, H_{42}, H_{48} and H_{53}), 3.77 – 3.41 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.30 – 2.86 (m, 6H, H_7, H_{15} and H_{23}), 2.76 – 2.64 (m, 4H, H_{33} and H_{55}), 2.43 – 1.87 (m, 20H, H_8, H_{16}, H_{24}, H_{34}, H_{36}, H_{41}, H_{56}, H_{58} and H_{63}), 1.59 – 1.38 (m, 36H, H_{47} and H_{52}), 0.91 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.31, 169.26, 161.91, 155.85, 155.76, 155.73, 155.11, 152.56, 152.00, 151.12, 150.94, 149.69, 148.80, 147.28, 147.09, 146.71, 144.54, 144.17, 144.12, 141.90, 141.37, 125.68, 125.19, 123.53, 123.44, 123.32, 122.71, 109.54, 109.49, 101.30, 96.84, 90.86, 84.16, 83.25, 77.00, 71.12, 71.06, 71.01, 70.91, 70.88, 69.11, 68.69, 68.49, 64.85, 64.78, 64.64, 59.65, 53.07, 50.94, 50.89, 50.66, 50.64, 47.59, 45.94, 37.83, 37.79, 36.15, 36.08, 30.20, 30.15, 29.82, 28.13, 28.02, 26.15, 25.17, 25.01, 24.64, 24.51, 16.55, -4.56. **TOF MS ES +** *m/z*= 2360.1295 (calcd. for $C_{103}H_{143}ClN_{38}O_{24}Si$ 2360.0668 $[M+H]^+$).

(*S, S, S, S*)-**17**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.42 – 8.42 (m, 4H, H_{36}, H_{40}, H_{58} and H_{62}), 8.41 (s, 1H, H_{51}), 7.98 – 7.39 (m, 14H, H_{10}, H_{18}, H_{26}, H_{32}, H_{37}, H_{38}, H_{39}, H_{43}, H_{45}, H_{49}, H_{54}, H_{59}, H_{60} and H_{61}), 7.04 (d, *J* = 7.4 Hz, 1H, H_{46}), 6.41– 5.90 (b, 3H, H_6, H_{14} and H_{22}), 5.52 (s, 2H, H_{50}), 5.30 – 5.21 (m, 1H, H_5), 5.16 – 4.93 (m, 4H, H_{13}, H_{21} and H_{44}), 4.77 – 4.11 (m, 25H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{29}, H_{31}, H_{42}, H_{48} and H_{53}), 3.80 – 3.36 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.22 – 2.87 (m, 6H, H_7, H_{15} and H_{23}), 2.77 – 2.63 (m, 4H, H_{33} and H_{55}), 2.48 – 1.86 (m, 20H, H_8, H_{16}, H_{24}, H_{34}, H_{36}, H_{41}, H_{56}, H_{58} and H_{63}), 1.52 – 1.42 (m, 36H, H_{47} and H_{52}), 0.91 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.25, 169.71, 162.73, 155.71, 155.64, 155.59, 155.30, 152.63, 151.86, 151.23, 151.15, 149.67, 148.60, 147.28, 146.82, 146.71, 144.50, 144.21, 144.12, 141.72, 141.28, 125.87, 125.27, 123.89, 123.69, 123.21, 122.66, 109.50, 109.46, 101.19, 96.99, 90.97, 85.37, 84.31, 71.54, 71.44, 71.15, 70.88, 70.86, 69.17, 68.72, 68.49, 64.73, 64.63, 64.53, 59.67, 53.03, 50.96, 50.89, 50.55, 50.52, 47.51, 45.67, 39.52, 37.88, 37.77, 36.25, 36.12, 30.24, 30.10, 29.82, 28.03, 27.77, 26.14, 25.16, 25.06, 24.66, 24.43, 16.55, -4.57. **TOF MS ES +** *m/z*= 2360.1712 (calcd. for $C_{103}H_{143}ClN_{38}O_{24}Si$ 2360.0668 $[M+H]^+$).



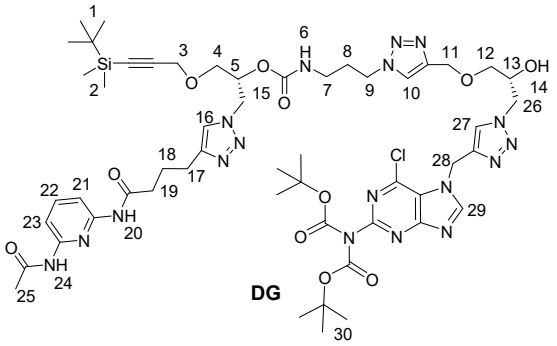
DCGD

Compound **17** (0.731 g, 0.31 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.57 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The residue was obtained and followed by adding TFA (3 mL) and Milli-Q water (1 mL) stirring at room temperature for 48 h. The crude product was precipitated from the solution with the neutralization of saturated $NaHCO_3$. Then, the solid product was wash with brine, water, acetone and Et_2O, respectively. The final product was dried under vacuum to give the final product all-*R* **DCGD** as foamy yellow solid (0.3 g, 51%). The products all-*S* **DCGD** (0.213 g, 92%) was prepared following the same protocol.

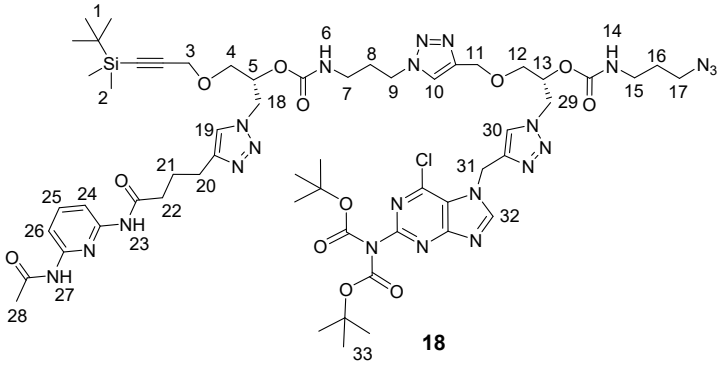
(*R, R, R, R*)-**DCGD**, **^{1}H NMR (500 MHz, DMSO)** δ ^{1}H NMR (500 MHz, DMSO) δ 11.10 (s, 1H, H_{50}), 10.20 – 9.85 (m, 4H, H_{35}, H_{39}, H_{58} and H_{62}), 8.13 – 8.06 (m, 3H, H_9, H_{17} and H_{25}), 7.98 – 7.91 (m, 2H, H_{48} and H_{52}), 7.83 – 7.77 (m, 2H, H_{42} and H_{44}), 7.74 – 7.64 (m, 8H, H_{31}, H_{36}, H_{37}, H_{38}, H_{54}, H_{59}, H_{60} and H_{61}), 7.40 (m, 5.6 Hz, 3H, H_{45} and H_{46}), 7.22 (s, 2H, H_{51}), 6.71 – 6.63 (b, 2H, H_5 and H_{13}), 5.68 (b, 1H, H_{21}), 5.21 (s, 2H, H_{49}), 5.13 – 5.05 (m, 3H, H_4, H_{12} and H_{20}), 4.93 – 4.83 (m, 2H, H_{43}), 4.62 – 4.47 (m, 13H, H_{10}, H_{18}, H_{26}, H_{30}, H_{41}, H_{47} and H_{53}), 4.39 (dd, *J* = 13.9, 3.7 Hz, 1H, H_{53}), 4.35 – 4.26 (m, 6H, H_8, H_{16} and H_{24}), 4.18 (d, *J* = 2.5 Hz, 2H, H_2), 4.10 (d, *J* = 5.5 Hz, 1H, H_{28}), 3.60 – 3.40 (m, 8H, H_3, H_{11}, H_{19} and H_{27}), 2.97 – 2.84 (m, 6H, H_6, H_{14} and H_{22}), 2.68 – 2.57 (m, 4H, H_{32} and H_{55}), 2.48 – 2.41(m, *J* = 7.9 Hz, 5H, H_1, H_{34} and H_{57}), 2.09 (s, 6H, H_{40} and H_{63}), 1.94 – 1.80 (m, 10H, H_7, H_{15}, H_{23}, H_{33} and H_{56}). **^{13}C NMR (126 MHz, DMSO)** δ 172.17, 169.67, 166.31, 157.51, 155.49, 153.92, 151.43, 150.51, 150.44, 146.66, 146.31, 146.15, 143.96, 143.65, 143.12, 142.80, 140.22, 137.53, 124.78, 124.64, 124.38, 124.34, 123.12, 123.07, 116.42, 109.19, 109.08, 94.22, 80.09, 77.80, 71.81, 70.78, 68.84, 68.55, 68.47, 64.01, 58.14, 52.89, 50.28, 50.06, 48.85, 47.21, 43.65, 37.61, 35.83, 35.73, 30.14, 25.04, 24.69, 24.65, 24.20. **TOF MS ES +** *m/z*= 1827,8045 (calcd. for $C_{77}H_{99}N_{38}O_{17}$ 1827,8045 $[M+H]^+$).

(*S, S, S, S*)-**DCGD**, **^{1}H NMR (500 MHz, DMSO)** δ 11.03 (s, 1H, H_{50}), 10.10 – 9.96 (m, 4H, H_{35}, H_{39}, H_{58} and H_{62}), 8.14 – 8.05 (m, 3H, H_9, H_{17}, H_{25}), 8.00 – 7.89 (m, 2H, H_{48} and H_{52}), 7.83 – 7.76 (m, 2H, H_{42} and H_{44}), 7.75 – 7.60 (m, 8H, H_{31}, H_{36}, H_{37}, H_{38}, H_{54}, H_{59}, H_{60} and H_{61}), 7.46 – 7.34 (m, 3H, H_{45} and H_{46}), 7.22 (s, 2H, H_{51}), 6.82 – 6.50 (b, 2H, H_5 and H_{13}), 5.68 (b,, H_{21}), 5.21 (s, 2H, H_{49}), 5.14 – 5.04 (m, 3H, H_4, H_{12} and H_{20}), 4.95 – 4.81 (m, 2H, H_{43}), 4.63 – 4.46 (m, 12H, H_{10}, H_{18}, H_{26}, H_{30}, H_{41} and H_{47}), 4.42 – 4.15 (m, 10H, H_2, H_8, H_{16}, H_{24} and H_{53}), 4.10 (d, *J* = 5.1 Hz, 1H, H_{28}), 3.64 – 3.40 (m, 7H, H_3, H_{11}, H_{19} and H_{27}), 2.91 (m, 6H, H_6, H_{14} and H_{22}), 2.62 – 2.57 (m, 5H, H_1, H_{32} and H_{55}), 2.47 – 2.40 (m, 4H, H_{34} and H_{57}), 2.09 (s, 6H, H_{40} and H_{63}), 1.94 – 1.80 (m, 10H, H_7, H_{15}, H_{23}, H_{33} and H_{56}). **^{13}C NMR (126 MHz, DMSO)** δ 171.87, 169.28, 166.09, 157.19, 155.20, 153.71, 151.19, 150.36, 150.28, 146.38, 146.02, 145.87, 143.70, 143.39, 142.97, 142.66, 139.86, 137.14, 124.47, 124.31, 124.12, 124.09, 122.80, 122.76, 116.32, 109.00, 108.87, 93.82, 79.85, 77.67, 71.66, 70.52, 70.46, 68.64, 68.33, 68.24, 63.85, 57.91, 52.69, 49.99, 49.78, 48.61, 46.95, 37.41, 35.57, 35.48, 29.96, 24.87, 24.54, 24.50, 24.00. **TOF MS ES +** *m/z*= 1827,7686 (calcd. for $C_{77}H_{99}N_{38}O_{17}$ 1827,8045 $[M+H]^+$).

