Supporting Information

Multifunctional imine-POSS as uncommon 3D nanobuilding blocks for supramolecular hybrid materials: Synthesis, structural characterization, and properties

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Experimental Section

General procedures and chemicals: Solvents: dichloromethane, chloroform, hexane, and methanol (HPLC grade) were used as received. (3-Aminopropyl)triethoxysilane (99%, Aldrich), HCl (36–38%, Avantor Performance Materials Poland S.A.), MgSO₄, NaHCO₃, (Avantor Performance Materials Poland S.A.), Na(CH₃COO)₂BH (97%, Aldrich), and triethylamine (99.5%, Aldrich) were used without further purification. Aldehydes: 2-hydroxy-1-naphthaldehyde, 4-bromobenzaldehyde, 4-nitrobenzaldehyde, benzaldehyde, and salicylaldehyde were of reagent-grade quality and were purchased from Sigma-Aldrich. Chromium(III) acetylacetone was prepared following the described procedure;¹ octa(3-aminopropyl)disilsesquioxane hydrochloride, and octa(3-aminopropyl)disilsesquioxane trifluoromethanesulfonate were prepared with a method based on a previously reported procedure.²

Methods: ¹H NMR and ¹³C NMR spectra were recorded using a Bruker Avance 500 or a Bruker Avance III 600 spectrometer equipped with broadband inverse gradient probe heads. ¹H NMR spectra were collected at 500.13 MHz using a relaxation delay of 1.0 s and a pulse width of 7°. Spectra were referred to the residual solvent signals (DMSO-d₆, 2.50; CDCl₃, 7.26; HOD, 4.79 for D₂O ppm) or TMS (0.00 ppm) as an internal reference. ¹³C NMR spectra were collected at 125.8 MHz using a relaxation delay of 2.0 s and a pulse width of 15° and referred to the solvent signals ((¹²CH₃)₂SO 39.52, ¹³CDCl₃ 77.16 ppm). ²⁹Si NMR spectra were recorded on a Bruker AMX-300 spectrometer using Wildmad PTFE-FEP 5 mm tube liners and were collected at 59.6 MHz using a relaxation delay of 10.0 s and a pulse width of 13°. Cr(aacac)₃ was added at a concentration of ~10⁻² mol/L as a shiftless relaxation agent. Chemical shifts were referenced to tetramethylsilane (TMS) (δ = 0.00 ppm). For proton and carbon assignments, COSY, HMBC, and HMQC experiments were performed on the Bruker Avance 500 spectrometer. Two-dimensional NMR spectra were recorded with a 1.0 s recovery delay and with gradient selection. Fourier-Transform Infrared Spectra (FTIR) were recorded on a Bruker Vertex 70 FTIR spectrometer in the transmission mode. The FTIR sample chamber was flushed continuously with N₂ prior to data acquisition in the range 4000–400 cm⁻¹ with a precision of ±1 cm⁻¹. Sample spectra were recorded as Nujol mulls sandwiched between CsI plates or as KBr pellets, optical grade; random cuttings of KBr ground with 1.0 wt % of the sample to be analyzed pressed. High resolution and accurate mass spectra were carried out on a Bruker microTOF-Q spectrometer equipped with an ESI source. Samples were dissolved in chloroform or methanol. The experimental parameters were as follows: scan range: 200–2500 m/z; drying gas: nitrogen; temperature: 200 °C; ion source voltage: 4500 V; in-source collision energy: 10 eV. The instrument operated in the positive ion mode and was calibrated externally with the Tunemix mixture (Bruker Daltonics). The analyzed solutions were introduced at a flow rate of 4.0 L/min. The Compass Data Analysis software was used to determine the formulae of the compounds. The distance between the isotopic peaks allowed the calculation of the charge of the analyzed ions. Elemental analyses (C, H, and N) were performed using a Vario EL III element analyzer. Quantitative analysis of Br was carried out using Mikro-K-Elemental by means of Schoeniger’s method. UV-Vis absorption spectra were recorded at room temperature in the wavelength range of 230–800 nm at intervals of 0.5 nm by a Cary 500 SCAN UV-VIS-NIR spectrophotometer. Measurements were performed on a 3.5 mL sample in a quartz cell with a path length of 10 mm, a bandwidth of 1.0 nm, and a scan speed of 250 nm/min. The concentration of the samples was ca. 10⁻⁵ mol·dm⁻³ to give absorption maximum for absorption studies to about 50% for a 1 cm path length. Thermogravimetry and differential thermal analyses (simultaneous TG-DTA) were recorded with a Setaram SETSYS 16/18 instrument. The calibrations of temperature and weight were performed following the procedure reported in the instruction manual of the equipment using indium (NIST SRM 2232) as the standard material for temperature and a set of exactly weighed samples supplied by Shimadzu for weight. Samples for thermogravimetric characterization were placed in open alumina crucibles in synthetic air (60% N₂, 40% O₂) or nitrogen dynamic atmosphere (flow rate: 1·dm⁻³·h⁻¹). A heating rate of 10 °C·min⁻¹ was applied, and all samples were studied between 30 and 1000 °C. For the compounds in which solvent molecules were found in the crystal lattice (3 and 5), additionally TG was conducted in the air atmosphere. Based on the weight
losses, the amount of the solvent was calculated. The decomposition onset temperature was
determined as the temperature at the maximum rate of weight loss (T_m) for the first weight loss. The
purity of all novel compounds was determined by combustion analysis, which confirmed that they
were at least 99% pure. Differential Scanning Calorimetry (DSC) traces were obtained using a
Perkin Elmer model 8500. Temperature and enthalpy calibrations were performed using high purity
standards (n-heptane and indium). The samples (2–5 mg, obtained via crystallization) were placed
in sealed Al-pans at a heating rate of 10 °C-min⁻¹ and a helium flow of 20.0 mL-min⁻¹. The images
were obtained using a FEI Tecnai G2 F20 X-TWIN Transmission Electron Microscope equipped
with a Penta FET EDX detector at an acceleration voltage of 200 kV. The colloidal suspension of
the sample with a concentration of about 5 mg·mL⁻¹ in methanol was drop-cast on a 3 mm holey
carbon copper grid and dried under an IR lamp for 15 min. The progress of the reaction was
monitored by thin layer chromatography (TLC). TLC was performed on Merck silica gel 60 F254
plates. Chromatograms were visualized using UV light (254 nm). For the detection of unreacted
amine, the chromatograms were first dipped in a 5% (w/v) solution of ninhydrin in 95% aqueous
ethanol, and finally charred on a hot plate. Preparative separations were performed on a Sepacore®
chromatography system (Büchi Labortechnik) consisting of two C-605 pump modules, a C-620
control unit, a C-640 UV-VIS detector, and a C-660 fraction collector. The system was controlled
by the SepacoreControl 1.3 software. Flash chromatography separations were performed on pre-
packed silica gel (40–63 μm) or silica HP (15–40 μm) polypropylene cartridges (21.0 × 129 mm,
Büchi) at a flow rate of 25 mL·min⁻¹. X-ray crystallography: the obtained crystals were immersed in
perfluoropolyalkylether, a single crystal was selected, mounted on a glass fiber, and placed in a
low-temperature N₂ stream. The crystallographic data collections for X-ray structure determinations
of compounds 1–5 were performed on a Xcalibur PX four-circle diffractometer with a Ruby CCD
detector with graphite monochromatized MoKa (λ = 0.71073 Å) radiation. The data were collected
at 100(2) K (for compound 1), 80(2) K (for compounds 2–3 and 5), and 110(2) K (for compound 4)
using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction and analysis
were carried out with the Xcalibur PX software, CrysAlis PRO (Agilent, 2012). The crystal
structures of all compounds were solved by the direct methods with SHELXS-2013³ and refined by
a full-matrix least squares technique on F² using SHELXL-2014⁴ with anisotropic thermal
parameters for the non-H-atoms, except for the low-occupied positions of disordered atoms. The
crystal data and the details of the data collection and the structure refinement are given in Tables
S1, S4, S7, S10, and S12. CCDC 1456557 (1), 146559 (2), 146561 (3) 1456558 (4), and 1456560
(5) contain the supplementary crystallographic data for this paper. These data are provided free of
charge by the Cambridge Crystallographic Data Centre. For compounds 1–5, powder XRD studies
were also performed. Such measurements were carried out to reveal if the resulting powders
confirmed the same compositions as single crystals. Powder X-ray diffraction (PXRD) patterns of
the dried powders were recorded on Bruker D8 ADVANCE diffractometer equipped with a copper
lamp (λCuKα = 1.5406 Å) at 30 kV and 40 mA with a slit of 0.1°. Standard measurements were done
for 2θ = 5°–50° with a 20 step of 0.008° and a counting time of 0.5 s.
Syntheses:

General procedure A – Synthesis of imine-functionalized POSS: An aldehyde (3.41 mmol, 8 equiv) was added dropwise to a solution of octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and MgSO₄ (0.100 g) in the mixture of methanol (20 mL) and chloroform (5 mL). The resulting solution was stirred for 5 h at room temperature or until the reaction was completed, which was confirmed by TLC. After that time, the solvent was evaporated. The crude product was washed with water (3 × 20 mL). Workup by recrystallization or flash column chromatography gave the product, which was dried in vacuo (25 °C, 0.5 mbar), affording spectroscopically pure product.

