Supporting Information for

Unraveling the Driving Forces in the Self-Assembly of Monodisperse Naphthalenediimide-Oligodimethylsiloxane Block Molecules

José Augusto Berrocal, † R. Helen Zha, † Bas F. M. de Waal, † Jody A. M. Lugger, † Martin Lutz, ‡ E. W. Meijer†*

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

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

* to whom correspondence should be addressed: e.w.meijer@tue.nl
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Experimental Section

Instrumentation

Microwave reactions were performed on a Biotage Initiator reactor. Column chromatography was performed using a Grace Reveleris instrument equipped with an evaporative light scattering detector. 

$^1$H NMR and $^{13}$C NMR spectra were recorded either on a Varian Mercury Vx 400 MHz (100 MHz for $^{13}$C) or Varian Oxford AS 500 MHz (125 MHz for $^{13}$C) NMR spectrometers. Chemical shifts are given in ppm (δ) values relative to residual solvent or tetramethylsilane (TMS). Splitting patterns are labelled as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet.

Matrix assisted laser desorption/ionisation mass spectra were obtained on a PerSeptive Biosystems Voyager DE-PRO spectrometer or a Bruker autoflex speed spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) and 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrices. Infrared spectra were recorded on a Perkin Elmer Spectrum One 1600 FT-IR spectrometer or a Perkin Elmer Spectrum Two FT-IR spectrometer, equipped with a Perkin Elmer Universal ATR Sampler Accessory.

Gel Permeation Chromatography (GPC) was performed using Shimadzu Prominence LC-2030C, and solutions were dissolved at 1 mg/mL and filtered through 0.2 μm Whatman Anatop 10 filters before injection.

Polarized Optical Microscopy (POM) measurements were performed with a Jenaval polarization microscope equipped with a Linkam THMS 600 heating device, with crossed polarizers.

Differential Scanning Calorimetry (DSC) measurements were carried out with a PerkinElmer Pyris 1 DSC under a nitrogen atmosphere with heating and cooling rates of 10 K/min.

Samples for Mid Angle and Wide Angle X Ray Scattering (MAXS and WAXS, respectively) measurements were mounted on V1 grade mica sheets 5-7 μm thick and measured using a SAXSLAB GANESHA system equipped with a GeniX-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of $1 \times 10^8$ photon × s$^{-1}$. Scattering patterns were collected using a Pilatus 300K silicon pixel detector with 487 x 619 pixels of
172 µm² placed at a sample to detector distance of 91 mm. The beam center and the q range were calibrated using the diffraction peaks of silver behenate (d(100) = 0.1076 Å⁻¹; 58.39 Å). Conversion of 2D images into 1D spectra was accomplished with Saxsgui software. Domain spacings (L₀) were calculated for various morphologies using primary scattering peak positions (q*) and interplanar spacings (d* = 2π/q*).

Fluorescence microscope images were obtained with an inverted Nikon Ti Eclipse microscope equipped with a white and black camera (Antor iXon Ultra). The filter used for excitation covers the 340-380 nm range, while that applied for emission operated in the 435-485 nm range.

UV-Vis measurements of drop cast films were performed with a Perkin Elmer Lambda 1050 UV/Vis/NIR spectrophotometer, while fluorescence measurements were carried out on a Perkin Elmer LS50B fluorimeter.

X-ray diffraction patterns were recorded with a Bruker Proteum diffractometer with rotating anode and Helios optics (λ = 1.54184 Å) at a temperature of 100(2) K up to a resolution of (sin θ/λ)max = 0.57 Å⁻¹. Further information about the XRD measurements are reported in the specific section.
Synthesis and Characterization

NDIs 1 and 9 and naphthalenemonoimides (NMIs) 6 and 7 were synthesized from commercially available 1,4,5,8-naphthalene tetracarboxylic dianhydride (NDA), n-decylamine and 10-undecen-1-amine via optimization of a previously reported microwave assisted protocol (Scheme S1). By means of the same microwave assisted protocol, asymmetric NDI 2 was obtained from 7 and n-decylamine, whereas the condensation of 7 with commercially available N-(tert-Butoxycarbonyl)-1,3-diaminopropane afforded 8 (Scheme S2). Boc group removal from 8 with trifluoroacetic acid (TFA), followed by microwave reaction with 7-6 in the presence of excess triethylamine in DMF yielded 3-4, in which two NDI units are connected via a three methylene linker (Scheme S2). Finally, Pt-catalyzed hydrosyliations between mono- and di-hydride ODMS and NDIs 1-4 afforded the monodisperse NDI-ODMS conjugates Si-NDI-Si, Si-NDI-Si, NDI-Si-NDI and NDI-Si-NDI (Scheme S3). The final block molecules were purified via column chromatography (SiO₂). In some cases recycling Gel Permeation Chromatography (GPC) was necessary to obtain pure products.

Scheme S1. Synthesis of NDIs 1 and 9 and NMIs 6 and 7.
Scheme S2. Synthesis of NDIs 2, 3 and 4.

Scheme S3. Synthesis of NDI-ODMS conjugates.

The molecular characterization of all new molecules was performed with proton and carbon Nuclear Magnetic Resonance ($^1$H and $^{13}$C NMR) spectroscopy, Matrix Assisted Laser Desorption Ionization-Time of Flight Mass (MALDI-TOF-MS) spectrometry, Fourier Transform Infrared (FT-IR) spectroscopy and, in some cases, Ultraviolet-Visible (UV-Vis) spectroscopy. The characteristic features of the $^1$H NMR spectra of the NDI blocks are summarized by the spectrum of 1 (Figure S1): proceeding from lower to higher magnetic fields the aromatic singlet at 8.75 ppm, the complex patterns of the terminal double bond protons in the 5.9-4.9 ppm range, the deshielded triplet of the methylene protons bound to the imide nitrogen atoms at 4.2 ppm, the quartet of the methylene protons α to the terminal double bond at 2.0 ppm, the quintet at 1.75 ppm and a large multiplet of the rest
of the aliphatic protons between 1.5 and 1.2 ppm, can be observed. Assignment of the alkyl chain signals was performed with two Dimensional Correlation Spectroscopy (2D-COSY) NMR experiments (Figure S4 and S8). The replacement of one ω-alkenyl chain with a fully hydrogenated alkyl chain in 2 only results in the variation of the relative intensity of signals and presence of the triplet of the final methyl group at 0.9 ppm (Figure S1b). No consequences are observed on the multiplicity of the aromatic signals of symmetrical 1 and asymmetrical 2, highlighting a very subtle structural change. In contrast, when two NDIs are connected via the three methylene spacer in 3, the multiplicity of the aromatic signal is significantly affected: the asymmetrical substitution on each NDI unit of 3 causes the generation of equivalent aromatic AB systems centered, once again, at 8.75 ppm (Figure S1c). New signals related to the three methylene linker, namely the triplet of the methylene protons α to the imide nitrogen atoms at 4.4 ppm and the quintet of their bridging methylene group at 2.3 ppm, are present in a 2:1 ratio (Figure S1c). The absence of intramolecular dimerization of the two NDI units of 3 and 4 was suggested by the lack of significant shifts in the aromatic regions of the 1H NMR spectra (vide supra) and, similarly to a previous report by Iverson et al on different NDI derivatives,51 the additivity of the extinction coefficients of 1 and 3 in CHCl3 (Figure S64 and S65). Upon coupling the NDI blocks to the ODMS via Pt-catalyzed hydrosylilation, the signals of the terminal double bond protons disappear. Key feature of the NDI-ODMS coupling is the A2B2 system (1H-1H and 29Si-1H couplings) at 0.5 ppm of the methylene protons directly connected to the ODMS chain as shown in the 1H NMR of Si7-NDI2-Si7 and NDI2-Si16-NDI2 (Figure S2d and S2e, respectively). Additionally, the quartet of the methylene protons α to the terminal double bond at 2.0 ppm disappears to become, in its new multiplicity, integrating part of the large multiplet in the 1.55-1.2 ppm range (Figure S1d and S1e).

Characteristic signals in the IR spectra of NDIs 1-4 are the C-H stretching vibrations at 2960-2850 cm−1 and the narrow and intense imide carbonyl vibrations at ~ 1710 cm−1 and ~ 1660 cm−1 (pages S84-S93). In the NDI-ODMS block molecules such vibrations are unaffected in shape and position, but their relative intensity is decreased due to the much more present siloxanes vibrations at ~ 1030 cm−1 and ~ 800 cm−1 (pages S84-S93).