2.3 Synthesis of all-R tetramer DGCD

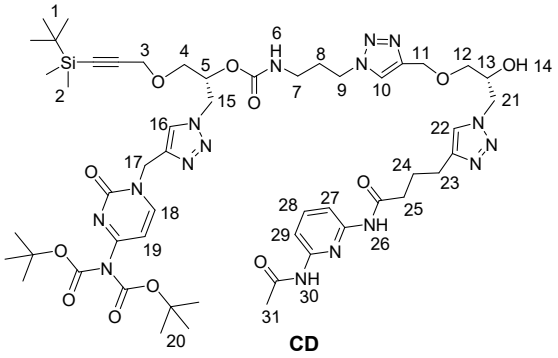


Compound **4** (0.541 g, 0.8 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (1.2 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **7** (0.513 g, 1 equiv.) was added into the residue followed by EtOH (5.6 mL) with stirring. Milli-Q water (2.4 mL), sodium ascorbate solution (32 mg in 1 mL water, 0.2 equiv.) and $CuSO_4$ solution (12.8 mg in 0.8 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 8/92) to give the final product **DG** as foamy yellow solid (0.78 g, 81%).**DG**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.41 – 8.89 (m, 2H, H_{20} and H_{24}), 8.43 (s, 1H, H_{29}), 7.99 (s, 1H, H_{10}), 7.86 – 7.72 (m, 3H, H_{21}, H_{23} and H_{27}), 7.65 – 7.51 (m, 2H, H_{16} and H_{22}), 6.14 (t, *J* = 6.1 Hz, 1H, H_6), 5.51 (s, 2H, H_{28}), 5.27 – 5.14 (m, 1H, H_5), 4.84 (d, *J* = 5.8 Hz, 1H, H_{15}), 4.66 – 4.07 (m, 10H, H_3, H_9, H_{11}, H_{13}, H_{15} and H_{26}), 3.72 – 3.40 (m, 4H, H_4 and H_{12}), 3.23 – 3.16 (m, 2H, H_7), 2.75 – 2.62 (t, 2H, H_{17}), 2.37 (q, *J* = 7.1 Hz, 2H, H_{19}), 2.16 (s, 3H, H_{25}), 2.07 – 1.91 (m, 4H, H_8 and H_{18}), 1.43 (s, 18H, H_{30}), 0.90 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.22, 169.58, 155.64, 152.58, 151.93, 151.12, 150.93, 150.07, 149.94, 147.23, 146.57, 144.44, 140.82, 140.50, 129.96, 125.23, 123.82, 122.88, 109.46, 101.20, 90.91, 84.00, 71.53, 71.19, 69.09, 68.45, 64.67, 59.02, 53.26, 50.89, 47.47, 39.32, 37.77, 36.20, 30.26, 28.00, 26.13, 25.12, 24.70, 24.49, 16.54, -4.59. **HRMS** *m/z*= 1203.5397 (calcd. for $C_{53}H_{75}ClN_{18}O_{11}Si$ 1203.5393 $[M+H]^+$)



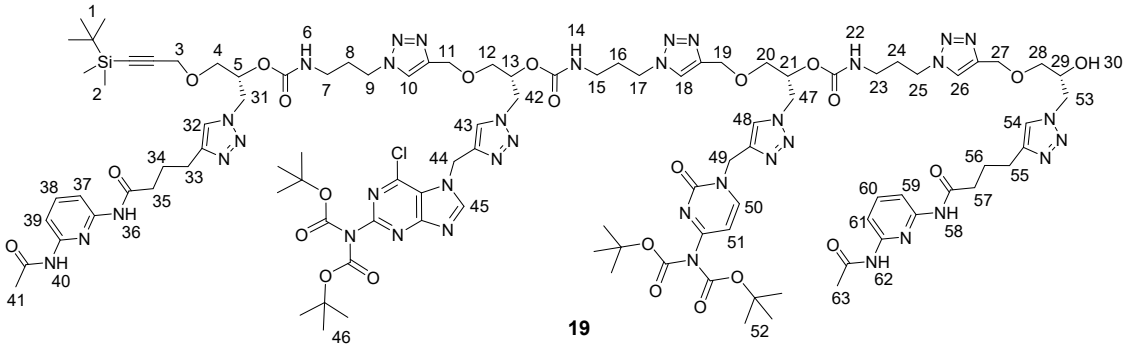
Compound **DC** (0.54 g, 0.45 mmol) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.227 g, 2.5 equiv.) and pyridine (98 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.135 g, 3 eq.) and Et_3N (0.314 mL, 5 eq.). The mixture was stirred for 2 h at room temperature, then DCM (50 mL) and Milli-Q water (50 mL) were added to the mixture. The organic phase was washed with water (2 × 50 mL) and brine (2 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **19** was obtained after passing the residue through a chromatography column (MeOH/DCM= 3/97 to 8/92) as a foamy-white solid (0.598 g, 100%). **18**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.61 (s, 1H, H_{27}), 8.51 – 8.32 (m, 2H, H_{23} and H_{32}), 7.93 – 7.77 (m, 3H, H_{10}, H_{24} and H_{30}), 7.73 – 7.62 (m, 2H, H_{25} and H_{26}), 7.42 (s, 1H, H_{19}), 5.64 – 5.48 (m, 3H, H_6 and H_{31}), 5.28 (t, *J* =

5.8 Hz, 1H, H_{14}), 5.10 (s, 1H, H_5), 4.74 – 4.11 (m, 10H, H_3, H_9, H_{11}, H_{13}, H_{18} and H_{29}), 3.86 – 3.37 (m, 4H, H_4 and H_{12}), 3.32 – 2.87 (m, 6H, H_7, H_{15} and H_{17}), 2.74 (d, *J* = 9.2 Hz, 2H, H_{20}), 2.36 (d, *J* = 4.7 Hz, 2H, H_{22}), 2.20 (s, 3H, H_{28}), 2.12 – 1.97 (m, 4H, H_8 and H_{21}), 1.62 (d, *J* = 1.4 Hz, 2H, H_{16}), 1.48 (s, 18H, H_{33}), 0.92 (s, 9H, H_1), 0.10 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 171.92, 169.21, 155.52, 155.27, 152.59, 151.91, 151.40, 151.28, 149.96, 149.80, 147.29, 146.41, 144.30, 141.36, 140.67, 130.19, 125.12, 123.62, 122.56, 109.61, 109.57, 101.10, 91.09, 84.33, 71.31, 70.97, 68.45, 68.38, 64.78, 59.74, 50.89, 50.86, 49.01, 47.42, 39.59, 38.50, 37.85, 36.06, 30.30, 28.94, 28.04, 26.15, 25.22, 24.77, 24.26, 16.56, -4.57. **HRMS** *m/z*= 1329.5743 (calcd. for $C_{57}H_{81}ClN_{22}O_{12}Si$ 1329.3935 $[M+H]^+$)



CD

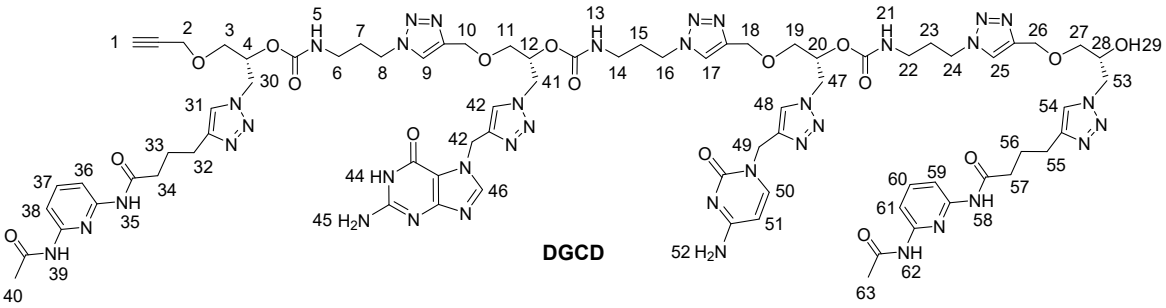
Compound **D** (0.468 g, 0.91 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (1.37 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **9** (0.68 g, 1 equiv.) was added into the residue followed by EtOH (6.37 mL) with stirring. Milli-Q water (2.73 mL), sodium ascorbate solution (36.4 mg in 1.5 mL water, 0.2 equiv.) and $CuSO_4$ solution (14.6 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 6/94) to give the final product **CD** as foamy yellow solid (0.624 g, 60%). **CD**, **^{1}H NMR (500 MHz, $CDCl_3$)** *δ* 9.43 – 9.17 (m, 2H, H_{26} and H_{30}), 8.12 (s, 1H, H_{10}), 8.04 – 7.96 (m, 2H, H_{16} and H_{18}), 7.85 – 7.75 (m, 2H, H_{27} and H_{28}), 7.66 (s, 1H, H_{29}), 7.58 (t, *J* = 8.1 Hz, 1H, H_{22}), 6.98 (d, *J* = 7.4 Hz, 1H, H_{19}), 6.57 (b, 1H, H_6), 5.19 – 5.01 (m, 4H, H_5 and H_{17}), 4.72 – 4.32 (m, 8H, H_9, H_{11}, H_{15} and H_{21}), 4.22 – 3.08 (m, 3H, H_3 and H_{13}), 3.68 – 3.45 (m, 4H, H_4 and H_{12}), 3.06 (dd, *J* = 14.4, 6.6 Hz, 2H, H_7), 2.73 (t, *J* = 6.8 Hz, 2H, H_{23}), 2.39 (dt, *J* = 7.2, 3.2 Hz, 2H, H_{25}), 2.18 (s, 3H, H_{31}), 2.10 – 1.98 (m, 4H, H_8 and H_{24}), 1.49 (s, 18H, H_{20}), 0.89 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 172.22, 169.68, 162.72, 155.64, 155.56, 155.24, 149.70, 149.66, 148.36, 147.32, 143.61, 141.74, 140.65, 125.70, 123.74, 122.60, 109.57, 109.54, 101.17, 96.92, 91.02, 85.28, 70.62, 68.48, 64.88, 59.69, 50.86, 50.47, 49.05, 47.64, 45.68, 38.57, 37.84, 36.10, 29.82, 27.79, 26.15, 25.21, 24.64, 24.30, 16.56, -4.57. **HRMS** *m/z*= 1145.5679 (calcd. for $C_{52}H_{76}N_{16}O_{12}Si$ 1145.5671 $[M+H]^+$).



19

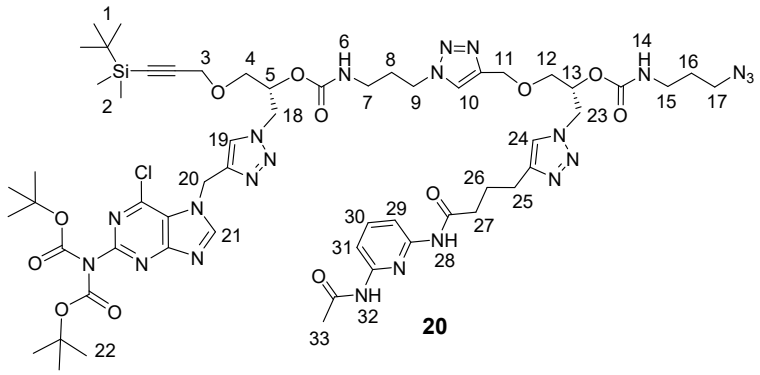
Compound **CD** (0.378 g, 0.33 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.66 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with

Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **18** (0.44 g, 1 equiv.) was added into the residue followed by EtOH (2.31 mL) with stirring. Milli-Q water (0.99 mL), sodium ascorbate solution (13.2 mg in 0.5 mL water, 0.2 equiv.) and $CuSO_4$ solution (5.3 mg in 0.3 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 3/97 to 12/88) to give the final product **19** as foamy yellow solid (0.584 g, 75%). **19**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.00 – 8.67 (m, 4H, H_{36}, H_{40}, H_{58} and H_{62}), 8.43 (s, 1H, H_{45}), 7.94 – 7.38 (m, 14H, H_{10}, H_{18}, H_{26}, H_{32}, H_{37}, H_{38}, H_{39}, H_{43}, H_{45}, H_{49}, H_{54}, H_{59}, H_{60} and H_{61}), 7.02 (d, J = 7.3 Hz, 1H, H_{51}), 6.31 – 6.06 (b, 2H, H_6 and H_{14}), 5.93 (b, 1H, H_{22}), 5.52 (s, 2H, H_{44}), 5.38 – 4.95 (m, 5H, H_5, H_{13}, H_{21} and H_{49}), 4.77 – 4.08 (m, 24H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{29}, H_{31}, H_{42}, H_{47} and H_{53}), 3.78 – 3.41 (m, 8H, H_4, H_{12}, H_{20} and H_{28}), 3.25 – 2.87 (m, 6H, H_7, H_{15} and H_{23}), 2.69 (d, J = 7.8 Hz, 4H, H_{33} and H_{55}), 2.44 – 1.83 (m, 20H, H_8, H_{16}, H_{24}, H_{34}, H_{36}, H_{41}, H_{56}, H_{58} and H_{63}), 1.55 – 1.38 (m, 36H, H_{46} and H_{52}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.15, 169.58, 162.69, 155.68, 155.65, 155.57, 155.27, 152.63, 151.87, 151.21, 151.15, 149.68, 148.58, 147.29, 146.83, 146.74, 144.48, 144.24, 144.09, 141.70, 141.29, 125.86, 125.24, 123.86, 123.79, 123.19, 122.65, 109.54, 109.50, 101.17, 96.93, 91.00, 85.36, 84.29, 71.42, 71.16, 70.93, 69.20, 68.62, 68.46, 64.65, 59.68, 53.00, 50.87, 50.56, 47.54, 45.60, 39.47, 37.82, 36.24, 36.11, 30.28, 30.17, 29.81, 28.02, 27.77, 26.13, 25.17, 25.09, 24.65, 24.42, 16.55, -4.58. **TOF MS ES +** *m/z*= 2360.1666 (calcd. for $C_{103}H_{143}ClN_{38}O_{24}Si$ 2360.0668 $[M+H]^+$).