General procedure B – Preparation of amines by a reduction reaction using Na(CH₃COO)₃BH: A mixture of the appropriate imine-POSS (1.0 equiv) and sodium triacetoxylborohydride (28 equiv) in the mixture of dichloromethane (20 mL) and methanol (1 mL) was stirred at room temperature for 2 h. The reaction mixture was neutralized with saturated NaHCO₃ and extracted with CHCl₃ (3 × 50 mL). The combined extracts were washed with brine, dried under MgSO₄, filtered, and evaporated in vacuo to give the final product.

Synthesis of 1. Benzaldehyde (0.347 mL, 0.362 g, 3.41 mmol, 8 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and methanol (20 mL) reacted according to General Procedure A for 2 h. Workup (recrystallization from chloroform) gave the product as a white solid in 92% yield (0.621 g, 0.391 mmol). Crystals suitable for single-crystal X-ray diffraction studies were obtained by recrystallization from a methanol solution. After 24 h, colorless, transparent needle-like crystals were obtained (size: 0.19 × 0.04 × 0.02 mm³). mp (obtained from DSC, He): 133 °C; fp (obtained from DSC, He): 75 °C; mp (obtained from DTA, N₂): 137 °C; mp (obtained from DTA, air): 137 °C; ¹H NMR (500 MHz, CDCl₃, 300 K): δ = 8.24 (s, 8H, CHN), 7.69 (d, 3JHH = 6.3 Hz, 16H, o-Ar), 7.38–7.33 (m, 24H, m-Ar and p-Ar), 3.59 (t, 3JHH = 6.6 Hz, 16H, CH₂N), 1.86–1.80 (m, 16H, CH₂), 0.69 (t, 3JHH = 8.3 Hz, 16H, SiCH₂); ¹³C{¹H} NMR (126 MHz, CDCl₃, 300 K): δ = 161.1 (s, C=N), 136.4 (s, 1-MeAr), 130.5 (s, p-Ar), 128.6 (s, m-Ar), 128.2 (s, o-Ar), 64.1 (s, CH₂N), 24.4 (s, CH₂), 9.8 (s, SiCH₂); ²⁹Si{¹H} NMR (59.6 MHz, CDCl₃, 20 °C): δ = -66.54 (s); HR-MS (ESI+, TOF/CHCl₃, m/z: 1585.5372 [M + H]+ (calcd 1585.5375), 793.2718 [M + 2H]²⁺ (calcd 793.2724), 529.1877 [M + 3H]³⁺ (calcd 529.1840); elemental analysis calcd (%) for C₈₀H₆₀N₈O₁₂Si₈ (1586.35): C 60.57, H 6.10, N 7.06; found: C 60.51, H 6.19, N 7.01; FTIR (nujol, KBr): v = 1647 (s, vC=O) and 1580 (w, vCN); 1112 (s, vNHasym Si-O-Si), 754 (m, Ar), 693 (m, Ar); UV–vis (dichloromethane, 293 K) λ [nm] (log ε in M⁻¹ cm⁻¹): 247 (5.10), 278 (3.96), 287 (3.78); decomposition onset temperature (DTG, 10 °C·min⁻¹): 352 °C (air), 343 °C (N₂); temperature of decomposition to SiO₂ (determined by TGA measurement, air, 10 °C·min⁻¹), residue yield: 638 °C, 30.50% (calcd 30.30%).

Synthesis of 2. 4-Bromobenzaldehyde (0.643 g, 3.41 mmol, 8 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and methanol (20 mL) reacted according to General Procedure A for 2 h. Workup (recrystallization from chloroform) gave the product as a white solid in 83% yield (0.788 g, 0.355 mmol). Single crystals were grown from methanol solution by slow evaporation at room temperature. After a month, colorless, transparent needle-like crystals were obtained (size: 0.51 × 0.46 × 0.37 mm³). mp (obtained from DSC, He): 169 °C; fp (obtained from DSC, He): 128 °C; mp (obtained from DTA, N₂): 180 °C; mp (obtained from DTA, air): 180 °C; ¹H NMR (500 MHz, CDCl₃, 300 K): δ = 8.16 (s, 8H, CHN), 7.53 (d, 3JHH = 8.5 Hz, 16H, o-Ar), 7.48 (d, 3JHH = 8.4 Hz, 16H, m-Ar), 3.55 (t, 3JHH = 6.6 Hz, 16H, CH₂N), 1.82–1.76 (m, 16H, CH₂), 0.66 (t, 3JHH = 8.4 Hz, 16H, SiCH₂); ¹³C{¹H} NMR (126 MHz, CDCl₃, 300 K): δ = 159.9 (s, C=N), 135.2 (s, 1-MePh), 132.0 (s, m-Ph), 129.6 (s, o-Ph), 125.1 (s, p-Ph), 64.1 (s, CH₂N), 24.4 (s, CH₂), 9.8 (s, SiCH₂); ²⁹Si{¹H} NMR (59.6 MHz, CDCl₃, 300 K): δ = -66.7 (s); FTIR (nujol, KBr): v = 1644 (s, vC=O), 1588 (w, vCN), 1158 (s, vNHasym Si-O-Si), 816 (w, vC=O); HRMS (ESI+, TOF/CHCl₃, m/z: 2212.8174 [M + H]+ (calcd 2212.8187), 1106.4249 [M + 2H]²⁺ (calcd 1106.4145), 738.2822 [M + 3H]³⁺ (calcd 738.2777); elemental analysis calcd (%) for C₈₀H₆₈Br₈N₈O₁₂Si₈ (2217.52): C 43.33, H 4.00, N 5.05;
found: C 43.38, H 4.09, N 5.01; UV–vis (dichloromethane, 293 K) λ [nm] (log ε in M⁻¹ cm⁻¹): 256 (3.89), 283 (3.03), 292 (2.80); decomposition onset temperature (DTG, 10 °C-min⁻¹): 300 °C (air), 303 °C (N₂); temperature of decomposition to SiO₂ (determined by TGA measurement, air, 10 °C-min⁻¹), residue yield: 625 °C, 25.82% (calcd 21.68%).

**Synthesis of 3.** 4-Nitrobenzaldehyde (0.543 g, 3.41 mmol, 8.0 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and the mixture of methanol (20 mL) and chloroform (5 mL) reacted according to General Procedure A for 2 h. Workup (flash column chromatography, eluent: hexane/CH₂Cl₂, 1:1 v/v) gave the product as a yellowish solid in 98% yield (0.716 g, 0.418 mmol). Single crystals were grown from methanol solution by slow evaporation at room temperature. After a week, yellow, transparent needle-like crystals were obtained (size: 0.35 × 0.1 × 0.1 mm³), mp (obtained from DSC, He): 206 °C; fp (obtained from DSC, He): 146 °C; mp (obtained from DTA, N₂): 204 °C; mp (obtained from DTA, air): 204 °C; ¹H NMR (500 MHz, CDCl₃, 300 K): δ = 8.32 (s, 8H, C=H), 7.19 (d, 3JHH = 8.8 Hz, 16H, Ar), 7.83 (d, 3JHH = 8.8 Hz, 16H, Ar), 3.63 (t, 3JHH = 6.5 Hz, 16H, CH₂N), 1.89–1.79 (m, 16H, CH₂), 0.72 (t, 2JHH = 8.1 Hz, 16H, SiCH₂); ¹³C¹H NMR (126 MHz, CDCl₃, 300 K): δ = 158.9 (s, C=N), 149.1, 141.7, 128.7, 124.0, (s, 6C, Ar), 64.3 (s, CH₂N), 24.4 (s, CH₂), 9.9 (s, SiCH₂); ²⁹Si¹H NMR (59.6 MHz, CDCl₃, 300 K): δ = -66.7 (s); FTIR (nujol, KBr): ν = 1645 (m, vC=O), 1601 (m, vN=O), 1523 (m, vC=N), 1343 (m, vC=N), 1189 (m, vC=N), 1108 (s, vC=N), HRMS (ESI⁺, TOF/CHCl₃), m/z: 1945.4211 [M + H]⁺ (calcd 1945.4181), 973.2254 [M + 2H]²⁺ (calcd 973.2127); elemental analysis calcd (%) for C₈₀H₇₆N₁₀O₂₅Si₈ (1946.33): C 49.37, H 4.56, N 11.51; found: C 49.42, H 4.51, N 11.57; UV–vis (dichloromethane, 293 K) λ [nm] (log ε in M⁻¹ cm⁻¹): 285 (5.33); decomposition onset temperature (DTG, 10 °C-min⁻¹): 272 °C (air), 278 °C (N₂); temperature of decomposition to SiO₂ (determined by TGA measurement, air, 10 °C-min⁻¹), residue yield: 662 °C, 24.40% (calcd 24.70%).