Purity and monodispersity of the synthesized block molecules was confirmed by MALDI-TOF spectrometry and Gel Permeation Chromatography (GPC).
Figure S1. $^1$H NMR spectra (400 MHz, CDCl$_3$) of (a) 1, (b) 2, (c) 3, (d) Si7-NDI$_2$-Si7 (e) and NDI$_2$-Si16-NDI$_2$. Chemical structures with colored circles for peak assignments are reported. The signal of tetramethylsilane is indicated with the TMS acronym.
General procedure for the synthesis of symmetrical NDIs 1, 9 and 5

1,4,5,8-Naphthalene tetracarboxylic dianhydride (1 mol eq) and the desired amine (2.1 eq) were loaded into a 20 mL microwave reaction vessel equipped with a magnetic stirrer. DMF (10 mL) was added and the suspension was sonicated for two minutes. The reaction vessel was sealed and the mixture was heated up to 75 °C for 5 minutes, followed by 25 minutes at 140 °C (maximum power 300 W). The reaction mixture was poured into 150 mL of a 1M NaOH aqueous solution and the precipitate was filtered and washed with H₂O several times. The NDIs were dried and filtered over a short path of silica gel (SiO₂, CH₂Cl₂) to remove the brown impurities. After this treatment 1, 5 and 9 were recovered as white/off yellow solids.

General procedure for the synthesis of NMIs 6 and 7

1,4,5,8-Naphthalene tetracarboxylic dianhydride (2.5 mol eq) and the desired amine (1 eq) were loaded into a 20 mL microwave reaction vessel equipped with a magnetic stirrer. DMF (10 mL) was added and the suspension was sonicated for two minutes. The reaction vessel was sealed and the mixture was kept at 140 °C for 5 minutes (maximum power 300 W). The reaction mixture was poured into 150 mL of a 1M NaOH aqueous solution and the unsoluble residue (NDIs 1 and 9) was filtered. The filtered solution was acidified to pH 5 with a 3M HCl aqueous solution until the formation of a precipitate was visible by eye. The acidic mixture was filtered and the solid was dried. NMIs 6 and 7 were used in the next step without further purification.

Procedure for the synthesis of NDI 8

NMI 7 (1 eq) and N-(tert-Butoxycarbonyl)-1,3-diaminopropane were loaded into a 20 mL microwave reaction vessel equipped with a magnetic stirrer and dissolved in DMF (10 mL). The reaction vessel was sealed and the mixture was heated up to 75 °C for 5 minutes, followed by 25 minutes at 140 °C (maximum power 300 W). The reaction mixture was poured into 150 mL of a 1M NaOH aqueous solution and the precipitate was filtered and washed with H₂O several times. NDI 8 was dried and filtered over a short path of silica gel (SiO₂, CH₂Cl₂) to remove the brown impurities.
General procedure for the synthesis of NDIs 3 and 4

NDI 8 (1 eq) was loaded into a microwave reaction vessel equipped with a magnetic stirrer and dissolved in a 5% v/v TFA:CHCl₃ mixture (10 mL). The solution was stirred at room temperature for 3 hours, after which the solvent was removed under vacuum without heating. The residue was dissolved in DMF (10 mL) and triethylamine (Et₃N) (10 eq) and NMI 6/7 (1 eq) were added to the solution. The reaction vessel was sealed and the mixture was heated up to 75 ºC for 5 minutes, followed by 25 minutes at 140 ºC (maximum power 300 W). The reaction mixture was poured into 150 mL of a 1M NaOH aqueous solution and the precipitate was filtered and washed with H₂O several times. NDIs 3 and 4 were obtained as off-yellow solids after column chromatography purification (SiO₂, CH₂Cl₂ → CH₂Cl₂:EtOAc in 10 column volumes).

General procedure for the hydrosilylation of NDIs with mono-hydride ODMS.

The reaction was performed under an Argon atmosphere, using oven dried glassware. NDIs 1/3 (1 eq) and mono-hydride ODMS (2.1 mol eq) were dissolved in toluene to reach a final 20 mM concentration of NDI. The solution was heated up to 70 ºC. Catalyst HS 432 from Umicore (1 mol % with respect to the NDI) was added and the mixture stirred overnight at 70 ºC.

The solvent was removed and the crude waxy product was purified with the Reveleris column chromatography system (SiO₂, gradient from 100% Heptane to 100% Ethyl acetate in 20 column volumes). In some cases the separation of Si-NDI-Si and Si-NDI₂-Si from side products (mostly monohydrosilylated-monoisomerized NDIs) was not satisfactory and some NDI-ODMS conjugates of family 1 were obtained in high purity with recycling gel permeation chromatography purification, using CHCl₃ as eluent.

General procedure for the hydrosilylation of NDIs with di-hydride ODMS.

The reaction was performed under an Argon atmosphere, using oven dried glassware. NDIs 2/4 (2 eq) and di-hydride ODMS (1 mol eq) were suspended in toluene to reach a final (nominal) 20 mM concentration of NDI. The solution was heated up to 70 ºC. Catalyst HS 432 from Umicore (1 mol % with respect to the NDI) was added and the mixture stirred overnight at 70 ºC.
The solvent was removed and the crude waxy product was purified with the Reveleris column chromatography system (SiO₂, gradient from 100% Heptane to 100% Ethyl acetate in 20 column volumes). In all cases the separation of NDI-Si-NDI and NDI₂-Si-NDI₂ from side products was not satisfactory and the NDI-ODMS conjugates of family 2 were obtained in high purity with recycling gel permeation chromatography purification, using CHCl₃ as eluent.

2,7-di(undec-10-en-1-yl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (1)

White solid. 98% yield.

\[^{1}H\] NMR (400 MHz, CDCl₃) \(\delta\): 8.75 (s, 4H), 5.85-5.75 (m, 2H), 5.00-4.90 (m, 4H), 4.19 (t, \(J = 8\) Hz, 4H), 2.04 (q, \(J = 8\) Hz, 4H), 1.74 (p, \(J = 8\) Hz, 4H), 1.46-1.25 (m, 24 H).

\[^{13}C\] NMR (100 MHz, CDCl₃) \(\delta\): 162.97, 139.36, 131.07, 126.84, 126.79, 114.25, 41.14, 33.95, 29.59, 29.55, 29.44, 29.24, 29.06, 28.23, 27.22.

UV-vis (CHCl₃, 25 ºC) \([\lambda_{max} (nm) \epsilon (L \times mol^{-1} \times cm^{-1})]\): 381 (28182), 360 (21847), 342 (12932).

FT-IR (ATR) \(\nu (cm^{-1})\): 3078, 2923, 2850, 1706, 1655, 1582, 1466, 1455, 1375, 1338, 1281, 1258, 1243, 1194, 1155, 1083, 992, 970, 908, 889, 769, 608, 567.

MALDI-ToF-MS for C₃₆H₄₆N₂O₄ calculated \(M_w\) 570.35 g/mol, found \(m/z\) 570.38 [M⁺].

2,7-didecylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (9)

White solid. 98% yield.

\[^{1}H\] NMR (400 MHz, CDCl₃) \(\delta\): 8.74 (s, 4H), 4.18 (t, \(J = 8\) Hz, 4H), 1.73 (p, \(J = 8\) Hz, 4H), 1.46-1.25 (m, 28 H), 0.87 (t, \(J = 8\) Hz, 6H).

\[^{13}C\] NMR (100 MHz, CDCl₃) \(\delta\): 162.95, 131.05, 126.81, 126.76, 41.14, 32.02, 29.69, 29.67, 29.47, 29.44, 28.23, 27.23, 22.82, 14.26.

FT-IR (ATR) \(\nu (cm^{-1})\): 2946, 2917, 2849, 1699, 1653, 1580, 1454, 1345, 1327, 1262, 1242, 1153, 1080, 983, 887, 767, 727, 605, 562.

MALDI-ToF-MS for C₃₆H₄₆N₂O₄ calculated \(M_w\) 546.35 g/mol, found \(m/z\) 546.35 [M⁺].

1,3-dioxo-2-(undec-10-en-1-yl)-2,3-dihydro-1H-benzo[de]isoquinoline-6,7-dicarboxylic acid (7)

Off-yellow solid. 68% yield.
$^1$H NMR (400 MHz, 4% CF$_3$CO$_2$D in CDCl$_3$) δ: 8.79 (d, J = 4 Hz, 2H), 8.42 (d, J = 4 Hz, 2H), 5.86-5.76 (m, 1H), 5.01-4.90 (m, 2H), 4.21 (t, J = 8 Hz, 2H), 2.03 (q, J = 8 Hz, 2H), 1.72 (p, J = 8 Hz, 2H), 1.46-1.27 (m, 12H).