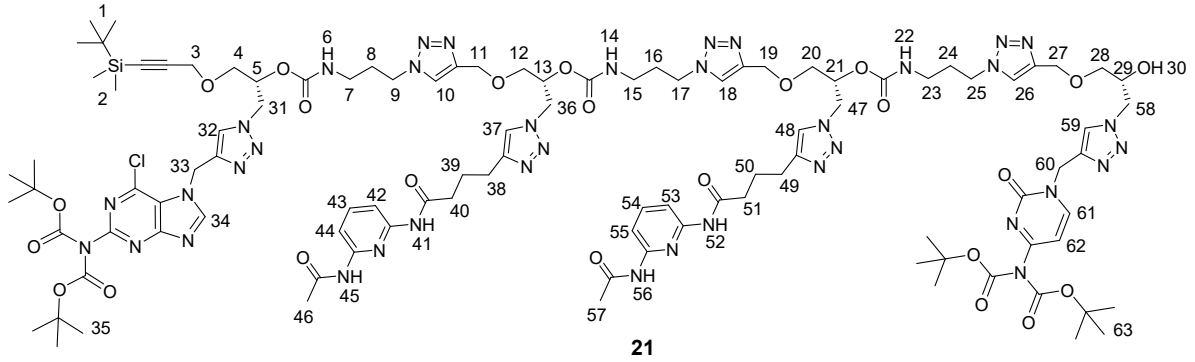
Compound **19** (0.5 g, 0.21 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.63 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The residue was obtained and followed by adding TFA (3 mL) and Milli-Q water (1 mL) stirring at room temperature for 48 h. The crude product was precipitated from the solution with the neutralization of saturated $NaHCO_3$. Then, the solid product was wash with brine, water, acetone and Et_2O, respectively. The final product was dried under vacuum to give the final product all-*R* **DGCD** as foamy yellow solid (0.32 g, 83%). **DGCD**, **^{1}H NMR (500 MHz, DMSO)** δ 11.17 (s, 1H, H_{44}), 10.03 (dd, J = 24.2, 8.0 Hz, 4H, 4H, H_{35}, H_{39}, H_{58} and H_{62}), 8.18 – 8.02 (m, 3H, H_9, H_{17} and H_{25}), 7.95 (d, J = 16.5 Hz, 2H, H_{44} and H_{46}), 7.86 – 7.59 (m, 10H, H_{31}, H_{36}, H_{37}, H_{38}, H_{42}, H_{44}, H_{54}, H_{59}, H_{60} and H_{61}), 7.48 – 7.32 (m, 3H, H_{51} and H_{52}), 7.22 (s, 1H, H_{45}), 7.05 (b, 1H, H_5), 6.72 (b, 1H, H_{13}), 5.68 (b, 1H, H_{21}), 5.37 – 5.02 (m, 5H, H_4, H_{12}, H_{20} and H_{49}), 4.87 (dd, J = 8.7, 6.1 Hz, 2H, H_{43}), 4.70 – 4.43 (m, 12H, H_{10}, H_{18}, H_{26}, H_{30}, H_{36} and H_{47}), 4.43 – 4.07 (m, 10H, H_2, H_8, H_{16}, H_{24} and H_{53}), 3.95 (d, J = 15.6 Hz, 1H, H_{28}), 3.61 – 3.39 (m, 8H, H_3, H_{11}, H_{19} and H_{27}), 3.03 – 2.78 (m, 6H, H_6, H_{14} and H_{22}), 2.70 – 2.56 (m, 4H, H_{32} and H_{55}), 2.45 (d, J = 8.3 Hz, 4H, H_{34} and H_{57}), 2.09 (s, 6H, H_{40} and H_{63}), 1.97 – 1.75 (m, 10H, H_7, H_{15}, H_{23}, H_{33} and H_{56}). **^{13}C NMR (126 MHz, DMSO)** δ 171.88, 169.29, 166.02, 157.33, 155.22, 153.80, 151.21, 150.37, 150.29, 146.39, 146.02, 145.92, 143.68, 143.39, 143.00, 142.65, 139.88, 137.12, 124.54, 124.26, 124.13, 122.82, 122.77, 116.28, 109.02, 108.88, 93.85, 79.85, 77.69, 71.65, 70.53, 70.48, 68.67, 68.34, 68.24, 63.85, 57.92, 52.70, 50.13, 49.94, 48.62, 46.96, 37.42, 35.58, 35.49, 29.99, 24.88, 24.55, 24.50, 24.01. **TOF MS ES +** *m/z*= 1827, 8105 (calcd. for $C_{77}H_{99}N_{38}O_{17}$ 1827,8045 $[M+H]^+$).

2.4 Synthesis of all-R tetramer GDDC



20

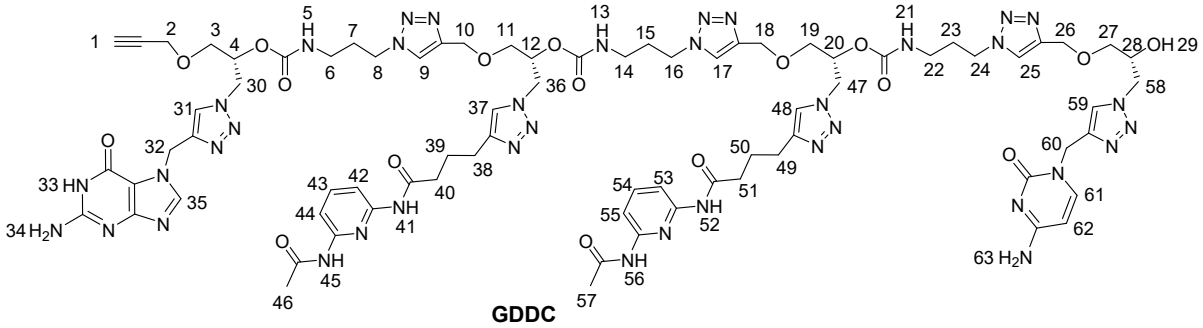
Compound **GD** (0.3 g, 0.25 mmol) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.126 g, 2.5 equiv.) and pyridine (51 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.75 g, 3 eq.) and Et_3N (0.139 mL, 5 eq.). The mixture was stirred for 2 h at room temperature, then DCM (30 mL) and Milli-Q water (30 mL) were added to the mixture. The organic phase was washed with water (2 × 30 mL) and brine (2 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **20** was obtained after passing the residue through a chromatography column (MeOH/DCM= 2/98 to 6/94) as a foamy-white solid (0.335 g, 100%).**20**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.37 – 8.18 (m, 3H, H_{21}, H_{28} and H_{32}), 7.99 – 7.55 (m, 5H, H_{10}, H_{19}, H_{29}, H_{30} and H_{31}), 7.41 (s, 1H, H_{24}), 5.93 – 5.64 (b, 2H, H_6 and H_{14}), 5.53 (s, 2H, H_{20}), 5.59– 5.46 (m, 2H, H_5 and H_{13}), 4.78 – 4.44 (m, 6H, H_{11}, H_{18} and H_{23}), 4.38 – 4.02 (m, 4H, H_3 and H_9), 3.69 – 3.57 (m, 2H, H_4), 3.33 (t, *J* = 6.5 Hz, 2H, H_{12}), 3.21 (q, *J* = 6.5 Hz, 2H, H_{17}), 3.14 – 3.05 (m, 4H, H_7 and H_{15}), 2.74 (d, *J* = 7.2 Hz, 2H, H_{25}), 2.38 (t, *J* = 7.4 Hz, 2H, H_{27}), 2.19 (s, 3H, H_{33}), 2.08 – 1.89 (m, 4H, H_8 and H_{26}), 1.73 (q, *J* = 6.6 Hz, 2H, H_{16}), 1.48 (s, 18H, H_{22}), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.05, 169.39, 155.44, 152.60, 151.87, 151.26, 151.26, 149.88, 149.69, 147.09, 146.58, 144.27, 141.31, 140.72, 130.14, 125.15, 123.65, 122.74, 109.50, 101.11, 90.90, 84.37, 71.06, 68.25, 68.14, 64.69, 59.61, 51.13, 50.22, 49.07, 47.44, 39.63, 38.62, 37.76, 36.13, 30.11, 29.03, 28.03, 26.11, 25.04, 24.71, 24.30, 16.52, -4.60. **HRMS** *m/z*= 1329.5933 (calcd. for $C_{57}H_{81}ClN_{22}O_{12}Si$ 1329.5935 $[M+H]^+$).



21

Compound **DC** (0.241 g, 0.21 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.42 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **20** (0.28 g, 1 equiv.) was added into the residue followed by EtOH (1.47 mL) with stirring. Milli-Q water (0.63 mL), sodium ascorbate solution (8.4 mg in 0.3 mL water, 0.2 equiv.) and $CuSO_4$ solution (3.4 mg in 0.2 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 3/97 to 14/86) to give the final product **21** as foamy yellow solid (0.43 g, 87%). **21**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.40 – 8.37 (m, 4H, H_{41}, H_{45}, H_{52} and H_{56}), 8.44 (s, 1H, H_{34}), 8.02 – 7.54 (m, 12H, H_{10}, H_{18}, H_{26}, H_{32}, H_{42}, H_{43}, H_{44}, H_{53}, H_{54}, H_{55}, H_{59} and H_{61}), 7.51– 7.39 (m, 2H, H_{37} and

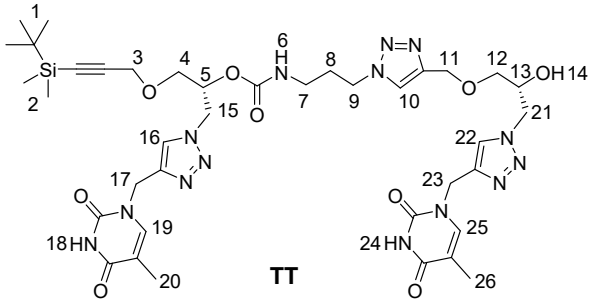
H_{48}), 7.03 (t, *J* = 7.2 Hz, 1H, H_{62}), 6.36 (b, 2H, H_6 and H_{14}), 5.86 (b, 1H, H_{22}), 5.54 (s, 2H, H_{33}), 5.12 (m,, 5H, H_5, H_{13}, H_{21} and H_{60}), 4.70 – 4.09 (m, 24H, H_3, H_9, H_{11}, H_{17}, H_{19}, H_{25}, H_{27}, H_{29}, H_{31}, H_{36}, H_{47} and H_{58}), 3.79 – 3.42 (m, 7H, H_4, H_{12}, H_{20} and H_{28}), 3.17 – 2.83 (m, 6H, H_7, H_{15} and H_{23}), 2.77 – 2.59 (m, 4H, H_{38} and H_{49}), 2.46 – 2.11 (m, 10H, H_{40}, H_{46}, H_{51} and H_{57}), 2.08 – 1.80 (m, 11H, H_8, H_{16}, H_{24}, H_{39} and H_{50}), 1.49 (m, 36H, H_{35} and H_{63}), 0.90 (s, 9H, H_1), 0.08 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** *δ* 172.35, 169.72, 162.67, 155.85, 155.80, 155.46, 155.24, 152.63, 151.86, 151.30, 151.18, 149.69, 148.53, 147.19, 146.91, 146.77, 144.60, 144.17, 144.12, 141.63, 141.36, 125.66, 125.26, 123.94, 123.78, 122.91, 109.65, 109.55, 101.16, 96.88, 90.90, 85.33, 84.41, 71.55, 71.06, 69.08, 68.67, 68.31, 64.71, 64.53, 59.61, 53.19, 51.17, 50.52, 47.58, 45.56, 39.62, 37.85, 37.78, 36.06, 29.82, 28.05, 27.78, 26.14, 25.05, 24.60, 24.46, 16.54, -4.58. **TOF MS ES +** *m/z*= 2360.2353 (calcd. for $C_{103}H_{143}ClN_{38}O_{24}Si$ 2360.0668 $[M+H]^+$).



GDDC

Compound **21** (0.283 g, 0.12 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.36 mL, 3 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (50 mL) and washed with brine (3 × 50 mL), dried with Na_2SO_4 and concentrated under vacuum. The residue was obtained and followed by adding TFA (3 mL) and Milli-Q water (1 mL) stirring at room temperature for 48 h. The crude product was precipitated from the solution with the neutralization of saturated $NaHCO_3$. Then, the solid product was wash with brine, water, acetone and Et_2O, respectively. The final product was dried under vacuum to give the final product all-*R* **GDDC** as foamy yellow solid (0.191 g, 87%). **GDDC**, **^{1}H NMR (500 MHz, DMSO)** *δ* 10.97 (s, 1H, H_{33}), 9.25 – 9.08 (m, 4H, H_{41}, H_{45}, H_{52} and H_{56}), 8.16 – 8.05 (m, 3H, H_9, H_{17} and H_{25}), 8.02 (s, 1H, H_{35}), 7.91 (s, 1H, H_{31}), 7.84 – 7.57 (m, 9H, H_{37}, H_{42}, H_{43}, H_{44}, H_{48}, H_{53}, H_{54}, H_{55} and H_{59}), 7.50 – 7.36 (m, 3H, H_{62} and H_{63}), 7.13 (d, *J* = 79.0 Hz, 2H, H_{34}), 6.87 – 6.66 (b, 2H, H_5 and H_{13}), 5.69 (b, 1H, H_{21}), 5.20 (s, 2H, H_{32}), 5.12 – 5.02 (m, 3H, H_4, H_{12} and H_{20}), 4.88 (d, *J* = 2.5 Hz, 2H, H_{60}), 4.73 – 4.04 (m, 22H, H_2, H_8, H_{10}, H_{16}, H_{18}, H_{24}, H_{26}, H_{30}, H_{36}, H_{47} and H_{58}), 4.00 – 3.89 (m, 1H, H_{28}), 3.71 – 3.41 (m, 8H, H_3, H_{11}, H_{19} and H_{27}), 2.91 (q, *J* = 6.4 Hz, 6H, H_6, H_{14} and H_{22}), 2.67 – 2.53 (m, 5H, H_1, H_{38} and H_{49}), 2.44 (t, *J* = 7.4 Hz, 4H, H_{40} and H_{51}), 2.08 (d, *J* = 3.4 Hz, 6H, H_{46} and H_{57}), 1.95 – 1.77 (m, 10H, H_7, H_{15}, H_{23}, H_{38} and H_{49}). **^{13}C NMR (126 MHz, DMSO)** *δ* 171.92, 169.36, 166.08, 156.95, 155.30, 155.22, 153.93, 150.39, 150.30, 146.40, 145.87, 143.71, 143.42, 142.80, 139.90, 137.06, 124.53, 124.45, 124.21, 124.12, 122.81, 109.03, 108.90, 93.78, 79.84, 79.29, 77.71, 71.62, 70.64, 70.45, 68.66, 68.23, 63.85, 57.94, 52.83, 50.03, 49.98, 48.62, 46.99, 37.43, 35.53, 30.03, 24.89, 24.52, 24.04. **TOF MS ES +** *m/z*= 1827, 7659 (calcd. for $C_{77}H_{99}N_{38}O_{17}$ 1827,8045 $[M+H]^+$).