**Synthesis of 4.** Salicylaldehyde (0.366 mL, 0.416 g, 3.41 mmol, 8.0 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and the mixture of methanol (20 mL) and chloroform (5 mL) reacted according to General Procedure A for 2 h. Workup (recrystallization from chloroform) gave the product as a yellow solid in 98% yield (0.716 g, 0.418 mmol). Single crystals were grown from methanol solution by slow evaporation at -8°C. After one month, yellow, transparent block crystals were obtained (size: 0.14 × 0.13 × 0.05 mm³), mp (obtained from DSC, He): 124 °C; fp (obtained from DSC, He): 124 °C; mp (obtained from DTA, N₂): 124 °C; mp (obtained from DTA, air): 124 °C; ¹H NMR (500 MHz, CDCl₃, 300 K): δ = 13.61 (s, 8H, OH), 8.27 (s, 8H, C=H), 7.27 (t, 3JHH = 7.2 Hz, 8H, 4-Ph), 7.17 (d, 3JHH = 7.7 Hz, 8H, 6-Ph), 6.90 (d, 3JHH = 8.0 Hz, 8H, 3-Ph), 6.82 (t, 3JHH = 7.5 Hz, 8H, 5-Ph), 3.55 (t, 3JHH = 6.6 Hz, 16H, CH₂N), 1.82–1.76 (m, 16H, CH₂), 0.72 (t, 2JHH = 8.3 Hz, 16H, SiCH₂); ¹³C¹H NMR (126 MHz, CDCl₃, 300 K): δ = 165.0 (s, C=O), 161.5 (s, Ph-OH), 132.2, 131.3 (s, 4.6-Ph), 118.9 (s, 5-Ph), 118.5 (s, 1-Ph), 117.1 (s, 3-Ph), 64.7 (s, CH₂N), 24.5 (s, CH₂), 9.6 (s, SiCH₂); ²⁹Si¹H NMR (59.6 MHz, CDCl₃, 300 K): δ = -66.7 (s); FTIR (nujol, KBr): ν = 2659 (m, vO=O), 1631 (s, vC=O), 1518 (w, vC=O), 1477 (m, vC-O), 1280 (s, vC-O), 1188 (m, vC=N), 1099 (s, vC=O), 788 (w, vC-N), 756 (m, vC=Cl), HRMS (ESI⁺, TOF/CHCl₃), m/z: 1713.4968 [M + H]⁺ (calcd 1713.5371), 857.2574 [M + 2H]²⁺ (calcd 857.2520), 571.8456 [M + 3H]³⁺ (calcd 571.8371); elemental analysis calcd (%) for C₆₀H₆₀N₁₀O₂₀Si₈ (1714.34): C 56.05, H 5.64, N 6.54; found: C 56.10, H 5.61, N 6.52; UV–vis (dichloromethane, 293 K) λ [nm] (log ε in M⁻¹ cm⁻¹): 253 (4.96), 316 (4.60), 416 (3.08); decomposition onset temperature (DTG, 10 °C-min⁻¹): 345 °C (air), 344 °C (N₂); temperature of decomposition to SiO₂ (determined by TGA measurement, air, 10 °C-min⁻¹), residue yield: 631 °C, 27.87% (calcd 28.04%).

**Synthesis of 5.** 2-Hydroxy-1-naphthaldehyde (0.587 g, 3.41 mmol, 8.00 equiv), octa(3-aminopropyl)silsesquioxane hydrochloride (0.500 g, 0.426 mmol), triethylamine (0.475 mL, 0.345 g, 3.41 mmol, 8 equiv), and methanol (20 mL) reacted according to General Procedure A for 2 h. Workup gave the product as a yellow solid of imine in 84% yield (0.755 g, 0.357 mmol). Crystals suitable for single-crystal X-ray diffraction studies were obtained by dissolving this compound (0.01 g) in methanol (20 mL), heating it up to melting, and slow cooling to -8°C; after a few
months, 5 crystallized as yellow needles (size: 0.23 × 0.2 × 0.04 mm³). mp (obtained from DSC, He): 89 °C; fp (obtained from DSC, He): 73 °C; mp (obtained from DTA, N2, recrystallized from methanol): 94 °C; mp (obtained from DTA, air, recrystallized from methanol): 95 °C; 1H NMR (500 MHz, CDCl₃, 300 K): δ = −14.45 (s, 8H, NH), 8.64 (s, 8H, CHN), 7.75 (d, JHH = 8.4 Hz, 8H, Nph), 7.61 (d, JHH = 9.3 Hz, 8H, Nph), 7.54 (d, JHH = 8.7 Hz, 8H, Nph), 7.30 (t, JHH = 8.3 Hz, 8H, Nph), 7.16 (t, JHH = 7.8 Hz, 8H, Nph), 6.85 (d, JHH = 8.0 Hz, 8H, Nph), 3.54 (t, JHH = 6.5 Hz, 16H, CH₂N), 1.79–1.85 (m, 16H, CH₂), 0.78 (t, JHH = 8.5 Hz, 16H, SiCH₂); 13C¹H NMR (126 MHz, CDCl₃, 300 K): δ = 177.1 (s, C=CN), 158.0 (s, Ph-OH), 137.4, 133.9, 129.2, 128.0, 126.1, 125.2, 122.7, 117.9, 106.6 (s, Nph), 54.9 (s, CH₂N), 24.6 (s, CH₂), 9.1 (s, SiCH₂); ²⁹Si¹H NMR (59.6 MHz, CDCl₃, 300 K): δ = −67.0 (s); FTIR (nujol, KBr): ν = 3348 (m, νNH), 1633 (s, νC=N), 1546 (w, νC=O), 1192 (m, νC=O), 1114 (s, νSiO-O-Si), 749 (m, δSiH); HRMS (ESI+, TOF/CHCl₃), m/z: 2113.6986 [M + H]+ (calcd 2113.6220), 1057.3229 [M + 2H]²⁺ (calcd 1057.3146), 705.2191 [M + 3H]³⁺ (calcd 705.2122); elemental analysis calcd (%) for C₁₁₂H₂₁₂N₈O₂Si₈ (2114.81): C 63.61, H 5.34, N 5.30; found: C 63.68, H 5.39, N 5.33; UV−vis (dichloromethane, 293 K) λ [nm] (log ε in M⁻¹ cm⁻¹): 308 (3.47), 402 (3.34), 422 (3.35); decomposition onset temperature (DTG, 10 °C·min⁻¹): 331 °C (air), 330 °C (N₂); temperature of decomposition to SiO₂ (determined by TGA measurement, air, 10 °C·min⁻¹), residue yield: 652 °C, 22.86% (calcd 22.73%).

**Synthesis of 6.** This compound was prepared by General Procedure B. Compound 1 (0.100 g, 0.0630 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.374 g, 1.77 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave 6 as a colorless liquid in 95% yield (0.096 g, 0.0598 mmol). ¹H NMR (500 MHz, CDCl₃, 300 K): δ = 7.29–7.31 (m, 40H, Ph), 3.77 (s, 16H, NCH₂Ph), 2.65 (t, JHH = 7.1 Hz, 16H, CH₂N), 1.59–1.65 (m, 16H, CH₂), 0.65 (t, JHH = 8.5 Hz, 16H, SiCH₃); ¹³C¹H NMR (126 MHz, CDCl₃, 300 K): δ = 140.5, 128.4, 128.1, 126.9 (s, 6C, Ph), 53.9 (s, NCH₂Ph), 52.0 (s, CH₂N), 23.3 (s, CH₃), 9.6 (s, SiCH₂); ²⁹Si¹H NMR (59.6 MHz, CDCl₃, 300 K): δ = −67.0 (s); HRMS (ESI+, TOF/CHCl₃), m/z: 1601.6829 [M + H]+ (calcd 1601.6768), 801.3403 [M + 2H]²⁺ (calcd 801.3350), 534.5599 [M + 3H]³⁺ (calcd 534.5591); elemental analysis calcd (%) for C₆₆H₁₁₂N₈O₂Si₈ (1602.48): C 59.96, H 7.04, N 6.99; found: 59.92, H 7.08, N 6.92.