$^{13}$C NMR (100 MHz, 4% CF$_3$CO$_2$D in CDCl$_3$) δ: 173.78, 163.77, 162.90, 159.31, 139.43, 139.41, 133.73, 133.62, 131.83, 131.61, 131.37, 129.16, 129.01, 127.86, 126.96, 125.97, 125.87, 123.00, 114.26, 114.24, 41.74, 41.61, 33.94, 29.56, 29.53, 29.39, 29.37, 29.23, 29.05, 28.10, 27.14.

FT-IR (ATR) ν (cm$^{-1}$): 3085, 2922, 2852, 1792, 1765, 1709, 1671, 1582, 1516, 1449, 1384, 1368, 1336, 1286, 1239, 1192, 1155, 1105, 1030, 910, 878, 763, 562.

MALDI-ToF-MS for C$_{25}$H$_{25}$NO$_5$ (M-H$_2$O) calculated M$_w$ 419.17 g/mol, found m/z 419.23 [(M-H$_2$O)$^-$].

2-decyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6,7-dicarboxylic acid (6)

Off-yellow solid. 69% yield.

$^1$H NMR (400 MHz, 4% CF$_3$CO$_2$D in CDCl$_3$) δ: 8.79 (d, J = 8 Hz, 2H), 8.43 (d, J = 8 Hz, 2H), 4.21 (t, J = 8 Hz, 2H), 1.74 (p, J = 8 Hz, 2H), 1.31-1.26 (m, 14H), 0.87 (t, J = 8 Hz, 3H).

$^{13}$C NMR (100 MHz, 4% CF$_3$CO$_2$D in CDCl$_3$) δ: 173.64, 163.84, 163.00, 159.37, 133.69, 131.91, 131.72, 131.46, 127.84, 126.00, 123.02, 41.82, 41.70, 32.02, 29.67, 29.64, 29.43, 29.40, 28.11, 28.06, 27.16, 22.82, 14.22.

FT-IR (ATR) ν (cm$^{-1}$): 2956, 2921, 2852, 1691, 1653, 1592, 1519,1455, 1332, 1243, 882, 768.

MALDI-ToF-MS for C$_{24}$H$_{25}$NO$_5$ calculated M$_w$ 407.17 g/mol, found m/z 407.20 [M$^-$].

2-decyl-7-(undec-10-en-1-yl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrione (2)

White solid. 98% yield

$^1$H NMR (400 MHz, CDCl$_3$) δ: 8.75 (s, 4H), 5.85-5.75 (m, 1H), 5.01-4.90 (m, 2H), 4.19 (t, J = 8 Hz, 4H), 2.03 (q, J = 8 Hz, 2H), 1.74 (p, J = 8 Hz, 4H), 1.46-1.26 (m, 26H), 0.87 (t, J = 8 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ: 162.99, 139.37, 131.07, 126.85, 126.80, 114.26, 41.15, 33.95, 32.03, 29.70, 29.68, 29.60, 29.55, 29.48, 29.45, 29.24, 29.06, 28.24, 27.24, 27.22, 22.83, 14.27.

FT-IR (ATR) ν (cm$^{-1}$): 2954, 2921, 2849, 1704, 1655, 1581, 1454, 1374, 1332, 1243, 1154, 1083, 908, 889, 768, 608, 566.

MALDI-ToF-MS for C$_{35}$H$_{46}$N$_2$O$_4$ calculated M$_w$ 558.35 g/mol, found m/z 558.37 [M$^+$].

tert-butyl (3-(1,3,6,8-tetraoxo-7-(undec-10-en-1-yl)-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthrolin-2(1H)-yl)propyl)carbamate (8)
Off-yellow solid. 95% yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ: 8.76 (s, 4H), 5.86-5.73 (m, 1H), 5.09 (br s, 1H), 5.00-4.91 (m, 2H), 4.28 (t, J = 8 Hz, 2H), 4.19 (t, J = 8 Hz, 2H), 3.21-3.11 (m, 2H), 2.07-1.90 (m, 2H), 1.81-1.67 (m, 2H), 1.45-1.29 (m, 21H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ: 163.26, 162.89, 139.35, 131.27, 131.08, 126.97, 126.87, 126.84, 126.50, 114.25, 41.17, 38.39, 33.94, 29.59, 29.54, 29.43, 29.23, 29.05, 28.68, 28.58, 28.22, 27.21.

FT-IR (ATR) ν (cm$^{-1}$): 3357, 2977, 2924, 2852, 1706, 1689, 1657, 1582, 1534, 1454, 1377, 1367, 1341, 1283, 1269, 1246, 1174, 1083, 1064, 1003, 769.

MALDI-ToF-MS for C$_{33}$H$_{41}$N$_{3}$O$_{6}$ calculated M$\text{w}$ 575.30 g/mol, found m/z 575.32 [M$^+$].

7,7'-{(propane-1,3-diyl)bis(2-(undec-10-en-1-yl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrone) (3)

Off-yellow solid. 90% yield.

$^1$H NMR (500 MHz, CDCl$_3$): δ: 8.75-8.69 (AB system, 8H), 5.85-5.75 (m, 2H), 5.00-4.90 (m, 4H), 4.37 (t, J = 8 Hz, 4H), 4.18 (t, J = 8 Hz, 4H), 2.28 (p, J = 8 Hz, 2H), 2.02 (q, J = 8 Hz, 4H), 1.73 (p, J = 8 Hz, 4H), 1.44-1.28 (m, 24).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ: 163.05, 162.98, 162.91, 139.36, 131.16, 131.07, 131.05, 126.93, 126.88, 126.86, 126.79, 126.58, 114.25, 41.16, 38.80, 33.95, 29.59, 29.55, 29.44, 29.24, 29.06, 28.22, 27.22.

UV-vis (CHCl$_3$, 25 ºC) [λ$_{max}$ (nm) e (L × mol$^{-1}$ × cm$^{-1}$): 381 (52150), 360 (44029), 343 (25137).

FT-IR (ATR) ν (cm$^{-1}$): 3076, 2923, 2852, 1703, 1657, 1581, 1455, 1378, 1339, 1245, 1222, 1154, 1084, 1059, 992, 969, 908, 890, 808, 768, 608, 564.

MALDI-ToF-MS for C$_{53}$H$_{56}$N$_{4}$O$_{8}$ calculated M$\text{w}$ 876.41 g/mol, found m/z 876.42 [M$^+$].

2-decyl-7-(3-(1,3,6,8-tetraoxo-7-(undec-10-en-1-yl)-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthroline-2(1H)-yl)propyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetrone (4)

Off-yellow solid. 90% yield.

$^1$H NMR (400 MHz, 4% CF$_3$CO$_2$D in CDCl$_3$): δ: 8.83-8.77 (AB system, 8H), 5.86-5.76 (m, 1H), 5.01-4.91 (m, 2H), 4.41 (t, J = 8 Hz, 4H), 4.21 (t, J = 8 Hz, 4H), 2.29 (p, J = 8 Hz, 2H), 2.03 (q, J = 8 Hz, 4H), 1.74 (p, J = 8 Hz, 4H), 1.46-1.26 (m, 26H), 0.87 (t, J = 8 Hz, 3H).

$^{13}$C NMR (100 MHz, 4% CF$_3$CO$_2$D in CDCl$_3$): δ: 163.80, 163.70, 139.44, 131.92, 131.87, 126.87, 126.83, 126.80, 126.66, 126.47, 114.24, 110.20, 41.78, 39.25, 33.95, 32.03, 29.67, 29.64, 29.56, 29.53, 29.44, 29.41, 29.38, 29.23, 29.05, 28.12, 27.15, 22.82, 14.21.
FT-IR (ATR) ν (cm\(^{-1}\)): 2955, 2923, 2852, 1703, 1581, 1454, 1379, 1341, 1247, 1221, 1154, 1059, 769.

MALDI-ToF-MS for C\(_{52}\)H\(_{66}\)N\(_{4}\)O\(_{8}\) calculated M\(_{w}\) 864.45 g/mol, found m/z 864.45 [M\(^+\)].

2,7-dipropylbenzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetaone (5)

White solid. 98% yield.

Compound already reported in literature.\(^5\)

Crystal structure in separate section.

2,7-bis(11-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,13-pentadecamethyloctaploroxanyl)undecyl)benzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetaone (Si\(_7\)-NDI-Si\(_7\))

Off-yellow wax. 23 % yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ: 8.75 (s, 4H), 4.19 (t, J = 8 Hz, 4H), 1.74 (p, J = 8 Hz, 4H), 1.46-1.26 (m, 32H), 0.52 (t, J = 8Hz), 0.09-0.04 (m, 90H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) δ: 162.97, 131.06, 126.84, 126.79, 41.16, 33.65, 29.82, 29.77, 29.73, 29.57, 29.52, 28.26, 27.28, 18.43, 1.95, 1.34, 1.31, 1.23, 1.23, 1.23, 0.35, 0.15.