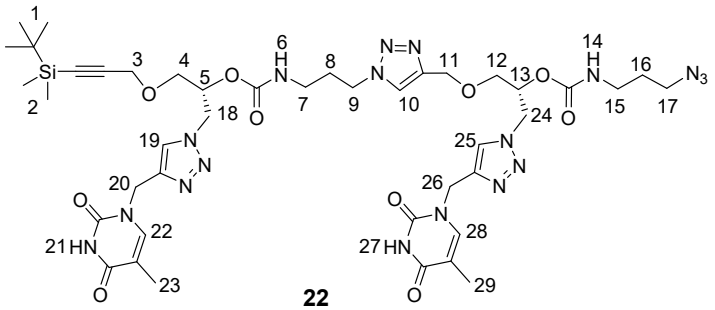
2.5 Synthesis of all-R tetramer TTTT



TT

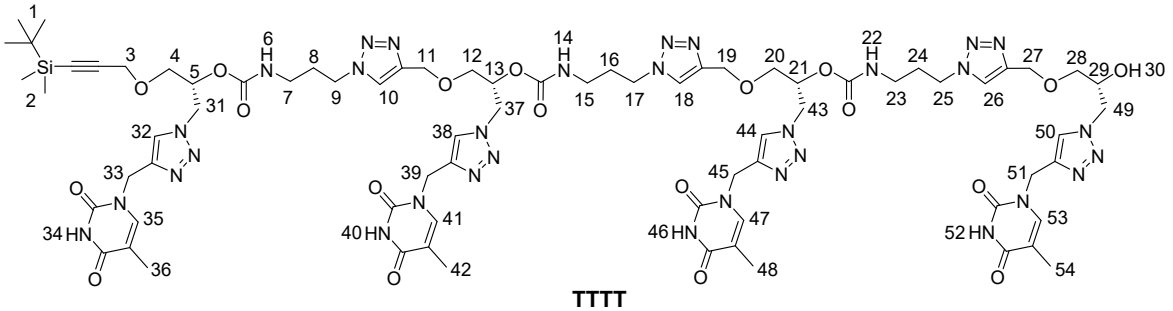
Compound **T** (0.334 g, 0.77 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (1.16 mL, 1.5 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification.

Compound **6** (0.431 g, 1 equiv.) was added into the residue followed by EtOH (5.39 mL) with stirring. Milli-Q water (2.31 mL), sodium ascorbate solution (30.8 mg in 1.2 mL water, 0.2 equiv.) and $CuSO_4$ solution (12.3 mg in 1 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 2/98 to 10/90) to give the final product **TT** as foamy white solid (0.59 g, 87%). **TT**, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.26 (s, 1H, H_{18}), 10.05 (s, 1H, H_{24}), 8.02 – 7.92 (m, 2H, H_{16} and H_{22}), 7.84 (s, 1H, H_{10}), 7.39 – 7.31 (m, 2H, H_{19} and H_{25}), 6.18 (t, *J* = 6.0 Hz, 1H, H_6), 5.16 (d, *J* = 3.6 Hz, 1H, H_5), 4.91 (d, *J* = 12.8 Hz, 4H, H_{17} and H_{23}), 4.72 – 4.35 (m, 8H, H_9, H_{11}, H_{15} and H_{21}), 4.25 – 4.13 (m, 3H, H_3 and H_{13}), 3.72 – 3.47 (m, 4H, H_4 and H_{12}), 3.15 – 3.00 (m, 2H, H_7), 2.12 – 1.97 (m, 2H, H_8), 1.84 (dd, *J* = 7.8, 1.1 Hz, 6H, H_{20} and H_{26}), 0.91 (s, 9H, H_1), 0.09 (s, 6H, H_2). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.82, 164.76, 155.60, 151.57, 151.49, 144.53, 142.26, 141.91, 140.67, 125.56, 123.88, 111.33, 111.27, 101.31, 90.78, 71.59, 71.13, 69.09, 68.27, 64.66, 59.59, 53.15, 50.99, 47.49, 43.19, 37.74, 30.21, 26.15, 16.54, 12.39, -4.58. **HRMS** *m/z*= 879.4043 (calcd. for $C_{38}H_{54}N_{14}O_9Si$ 879.4040 $[M+H]^+$).



22

Compound (*R*)-**TT** (0.282 g, 0.32 mmol) was added in a flask followed by DCM (5 mL), 4-nitrophenyl chloroformate (0.161 g, 2.5 equiv.) and pyridine (65 µL, 2.5 equiv.). The mixture was stirred for 2 h at room temperature followed by solvent evaporation. The residue was dissolved in CH_3CN (5 mL) and added to a flask followed by 3-azido-1-propylamine (0.96 g, 3 eq.) and Et_3N (0.162 mL, 5 eq.). The mixture was stirred for 2 h at room temperature, then DCM (30 mL) and Milli-Q water (30 mL) were added to the mixture. The organic phase was washed with water (2 × 30 mL) and brine (2 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The final product **23** was obtained after passing the residue through a chromatography column (MeOH/DCM= 2/98 to 10/90) as a foamy-white solid (0.28 g, 87%). **22, ^{1}H NMR (500 MHz, DMSO)** δ 11.30 (s, 2H, H_{21} and H_{27}), 8.12 – 7.96 (m, 3H, H_{10}, H_{16} and H_{22}), 7.56 (dd, *J* = 2.3, 1.3 Hz, 2H, H_{19} and H_{25}), 7.46 – 7.27 (b, 2H, H_6 and H_{14}), 5.24 – 4.99 (m, 2H, H_5 and H_{13}), 4.88 (t, *J* = 1.7 Hz, 4H, H_{20} and H_{26}), 4.70 – 4.46 (m, 6H, H_{11}, H_{18} and H_{24}), 4.40 – 4.16 (m, 4H, H_3 and H_9), 3.70 – 3.46 (m, 4H, H_4 and H_{12}), 3.29 (t, *J* = 6.7 Hz, 2H, H_{17}), 3.02 – 2.81 (m, 4H, H_7 and H_{15}), 1.93 – 1.83 (m, 2H, H_8), 1.74 (dd, *J* = 5.6, 1.2 Hz, 6H, H_{23} and H_{29}), 1.56 (t, *J* = 6.8 Hz, 2H, H_{16}), 0.89 (s, 9H, H_1), 0.07 (s, 6H, H_2). **^{13}C NMR (126 MHz, DMSO)** δ 164.28, 155.16, 150.72, 143.42, 142.39, 142.34, 141.03, 124.41, 124.12, 108.85, 102.78, 89.27, 70.49, 70.44, 68.70, 68.27, 63.87, 58.61, 50.12, 48.18, 46.97, 42.01, 37.52, 37.42, 29.99, 28.49, 25.85, 16.11, 11.96, -4.79. **HRMS** *m/z*= 1005.4585 (calcd. for $C_{42}H_{60}N_{18}O_{10}Si$ 1005.4582 $[M+H]^+$).



TTTT

Compound **TT** (0.193 g, 0.22 mmol) was added in a flask followed by EtOAc (5 mL) and TBAF (0.44 mL, 2 equiv.). The mixture was stirred for 30 min at room temperature. 5 mL MeOH was added to quench the reaction followed by

solvent evaporation. The residue was dissolved in DCM (30 mL) and washed with brine (3 × 30 mL), dried with Na_2SO_4 and concentrated under vacuum. The crude product was obtained without any further purification. Compound **22** (0.201 g, 1 equiv.) was added into the residue followed by EtOH (1.54 mL) with stirring. Milli-Q water (0.66 mL), sodium ascorbate solution (8.8 mg in 0.3 mL water, 0.2 equiv.) and $CuSO_4$ solution (3.5 mg in 0.2 mL water, 0.1 equiv.) were successively added to the reaction mixture. The reaction was stirred for 2 h at 50 °C followed by cooling to room temperature. Then, DCM (30 mL) and Na_2EDTA (0.05 M, 30 mL) were added into the mixture followed by air bubbling for 30 min. After that, the organic phase was collected, and the water phase was extracted with DCM (30 × 3 mL). The organic phases were combined, dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (MeOH /DCM = 3/97 to 14/86) to give the final product **TTTT** as foamy white solid (0.322 g, 83%). **TTTT**, **^{1}H NMR (500 MHz, DMSO)** δ 11.30 (d, J = 2.1 Hz, 4H, H_{34}, H_{40}, H_{46}, H_{52}), 8.10 (d, J = 3.3 Hz, 3H, H_{32}, H_{38} and H_{44}), 8.05 – 7.94 (m, 4H, H_{10}, H_{18}, H_{26} and H_{50}), 7.63 – 7.53 (m, 4H, H_{35}, H_{41}, H_{47} and H_{53}), 7.36 – 7.44 (b, 3H, H_6, H_{14} and H_{22}), 5.17 – 5.06 (m, 3H, H_5, H_{13} and H_{21}), 4.88 (d, J = 6.1 Hz, 8H, H_{33}, H_{39}, H_{45} and H_{51}), 4.65 – 4.46 (m, 12H, H_{11}, H_{19}, H_{27}, H_{32}, H_{37} and H_{43}), 4.45 – 4.20 (m, 10H, H_3, H_9, H_{17}, H_{25} and H_{49}), 4.00 – 3.92 (m, 1H, H_{29}), 3.56 (t, J = 24.1, 10.6, 4.7 Hz, 6H, H_4, H_{12} and H_{20}), 3.44 – 3.36 (m, 2H, H_{17}), 2.90 (d, J = 7.4 Hz, 6H, H_7, H_{15} and H_{23}), 1.94 – 1.82 (m, 6H, H_8, H_{16} and H_{24}), 1.78 – 1.67 (m, 12H, H_{36}, H_{42}, H_{48} and H_{54}), 0.88 (s, 9H, H_1), 0.07 (s, 6H, H_2). **^{13}C NMR (126 MHz, DMSO)** δ 164.28, 155.21, 150.73, 143.70, 143.41, 142.38, 142.13, 141.18, 141.04, 124.47, 124.43, 124.14, 124.09, 108.86, 102.78, 89.27, 71.64, 70.56, 70.43, 68.69, 68.26, 68.21, 63.88, 63.86, 58.61, 54.94, 52.90, 50.11, 46.96, 42.15, 42.03, 37.41, 29.97, 25.84, 16.10, 11.95, -4.79. **TOF MS ES +** m/z= 1769,7665 (calcd. for $C_{74}H_{100}N_{32}O_{19}Si$ 1769,7685 $[M+H]^+$).

S3. TOF-MS/MS of the oligomers

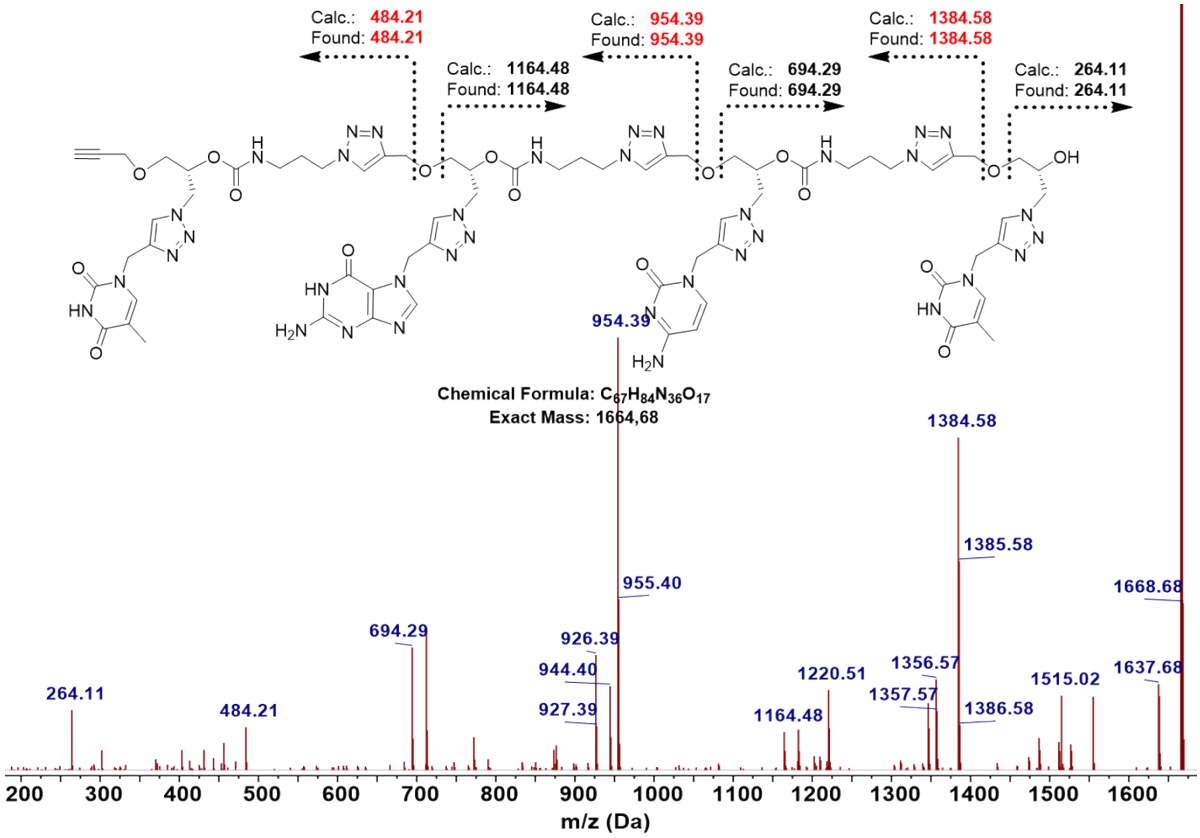


Figure S3.1 - TOF-MS/MS of TGCT.