**Synthesis of 7.** This compound was prepared by General Procedure B. Compound 2 (0.100 g, 0.0451 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.268 g, 1.26 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave 7 as a colorless solid in 91% yield (0.092 g, 0.0412 mmol). ¹H NMR (500 MHz, CDCl₃, 300 K): δ = 7.37 (d, JHH = 8.3 Hz, 16H, o-AR), 7.13 (d, JHH = 8.3 Hz, 16H, m-AR), 3.67 (s, 16H, NCH₂Ph), 2.57 (t, JHH = 6.2 Hz, 16H, CH₂N), 1.63–1.48 (m, 16H, CH₂), 0.60 (t, JHH = 7.1 Hz, 16H, SiCH₃); ¹³C¹H NMR (126 MHz, CDCl₃, 300 K): δ = 139.4 (s, -i-Ph), 131.3 (s, -m-Ph), 129.7 (s, -o-Ph), 120.5 (s, -p-Ph), 53.1 (s, NCH₂Ph), 51.7 (s, CH₂N), 23.2 (s, CH₂), 9.4 (s, SiCH₂); ²⁹Si¹H NMR (59.6 MHz, CDCl₃, 300 K): δ = −66.7 (s); HRMS (ESI+, TOF/CHCl₃), m/z: 2228.9452 [M + H]+ (calcd 2228.9439), 1116.9735 [M + 2H]²⁺ (calcd 1116.9742), 745.6529 [M + 3H]³⁺ (calcd 745.6515); elemental analysis calcd (%) for C₆₅H₁₂₇Br₂N₉O₁₂Si₈ (2233.64): C 42.73, H 4.68, N 5.05, Br 28.79; found: C 42.68, H 4.70, N 5.11, Br 28.72.

**Synthesis of 8.** This compound was prepared by General Procedure B. Compound 3 (0.100 g, 0.0514 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.305 g, 1.44 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave 8 as a beige solid in 90% yield (0.089 g, 0.046 mmol). ¹H NMR (500 MHz, CDCl₃, 300 K): δ = 8.09 (d, JHH = 8.5 Hz, 16H, m-AR), 7.49 (d, JHH = 8.4 Hz, 16H, o-AR), 3.84 (s, 16H, NCH₂Ph), 2.56 (t, JHH = 6.5 Hz, 16H, CH₂N), 1.60–1.50 (m, 16H, CH₂), 0.58 (t, JHH = 7.3 Hz, 16H, SiCH₂); ¹³C¹H NMR (126 MHz, CDCl₃, 300 K): δ = 146.9, 130.7, 128.5, 123.6, (s, 6C, AR), 53.1 (s, NCH₂Ph), 51.9 (s, CH₂N), 23.4 (s, CH₂), 9.4 (s, SiCH₂); ²⁹Si¹H NMR (59.6 MHz, CDCl₃, 300 K): δ = −66.7 (s); HRMS (ESI+, TOF/CHCl₃), m/z: 1945.4175 [M + H]+ (calcd 1945.4181), 973.7125 [M + 2H]²⁺ (calcd 973.7137), 649.4775 [M + 3H]³⁺ (calcd 649.4782); elemental analysis
calcd (%) for C$_{86}$H$_{88}$N$_{16}$O$_{28}$Si$_{8}$ (1943.63): C 49.37, H 4.56, N 11.51; found C 49.42, H 4.51, N 11.40. UV−vis (dichloromethane, 293 K) $\lambda$ [nm] (log $\varepsilon$ in M$^{-1}$ cm$^{-1}$): 277 (4.52).

**Synthesis of 9.** This compound was prepared by General Procedure B. Compound 4 (0.100 g, 0.0583 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.346 g, 1.63 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave 9 as a white solid in 97% yield (0.098 g, 0.0566 mmol).$^1$H NMR (500 MHz, CDCl$_3$, 300 K): $\delta$ = 7.12 (td, $^3$J$_{HH}$ = 7.9, $^4$J$_{HH}$ = 1.6 Hz, 8H, Ph), 6.95 (d, $^3$J$_{HH}$ = 7.5 Hz, 8H, Ph), 6.75 − 6.75 (m, 8H, Ph), 6.74 − 6.72 (m, 16H, Ph), 3.97 (s, 16H, NCH$_2$Ph), 2.67 (t, $^3$J$_{HH}$ = 7.1 Hz, 16H, CH$_2$N), 1.59 − 1.66 (m, 16H, CH$_2$), 0.64 (t, $^3$J$_{HH}$ = 8.5 Hz, 16H, SiCH$_2$); $^{13}$C{[H]} NMR (126 MHz, CDCl$_3$, 300 K): $\delta$ = 159.2 (s, Ph-OH), 151.4, 150.5, 142.9, 122.2, 121.9 (s, 5xPh), 64.1 (s, CH$_2$N), 45.9 (s, NCH$_2$Ph), 24.2 (s, CH$_2$), 9.8 (s, SiCH$_2$); $^{29}$Si{[H]} NMR (59.6 MHz, CDCl$_3$, 300 K): $\delta$ = −66.6 (s); FTIR (nujol, KBr): $\tilde{\nu}$ = 3311 (m, ν$_{NH}$), 2723 (m, ν$_{O-H}$), 1739, 1589 (m, δ$_{N-H}$), 1260 (s, ν$_{Si-O-Si}$), 1097 (s, ν$_{ring}$-asym Si-O-Si), 800 (w, ν$_{C-N}$), 751 (m, δ$_{O-H}$); HRMS (ESI+, TOF/CHCl$_3$), $m/z$: 1729.6275 [M + H]$^+$ (calcd 1729.6220), 865.3137 [M + 2H]$^{2+}$ (calcd 865.3146); elemental analysis calcd (%) for C$_{86}$H$_{88}$N$_{16}$O$_{28}$Si$_{8}$ (1730.47): C 55.53, H 6.52, N 6.48. found: C 55.50, H 6.58, N 6.41; UV−vis (dichloromethane, 293 K) $\lambda$ [nm] (log $\varepsilon$ in M$^{-1}$ cm$^{-1}$): 232 (4.32), 278 (4.20).

**Synthesis of 10.** This compound was prepared by General Procedure B. Compound 5 (0.100 g, 0.0473 mmol), methanol (20 mL), and sodium triacetoxyborohydride (0.281 g, 1.32 mmol, 28 equiv) reacted according to the general procedure for 3 h. Workup (filtering through a short alumina plug) gave 10 as a yellowish solid in 86% yield (0.087 g, 0.0408 mmol).$^1$H NMR (500 MHz, CDCl$_3$, 300 K): $\delta$ = 7.72 (d, $^3$J$_{HH}$ = 8.4 Hz, 8H, Nph), 7.59 (d, $^3$J$_{HH}$ = 9.3 Hz, 8H, Nph), 7.37 (d, $^3$J$_{HH}$ = 8.7 Hz, 8H, Nph), 7.26 (t, $^3$J$_{HH}$ = 8.3 Hz, 8H, Nph), 7.24 (t, $^3$J$_{HH}$ = 7.8 Hz, 8H, Nph), 7.00 (d, $^3$J$_{HH}$ = 8.0 Hz, 8H, Nph), 4.38 (s, 16H, NCH$_2$Ph), 2.68 (t, $^3$J$_{HH}$ = 6.5 Hz, 16H, CH$_2$N), 1.60−1.71 (m, 16H, CH$_2$), 0.64 (t, $^3$J$_{HH}$ = 8.5 Hz, 16H, SiCH$_2$); $^{13}$C{[H]} NMR (126 MHz, CDCl$_3$, 300 K): $\delta$ = 157.0 (s, Ph-OH), 132.5, 129.1, 128.9, 128.5, 126.4, 122.5, 121.0, 119.5, 111.9. (s, Nph), 51.4 (s, CH$_2$N), 47.8 (s, NCH$_2$Ph), 23.1 (s, CH$_2$), 9.4 (s, SiCH$_2$); $^{29}$Si{[H]} NMR (59.6 MHz, CDCl$_3$, 300 K): $\delta$ = −66.3 (s); HRMS (ESI+, TOF/MeOH), $m/z$: 2129.7472 [M + H]$^+$ (calcd 2129.7472); elemental analysis calcd (%) for C$_{121}$H$_{129}$N$_{8}$O$_{20}$Si$_{8}$ (2130.94): C 63.21, H 6.14, N 5.19. found: C 63.13, H 6.05, N 5.26; UV−vis (dichloromethane, 293 K) $\lambda$ [nm] (log $\varepsilon$ in M$^{-1}$ cm$^{-1}$): 237 (4.39), 279 (8.87), 290 (3.77), 320 (3.47), 332 (3.55).