FT-IR (ATR) ν (cm\(^{-1}\)): 2961, 2922, 2853, 1707, 1657, 1582, 1455, 1412, 1377, 1339, 1258, 1079, 1025, 840, 795, 771, 754, 686.

MALDI-ToF-MS for C\(_{66}\)H\(_{138}\)N\(_{2}\)O\(_{16}\)Si\(_{14}\) calculated M\(_{w}\) = 1606.68 g/mol, found m/z = 1606.69 [M\(^+\)].

7,7’-(propane-1,3-diyl)bis(2-(11-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,13-pentadecamethyloctaploroxanyl)undecyl)benzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetaone) (Si\(_7\)-NDI\(_2\)-Si\(_7\))

Off-yellow wax. 20 % yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ: 8.75-8.70 (AB system, 8H), 4.37 (t, J = 8Hz, 4H), 4.18 (t, J = 8Hz, 4H) 2.28 (p, J = 8Hz, 2H), 1.74 (p, J = 8 Hz, 4H), 1.45-1.26 (m, 32, 0.52 (t, J = 8Hz, 4H), 0.08-0.04 (m, 90H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) δ: 163.05, 162.89, 131.16, 131.04, 126.93, 126.88, 126.85, 126.56, 41.19, 38.80, 33.64, 29.82, 29.76, 29.73, 29.57, 29.52, 28.25, 27.28, 27.04, 23.39, 18.43, 1.94, 1.34, 1.30, 1.22, 0.35, 0.15.

FT-IR (ATR) ν (cm\(^{-1}\)): 2961, 2922, 2853, 1704, 1661, 1582, 1456, 1412, 1377, 1342, 1258, 1248, 1221, 1153, 1048, 1027, 840, 796, 771, 754, 687.
MALDI-ToF-MS for C_{86}H_{148}N_{4}O_{20}Si_{14} calculated M_w = 1912.75 g/mol, found m/z = 1912.76 [M^+].

2,7-bis(11-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,29-hentriacontamethylpentadecasiloxanyl)undecyl)benzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (Si15-NDI-Si15)

Off-yellow wax. 28 % yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.75 (s, 4H), 4.19 (t, J = 8 Hz, 4H), 1.74 (p, J = 8Hz, 4H), 1.45-1.26 (m, 32H), 0.52 (t, J = 8Hz, 4H), 0.09-0.04 (m, 186H).

\(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 162.99, 131.07, 126.86, 126.82, 41.18, 33.65, 29.83, 29.78, 29.74, 29.58, 29.53, 28.27, 27.29, 23.41, 18.44, 1.94, 1.33, 1.30, 1.23, 1.21, 0.35.

FT-IR (ATR) \(\nu\) (cm\(^{-1}\)): 2962, 2924, 2854, 1708, 1668, 1582, 1455, 1412, 1376, 1340, 1258, 1076, 1013, 868, 841, 789, 702, 687.

MALDI-ToF-MS for C_{98}H_{234}N_{2}O_{32}Si_{30} calculated M_w = 2790.98 g/mol, found m/z = 2790.89 [M^+].

7,7’-(propane-1,3-diyl)bis(2-(11-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,29-hentriacontamethylpentadecasiloxanyl)undecyl)benzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (Si15-NDI\(_2\)-Si15)

Off-yellow wax. 30 % yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.76-8.70 (AB system, 8H), 4.37 (t, J = 8 Hz, 4H), 4.19 (t, J = 8 Hz, 4H), 2.28 (p, J = 8 Hz, 2H), 1.74 (p, J = 8 Hz, 4H), 1.46-1.26 (m, 32H), 0.52 (t, J = 8 Hz, 4H), 0.10-0.04 (m, 186H).

\(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 163.06, 162.90, 131.17, 131.04, 126.95, 126.90, 126.87, 126.58, 41.20, 38.82, 33.65, 29.83, 29.78, 29.75, 29.58, 29.53, 28.27, 27.30, 27.06, 23.40, 18.44, 1.94, 1.33, 1.30, 1.23, 1.21, 0.35.

FT-IR (ATR) \(\nu\) (cm\(^{-1}\)): 2962, 2923, 2853, 1704, 1661, 1582, 1456, 1412, 1377, 1342, 1258, 1014, 863, 840, 790, 771, 701, 686, 663.

MALDI-ToF-MS for C_{115}H_{244}N_{4}O_{36}Si_{30} calculated M_w = 3097.05 g/mol, found m/z = 3097.04 [M^+].

2,7-bis-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31,33,33,35,35,37,37,39,39,41,41,43,43,45,45,45-heptatettrarcontamethyltricosasiloxanyl)undecyl)benzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (Si23-NDI-Si23)
Off-yellow wax. 10 % yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\))  \(\delta\): 8.76 (s, 4H), 4.19 (t,  \(J = 8\) Hz, 4H), 1.74 (p,  \(J = 8\) Hz, 4H), 1.44-1.26 (m, 32H), 0.52 (t,  \(J = 8\) Hz, 4H), 0.09-0.04 (m, 282H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\))  \(\delta\): 162.98, 131.07, 126.80, 33.66, 33.36, 29.83, 29.78, 29.74, 29.58, 29.52, 28.27, 27.29, 23.40, 18.43, 1.94, 1.33, 1.30, 1.22, 1.20, 0.34, 0.15.

FT-IR (ATR)  \(\nu\) (cm\(^{-1}\)): 2962, 2924, 2855, 1708, 1669, 1582, 1455, 1412, 1376, 1340, 1258, 1078, 1012, 841, 789, 701, 686.

MALDI-ToF-MS for C\(_{130}\)H\(_{330}\)N\(_2\)O\(_4\)Si\(_4\) calculated  \(M_w\) = 3975.28 g/mol, found  \(m/z\) = 3977.23 [M\(^+\)].

7,7'-(propane-1,3-diyl)bis(2-(11-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31,33,33,35,35,37,37,39,39,41,41,43,43,45,45,45-heptatetracontamethyltricosasiloxanyl)undecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (Si23-NDI2-Si23)

Off-yellow wax. 20 % yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\))  \(\delta\): 8.76-8.70 (AB system, 8H), 4.37 (t,  \(J = 8\) Hz, 4H), 2.28 (p,  \(J = 8\) Hz, 2H), 1.74 (p,  \(J = 8\) Hz, 4H), 1.45-1.26 (m, 32H), 0.52 (t,  \(J = 8\) Hz, 4H), 0.10-0.04 (m, 282H).

\(^{13}\)C NMR (50 MHz, CDCl\(_3\))  \(\delta\): 163.06, 162.91, 131.18, 131.06, 126.94, 126.90, 126.86, 126.57, 77.80, 33.66, 29.83, 29.78, 29.77, 29.58, 23.40, 18.42, 1.94, 1.33, 1.20, 0.34.

FT-IR (ATR)  \(\nu\) (cm\(^{-1}\)): 2962, 2923, 2853, 1704, 1661, 1582, 1456, 1412, 1377, 1343, 1258, 1079, 1012, 841, 790, 701, 686.

MALDI-ToF-MS for C\(_{147}\)H\(_{340}\)N\(_4\)O\(_5\)Si\(_{4}\) calculated  \(M_w\) = 4281.35 g/mol, found  \(m/z\) = 4282.12 [M\(^+\)].

7,7'-(1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyloctasiloxane-1,15-diyl)bis(undecane-11,1-diyl)bis(2-decylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (NDI8-Si8-NDI)

Off-yellow wax. 20 % yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\))  \(\delta\): 8.73 (s, 8H), 4.17 (t,  \(J = 8\) Hz, 8H), 1.73 (p,  \(J = 8\) Hz, 8H), 1.45-1.25 (m, 60H), 0.86 (t,  \(J = 8\) Hz, 6H), 0.52 (t,  \(J = 8\) Hz, 4H), 0.07-0.04 (m, 48H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\))  \(\delta\): 162.93, 131.04, 126.79, 126.75, 41.14, 33.64, 32.02, 29.81, 29.76, 29.72, 29.69, 29.67, 29.56, 29.51, 29.47, 29.44, 28.24, 28.22, 27.26, 27.23, 23.38, 22.82, 18.42, 14.27, 1.33, 1.33, 1.23, 1.20, 0.34.

FT-IR (ATR)  \(\nu\) (cm\(^{-1}\)): 2960, 2922, 2853, 1704, 1660, 1582, 1456, 1380, 1345, 1249, 1221, 1154, 1088, 1057, 1025, 798, 770.
MALDI-ToF-MS for C₈₆H₄₂N₄O₁₅Si₈ calculated Mₘ 1694.86 g/mol, found m/z 1694.87.