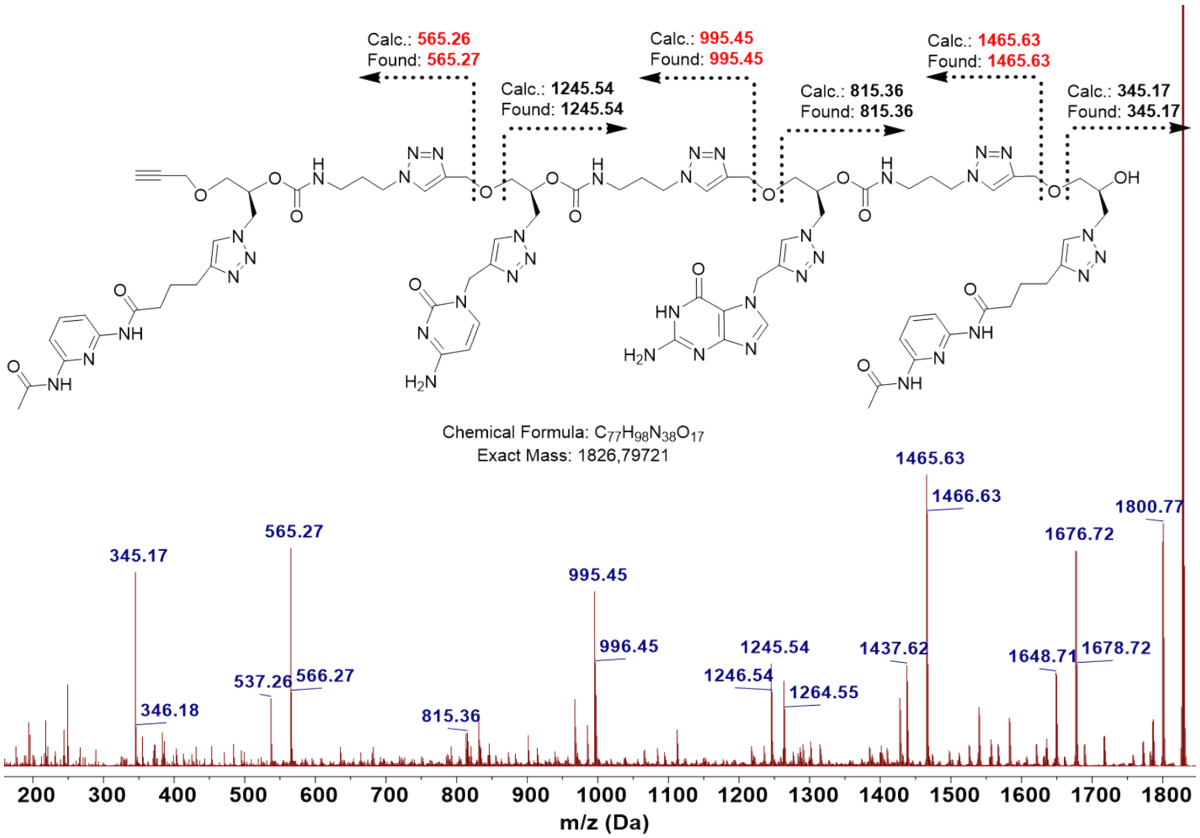


Figure S3.2 - TOF-MS/MS of all-*R* DCGD.

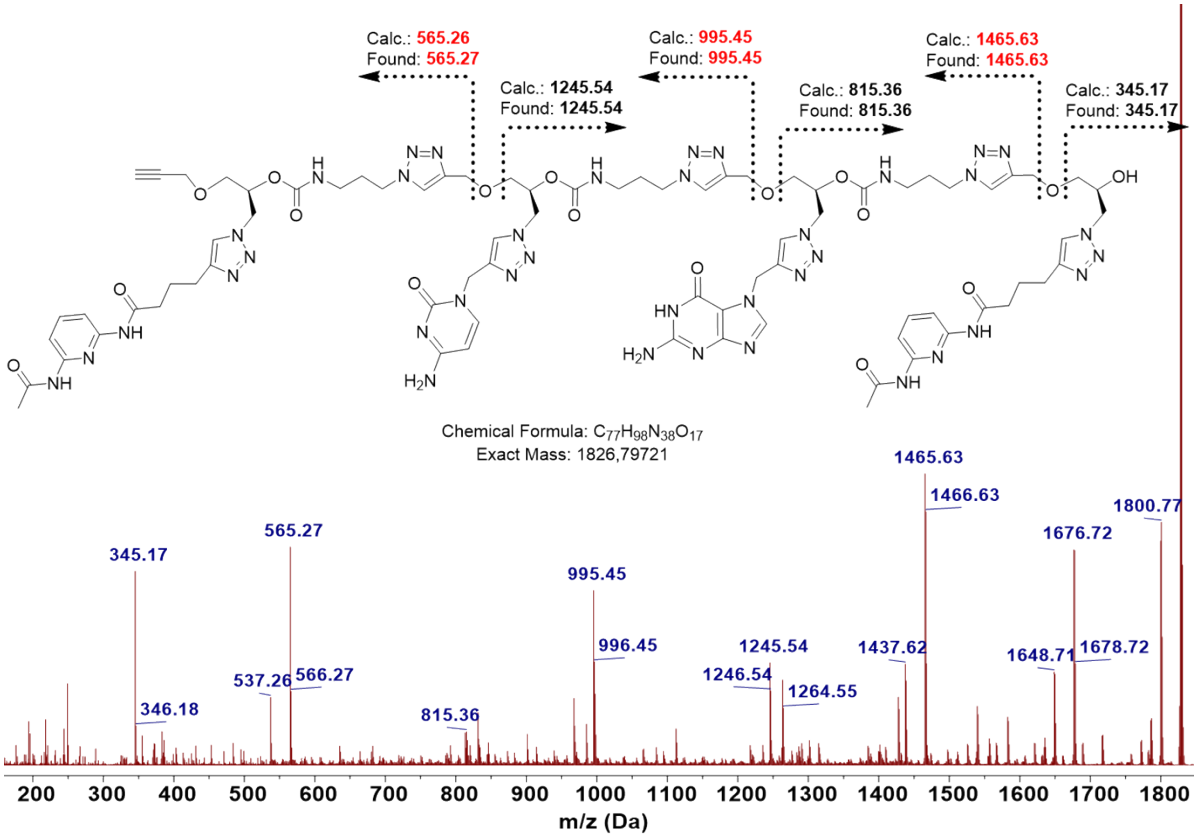


Figure S3.3 - TOF-MS/MS of all-*S* DCGD.

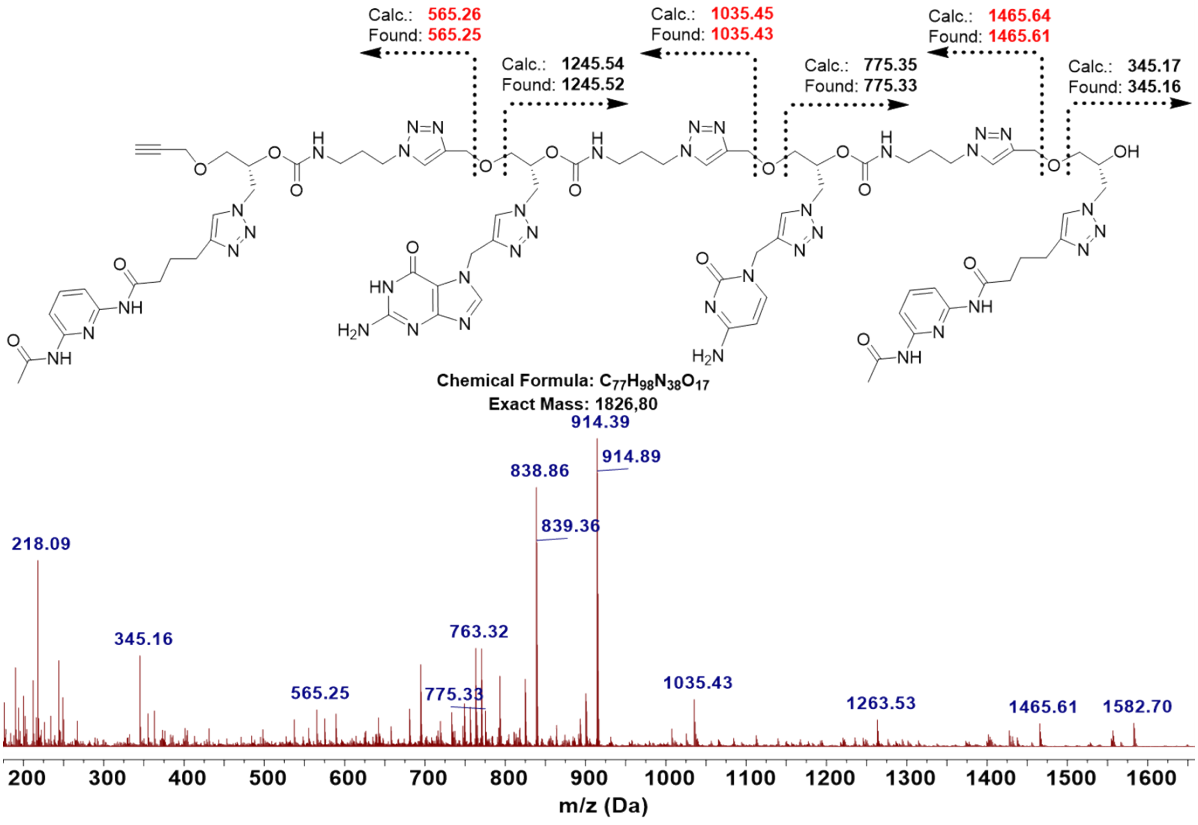


Figure S3.4 - TOF-MS/MS of DGCD.

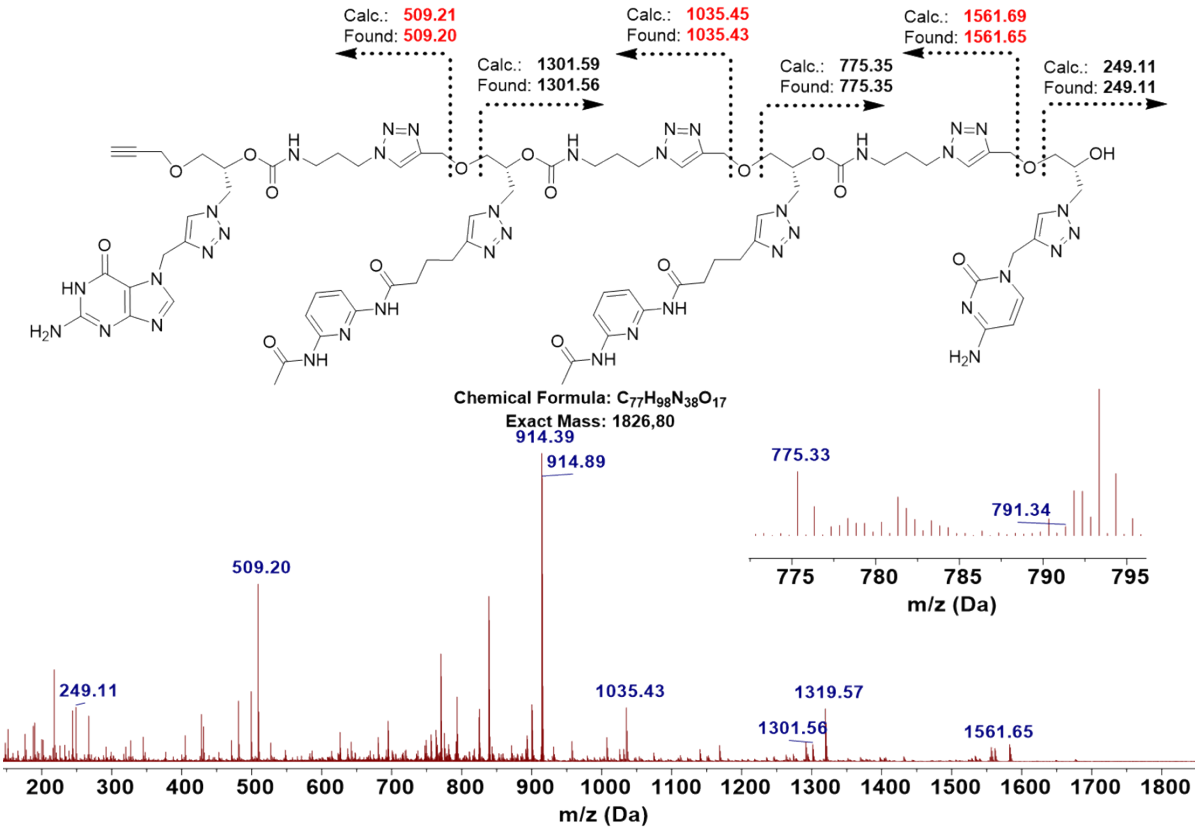


Figure S3.5 - TOF-MS/MS of GDDC.