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Table S1. Crystal data and structure refinement for 1.

| Property                                | Value                        |
|------------------------------------------|------------------------------|
| Identification code                      | mj661                        |
| Empirical formula                       | C₈₀H₉₆N₈O₁₂Si₈               |
| Formula weight                           | 1586.36                      |
| Temperature/K                            | 100                          |
| Crystal system                           | triclinic                    |
| Space group                              | P-1                          |
| a/Å                                      | 9.982(3)                     |
| b/Å                                      | 13.141(4)                    |
| c/Å                                      | 16.763(5)                    |
| α/°                                      | 82.27(3)                     |
| β/°                                      | 82.12(3)                     |
| γ/°                                      | 77.37(3)                     |
| Volume/Å³                                | 2112.9(11)                   |
| Z                                        | 1                            |
| ρ_calc g/cm³                             | 1.247                        |
| μ/mm⁻¹                                   | 0.19                         |
| F(000)                                   | 840                          |
| Crystal size/mm³                         | 0.19 × 0.04 × 0.02           |
| Radiation                                | MoKα (λ = 0.71073)           |
| 2Θ range for data collection/°           | 5.6 to 61.6                  |
| Index ranges                             | -14 ≤ h ≤ 13, -18 ≤ k ≤ 12, -23 ≤ l ≤ 23 |
| Reflections collected                    | 15995                        |
| Independent reflections                  | 11237 [R_int = 0.0384, R_sigma = 0.1040] |
| Data/restraints/parameters               | 11237/0/487                  |
| Goodness-of-fit on F²                    | 1.006                        |
| Final R indexes [I>=2σ(I)]               | R₁ = 0.0628, wR₂ = 0.1128    |
| Final R indexes [all data]               | R₁ = 0.1169, wR₂ = 0.1337    |
| Largest diff. peak/hole / e Å⁻³          | 0.51/-0.42                   |
Table S2. Selected bond distances (Å) and bond angles (°) of 1.

| Atom | Atom | Length     | Atom | Atom | Atom | Angle  |
|------|------|------------|------|------|------|--------|
| Si   | O    | 1.6267(18) | O    | Si   | O    | 108.97(9) |
| Si   | O    | 1.6220(18) | O    | Si   | O    | 109.31(9) |
| Si   | O    | 1.6215(18) | O    | Si   | O    | 108.84(9) |
| Si   | O    | 1.6213(18) | O    | Si   | O    | 109.34(10) |
| Si   | O    | 1.6185(18) | O    | Si   | O    | 109.94(9) |
| Si   | O    | 1.6212(19) | O    | Si   | O    | 108.96(9) |
| Si   | O    | 1.6237(19) | O    | Si   | O    | 109.40(9) |
| Si   | O    | 1.6226(17) | O    | Si   | O    | 108.46(9) |
| Si   | O    | 1.6180(18) | O    | Si   | O    | 109.01(9) |
| Si   | O    | 1.6271(18) | O    | Si   | O    | 108.98(9) |
| Si   | O    | 1.6256(17) | O    | Si   | O    | 109.16(9) |
| Si   | O    | 1.6253(18) | O    | Si   | O    | 108.99(9) |

Si-C

| Atom | Atom | Length     | Atom | Atom | Atom | Angle  |
|------|------|------------|------|------|------|--------|
| Si   | C1A  | 1.839(2)   | Si   | C1B  | 1.839(2) |
| Si   | C1C  | 1.846(2)   | Si   | C1D  | 1.840(3) |
| N1A  | C4A  | 1.263(3)   | N1B  | C4B  | 1.269(3) |
| N1C  | C4C  | 1.268(3)   | N1D  | C4D  | 1.263(3) |

C-N

| Atom | Atom | Length     | Atom | Atom | Atom | Angle  |
|------|------|------------|------|------|------|--------|
| N1A  | C3A  | 1.464(3)   | N1B  | C3B  | 1.458(3) |
| N1C  | C3C  | 1.466(3)   | N1D  | C3D  | 1.460(3) |

Symmetry code: 12-X,1-Y,1-Z

Table S3. Geometry of hydrogen bonds and close contacts for 1.

| D—H···A   | d(D—H)/Å | d(H···A)/Å | d(D···A)/Å | D—H···A/° |
|-----------|----------|------------|------------|-----------|
| Intermolecular, weak |
| C2B—H2BB···N1A² | 0.99     | 2.53       | 3.391(4)   | 146       |

Symmetry code: 12+X,+Y,+Z
| Identification code       | mj488a          |
|--------------------------|-----------------|
| Empirical formula        | C_{80}H_{88}Br_{8}N_{8}O_{12}Si_{8} |
| Formula weight           | 2217.58         |
| Temperature/K            | 80              |
| Crystal system           | triclinic       |
| Space group              | P-1             |
| Unit cell dimensions:    |                 |
| a = 11.895(3) Å         | α = 66.17(5)°   |
| b = 14.061(4) Å         | β = 85.35(5)°   |
| c = 15.763(4) Å         | γ = 68.70(5)°   |
| Volume/Å³                | 2240.3(15)      |
| Z                        | 1               |
| ρ<sub>calc</sub>/g/cm³   | 1.644           |
| μ/mm⁻¹                   | 3.75            |
| F(000)                   | 1112            |
| Crystal size/mm³         | 0.51 × 0.46 × 0.37 |
| Radiation                | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 5.5 to 56.1 |
| Index ranges             | -15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20 |
| Reflections collected    | 20253           |
| Independent reflections  | 10851 [R<sub>int</sub> = 0.0347, R<sub>sigma</sub> = 0.0735] |
| Data/restraints/parameters | 10851/16/598   |
| Goodness-of-fit on F²    | 1.06            |
| Final R indexes [I>2σ (I)] | R₁ = 0.0497, wR₂ = 0.0954 |
| Final R indexes [all data] | R₁ = 0.0720, wR₂ = 0.1104 |
| Largest diff. peak/hole / e Å⁻³ | 1.06/-1.24 |
| Absorption correction    | Analytical      |
| Max. and min. transmission | 0.366 to 0.260 |
| Refinement method        | Full-matrix least-squares on F² |

**Table S4.** Crystal data and structure refinement for 2.
Table S5. Selected bond distances (Å) and bond angles (°) of 2.

| Atom | Atom | Length  | Atom | Atom | Atom | Angle   |
|------|------|---------|------|------|------|---------|
| Si-O |     |         | O-Si-O |     |      |         |
| O1   | Si3^1| 1.619(3)| O1   | Si1  | O2   | 108.78(14) |
| O1   | Si1  | 1.620(3) | O1^1 | Si3  | O4   | 109.79(14) |
| O2   | Si1  | 1.622(3) | O1   | Si3  | O3   | 108.87(14) |
| O2   | Si2  | 1.623(2) | O3   | Si2  | O2   | 108.68(14) |
| O3   | Si2  | 1.617(2) | O4   | Si3  | O3   | 108.95(13) |
| O3   | Si3  | 1.626(2) | O5   | Si1  | O1   | 109.68(14) |
| O4   | Si3  | 1.620(2) | O5   | Si1  | O2   | 109.24(13) |
| O4   | Si4  | 1.624(2) | O5   | Si4  | O4   | 108.20(13) |
| O5   | Si1  | 1.616(3) | O6   | Si4  | O5   | 109.35(13) |
| O5   | Si4  | 1.624(2) | O6   | Si4  | O4   | 108.14(13) |
| O6   | Si2^1| 1.612(3) | O6^1 | Si2  | O3   | 109.48(13) |
| O6   | Si4  | 1.614(3) | O6^1 | Si2  | O2   | 108.83(14) |
| Si-C | Si1  | C1A     | Si   | O2   | Si2  | 151.76(16) |
| Si1  | C1B  | 1.839(4) | Si1  | O5   | Si4  | 143.18(16) |
| Si3  | C1C  | 1.837(3) | Si2  | O3   | Si3  | 143.04(16) |
| Si4  | C1D  | 1.835(4) | Si2^1| O6   | Si4  | 152.45(17) |
| C-N  | Si3  | N1A     | Si3  | O1   | Si1  | 150.86(15) |
| C4A  | N1A  | 1.254(5) | Si3^1| O1   | Si1  | 150.86(15) |
| C4B  | N1B  | 1.266(4) |       |      |      |         |
| C4C  | N1C  | 1.266(5) |       |      |      |         |
| C4D  | N1D  | 1.251(12) |      |      |      |         |
| C4E  | N1E  | 1.256(11) |      |      |      |         |
| C-N  | C3A  | N1A     | C3   | N1A  | 1.461(5) |
| C3B  | N1B  | 1.447(5) | C3   | N1B  | 1.447(5) |
| C3C  | N1C  | 1.442(5) | C3   | N1C  | 1.442(5) |
| C3D  | N1D  | 1.439(18) | C3   | N1D  | 1.439(18) |
| C3E  | N1E  | 1.47(2)  | C3   | N1E  | 1.47(2)  |
| C-Br | Br1  | C8A     | Br2  | C8B  | 1.903(4) |
| Br2  | C8B  | 1.881(4) | Br3  | C8C  | 1.898(5) |
| Br3  | C8C  | 1.898(5) | Br4  | C8D  | 1.776(11) |

Symmetry code: ^1^2-X,-Y,-Z
**Figure S1.** The simulated XRD patterns from the single crystal data and the experimental powder XRD patterns of compound 2.
**Table S6.** Crystal data and structure refinement for 3.