7,7’-((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyloctasiloxane-1,15-diy)bis(undecane-11,1-diyl))bis(2-(3-(7-decyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthroline-2(1H)-yl)propyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (NDI₂-Si₈-NDI₂)

Off-yellow wax. 10 % yield.

¹H NMR (400 MHz, CDCl₃) δ: 8.75-8.71 (AB system, 8H), 8.74-8.69 (AB system, 8H), 4.18 (t, J = 8 Hz, 8H), 2.27 (p, J = 8 Hz, 4H), 1.73 (p, J = 8 Hz, 8H), 1.42-1.26 (m, 60H), 0.87 (t, J = 8 Hz, 6H), 0.52 (t, J = 8 Hz, 4H), 0.14-0.04 (m, 48H).

¹³C NMR (100 MHz, CDCl₃) δ: 163.04, 162.89, 131.16, 131.09, 131.06, 131.04, 126.92, 126.83, 126.55, 126.51, 41.20, 38.80, 33.22, 32.03, 29.82, 29.78, 29.77, 29.73, 29.70, 29.68, 29.57, 29.52, 29.47, 29.45, 28.25, 27.28, 22.83, 18.95, 14.28, 1.35, 1.23, 0.35.

FT-IR (ATR) ν (cm⁻¹): 2959, 2922, 2853, 1704, 1660, 1582, 1456, 1377, 1341, 1247, 1221, 1154, 1047, 1020, 798, 768, 722, 614.

MALDI-ToF-MS for C₁₂₀H₁₆₂N₈O₂₃Si₈ calculated Mₘ 2306.99 g/mol, found m/z 2307.03 [M⁺].

7,7’-
((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-dotriacontamethylhexadecasiloxane-1,31-diyl)bis(undecane-11,1-diyl))bis(2-decylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (NDI-Si₁₆-NDI)

Off-yellow wax. 19 % yield.

¹H NMR (400 MHz, CDCl₃) δ: 8.73 (s, 8H), 4.17 (t, J = 8 Hz, 8H), 1.73 (p, J = 8 Hz, 8H), 1.42-1.25 (m, 60H), 0.86 (t, J = 8 Hz, 6H), 0.52 (t, J = 8 Hz, 4H), 0.13-0.04 (m, 96H).

¹³C NMR (100 MHz, CDCl₃) δ: 162.91, 131.03, 126.78, 126.74, 41.13, 33.63, 32.02, 29.80, 29.75, 29.71, 29.69, 29.66, 29.56, 29.50, 29.46, 29.43, 28.24, 28.22, 27.26, 22.38, 22.82, 18.41, 14.26, 1.32, 1.31, 1.19, 1.13, 0.46, 0.33.

FT-IR (ATR) ν (cm⁻¹): 2962, 2922, 2851, 1708, 1657, 1582, 1455, 1376, 1348, 1337, 1258, 1082, 1016, 792, 769.

MALDI-ToF-MS for C₁₉₀H₁₉₀N₈O₂₃Si₁₆ calculated Mₘ 2287.01 g/mol, found m/z 2287.01 [M⁺].

7,7’-
((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-dotriacontamethylhexadecasiloxane-1,31-diyl)bis(undecane-11,1-diyl))bis(2-(3-(7-decyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthroline-2(1H)-yl)propyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (NDI₂-Si₁₆-NDI₂)

Off-yellow wax. 5 % yield.
$^1$H NMR (400 MHz, CDCl$_3$) δ: 8.75-8.69 (AB system, 16H), 4.37 (t, J = 8 Hz, 8H), 4.19 (t, J = 8 Hz, 8H), 2.28 (p, J = 8 Hz, 4H), 1.74 (p, J = 8 Hz, 8H), 1.44-1.26 (m, 60H), 0.87 (t, J = 8 Hz, 6H), 0.52 (t, J = 8 Hz, 4H), 0.21-0.04 (m, 96H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ: 163.06, 162.91, 131.17, 131.16, 131.05, 126.93, 126.88, 126.85, 126.57, 41.19, 38.81, 33.65, 32.03, 29.83, 29.78, 29.74, 29.70, 29.68, 29.61, 29.58, 29.52, 29.48, 29.45, 28.23, 27.28, 22.83, 18.43, 14.27, 1.33, 1.20, 0.34.

FT-IR (ATR) ν (cm$^{-1}$): 2962, 2923, 2854, 1705, 1660, 1582, 1456, 1379, 1346, 1258, 1249, 1083, 1014, 791, 770.

MALDI-ToF-MS for C$_{136}$H$_{210}$N$_8$O$_3$Si$_{16}$ calculated M$_w$ 2899.14 g/mol, found m/z 2900.10 [M$^+$].

7,7’-

((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31,33, 33,35,35,37,37,39,39,41,41,43,43,45,45,47,47-octatetracontamethyltetracosasiloxane-1,47-diy)bis(undecane-11,1-diy))bis(2-decylbenzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (NDI-Si$_{24}$-NDI)

Off-yellow wax. 10 % yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ: 8.75 (s, 8H), 4.18 (t, J = 8 Hz, 8H), 1.73 (p, J = 8 Hz, 8H), 1.42-1.26 (m, 60H), 0.87 (t, J = 8 Hz, 4H), 0.52 (t, J = 8 Hz, 4H), 0.21-0.04 (m, 144H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ: 162.97, 131.07, 126.82, 126.77, 41.15, 33.65, 32.03, 29.69, 29.45, 28.25, 27.26, 23.38, 22.84, 18.41, 2.14, 1.84, 1.61, 1.34, 1.25, 1.14, 0.55, 0.23.

FT-IR (ATR) ν (cm$^{-1}$): 2962, 2922, 2850, 1707, 1657, 1582, 1455, 1376, 1348, 1337, 1258, 1082, 1014, 790, 769.

MALDI-ToF-MS for C$_{102}$H$_{190}$N$_4$O$_{23}$Si$_{16}$ calculated M$_w$ 2879.16 g/mol, found m/z 2879.16 [M$^+$].

7,7’-

((1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15,17,17,19,19,21,21,23,23,25,25,27,27,29,29,31,31,33, 33,35,35,37,37,39,39,41,41,43,43,45,45,47,47-octatetracontamethyltetracosasiloxane-1,47-diy)bis(2-[3-(7-decyl-1,3,6,8-tetraoxo-3,6,7,8- tetrahydrobenzo[lnn][3,8]phenanthroline-2(1H-yl)propyl]benzo[lnn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (NDI$_2$-Si$_{24}$-NDI$_2$)

Off-yellow wax. 3 % yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ: 8.75-8.69 (AB system, 16H), 4.37 (t, J = 8 Hz, 8H), 4.18 (t, J = 8 Hz, 8H), 2.28 (p, J = 8 Hz, 4H), 1.75 (p, J = 8 Hz, 8H), 1.42-1.26 (m, 60H), 0.87 (t, J = 8 Hz, 6H), 0.52 (t, J = 8 Hz, 4H), 0.21-0.04 (m, 144H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ: 163.05, 162.90, 131.17, 131.05, 126.92, 126.87, 126.85, 126.56, 41.18, 38.80, 33.65, 32.03, 29.83, 29.75, 29.74, 29.69, 29.57, 29.52, 29.47, 29.44, 28.25, 28.23, 27.28, 27.24, 27.03, 23.39, 22.83, 18.42, 14.27, 1.32, 1.19, 0.34.
FT-IR (ATR) ν (cm⁻¹): 2961, 2923, 2853, 1704, 1659, 1582, 1456, 1379, 1345, 1258, 1248, 1084, 1015, 792, 770.

MALDI-ToF-MS for C₁₅₂H₂₅₈N₈O₃₉Si₂₄ calculated Mₘ 3491.29 g/mol, found m/z 3492.37 [M⁺].
Figure S2. $^1$H NMR spectrum of 1.
Figure S3. $^{13}$C NMR spectrum of 1.
Figure S4. 2D COSY spectrum of 1.
Figure S5. MALDI-TOF-MS spectrum of 1.

Chemical Formula: $C_{36}H_{46}N_2O_4$
Exact Mass: 570.35
Molecular Weight: 570.77
Figure S6. $^1$H NMR spectrum of 9.
Figure S7. $^{13}$C NMR spectrum of 9.
Figure S8. 2D COSY spectrum of 9.
Figure S9. MALDI-TOF-MS spectrum of 9.