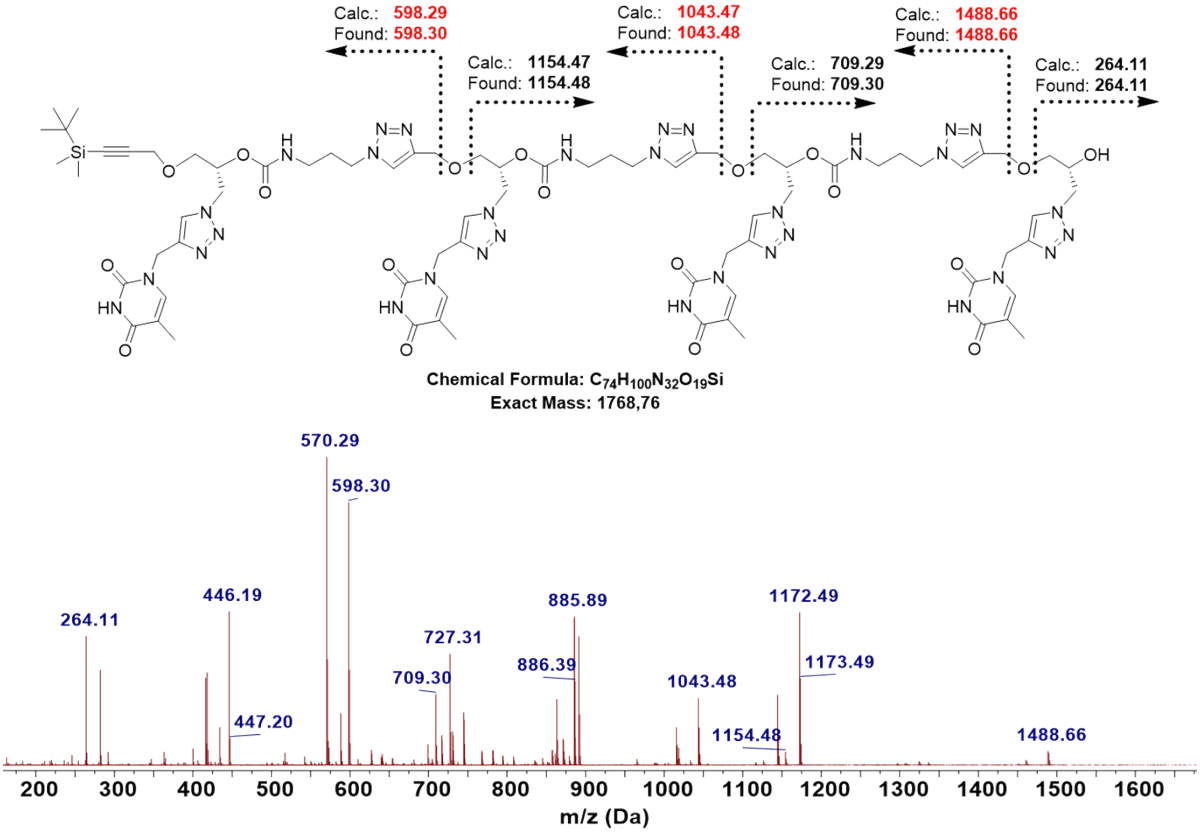


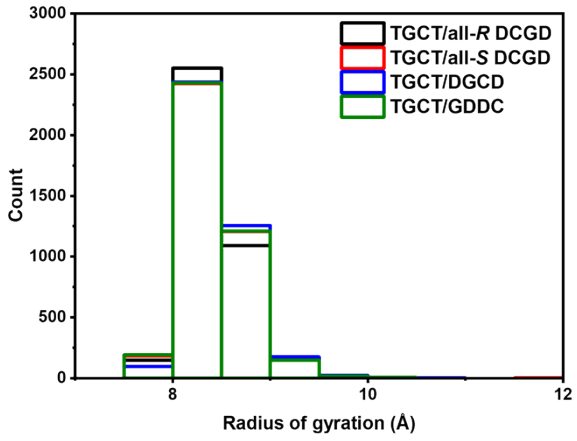
Figure S3.6 - TOF-MS/MS of TTTT.

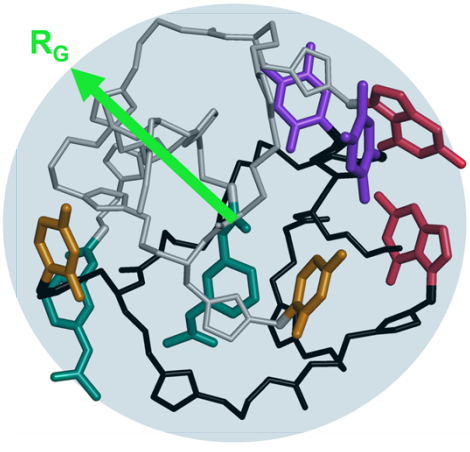
S4. Determination by NMR of the binding constants of the monomer units

S5. All-atom molecular dynamics (MD) simulations

All-atom molecular dynamics (MD) simulations were performed using the GPU version of AMBER16 package. The five oligomeric strands (all-*R* TGCT, all-*R* DCGD, all-*S* DCGD, all-*R* DGCD and all-*R* GDDC) studied by MD were built by joining small molecular fragments together. The monomers were first constructed within the Avogadro software.[4] The partial atomic charges of each fragment were calculated using the semi-empirical AM1-BCC model[5] as implemented within the antechamber module of AMBER16, whereas other force field parameters are from the 'General AMBER Force Field (GAFF 2.1, version updated in April 2016).[6] The individual molecular fragments were then connected in the desired sequence with the LEaP module of AMBER16 to constitute the complete oligomeric chains. When building the target chain/probe chain assemblies, the latter was translated by 25 Å in the x, y and z directions to avoid intermolecular contacts in the starting structure. A geometry optimization was then performed by molecular mechanics, with a total of 10,000 steps distributed in 1,000 steps of steepest descent and 9,000 steps of conjugated gradient, to get a stable starting point for the subsequent MD simulations. These were carried out with an implicit solvent model, the Generalized Born (GB) model,[7] to ensure a sufficient conformational sampling in a reasonable computational time. A dielectric constant of 37.5 was considered, i.e., the dielectric constant of acetonitrile at room temperature. The temperature in all MD simulations was set to 300 K and controlled by the Langevin thermostat with a coupling constant of 1.0 ps and combined with a pseudo-random seed generator. Frames were collected at 1-ns intervals for a total simulation length of 1 µs, resulting in a set of 1,000 conformations per replica. Four independent replicas were launched for each heteromolecular assembly, leading to a total of 4,000 conformations by duplex. The four duplexes studied by MD are hereafter referred to as **TGCT/all-*R* DCGD**, **TGCT/all-*S* DCGD**, **TGCT/DGCD** and **TGCT/GDDC**. The resulting trajectories were visualized and the MD snapshots were created with PyMOL.[8]

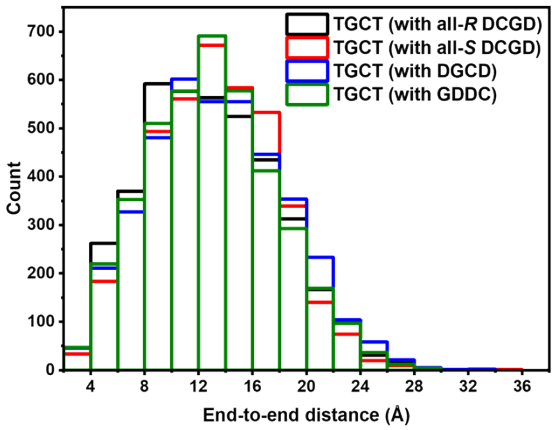
The analyses of the MD trajectories were performed using the cpptraj module available in AmberTools. The Radii of gyration (R_G) were calculated in reference to the heavy atoms, with omission of hydrogen atoms. The end-to-end distances were measured between the first carbon atom of the oligomers and a carbon atom of the last nucleobase analog. A cut-off of 3.0 Å for the donor (D)-acceptor (A) distance and 135° for the A-H-D angle were set as criteria to detect possible hydrogen-bonds. An H-bond is described as "complementary" if it is intermolecular and occurs between a T-D or G-C pair of nucleobase analogs. An aromatic interaction between two cycles was detected if two geometric criteria were satisfied: the distance between the center-of-mass (COM) is less than 5 Å and the angle between the planes of the cycles is less than 45° or more than 135°.

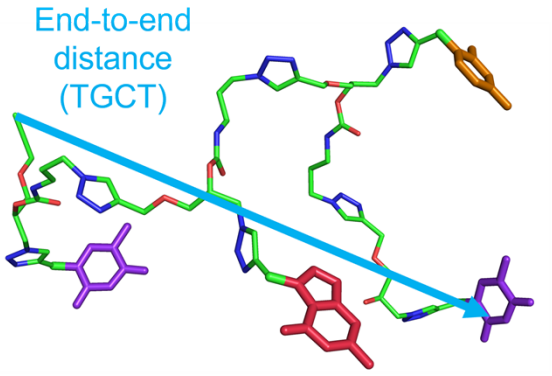




	TGCT/all-*R* DCGD	TGCT/all-*S* DCGD	TGCT/DGCD	TGCT/GDDC
Average ± Std dev (Å)	8.5 ± 1.1	8.5 ± 0.8	8.5 ± 0.9	8.4 ± 0.6
Max (Å)	27.4	30.5	27.4	24
Min (Å)	7.8	7.7	7.8	7.7

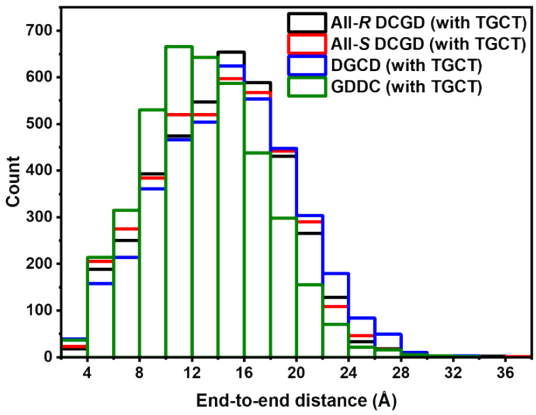
Figure S5.1 - Distribution profiles of the radius of gyration (R_G, illustrated on a snapshot on the right) for a total of 4,000 conformations for the pairs of oligomers **TGCT/all-*R* DCGD**, **TGCT/all-*S* DCGD**, **TGCT/DGCD** and **TGCT/GDDC**. Bin sizes were set to 0.5 Å for all distributions. Averages, standard deviations, minimum and maximum values of the radii of gyration for the different sequences are gathered in the table.

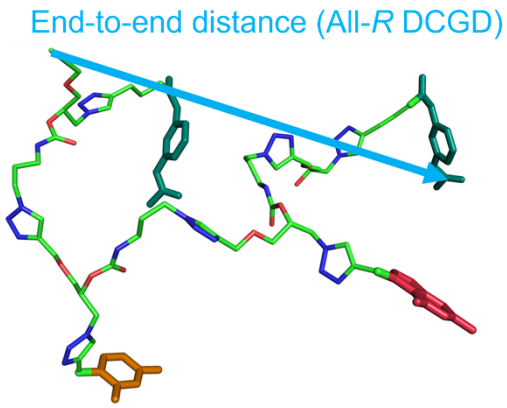




	TGCT (with all-*R* DCGD)	TGCT (with all-*S* DCGD)	TGCT (with DGCD)	TGCT (with GDDC)
Average ± Std dev (Å)	12.8 ± 4.9	13.2 ± 4.5	13.5 ± 5	13 ± 4.7
Max (Å)	34.2	34.2	32	29.7
Min (Å)	3.3	3.2	3.2	3.2

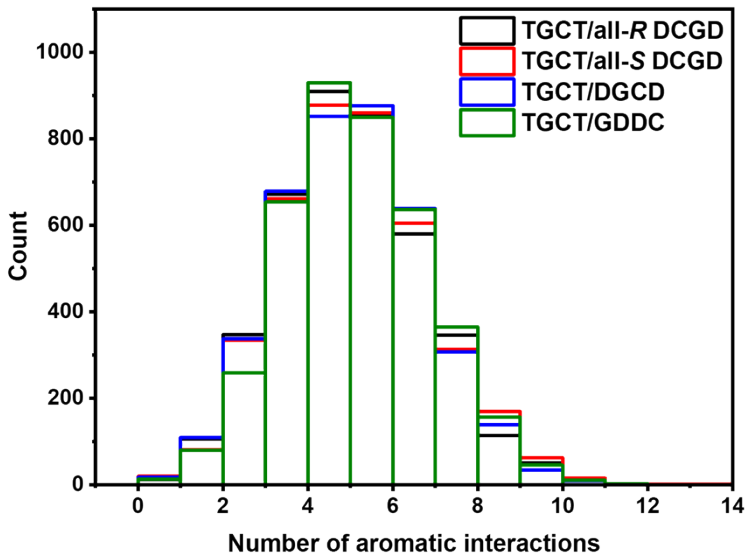
Figure S5.2 - Distribution profiles of the end-to-end distance for a total number of 4,000 conformations for the target chain TGCT, when assembled with the four different probe chains. Bin sizes were set to 2 Å for all distributions. Averages, standard deviations, minimum and maximum values of the end-to-end distances for the different sequences are gathered in the table. The carbon atoms of the target chain, TGCT, between which the distance is measured are shown by the cyan arrow, on the snapshot on the right of the figure.





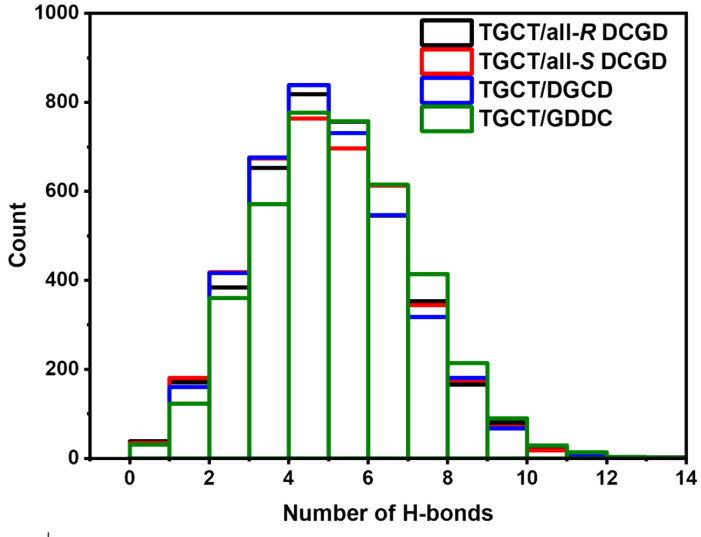
	All-*R* DCGD (with TGCT)	All-*S* DCGD (with TGCT)	DGCD (with TGCT)	GDDC (with TGCT)
Average ± Std dev (Å)	14.2 ± 4.8	14.1 ± 4.9	14.8 ± 5.2	13 ± 4.6
Max (Å)	35.8	37.4	33	39
Min (Å)	3.2	3.4	3.4	3.1

Figure S5.3 - Distribution profiles of the end-to-end distance for a total number of 4,000 conformations for the four different probe chains, when assembled with the target chain, TGCT. Bin sizes were set to 2 Å for all distributions. Averages, standard deviations, minimum and maximum values of the end-to-end distances for the different sequences are gathered in the table. The carbon atoms between which the distance is measured are shown for the All-*R* DCGD probe chain by the cyan arrow, on the snapshot on the right of the figure.