| Property                  | Value                          |
|---------------------------|--------------------------------|
| Identification code       | MJ517a                         |
| Empirical formula         | C$_{380}$H$_{86}$N$_{16}$O$_{28}$Si$_{8}$$\cdot$4(CHCl)$_3$ |
| Formula weight            | 2421.83                        |
| Temperature/K             | 80                             |
| Crystal system            | triclinic                      |
| Space group               | P-1                            |
| a/Å                       | 9.578(4)                       |
| b/Å                       | 16.150(7)                      |
| c/Å                       | 18.867(7)                      |
| α/°                       | 108.08(4)                      |
| β/°                       | 98.79(3)                       |
| γ/°                       | 92.53(3)                       |
| Volume/Å$^3$              | 2729(2)                        |
| Z                         | 1                              |
| ρ$_{\text{calc}}$/cm$^3$  | 1.474                          |
| μ/mm$^{-1}$               | 0.47                           |
| F(000)                    | 1246                           |
| Crystal size/mm$^3$       | 0.35 × 0.1 × 0.1               |
| Radiation                 | MoKα ($\lambda = 0.71073$)     |
| 2Θ range for data collection/° | 5.7 to 61.6             |
| Index ranges              | -13 ≤ h ≤ 12, -22 ≤ k ≤ 21, -25 ≤ l ≤ 24 |
| Reflections collected    | 22452                          |
| Independent reflections   | 14558 [R$_{\text{int}}$ = 0.024, R$_{\text{sigma}}$ = 0.052] |
| Data/restraints/parameters| 14558/9/817                    |
| Goodness-of-fit on F$^2$  | 1.02                           |
| Final R indexes [I>2σ (I)] | R$_1$ = 0.067, wR$_2$ = 0.170 |
| Final R indexes [all data]| R$_1$ = 0.096, wR$_2$ = 0.189 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.00/-0.54         |
| Atom | Atom | Length  | Atom | Atom | Atom | Angle   |
|------|------|---------|------|------|------|---------|
| Si-O | O-Si-O |
| Si1  | O1   | 1.628(2) | O4   | Si1  | O1   | 108.78(10) |
| Si1  | O4   | 1.626(2) | O5   | Si1  | O1   | 109.06(10) |
| Si1  | O5   | 1.618(2) | O2   | Si2  | O1   | 109.31(10) |
| Si2  | O1   | 1.6241(19) | O6<sup>1</sup> | Si2  | O1   | 108.79(10) |
| Si2  | O2   | 1.617(2) | O3   | Si3  | O2   | 108.99(10) |
| Si2  | O6<sup>1</sup> | 1.624(2) | O5<sup>1</sup> | Si3  | O2   | 108.28(11) |
| Si3  | O2   | 1.624(2) | O5<sup>1</sup> | Si3  | O3   | 108.62(11) |
| Si3  | O3   | 1.623(2) | O6   | Si4  | O3   | 109.15(10) |
| Si3  | O5<sup>1</sup> | 1.623(2) | O5   | Si1  | O4   | 109.26(11) |
| Si4  | O3   | 1.6251(19) | O3   | Si4  | O4   | 108.68(10) |
| Si4  | O4   | 1.626(2) | O6   | Si4  | O4   | 109.32(11) |
| Si4  | O6   | 1.625(2) | O2   | Si2  | O6<sup>1</sup> | 109.45(10) |
| Si-C | Si-O-Si |
| Si1  | C1A  | 1.836(2) | Si1  | O5   | Si3<sup>1</sup> | 148.60(12) |
| Si2  | C1B  | 1.837(3) | Si2  | O1   | Si1  | 144.77(12) |
| Si3  | C1C  | 1.886(10) | Si2  | O2   | Si3  | 152.96(13) |
| Si3  | C1E  | 1.72(2) | Si2<sup>1</sup> | O6   | Si4  | 147.36(12) |
| Si4  | C1D  | 1.837(3) | Si3  | O3   | Si4  | 145.41(13) |
|     | C≡N  |        | Si4  | O4   | Si1  | 152.17(13) |
| C-N |       |
| C3A  | N1A  | 1.458(4) |
| C3B  | N1B  | 1.474(4) |
| C3C  | N1C  | 1.589(8) |
| C3D  | N1D  | 1.456(4) |
| C3E  | N1E  | 1.76(3) |

Symmetry code: 1<sup>2</sup>-X,Y,Z;
Table S8. Geometry of hydrogen bonds and close contacts for 3.

| D—H⋯A          | d(D—H)/Å | d(H⋯A)/Å | d(D⋯A)/Å | D—H⋯A /° |
|----------------|-----------|-----------|-----------|-----------|
|                | Intermolecular, moderate |          |           |           |
| C4B—H4B⋯O1A³  | 0.95      | 2.48      | 3.365(4)  | 154       |
|                | Intramolecular, moderate |          |           |           |
| C3A—H3A⋯Cl19² | 0.99      | 2.73      | 3.68(2)   | 161       |
| C7B—H7B⋯Cl18² | 0.95      | 2.88      | 3.541(13) | 128       |

Symmetry codes: ³1-X,2-Y,-Z; ²2-X,2-Y,1-Z

Figure S2. The simulated XRD patterns from the single crystal data and the experimental powder XRD patterns of compound 3 after remove of solvent.
**Table S9.** Crystal data and structure refinement for 4.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | MJ487                                      |
| Empirical formula               | C<sub>80</sub>H<sub>96</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>8</sub> |
| Formula weight                  | 1714.36                                    |
| Temperature/K                   | 110                                        |
| Crystal system                  | triclinic                                  |
| Space group                     | P-1                                        |
| a/Å                             | 9.381(3)                                   |
| b/Å                             | 14.034(4)                                  |
| c/Å                             | 16.112(5)                                  |
| α/°                             | 91.48(3)                                   |
| β/°                             | 94.07(3)                                   |
| γ/°                             | 90.06(3)                                   |
| Volume/Å³                       | 2115.1(11)                                 |
| Z                               | 1                                          |
| ρ<sub>calc</sub> g/cm³          | 1.346                                      |
| μ/mm⁻¹                          | 0.20                                       |
| F(000)                          | 904                                        |
| Crystal size/mm³                | 0.14 × 0.13 × 0.05                         |
| Radiation                       | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/°  | 5.7 to 61.3                                |
| Index ranges                    | -12 ≤ h ≤ 13, -20 ≤ k ≤ 11, -20 ≤ l ≤ 22  |
| Reflections collected           | 19597                                      |
| Independent reflections         | 11718 [R<sub>int</sub> = 0.0244, R<sub>sigma</sub> = 0.0529] |
| Data/restraints/parameters      | 11718/0/527                                |
| Goodness-of-fit on F²           | 1.01                                       |
| Final R indexes [I>2σ(I)]       | R<sub>1</sub> = 0.0475, wR<sub>2</sub> = 0.1042 |
| Final R indexes [all data]      | R<sub>1</sub> = 0.0737, wR<sub>2</sub> = 0.1163 |
| Largest diff. peak/hole / e Å⁻³ | 0.41/-0.26                                |
Table S10. Selected bond distances (Å) and bond angles (°) of 4.

| Atom | Atom | Length | Atom | Atom | Atom | Angle |
|------|------|--------|------|------|------|-------|
| Si   | O1   | 1.6302(14) | O5   | Si1  | O2   | 109.20(7) |
| Si1  | O2   | 1.6265(13) | O5   | Si1  | O1   | 109.76(7) |
| Si1  | O5   | 1.6206(14) | O2   | Si1  | O1   | 108.86(7) |
| Si2  | O2   | 1.6234(14) | O3   | Si2  | O6   | 109.13(7) |
| Si2  | O3   | 1.6206(14) | O3   | Si2  | O2   | 109.74(7) |
| Si2  | O6   | 1.6233(13) | O6   | Si2  | O2   | 108.95(7) |
| Si3  | O1   | 1.6314(14) | O3   | Si3  | O4   | 109.50(7) |
| Si3  | O3   | 1.6232(14) | O3   | Si3  | O1   | 108.60(7) |
| Si3  | O4   | 1.6255(13) | O4   | Si3  | O1   | 108.86(7) |
| Si4  | O4   | 1.6265(13) | O5   | Si4  | O6   | 108.82(7) |
| Si4  | O5   | 1.6231(14) | O5   | Si4  | O4   | 109.43(7) |
| Si4  | O6   | 1.6245(14) | O6   | Si4  | O4   | 108.39(7) |

| Si-C | Si-O-Si |
|------|---------|
| Si1  | C1A     | 1.8444(19) | Si1  | O1   | Si3   | 144.98(8) |
| Si2  | C1B     | 1.8381(18) | Si1  | O5   | Si4   | 152.16(9) |
| Si3  | C1C     | 1.8486(18) | Si2  | O2   | Si1   | 143.90(9) |
| Si4  | C1D     | 1.8425(18) | Si2  | O3   | Si3   | 152.46(9) |

