Conformationally pre-organized and pH-responsive flat dendrons:

Synthesis and self-assembly at the liquid-solid interface

Tamer El Malah,[a,#] Artur Ciesielski,[b,#] Luc Piot,[b] Sergey I. Troyanov,[c] Uwe Mueller,[d]

Steffen Weidner,[e] Paolo Samorì,[b,*] and Stefan Hecht[a,*]

[a] *Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany, Email: sh@chemie.hu-berlin.de*

[b] *ISIS/UMR CNRS 7006, Université de Strasbourg, 8 allée Gaspard Monge, 67000 Strasbourg, France; Email: samori@unistra.fr*

[c] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

[d] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Elektronenspeicherring BESSY II, Albert-Einstein-Str. 15, 12489 Berlin, Germany*

[e] *Bundesanstalt für Materialforschung und –prüfung (BAM), Richard-Willstätter-Str. 11, 12489 Berlin, Germany*

[#] Both authors contributed equally to this work.

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General Methods

Solvents and starting materials were used as received. 2-Nitrophenol, 3-nitrophenol, 4-nitrophenol, 1-bromooctadecane, citrazinic acid, 1-hexadecanol, triisopropylsilylacetylene (TIPS acetylene), 18-crown-6, tert-Butyl nitritr (t-BuONO), Azidotrimethylsilane (TMS-N_3), copper(I) iodide, triphenylphosphine, palladium on activated carbon (pd on charcoal) and tetrabutylammonium iodide (TBAI). Tetrahydrofuran (THF) and triethylamine (TEA) were distilled under an inert gas (Ar) atmosphere from sodium/benzophenone and CaH_2, respectively, prior to use. Esterification catalyst 4-dimethylaminopyridinium *p*-toluenesulfonate (DPTS),[1] 2,6-diethynyl-4-(*n*-hexadecyloxycarbonyl)pyridine,[2] 2,6-dibromo-4-nitropyridine-1-oxide[3], 2,6-dibromo-4-nitropyridine-1-oxide[3] and 2,6-dibromo-4-nitropyridine[4] were prepared using previously published procedures. $Pd(PPh_3)_4$ was freshly prepared.[5] All reactions requiring inert gas atmosphere were performed under Ar atmosphere. The Cu-catalyzed cycloaddition reaction was performed in the dark under Ar atmosphere using solid sodium ascorbate An aqueous EDTA-disodium salt solution (16 g/L Na_2-EDTA), adjusted to a pH ~ 8-9, was used to remove Cu-ions in aqueous extraction steps. Column chromatography was carried out with 130-400 mesh silica gel using the eluents specified (PE = petroleum ether, EtOAc = ethyl acetate).

Spectroscopy. NMR spectra were recorded on a 300 MHz (75.6 MHz for 13C) Bruker DPX 300 spectrometer or a 300 MHz Bruker Avance II spectrometer at 23 °C using residual protonated solvent signals as internal standard (^{1}H: δ($CHCl_3$) = 7.26 ppm and ^{13}C: δ($CHCl_3$) = 77.11 ppm). Assignments are based on chemical shifts (Ar is used as abbreviation for assigning signals of both aromatic as well as triazole moieties). Mass spectrometry was performed on Thermo LTQ FT (ESI-HRMS; additives of mixtures of MeOH/H_2O 75/25 + 0.5 % HCO_2H), QSTARXL Applied Biosystems ESI Q-TOF (950 V ISV) and MSI Concept 1H instruments (EI, 70 eV ionization) as well as a Bruker-Apex III (MALDI-TOF, 365 nm laser wavelength, dithranol matrix). HPLC separations were performed with Waters Alliance systems (mixtures and gradient mixtures of CH_3CN/H_2O) equipped with 150 x 2 mm Luna columns (3 µm, phenyl-hexyl material) and consisted of a Waters Separations Module 2695, a Waters Diode Array detector 996, and a Waters Mass Detector ZQ 2000. Conditions