	TGCT/all-*R* DCGD	TGCT/all-*S* DCGD	TGCT/DGCD	TGCT/GDDC
Average ± Std dev	4.5 ± 1.7	4.6 ± 1.8	4.5 ± 1.7	4.7 ± 1.7
Max	11	13	11	11
Min	0	0	0	0

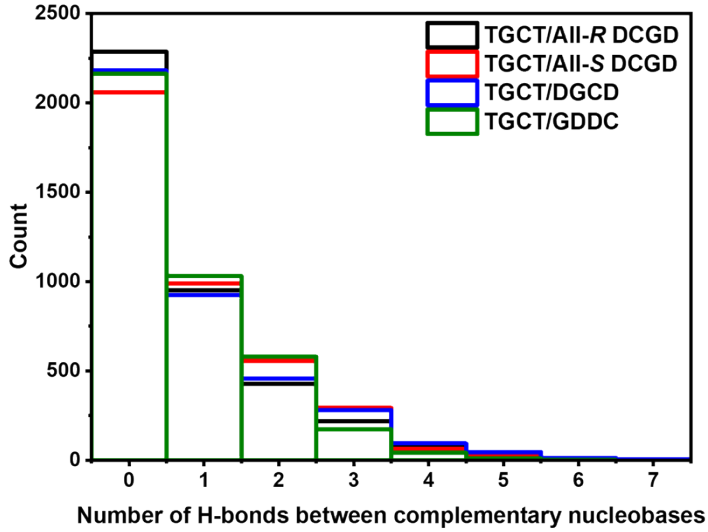
Figure S5.4 - Distribution profiles of the number of aromatic interactions for a total number of 4,000 conformations for the pairs of oligomers **TGCT/all-*R* DCGD**, **TGCT/all-*S* DCGD**, **TGCT/DGCD** and **TGCT/GDDC**. Bin sizes were set to one interaction for all distributions. Averages, standard deviations, minimum and maximum values of the number of aromatic interactions for the different sequences are gathered in the table.



	TGCT/all-*R* DCGD	TGCT/all-*S* DCGD	TGCT/DGCD	TGCT/GDDC
Average ± Std dev	4.5 ± 2	4.5 ± 2	4.5 ± 1.9	4.8 ± 2
Max	13	12	11	13
Min	0	0	0	0

Figure S5.5 - Distribution profiles of the number of hydrogen bonds for a total number of 4,000 conformations for the pairs of oligomers **TGCT/all-*R* DCGD**, **TGCT/all-*S* DCGD**, **TGCT/DGCD** and **TGCT/GDDC**. Bin sizes were set to one

interaction for all distributions. Averages, standard deviations, minimum and maximum values of the number of H-bonds for the different sequences are gathered in the table.



	TGCT/all-*R* DCGD	TGCT/all-*S* DCGD	TGCT/DGCD	TGCT/GDDC
Average ± Std dev	0.7 ± 1.1	0.9 ± 1.1	0.8 ± 1.2	0.7 ± 1
Max	13	12	11	13
Min	0	0	0	0

Figure S5.6 - Distribution profiles of the number of hydrogen bonds between complementary nucleobase pairs (T-D and G-C) for a total number of 4,000 conformations for the pairs of oligomers **TGCT/all-*R* DCGD**, **TGCT/all-*S* DCGD**, **TGCT/DGCD** and **TGCT/GDDC**. Bin sizes were set to one interaction for all distributions. Averages, standard deviations, minimum and maximum values of the number of H-bonds for the different sequences are gathered in the table.

	TGCT/all-*R* DCGD	TGCT/all-*S* DCGD	TGCT/DGCD	TGCT/GDDC
R_G (Å)	8.5 ± 1.1	8.5 ± 0.8	8.5 ± 0.9	8.4 ± 0.6
End-to-end distance: target chain (Å)	12.8 ± 4.9	13.2 ± 4.5	13.5 ± 5	13 ± 4.7
End-to-end distance: probe chain (Å)	14.2 ± 4.8	14.1 ± 4.9	14.8 ± 5.2	13 ± 4.6
Number of aromatic interactions per conformation	4.5 ± 1.7	4.6 ± 1.8	4.5 ± 1.7	4.7 ± 1.7
Number of H-bonds per conformation	4.5 ± 2	4.5 ± 2	4.5 ± 1.9	4.8 ± 2
Number of complementary H-bonds per conformation	0.7 ± 1.1	0.9 ± 1.1	0.8 ± 1.2	0.7 ± 1

Table S5.1 – Summary table of the MD data presented in the figures above.

S6. X-ray reflectometry results

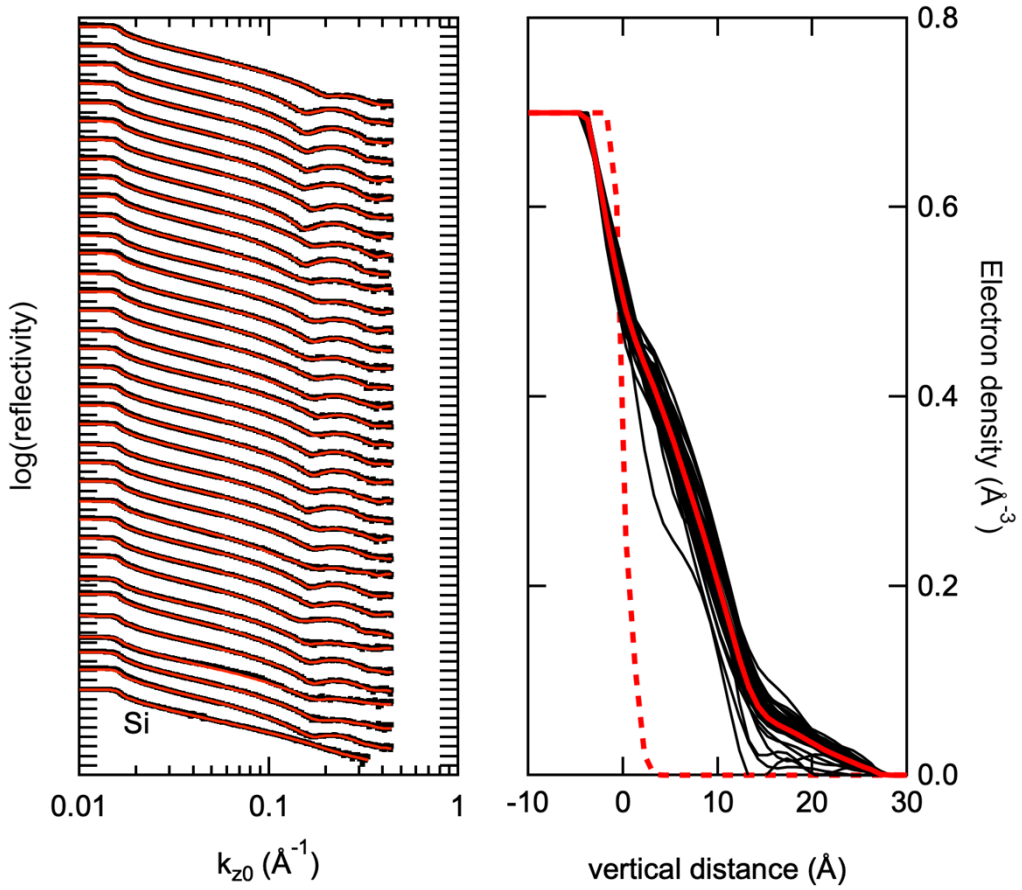


Figure S6.1 – **Left.** X-ray reflectograms (black dots) and fits (red lines) of thirty-fiveSi wafers ((100), native oxide-covered) gas-phase silanized by AzUTMS. The bottom curve is the XRR of a bare Si wafer. The curves are displaced vertically for clarity. **Right.** Electron density profiles corresponding to the fits of the XRR (black lines except for the bare Si wafer which is dislayed as the dashed red line). The thick red line is the average electron density profile of these thirty-five AzUTMS-silanized wafers.

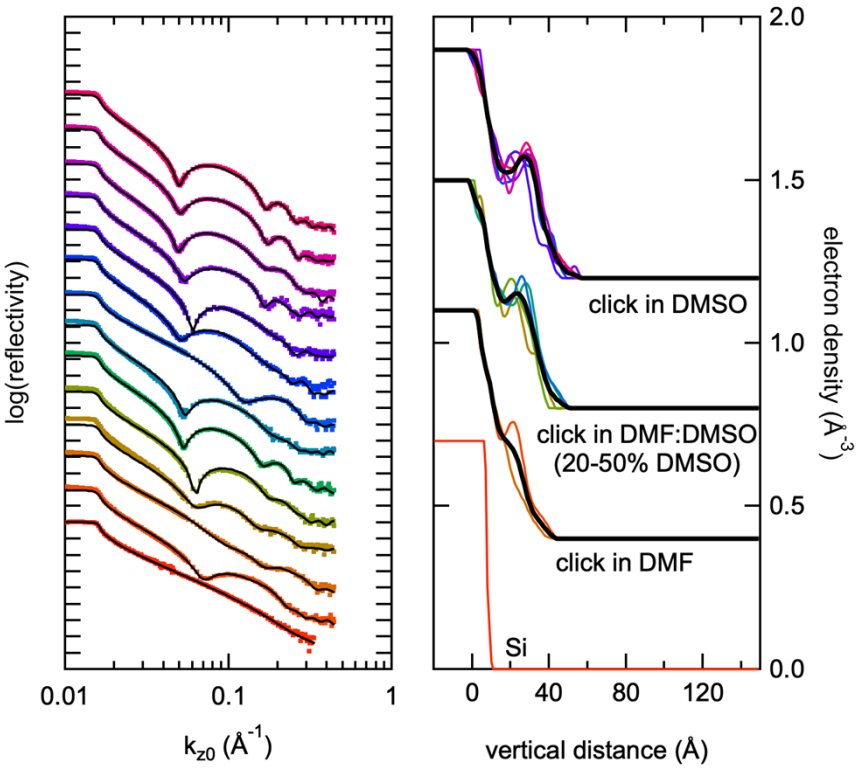


Figure S6.2 – **Left.** X-ray reflectograms (colored dots) and fits (black lines) all-R TGCT layers clicked in different solvents onto AzUTMS-silanized Si wafers. The bottom curve is the XRR of a bare Si wafer. The curves are displaced vertically for clarity. **Right.** Electron density profiles corresponding to the fits of the XRR (colored lines; same color code as in the left panel). The thick black lines are the average electron density profiles of the modified wafers.

S7. XPS of grafted layers

S7.1. AzUTMS layers

The AzUTMS layer grafted on a silicon wafer was characterized by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum is shown in Figure S7.1, showing the presence of Si, O, C, N and adventitious contaminants such as Na or Zn.

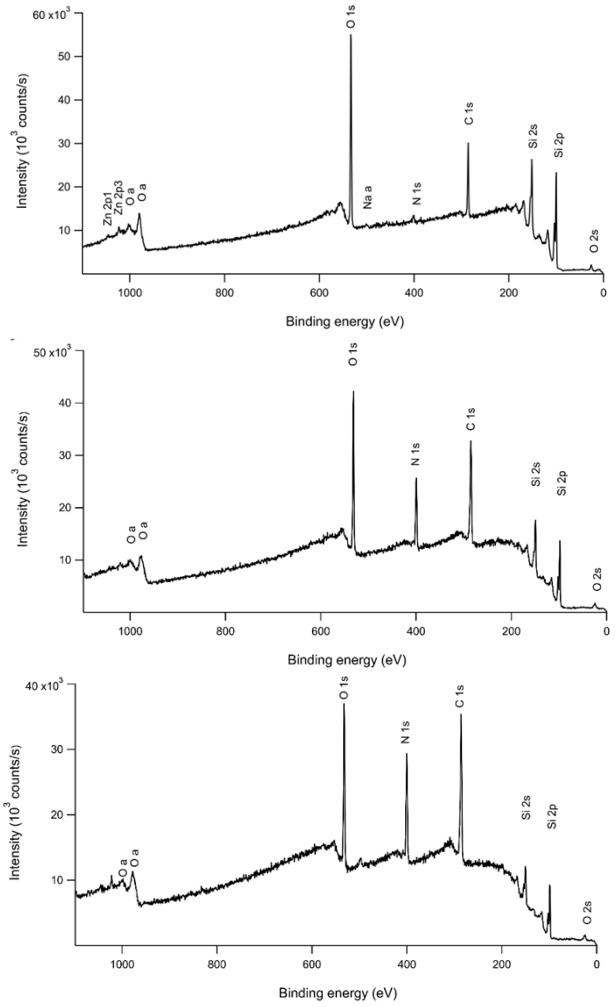


Figure S7.1 - XPS survey scans of (**top**) a monolayer assembled from AzUTMS on a Si (100) wafer with its native oxide layer; (**middle**) the same after clicking the TGCT oligomer in DMSO; (**bottom**) the same after recognition with all-*R* DCGD.