Chemical Formula: C₃₄H₄₆N₂O₄
Exact Mass: 546.35
Molecular Weight: 546.75
Figure S10. $^1$H NMR spectrum of 7.
Figure S11. $^{13}$C NMR spectrum of 7.
Figure S12. MALDI-TOF-MS spectrum of 7.
Figure S13. $^1$H NMR spectrum of 6.
Figure S14. $^{13}$C NMR spectrum of 6.
Figure S15. MALDI-TOF-MS spectrum of 6.
Figure S16. $^1$H NMR spectrum of 2.
Figure S17. $^{13}$C NMR spectrum of 2.
Figure S18. MALDI-TOF-MS spectrum of 2.
Figure S19. $^1$H NMR spectrum of 8.
Figure S20. $^{13}$C NMR spectrum of 8.
Figure S21. MALDI-TOF-MS spectrum of 8.
Figure S22. $^1$H NMR spectrum of 3.
Figure S23. $^{13}$C NMR spectrum of 3.
Figure S24. MALDI-TOF-MS spectrum of 3.
Figure S25. $^1$H NMR spectrum of 4.
Figure S26. $^{13}$C NMR spectrum of 4.
Figure S27. MALDI-TOF-MS spectrum of 4.
Figure S28. $^1$H NMR spectrum of Si7-NDI-Si7.
Figure S29. $^{13}$C NMR spectrum of Si7-NDI-Si7.
Figure S30. MALDI-TOF-MS spectrum of Si7-NDI-Si7.

Si7-NDI-Si7
Chemical Formula: C_{66}H_{138}N_{2}O_{16}Si_{14}
Exact Mass: 1606.68
Molecular Weight: 1609.02
Figure S31. $^1$H NMR spectrum of Si7-NDI$_2$-Si7.
Figure S32. $^{13}$C NMR spectrum of Si7-NDI$_2$-Si7.
Figure S33. MALDI-TOF-MS spectrum of Si7-NDI2-Si7.
Figure S34. $^1$H NMR spectrum of Si15-NDI-Si15.
Figure S35. $^{13}$C NMR spectrum of Si15-NDI-Si15.
Figure S36. MALDI-TOF-MS spectrum of Si15-NDI-Si15.
Figure S37. $^1$H NMR spectrum of Si15-NDI$_2$-Si15.
Figure S38. $^{13}$C NMR spectrum of Si15-NDI$_2$-Si15.
Figure S39. MALDI-TOF-MS spectrum of Si15-NDI2-Si15.

Si15-NDI2-Si15
Chemical Formula: C_{115}H_{244}N_{36}O_{36}Si_{30}
Exact Mass: 3097.85
Molecular Weight: 3101.76
Figure S40. $^1$H NMR spectrum of Si23-NDI-Si23.
Figure S41. $^{13}$C NMR spectrum of Si23-NDI-Si23.
Figure S42. MALDI-TOF-MS spectrum of Si23-NDI-Si23.
Figure S43. $^1$H NMR spectrum of Si23-NDI$_2$-Si23.
Figure S44. $^{13}$C NMR spectrum of Si23-NDl$_{2}$-Si23.
Figure S45. MALDI-TOF-MS spectrum of Si23-NDI2-Si23.
Figure S46. $^1$H NMR spectrum of NDI-Si8-NDI.
Figure S47. $^{13}$C NMR spectrum of NDI-Si8-NDI.
Figure S48. MALDI-TOF-MS spectrum of NDI-Si8-NDI.

Chemical Formula: C_{68}H_{142}N_{14}O_{15}Si_{8}
Exact Mass: 1694.66
Molecular Weight: 1696.78
Figure S49. $^1$H NMR spectrum of NDI$_2$-Si8-NDI$_2$. 
Figure S50. $^{13}$C NMR spectrum of NDI$_2$-Si8-NDI$_2$. 
Figure S51. MALDI-TOF-MS spectrum of NDI$_2$-Si8-NDI$_2$. 

NDI$_2$-Si8-NDI$_2$

Chemical Formula: C$_{120}$H$_{122}$N$_2$O$_{23}$Si$_9$

Exact Mass: 2306.99
Molecular Weight: 2309.33
Figure S52. $^1$H NMR spectrum of NDI-Si16-NDI.
Figure S53. $^{13}$C NMR spectrum of NDI-Si16-NDI.
Figure S54. MALDI-TOF-MS spectrum of NDI-Si16-NDI.

NDI-Si16-NDI

Chemical Formula: C_{102}H_{118}N_{10}O_{22}Si_{16}

Exact Mass: 2287.01

Molecular Weight: 2290.01
Figure S55. $^1$H NMR spectrum of NDI$_2$-Si16-NDI$_2$. 
Figure S56. $^{13}$C NMR spectrum of NDI$_2$-Si16-NDI$_2$. 
Figure S57. MALDI-TOF-MS spectrum of NDI$_2$-Si16-NDI$_2$. 
Figure S58. $^1$H NMR spectrum of NDI-Si24-NDI.
Figure S59. $^{13}$C NMR spectrum of NDI-Si24-NDI.
Figure S60. MALDI-TOF-MS spectrum of NDI-Si24-NDI.
Figure S61. $^1$H NMR spectrum of NDI$_2$-Si24-NDI$_2$. 
Figure S62. $^{13}$C NMR spectrum of NDI$_2$-Si24-NDI$_2$. 
Figure S63. MALDI-TOF-MS spectrum of NDI$_2$-Si24-NDI$_2$. 
UV-Vis comparison between 1 and 3

Figure S64. UV-Vis spectra of 1 and 3 in CHCl₃ (5 × 10⁻⁵M; 25 °C; 1 cm optical path).

Figure S65. UV-Vis spectra of 1 (multiplied by 2) and 3 in CHCl₃ (5 × 10⁻⁵M; 25 °C; 1 cm optical path).
Figure S66. FT-IR spectrum of 1.

Figure S67. FT-IR spectrum of 2.
Figure S68. FT-IR spectrum of 3.

Figure S69. FT-IR spectrum of 4.
Figure S70. FT-IR spectrum of 6

Figure S71. FT-IR spectrum of 7
Figure S72. FT-IR spectrum of 8

Figure S73. FT-IR spectrum of 9
Figure S74. FT-IR spectrum of Si7-NDI-Si7

Figure S75. FT-IR spectrum of Si7-NDI$_2$-Si7
Figure S76. FT-IR spectrum of Si15-NDI-Si15

Figure S77. FT-IR spectrum of Si15-NDI2-Si15
Figure S78. FT-IR spectrum of Si23-NDI-Si23

Figure S79. FT-IR spectrum of Si23-NDI$_2$-Si23
Figure S80. FT-IR spectrum of NDI-Si8-NDI

Figure S81. FT-IR spectrum of NDI$_2$-Si8-NDI$_2$
Figure S82. FT-IR spectrum of NDI-Si16-NDI

Figure S83. FT-IR spectrum of NDI2-Si16-NDI2
Figure S84. FT-IR spectrum of NDI-Si24-NDI

Figure S85. FT-IR spectrum of NDI2-Si24-NDI2
Gel Permeation Chromatography traces of Si-NDI-Si and Si-NDI$_2$-Si block molecules

Figure S86. GPC traces of Si-NDI-Si featuring one NDI unit and different ODMS length.

Figure S87. GPC traces of Si-NDI-Si featuring two NDI units and different ODMS length.
Differential Scanning Calorimetry

Figure S88. DSC trace of 1 (exo up, second heating and cooling cycle, rate 10 °C/min).

Figure S89. DSC trace of 2 (exo up, second heating and cooling cycle, rate 10 °C/min).
Figure S90. DSC trace of Si7-NDI-Si7 (exo up, second heating and cooling cycle, rate 10 °C/min).

Figure S91. DSC trace of Si7-NDI2-Si7 (exo up, second heating and cooling cycle, rate 10 °C/min).
Figure S92. DSC trace of Si15-NDI-Si15 (exo up, second heating and cooling cycle, rate 10 °C/min).

Figure S93. DSC trace of Si15-NDI₂-Si15 (exo up, second heating and cooling cycle, rate 10 °C/min).
Figure S94. DSC trace of Si23-NDI-Si23 (exo up, second heating and cooling cycle, rate 10 °C/min).

Figure S95. DSC trace of Si23-NDI2-Si23 (exo up, second heating and cooling cycle, rate 10 °C/min).
Figure S96. DSC trace of NDI-Si8-NDI (exo up, second heating and cooling cycle, rate 10 °C/min).