Table S11. Geometry of hydrogen bonds and close contacts for 4.

| D—H···A  | d(D—H)/Å | d(H···A)/Å | d(D···A)/Å | D—H···A/° |
|----------|-----------|-----------|------------|-----------|
| Intramolecular, strong |
| O1B—H1B···N1B | 0.84 | 1.83 | 2.575(2) | 148 |
| O1D—H1D···N1D | 0.84 | 1.85 | 2.596(2) | 148 |
| O1C—H1C···N1C | 0.84 | 1.86 | 2.596(2) | 146 |
| O1A—H1A···N1A | 0.84 | 1.90 | 2.641(2) | 147 |
| Intermolecular, weak |
| C2A—H2AB···O1B | 0.99 | 2.39 | 3.150(2) | 134 |

Symmetry code: 12-X,-Y,-Z
Figure S3. The simulated XRD patterns from the single crystal data and the experimental powder XRD patterns of compound 4.
Table S12. Crystal data and structure refinement for 5.

| Parameter                      | Value                                      |
|--------------------------------|--------------------------------------------|
| Identification code           | MJ491b                                     |
| Moiety formula                | C_{112}H_{112}N_{8}O_{20}Si_{8}·6.1(CH_{3}OH) |
| Formula weight                | 2310.26                                    |
| Temperature/K                 | 80                                         |
| Radiation                     | MoKα (λ = 0.71073)                         |
| Crystal system                | triclinic                                  |
| Space group                    | P-1                                        |
| Unit cell dimensions          | a = 14.292(6) Å, α = 97.14(4)°             |
|                                | b = 14.663(7) Å, β = 97.17(4)°             |
|                                | c = 15.109(7) Å, γ = 110.39(4)°           |
| Volume/Å^3                    | 2896(2)                                    |
| Z                              | 1                                          |
| \( \rho_{\text{calc}} \)/g/cm\(^3\) | (calculated) 1.325                         |
| Absorption coefficient \(\mu/\text{mm}^1\) | 0.17                                       |
| F(000)                         | 1222                                       |
| Crystal size/mm\(^3\)        | 0.23 × 0.2 × 0.04                          |
| 2\(\Theta\) range for data collection/° | 5.5 to 51.0                               |
| Index ranges                  | -17 ≤ h ≤ 17, -16 ≤ k ≤ 17, -12 ≤ l ≤ 18 |
| Reflections collected         | 18913                                      |
| Independent reflections       | 10761 [R\(_{\text{int}}\) = 0.0562, R\(_{\text{sigma}}\) = 0.1430] |
| Data/restraints/parameters    | 10761/7/772                                |
| Goodness-of-fit on F\(^2\)    | 1.01                                       |
| Final R indexes [I≥2\(\sigma\) (I)] | R\(_1\) = 0.0721, wR\(_2\) = 0.1426       |
| Final R indexes [all data]    | R\(_1\) = 0.1485, wR\(_2\) = 0.1770       |
| Largest diff. peak/hole / e Å\(^{-3}\) | 0.46/-0.42                                |
| Absorption correction         | none                                       |
| Refinement method             | Full-matrix least-squares on F\(^2\)      |
Table S13. Selected bond distances (Å) and bond angles (°) of 5.

| Atom | Atom | Length  | Atom | Atom | Angle    |
|------|------|---------|------|------|----------|
|      |      | Si-O    |      |      | O-Si-O   |
| O1   | Si1  | 1.623(3) | O1   | Si4  | 109.39(16) |
| O1   | Si4  | 1.619(3) | O2   | Si1  | O5       | 109.76(16) |
| O2   | Si1  | 1.622(3) | O2   | Si1  | O1       | 108.79(16) |
| O2   | Si2  | 1.625(3) | O2   | Si2  | O6       | 109.01(16) |
| O3   | Si2  | 1.628(3) | O2   | Si2  | O3       | 109.42(16) |
| O3   | Si3  | 1.618(3) | O3   | Si3  | O51      | 109.48(16) |
| O4   | Si3  | 1.625(3) | O3   | Si3  | O4       | 109.64(16) |
| O4   | Si4  | 1.625(3) | O5   | Si1  | O1       | 108.56(16) |
| O5   | Si1  | 1.623(3) | O51  | Si3  | O4       | 109.15(16) |
| O5   | Si31 | 1.619(3) | O6   | Si2  | O3       | 109.20(16) |
| O6   | Si2  | 1.627(3) | O61  | Si4  | O1       | 109.11(15) |
| O6   | Si41 | 1.615(3) | O61  | Si4  | O4       | 109.26(16) |
|      |      | Si-C    |      |      | Si-O-Si  |
| Si1  | C1A  | 1.844(4) | Si1  | O2   | Si2      | 149.0(2)   |
| Si2  | C1B  | 1.837(4) | Si3  | O3   | Si2      | 148.82(19) |
| Si3  | C1C  | 1.841(4) | Si3  | O4   | Si4      | 148.52(19) |
| Si4  | C1D  | 1.842(4) | Si31 | O5   | Si1      | 148.37(19) |
|      |      | C-N     |      |      | Si-O-N   |
| C4A  | N1A  | 1.304(6) | Si4  | O6   | Si2      | 150.1(2)   |
| C4B  | N1B  | 1.306(5) |      |      |          |            |
| C4C  | N1C  | 1.303(5) |      |      |          |            |
| C4D  | N1D  | 1.307(5) |      |      |          |            |
|      |      | C-N     |      |      |          |
| C3A  | N1A  | 1.463(6) |      |      |          |            |
| C3B  | N1B  | 1.458(5) |      |      |          |            |
| C3C  | N1C  | 1.454(5) |      |      |          |            |
| C3D  | N1D  | 1.466(5) |      |      |          |            |
|      |      | C=O     |      |      |          |
| C6A  | O1A  | 1.305(6) |      |      |          |            |
| C6B  | O1B  | 1.273(5) |      |      |          |            |
| C6C  | O1C  | 1.270(5) |      |      |          |            |
| C6D  | O1D  | 1.289(5) |      |      |          |            |

Symmetry code: 11-X,-Y,1-Z
Table S14. Geometry of hydrogen bonds and close contacts for 5.

| D—H···A      | d(D—H)/Å | d(H···A)/Å | d(D···A)/Å | D—H···A /° |
|--------------|-----------|-----------|------------|------------|
|              | Intramolecular, strong | | | |
| N1D—H1D···O1D | 0.88      | 1.80      | 2.519(5)   | 138        |
| N1A—H1A···O1A | 0.88      | 1.85      | 2.545(6)   | 134        |
| N1C—H1C···O1C | 0.88      | 1.92      | 2.595(5)   | 132        |
| N1B—H1B···O1B | 0.88      | 1.92      | 2.606(5)   | 133        |
|              | Intramolecular, moderate | | | |
| N1C—H1C···O1B<sup>6</sup> | 0.88 | 2.23 | 2.842(5) | 127 |
| N1B—H1B···O1C<sup>4</sup> | 0.88 | 2.38 | 3.066(5) | 135 |
|              | Intermolecular, moderate | | | |
| O1M—H1M···O1D | 0.84      | 1.84      | 2.679(5)   | 174        |
| O4M—H4M···O1A | 0.84      | 1.96      | 2.715(9)   | 148        |
| O2M—H2M···O1C | 0.85      | 1.92      | 2.766(9)   | 179        |
| O3M—H3M···O1C | 0.84      | 2.24      | 2.816(12)  | 126        |
| O5M—H5M···O1  | 0.84      | 2.52      | 3.32(2)    | 159        |
|              | Intermolecular, weak | | | |
| C4A—H4A···O6M<sup>2</sup> | 0.95 | 2.25 | 3.16(4) | 160 |
| C4B—H4B···O1M<sup>3</sup> | 0.95 | 2.40 | 3.299(6) | 157 |
| C2A—H2A···O8M<sup>7</sup> | 0.99 | 2.45 | 3.35(2) | 150 |
| C3C—H3CB···O1M<sup>6</sup> | 0.99 | 2.53 | 3.446(6) | 153 |

Symmetry codes: <sup>2</sup>1+X,Y,Z; <sup>1</sup>1-X,-Y,1-Z; <sup>4</sup>1+X,+Y,-1+Z; <sup>3</sup>1-X,-Y,1-Z; <sup>5</sup>1+X,-Y,-1+Z; <sup>4</sup>1+X,+Y,1+Z; <sup>7</sup>1-X,1-Y,1-Z;
Table S15. Thermal properties of 1-5 based on TG-DTA studies.