High resolution XPS spectra in the N 1s and C 1s regions are shown in Fig.S7.2 (top). In the N 1s region (Fig.S7.2, top left), the AzUTMS layer shows two azide peaks in a 2:1 ratio, the larger one arising from N and N^- atoms and the smaller one from N^+ atoms. An additional peak (400.3 eV) corresponding to decomposed azide groups upon X-ray exposure is also observed.[9] In the C 1s region (Fig.S7.2 right), the high-resolution spectrum consists of a broad signal at a mean binding energy of 285.0 eV. The large dispersion value (1.4 eV FWHM) of the fitted function is consistent with a peak essentially resulting from contributions of C-C, C-H and C-N bonds.

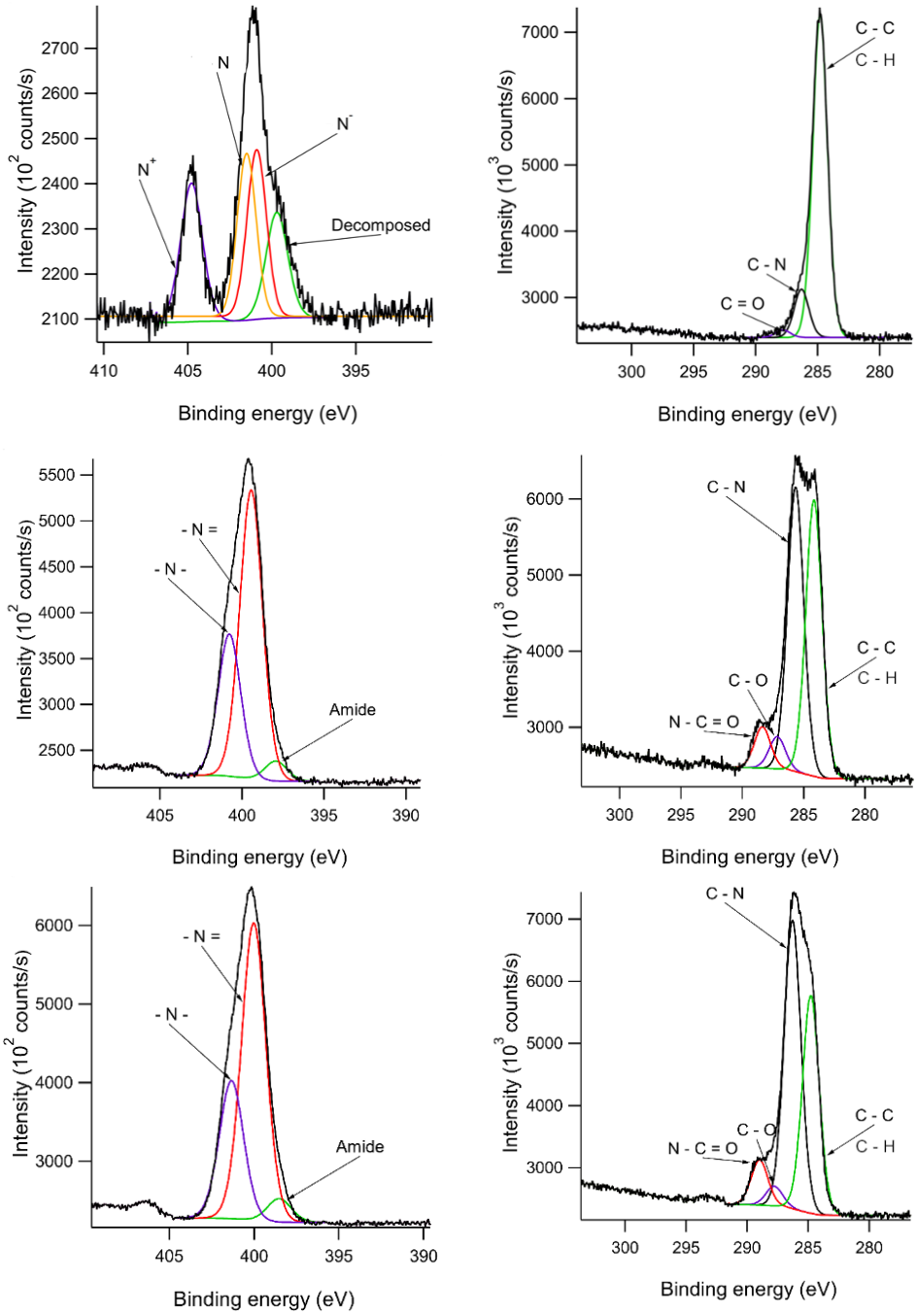


Figure S7.2 – High resolution XPS spectra in the N 1s (**left**) and C 1s (**right**) regions of (**top**) a monolayer assembled from 11-azidoundecyltrimethoxysilane on a Si (100) wafer with its native oxide layer; (**middle**) the same after clicking TGCT in DMSO; (**bottom**) the same after recognition with all-*R* DCGD. Black curves are experimental spectra, colored curves show the components as obtained from spectral decomposition by fitting.

S7.2. TGCT layers

The sample obtained after clicking TGCT target chains on the AzUTMS layer in DMSO was also measured by XPS. The survey scan and high-resolution scans are displayed in the middle panels of Fig.S7.1 and Fig.S7.2, respectively. The decrease of the Si 2p signals together with the increase of N 1s and C 1s signals correspond to the burial of the Si wafer below a layer of TGCT. On the high-resolution scan of the N 1s region, the azide signal vanishes (signal at 405.4 eV), and new peaks corresponding to the nucleobases and triazole rings appear, together with a smaller signal from the urethane and amide groups. Simultaneously, the C 1s region of the XPS spectra exhibits a major component at 287.5 - 287.6 eV which is assigned to C–N. Additionally, N-C=O groups appear at 290.2-290.3 eV. These observations fully confirm the grafting of the TGCT layer on the surface.

S7.3. TGCT layer after recognition by all-R DCGD

The sample grafted by TGCT then exposed to all-*R* DCGD probe chains was also measured by XPS. The comparison of survey scans of both AzUTMS (Fig.S7.1, top panel) and TGCT samples (Fig.S7.1, middle panel) shows a significant decrease of Si 2p signals and an increase of N 1s and C 1s signals, confirming the adsorption of the probe oligomer on the surface. The N 1s spectrum of this sample (Fig.S7.2, bottom left) is similar to the one of the TGCT-grafted layer whereas the C 1s spectrum shows an increase of the C-N signal and a decrease of the C-C/H signal, resulting from a decreased contribution of the AzUTMS layer.

S8. In-situ ellipsometry

S8.1. Determination of the relationship between the change of Δ and the amount of adsorbed probe oligomer.
The amount of oligomer irreversibly-adsorbed over a TGCT-modified wafer was obtained from the variation of the ellipsometric angle Δ before and after adsorption/rinsing of the oligomer over the TGCT layer. Simulations of the (Ψ,Δ) ellipsometric trajectories parametrized by wavelength λ (from 400 to 700 nm) are shown in Fig.S8.1 (left). To draw these trajectories, we considered a model consisting of a Si wafer with 1.3 nm of native oxide, modified by a layer of AzUTMS of 1.05 nm thickness (the average experimental value) covered by a solvated layer of thickness d_{layer} made of a mixture of target/probe oligomers in acetonitrile:DMSO 5:1 at 25°C; this solvated layer contains a volume fraction f_{oligo} of oligomers, the remaining part being the solvent. The indices of refraction used for each layer are detailed in section S8.2. The simulations were performed with a home-made program written in the Igor Pro (Wavemetrics) macro-programming language based on standard ellipsometry equations.[10] The program is available upon request.

In Fig.S8.1, the black dotted line shows the trajectory for an AzUTMS-modified wafer measured in the ACN:DMSO 5:1 solvent. When adding a layer of precision oligomers containing no solvent (red curves), the trajectories shift towards lower values of Δ without significant changes of Ψ, the trajectories staying parallel within experimental precision. If layers containing 50% oligomer and 50% solvent are considered (blue curves), the trajectories behave similarly but the amplitude of the shift of Δ is approximately decreased by a factor of two. A master curve is drawn in Fig.S8.1 (right), in which the average value of Δ computed over the 400-700 nm wavelength range is plotted versus the product d_{layer} x f_{oligo} for different values of f_{oligo}. All data points fall over a single line of slope -1.2615 °/nm, in the range of possible values for d_{layer} x f_{oligo}.

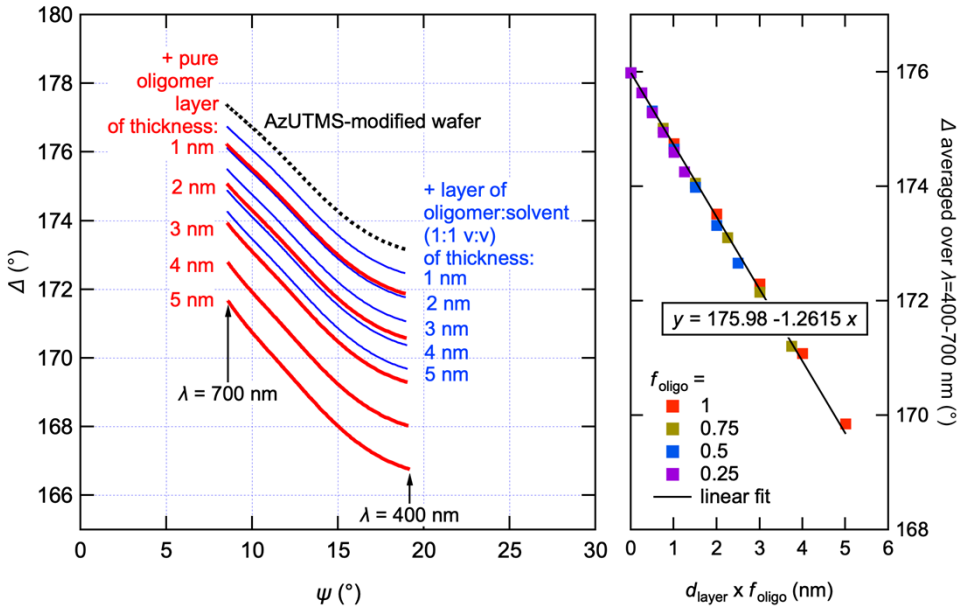


Figure S8.1. (**left**) Simulated ellipsometric trajectories drawn with wavelength as parameter for AzUTMS-modified wafers covered by layers of oligomer:solvent of varying thickness and solvent content, as indicated, measured in ACN:DMSO 5:1 v:v solvent. (**right**) Master line relating the average value of the ellipsometric angle Δ to the product of thickness and oligomer volume fraction in the layer.

The product d_{layer} x f_{oligo} is the volume of oligomer resting over the silanized wafer, per surface area of wafer. Therefore, suppose an average value Δ_A is measured for a sample grafted by a TGCT target layer at equilibrium with the solvent, and an average value Δ_B is measured after adsorption of a probe chain and rinsing; then, the difference (Δ_B - Δ_A)/(-1.2615) [nm] is the adsorbed volume of probe chain per unit area of wafer. The advantage of subtracting these two numbers is that systematic errors due to the presence of cell windows cancel out.

S8.2. Indices of refraction.
The simulations of Fig.S8.1 require the complex indices of refraction of the different materials in the 400-700 nm wavelength range.

- For Si and silicon oxide, the values tabulated in Palik's handbook were used.[11]
- For the AzUTMS layer, a constant value of 1.458 was taken for the real part of the index of refraction, with no absorption, as derived from the ellipsometric analysis of the AzUTMS-silanized wafers discussed in the companion article. Note that the conclusions of section S8.1 are insensitive to the exact values taken for this index of refraction owing to the subtraction of two values of Δ.
- For the ACN:DMSO 5:1 mixture, the refractive index was obtained by the Newton approximation (eq.1)[12] and the empirical dependences on wavelength of DMSO and ACN refractive indices described elsewhere (eqs.2 and 3):[13]

$$n_{solvent}^{2} = \frac{n_{DMSO}^{2} + 5n_{ACN}^{2}}{6} \quad (1)$$

$$n_{ACN}(\lambda) = 1.33212 + \frac{3525.78231}{\lambda^2} - \frac{32631699.6}{\lambda^4} + \frac{2.267 \cdot 10^{12}}{\lambda^6} \quad (2)$$

$$n_{DMSO}(\lambda) = \sqrt{1 + \frac{0.04419\,\lambda^2}{\lambda^2 - 46390.67309} + \frac{1.09101\,\lambda^2}{\lambda^2 - 12215.43949}} \quad (3),$$

with the wavelength λ expressed in nm.

- For the oligomers, we assumed that all of them have very similar refractive indices owing to their close chemical compositions. Therefore, we deposited by spin-coating a TGCT solution in methanol (10 mg/mL, spin rate 500 rpm) on a silicon wafer, and measured the thickness of the layer by XRR. The sample was then measured by spectroscopic ellipsometry. The XRR-determined value of thickness was then used to extract the index of refraction of the TGCT layer from the ellipsometric data, using a Cauchy transparent model to express the dependence of index of refraction with wavelength. The final result at 25°C is:

$$n_{TGCT} = 1.49944 - \frac{1503.02}{\lambda^2} + \frac{1.32138\,10^{9}}{\lambda^4}$$

, with λ the wavelength in vacuum, expressed in nm.

- For the solvent-swollen layer of oligomers with an oligomer volume fraction f_{oligo}, the index of refraction was computed with Bruggeman's effective medium approximation.[14]

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