[1] J. S. Moore, S. I. Stupp, *Macromolecules* **1990**, *23*, 65.
[2] L. Piot, R. M. Meudtner, T. El Malah, S. Hecht, P. Samori, *Chem. Eur. J.* **2009**, 15, 4788.
[3] U. Neumann, F. Vögtle, *Chem. Ber.* **1989**, *122*, 589.
[4] R. Shetty, D. Nguyen, D. Flubacher, F. Ruggle, A. Schumacher, M. Kelly, E. Michelotti, *Tetrahedron Letter.* **2007**, *48,* 113.
[5] D. R. Coulson, *Inorg. Syn.* **1971**, *13*, 121.

are specified when describing the corresponding substances. Peak areas were quantified using UV-detection over the range of 200-400 nm (MaxPlot). UV-visible absorption spectra were recorded in quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer each equipped with a Peltier thermostated cell holder at 25 ± 0.05 °C using spectrophotometric grade solvents.

Single Crystal X-ray Diffraction. Data collection was performed on a MX225 CCD detector at 100 K using synchrotron radiation at the BESSY II storage ring (λ = 0.9000 Å, BL14.2, operated by HZB and the Free University of Berlin, Germany). The structure was solved using direct methods with SHELXS-97 and refined by full-matrix least-square procedures using SHELXL-97.[6] The crystal structure contains two crystallographically independent BTP-a molecules. One of them is fully ordered, but another is characterized by disorder of one of its $C_{18}H_{37}$ alkyl chains between two close positions with occupation factors of 0.76 and 0.24, respectively. Figure S1 shows molecular packing of *ortho* **G-1_a** and Figure S2 reveals that the BTP cores adopt the "kinked" *anti,anti* conformation. Crystal data together with some details of data collection and refinement are summarized in Table S1.

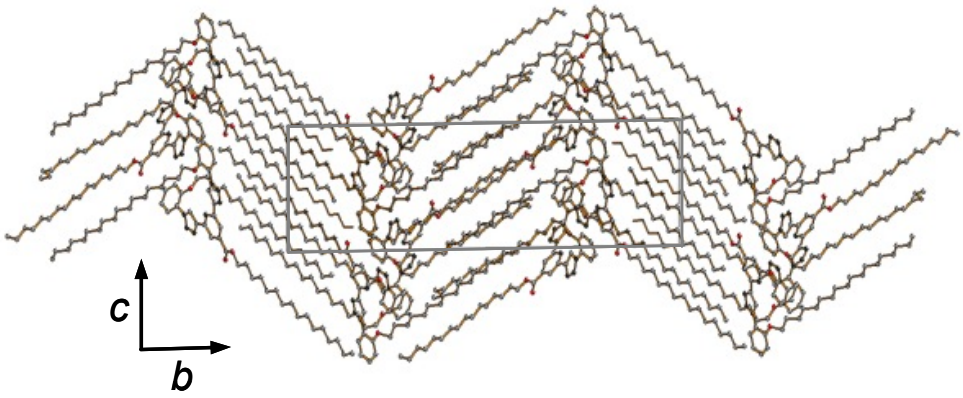


Figure S1. Molecular packing of **G-1_a** within a single crystal showing a lamellar structure.

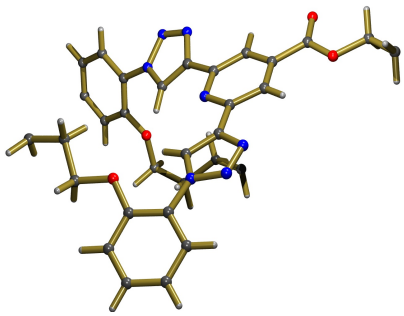


Figure S2. Zoom-in of the BTP core illustrating its conformational preferences for the "kinked" *anti,anti* conformation and the interactions of the O atoms of the *ortho*-alkoxy groups.

[6] Sheldrick G.M., SHELXS-97/SHELXL-97, University of Göttingen, Germany, 1997.

Table S1. Crystal data for **BTP-a**.