Figure S97. DSC trace of NDI-Si16-NDI (exo up, second heating and cooling cycle, rate 10 °C/min).
Figure S98. DSC trace of NDI-Si24-NDI (exo up, second heating and cooling cycle, rate 10 °C/min).
Figure S99. POM micrographs of 1, 3 and selected NDI-ODMS conjugates.
Mid Angle and Wide Angle X Ray Scattering measurements

Si7-NDI-Si7

Figure S100. MAXS (top) and WAXS (bottom) profile of Si7-NDI-Si7 with unit cell pictorial representation (top right). In the MAXS profile the [xyz] notation indicates the direction of the diffraction plane normal.

| Index | q value (nm⁻¹) |
|-------|----------------|
| [200] | 1.34526        |
| [010] | 2.11945        |
| [210] | 2.58977        |
| [400] | 2.6992         |
| [310] | 2.87096        |
| [500] | 3.32694        |
| [510] | 3.83509        |
| [600] | 4.047          |
| [020] | 4.30226        |
| [710] | 5.1338         |
| [800] | 5.3909         |
Figure S101. MAXS (top) and WAXS (bottom) profile of Si7-NDI$_2$-Si7 with pictorial representation of the Col$_h$ packing (top right). Observed reflections of the Col$_h$ are indexed.

| Index | q value (nm$^{-1}$) |
|-------|---------------------|
| q$^*$ | 1.19178             |
| v3    | 2.05393             |
Si15-NDI-Si15

Figure S102. MAXS (top) and WAXS (bottom) profile of Si15-NDI-Si15 with pictorial representation of the Col$_h$ packing (top right). Observed reflections of the Col$_h$ are indexed.

| Index | q value (nm$^{-1}$) |
|-------|---------------------|
| q$^*$ | 1.10726             |
| $\sqrt{3}$ | 1.90178       |
| $\sqrt{4}$ | 2.17226       |
| $\sqrt{7}$ | 2.89916       |
| $\sqrt{9}$ | 3.25416       |
| $\sqrt{12}$ | 3.91345      |
| $\sqrt{16}$ | 4.33607       |
Si15-NDI$_2$-Si15

Figure S103. MAXS (top) and WAXS (bottom) profile of Si15-NDI$_2$-Si15 with pictorial representation of the Col$_h$ packing (top right). Observed reflections of the Col$_h$ are indexed.

| Index | q value (nm$^{-1}$) |
|-------|---------------------|
| q*    | 0.97202             |
| v3    | 1.69893             |
| v4    | 1.9525              |
Si23-NDI-Si23

Figure S104. MAXS (top) and WAXS (bottom) profile of Si23-NDI-Si23 with unit cell pictorial representation (top right). In the MAXS profile the [xyz] notation indicates the direction of the diffraction plane normal.

| Index | q value (nm⁻¹) |
|-------|----------------|
| [100] | 0.96556        |
| [020] | 1.64603        |
| [120] | 1.74512        |
| [200] | 1.86046        |
| [210] | 1.97216        |
| [030] | 2.49247        |
| [300] | 2.79073        |
| [140] | 3.18876        |
| [040] | 3.36543        |
| [400] | 3.73255        |
| [050] | 4.11171        |
Figure S105. MAXS (top) and WAXS (bottom) profile of Si23-NDI$_2$-Si23 with pictorial representation of the Col$_h$ packing (top right). Observed reflections of the Col$_h$ are indexed.

| Index | q value (nm$^{-1}$) |
|-------|---------------------|
| $q^*$ | 0.81988             |
| $\sqrt{3}$ | 1.42845         |
| $\sqrt{4}$ | 1.64821         |
| $\sqrt{7}$ | 2.15536         |
Figure S106. WAXS profile of 1.

Figure S107. WAXS profile of 3.
**NDI-Si8-NDI**

Figure S108. MAXS profile of NDI-Si8-NDI with pictorial representation of the LAM packing (top right). Observed reflections of the LAM packing are indexed.

| Index | q value (nm⁻¹) |
|-------|----------------|
| q*    | 1.36           |
| √4   | 2.87           |
| √9   | 4.29           |

**NDI₂-Si8-NDI₂**

Figure S109. MAXS profile of NDI-Si8-NDI with pictorial representation of the LAM packing (top right). Observed reflections of the LAM packing are indexed.

| Index | q value (nm⁻¹) |
|-------|----------------|
| q*    | 1.21137        |
| √4   | 2.42274        |
Figure S110. MAXS (top) and WAXS (bottom) profile of NDI-Si16-NDI with pictorial representation of the LAM packing (top right). Observed reflections of the LAM packing are indexed.

| Index | q value (nm$^{-1}$) |
|-------|---------------------|
| q*    | 1.11                |
| √4    | 2.22                |
| √9    | 3.33                |
| √16   | 4.44                |
Figure S111. MAXS (top) and WAXS (bottom) profile of NDI$_2$-Si16-NDI$_2$ with pictorial representation of the LAM packing (top right). Observed reflections of the LAM packing are indexed.

| Index | q value (nm$^{-1}$) |
|-------|---------------------|
| $q^*$ | 0.98515             |
| $\sqrt{4}$ | 1.96173         |
Figure S112. MAXS (top) and WAXS (bottom) profile of NDI-Si24-NDI with pictorial representation of the LAM packing (top right). Observed reflections of the LAM packing are indexed.

| Index | q value (nm⁻¹) |
|-------|----------------|
| q*    | 0.97081        |
| √4    | 1.91585        |
| √9    | 2.86089        |
| √16   | 3.75438        |
| √25   | 4.83687        |
Figure S113. MAXS (top) and WAXS (bottom) profile of NDI$_2$-Si24-NDI$_2$ with pictorial representation of the LAM packing (top right). Observed reflections of the LAM packing are indexed.

| Index | q value (nm$^{-1}$) |
|-------|-------------------|
| q*    | 0.88235           |
| √4    | 1.739             |
| √9    | 2.64705           |
Influence of Structural Variations on Domain Spacing

Table S1. Domain spacings ($L_0$) and phase characterizations of NDI-ODMS conjugates of family 1 and 2.

| Entry | Compound     | $L_0$ (nm)$^a$ | Phase   |
|-------|--------------|---------------|---------|
| 1     | Si7-NDI-Si7  | 9.3 (A), 2.9 (B), 86.9 $^\circ$(γ) | Col$_{ob}$ |
| 2     | Si15-NDI-Si15| 6.5           | Col$_h$ |
| 3     | Si23-NDI-Si23| 7.8 (A), 6.8 (B), 80 $^\circ$(γ) | Col$_{ob}$$^b$ |
| 4     | Si7-NDI$_2$-Si7| 6.1         | Col$_h$ |
| 5     | Si15-NDI$_2$-Si15| 7.4           | Col$_h$ |
| 6     | Si23-NDI$_2$-Si23| 8.8           | Col$_h$ |
| 7     | NDI-Si8-NDI  | 4.4           | LAM     |
| 8     | NDI-Si16-NDI | 5.7           | LAM     |
| 9     | NDI-Si24-NDI | 6.9           | LAM     |
| 10    | NDI$_2$-Si8-NDI$_2$ | 5.2 | LAM$^c$   |
| 11    | NDI$_2$-Si16-NDI$_2$ | 6.3 | LAM$^c$   |
| 12    | NDI$_2$-Si24-NDI$_2$ | 7.2 | LAM$^c$   |

$^a$ $L_0$ is the lattice parameter(s) in Col$_h$ and Col$_{ob}$ and the bilayer thickness in LAM.

$^b$ Measured at 5 $^\circ$C.

$^c$ Samples annealed for 30 minutes at 300 $^\circ$C.
X-ray crystal structure determination of 5

C_{20}H_{18}N_{2}O_{4}, Fw = 350.36, colourless needle, 0.36 × 0.14 × 0.04 mm³, orthorhombic, Pbca (no. 61), a = 6.9724(3), b = 17.2520(7), c = 27.5875(11) Å, V = 3319.6(2) Å³, Z = 8, D_x = 1.402 g/cm³, μ = 0.81 mm⁻¹. 23670 Reflections were measured on a Bruker Proteum diffractometer with rotating anode and Helios optics (λ = 1.54184 Å) at a temperature of 100(2) K up to a resolution of (sin θ/λ)_{max} = 0.57 Å⁻¹. The Saint software was used for the integration of the intensities. Multiscan absorption correction and scaling was performed with SADABS (correction range 0.64-0.75). 2630 Reflections were unique (R_{int} = 0.037), of which 2512 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT. Least-squares refinement was performed with SHELXL-2014 against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 237 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0328 / 0.0953. R1/wR2 [all refl.]: 0.0335 / 0.0962. S = 1.052. Residual electron density between -0.24 and 0.17 e/Å³. Geometry calculations and checking for higher symmetry were performed with the PLATON program.
Figure S114. Packing of 5 in the crystal viewed along the b-axis. Displacement ellipsoids are drawn at the 50% probability level. By \( \pi-\pi \) stacking the molecules form chains in the direction of the a-axis. The shortest perpendicular distance between the ring planes is 3.2828(4) Å. Symmetry codes: \( i: x-0.5, y, 0.5-z; ii: x+0.5, y, 0.5-z. \)
Fluorescence Microscopy

Figure S115. Fluorescence microscopy micrographs of reference NDIs 1, 3 and 5 and selected NDI-ODMS conjugates (artificial colors; excitation range 340-380 nm, scale bars 100 μm).
Real color pictures of 5 and Si15-NDI-Si15 under 365 nm excitation

Figure S116. Real color pictures upon 365 nm excitation of crystals of 5 (left) and Si15-NDI-Si15 (right).
UV-Vis and Fluorescence of drop cast films

Figure S117. UV-Vis (black trace) and emission (green trace, $\lambda_{ex}$ 365 nm) spectra of the drop cast film of 1.