| Comp. | Atm. | Melting temperature [°C] | Calculated residue yield [%] | Residue yield [%] | Δ | T5% | T1 | T2 | T3 |
|-------|------|--------------------------|-------------------------------|------------------|---|-----|----|----|----|
| 1     | Air  | 137                      | 30.30                         | 30.50            | 0.20 | 292 | 352 | 638 |
| 1     | N₂   | 137                      | 30.30                         | 34.44            | 4.14 | 304 | 343 | 666 |
| 2     | Air  | 180                      | 21.68                         | 25.82            | 4.14 | 293 | 300 | 443 | 625 |
| 2     | N₂   | 180                      | 21.68                         | 30.34            | 8.66 | 302 | 303 | 419 | 649 |
| 3     | Air  | 204                      | 24.70                         | 24.40            | -0.30 | 270 | 272 | 662 |
| 3     | N₂   | 204                      | 24.70                         | 38.32            | 13.62 | 271 | 278 | 661 |
| 4     | Air  | 124                      | 28.04                         | 27.87            | -0.17 | 306 | 343 | 631 |
| 4     | N₂   | 124                      | 28.04                         | 45.16            | 17.12 | 322 | 344 | 631 |
| 5     | Air  | 78                       | 22.73                         | 22.86            | 0.13  | 298 | 330 | 652 |
| 5     | N₂   | 78                       | 22.73                         | 29.63            | 6.90  | 299 | 326 | 665 |

Calculated residue yield [%] calculated based on the decomposition to silicon dioxide SiO₂. Δ = The difference between the determined and calculated values. T5% refers to the temperature at which a 5% loss in weight is observed. The T₁, T₂, T₃, T₄ temperatures correspond to the maximum rate of decomposition for each stage evaluated from the peaks of the DTG curves.
Figure S4. TG (black line), and DTA (blue line) thermogram of 1 at a heating rate of 10 °C/min. Left graph in the air atmosphere (60% N₂, 40% O₂).

Figure S5. TG (black line), and DTA (blue line) thermogram of 1 at a heating rate of 10 °C/min. In nitrogen.
Figure S6. TG (black line), and DTA (blue line) thermogram of 2 at a heating rate of 10 °C/min. Left graph in the air atmosphere (60% N₂, 40% O₂).

Figure S7. TG (black line), and DTA (blue line) thermogram of 2 at a heating rate of 10 °C/min. In nitrogen.
Figure S8. TG (black line), and DTA (blue line) thermogram of 3 at a heating rate of 10 °C/min. Left graph in the air atmosphere (60% N₂, 40% O₂).

Figure S9. TG (black line), and DTA (blue line) thermogram of 3 at a heating rate of 10 °C/min. In nitrogen.
Figure S10. TG (black line), and DTA (blue line) thermogram of 4 at a heating rate of 10 °C/min. In the air atmosphere (60% N₂, 40% O₂).

Figure S11. TG (black line), and DTA (blue line) thermogram of 4 at a heating rate of 10 °C/min. In the in nitrogen.
Figure S12. TG (black line), and DTA (blue line) thermogram of 5 at a heating rate of 10 °C/min. In the air atmosphere (60% N₂, 40% O₂).

Figure S13. TG (black line), and DTA (blue line) thermogram of 5 at a heating rate of 10 °C/min. In nitrogen.
Figure S14. DSC of 1, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).

Figure S15. DSC of 2, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).
Figure S16. DSC of 3, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).

Figure S17. DSC of 4, 1st and 2nd heat & cooling cycle (10 °C/min in the helium atmosphere).
Figure S18. DSC of 5 (recrystallized from chloroform), 1\textsuperscript{st} and 2\textsuperscript{nd} heat & cooling cycle (10 °C/min in the helium atmosphere).
Figure S19. The electronic absorption spectra of 1-5 (dichloromethane, 298K).

Figure S20. The electronic absorption spectra (dichloromethane, 298K) of 6 (red) and 1 (black).
Figure S21. The electronic absorption spectra (dichloromethane, 298K) of 8 (red) and 3 (black).

Figure S22. The electronic absorption spectra (dichloromethane, 298K) of 9 (red) and 4 (black).
Figure S23. The electronic absorption spectra (dichloromethane, 298K) of 10 (red) and 5 (black).
Table S16. Selected NMR and FT-IR data.

| Compound | $^1$H NMR[a] N=CH | $^{13}$C NMR[a] C=N | $^{29}$Si NMR[a] | FT-IR[b] N=CH; Si-O-Si |
|----------|-------------------|---------------------|-----------------|------------------------|
| 1        | 8.27              | 165.0               | -66.7           | 1631; 1099             |
| 2        | 8.22              | 164.8               | -66.6           | 1634; 1116             |
| 3        | 8.27              | 164.7               | -66.7           | 1632; 1115             |
| 4        | 8.27              | 160.8               | -67.0           | 1624; 1113             |
| 5        | 8.33              | 166.0               | -66.6           | 1634; 1099             |
| 6        | 10.40             | 160.5               | -66.7           | 1632; 1089             |
| 7        | 8.64              | 158.1               | -67.0           | 1633[c]; 1114          |
| 8        | 8.24              | 161.1               | -66.5           | 1647; 1112             |
| 9        | 8.16              | 159.9               | -66.7           | 1644; 1158             |
| 10       | 8.26              | 159.3               | -67.2           | 1646; 1094             |
| 11       | 8.32              | 158.9               | -66.7           | 1645; 1108             |
| 12       | 7.00              | 158.9               | -66.7           | 1645; 1108             |
| 13       | 8.11              | 160.9               | -67.1           | 1639; 1121             |
| 14       | 8.34              | 162.0               | -66.6           | 1648; 1113             |
| 15       | 8.20              | 159.3               | -66.7           | 1647; 1098             |
| 16       | 7.94              | 153.5               | -67.3           | 1675; 1098             |
| 17       | 8.33              | 154.4               | -66.7           | 1634; 1107             |
| 18       | 8.01              | 153.1               | -66.3           | 1637; 1095             |
| 19       | 8.83              | 155.5               | -66.5           | 1645; 1113             |

[a] Measured in CDCl$_3$. [b] Powder measured in Nujol mull. [c] C=C-NH moiety.

Figure S24. $^1$H (500 MHz, CDCl$_3$) spectrum of the crude product of reaction of OAS-POSS-CF$_3$SO$_3$ with benzoic aldehyde.
**Figure S25.** $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 1.

**Figure S6.** $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 1.
Figure S27. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 1.

Figure S28. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 2.
Figure S29. $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 2.

Figure S30. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 2.
Figure S31. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 3.

Figure S32. $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 3.
Figure S33. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 3.

Figure S34. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 4.
Figure S35. $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 4.

Figure S36. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 4.
Figure S37. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 5.

Figure S38. $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 5.
Figure S39. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 5.
Figure S40. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 6.

Figure S41. $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 6.
Figure S42. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 6.

Figure S43. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 7.
**Figure S44.** $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 7.

**Figure S45.** $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 7.
Figure S46. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 8.

Figure S47. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 8.
Figure S48. $^1$H NMR (500 MHz, CDCl$_3$, 300 K) spectrum of 9.

Figure S49. $^{13}$C NMR (126 MHz, CDCl$_3$, 300 K) spectrum of 9.
Figure S50. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 9.

Figure S51. $^{29}$Si NMR (59.6 MHz, CDCl$_3$, 300 K) spectrum of 10.
Figure S51. FT-IR (nujol) spectrum of 1.

Figure S52. FT-IR (nujol) spectrum of 2.

Figure S53. FT-IR (nujol) spectrum of 3.
Figure S54. FT-IR (nujol) spectrum of 4.

Figure S55. FT-IR (nujol) spectrum of 5.
Figure S56. FT-IR (KBr pellets) spectrum of 9.
Figure S57. HR-MS (ESI+, TOF, CHCl₃) spectrum of 1.

Figure S58. Simulated (top) and measured (bottom) MS (ESI+, TOF, CHCl₃) spectra of 1.

Figure S59. HR-MS (ESI+, TOF, CHCl₃) spectrum of 2.

Figure S60. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, CHCl₃) spectra of 2.
Figure S61 HR-MS (ESI+, TOF, CHCl₃) spectrum of 3.

Figure S62. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, CHCl₃) spectra of 3.

Figure S63. HR-MS (ESI+, TOF, CHCl₃) spectrum of 4.

Figure S64. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, CHCl₃) spectra of 4.
Figure S65. HR-MS (ESI+, TOF, CHCl₃) spectrum of 5.

Figure S66. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, CHCl₃) spectra of 5.

Figure S67. Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, CHCl₃) spectra of 6.
**Figure S68.** Simulated (top) and measured (bottom) HR-MS (ESI+, TOF, CHCl₃) spectra of 9.

**Figure S69.** MS spectrum of 3 showing hexa-T₃R₆ and hepta-T₃R₇ derivatives. Spectrum was measured for crude product after the reaction of OAS-POSS-Cl with 4-nitrobenzoic aldehyde.

**Figure S70.** HR-MS spectra of the crude product of reaction of OAS-POSS-CF₃SO₃ with benzoic aldehyde.
**Figure S71.** EDS spectrum of 2 after heating to the decomposition temperature (copper content is derived from the high-purity conducting Cu grid).