Figure S118. UV-Vis (black trace) and emission (green trace, $\lambda_{ex}$ 365 nm) spectra of the drop cast film of NDI-Si8-NDI.
Figure S119. UV-Vis (black trace) and emission (green trace, $\lambda_{\text{ex}}$ 365 nm) spectra of the drop cast film of 3.

Figure S120. UV-Vis (black trace) and emission (green trace, $\lambda_{\text{ex}}$ 365 nm) spectra of the drop cast film of NDI$_2$-Si8-NDI$_2$. 
Figure S121. UV-Vis (black trace) and emission (green trace, $\lambda_{\text{ex}}$ 365 nm) spectra of the drop cast film of 5.

Figure S122. UV-Vis (black trace) and emission (green trace, $\lambda_{\text{ex}}$ 365 nm) spectra of the drop cast film of Si15-NDI-Si15.
Figure S123. UV-Vis (black trace) and emission (green trace, $\lambda_{\text{ex}}$ 365 nm) spectra of the drop cast film of Si$_{15}$-NDI$_{2}$-Si$_{15}$. 
Mixing experiments: POM measurements

Figure S124. POM micrographs of selected mixing experiments with NDI-ODMS conjugates.
Mixing experiments: MAXS measurements

**Si15-NDI₂-Si15 : Si23-NDI₂-Si23 1:1**

Figure S125. MAXS profile of 1:1 mixture of Si15-NDI₂-Si15 and Si23-NDI₂-Si23 with pictorial representation of the Col₇ packing (right). Observed reflections of the Col₇ packing are indexed.

| Index | q value (nm⁻¹) |
|-------|---------------|
| q*    | 0.91926       |
| √3    | 1.58938       |
| √4    | 1.82294       |
| √7    | 2.41414       |

$L_0 = 7.9$ nm
Si15-NDI-Si15 : Si23-NDI2-Si23 1:1

Figure S126. MAXS profile of 1:1 mixture of Si15-NDI-Si15 and Si23-NDI2-Si23 with pictorial representations of the two self-sorting Col₉ packings (right). Observed reflections of the Col₉ packings are indexed (black for Si23-NDI2-Si23 and red for Si15-NDI-Si15).

| Index | q value (nm⁻¹) |
|-------|---------------|
| q*    | 0.84808       |
| q*    | 1.13935       |
| √3    | 1.44774       |
| √4    | 1.6876        |
| √3    | 1.92746       |
| √7, √4| 2.21872       |
| √9    | 2.50998       |
| √12, √7| 2.92118      |
| √9    | 3.28097       |
| √12   | 3.96629       |

L₀ = 8.6 nm
L₀ = 6.5 nm
Si15-NDI₂-Si15 : Si15-NDI-Si15 1:1

Figure S127. MAXS profile of Si15-NDI-Si15 and Si23-NDI₂-Si23 1:1 mixture with pictorial representations of the two self-sorting Col₉ packings (right). Observed reflections of both Col₉ packings are indexed (black for Si15-NDI₂-Si15 and red for Si15-NDI-Si15).

| Index | q value (nm⁻¹) |
|-------|---------------|
| q²     | 0.95088       |
| q₄     | 1.12221       |
| √3    | 1.65334       |
| √4, √3 | 1.91033     |
| √4    | 2.18446       |
| √7    | 2.50998       |
| √7    | 2.90404       |
| √12   | 3.28097       |
NDI-Si8-NDI : NDI$_2$-Si24-NDI$_2$ 1:1

Figure S12. MAXS profile of NDI-Si8-NDI and NDI$_2$-Si24-NDI$_2$ 1:1 mixture with pictorial representations of the two self-sorting LAM packings (right). Observed reflections of both LAM packings are indexed (black for NDI$_2$-Si24-NDI$_2$ and red for NDI-Si8-NDI).

| Index | q value (nm$^{-1}$) |
|-------|---------------------|
| q*    | 0.86522             |
| q*    | 1.43061             |
| √4    | 1.70473             |
| √9    | 2.56138             |
| √4    | 2.85264             |
| √9    | 4.27468             |
**Si15-NDI-Si15 : NDI-Si24-NDI 1:1**

Figure S129. MAXS profile of Si15-NDI-Si15 and NDI-Si24-NDI 1:1 mixture with pictorial representation of the LAM packing (right). Observed reflections of the LAM packing are indexed.

| Index | q value (nm\(^{-1}\)) |
|-------|------------------------|
| q*    | 0.95088                |
| √4    | 1.87606                |
| √9    | 2.78411                |
| √16   | 3.64076                |
**Si15-NDI-Si15 : NDI-Si24-NDI 1:4**

![MAXS profile of Si15-NDI-Si15 and NDI-Si24-NDI 1:4 mixture with pictorial representation of the LAM packing (right). Observed reflections of the LAM packing are indexed.](image)

| Index | q value (nm⁻¹) |
|-------|---------------|
| q⁺    | 0.95088       |
| √4    | 1.87606       |
| √9    | 2.76698       |

Figure S130. MAXS profile of Si15-NDI-Si15 and NDI-Si24-NDI 1:4 mixture with pictorial representation of the LAM packing (right). Observed reflections of the LAM packing are indexed.
Si15-NDI-Si15 : NDI-Si24-NDI 4:1

Figure S131. MAXS profile of Si15-NDI-Si15 and NDI-Si24-NDI 4:1 mixture with pictorial representation of the two self-sorting Colh and LAM packings (right). Observed reflections of the LAM and Colh packings (black and red color, respectively) are indexed.

| Index   | q value (nm⁻¹) |
|---------|----------------|
| q*      | 0.93375        |
| q*      | 1.10508        |
| √4, √3  | 1.87606        |
| √4      | 2.18446        |
| √9      | 2.73271        |
| √7      | 2.90404        |
| √9      | 3.28097        |
| √16     | 3.64076        |
Mixing experiments: DSC measurements

Figure S132. DSC trace of Si15-NDI2-Si15 and Si23-NDI2-Si23 1:1 mixture (exo up, second heating and cooling cycle, rate 10 °C/min).
**Packing Models**

**Formulation of the hypothesis for Colₙ/Colₜ and LAM morphologies**

The d-spacings and Miller indexes were obtained by fitting the diffraction peaks obtained from the X Ray Scattering profiles of the block molecules to the crystal geometry equations for different morphologies using a Matlab script. The optimized morphology was then verified with LCDiXRay v1.0 software.

The unit cell volume for the Colₙ/Colₜ morphologies was determined using the exact 2D-morphology determined from MAXS, and assuming the peak consistently observed at roughly 15 nm⁻¹ (0.42 nm) in the WAXS profiles as π-π stacking distance between the NDIs in the columns. This was done in conjecture with the crystal packing of 5, for which a π-π stacking distance of 0.36 nm was measured.

The number of molecules in the unit cell of the Colₙ/Colₜ morphologies was calculated by means of LCDiXRay v1.0 software, by comparing the volume of the unit cell with that of the block molecules. The latter was estimated considering the density and molecular weight of the block molecules. The density of the block molecules was assumed to be lying in between that of polydimethylsiloxane (PDMS) (\(\rho = 965 \text{ kg/m}^3\)) and 5 in the crystal (\(\rho = 1402 \text{ kg/m}^3\)).
**Alternative Hypothetical Packing Model for the LAM morphology**

In alternative to the interdigitated packing model proposed for the block molecules of family 2 (Fig 5b), a non-interdigitated packing of the LAM morphology can be considered (Figure S133). The layered structure is still preserved in such a configuration, as an alternation of ODMS and NDI layers is present. However, the influence of structural variations on $L_0$ obtained from the MAXS profiles suggests to rule out the alternative non-interdigitated packing. The experimental evidences reported in Table 2 and Table S1 show an approximate increase in $L_0$ of 0.8 nm when the length of the ODMS block is preserved and the length of the NDI blocks is extended by one unit (compare NDI-Si8-NDI and NDI$_2$-Si8-NDI$_2$, for example). In the hypothesis that the correct packing model was the non-interdigitated one, such a structural variation would result in an approximate increase in $L_0$ equal to 2 NDI units (approximately 1.6 nm), instead of the experimentally observed 0.8 nm.

![Figure S133. Alternative non-interdigitated packing model for the LAM morphology.](image-url)
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