Formula	$C_{74}H_{119}N_7O_4$		
Formula Weight	1170.76		
Crystal System	Triclinic		
Space group	P $\bar{1}$ (No. 2)		
a, *b*, *c* [Å]	12.483(3)	13.549(3)	45.658(9)
α, *β*, *γ* [deg]	86.73(3)	83.86(3)	66.01(3)
V [Å^3]	7014(3)		
Z	4		
D(calc) [g cm^{-3}]	1.107		
Mu(X) [mm^{-1}]	0.068		
F(000)	2564		
Crystal Size [mm]	0.04 x 0.06 x 0.005		
Data Collection:			
Temperature (K)	100		
Radiation [Å]	0.90000		
Theta Min-Max [Deg]	2.3, 36.7		
Dataset	-15 : 15; -14 : 17; -56 : 57		
Tot., Uniq. Data, R(int)	124567, 27783, 0.066		
Observed data [$I > 2.0\ \sigma(I)$]	25890		
Data Refinement:			
Nrefl, Npar	27783, 1674		
R_1, wR_2, S	0.0555, 0.1444, 1.097		
w = 1/[\s^2^(Fo^2^)+(0.0600P)^2^+2.0000P] where P=(Fo^2^+2Fc^2^)/3			
Max. and av. Shift/Error	0.02, 0.00		
Δρ (min. / max.) [e/Å^3]	-0.41, 0.41		

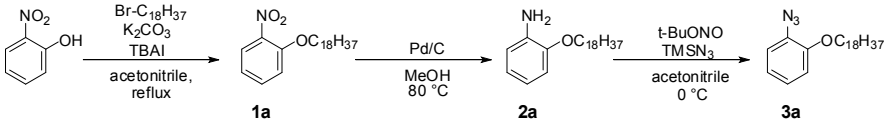
STM Measurements

Scanning Tunnelling Microscopy (STM) measurements at the liquid-solid interface have been carried out both in constant height and constant current mode using a DI Multimode microscope. The STM tips have been mechanically cut from a Pt:Ir (80:20) wire. Samples have been prepared by applying a droplet of solution on freshly cleaved highly oriented pyrolytic graphite (HOPG). The molecules were dissolved in 1-phenyloctane with an approximate concentration of 1.10^{-5} M. The raw STM data have been processed by the application of background flattening and the drift has been corrected using the underlying graphite lattice as a reference. The latter lattice is imaged underneath the molecules by lowering the bias voltage to 20 mV and raising the current to 65 pA.

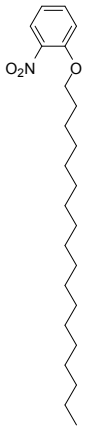
Synthesis

The preparation and characterization of G-1 and G-2 derivatives and its precursors are provided below:

Synthesis scheme of 1-azido-2-(n-octadecyloxy)benzene 3a

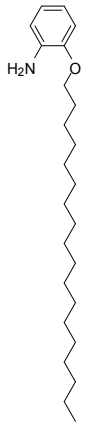


1-Nitro-2-(*n*-octadecyloxy)benzene 1a.



In a 3-necked flask equipped with a condenser 4.17 g (30.0 mmol, 1 equiv.) of 2-nitrophenol, 10.31 g (30.0 mmol, 1 equiv.) of 1-bromooctadecane, 10.36 g (75 mmol, 2.5 equiv.) of potassium carbonate, 0.39 g (1.5 mmol, 0.05 equiv.) of 18-crown-6, and 0.55 g (1.5 mmol, 0.05 equiv.) of tetrabutylammonium iodide (TBAI) were suspended in 600 mL of acetonitrile and the mixture was degassed at rt by evacuating under stirring and flushing with argon (4 cycles). The suspension was stirred at 80 °C over night and after TLC monitoring the yellow solution was transferred into a separation funnel and diluted with EtOAc. The organic phase was washed with sat. aq. $NaHCO_3$ solution (3 x), water (3 x), and brine (1 x). After drying over $MgSO_4$ and filtration the solvent was removed *in vacuo*. Purification by column chromatography (PE/EtOAc 25/1) gave 11.7 g (quant. yield) of the title compound as pale yellow solid. **TLC** (PE/EtOAc 25/1) $R_f = 0.58$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.83 (dd, $^3J = 8.08$, $^4J = 1.58$ Hz, 1H, Ar*H*), 7.54-7.48 (m, 1H, Ar*H*), 7.09-6.98 (m, 2H, Ar*H*), 4.10 (t, $^3J = 6.45$ Hz, 2H, OCH_2), 1.89-1.79 (m, 2H, OCH_2CH_2), 1.51-1.27 (m, 30H, CH_2), 0.89 (t, $^3J = 6.34$ Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 152.49 (OC_{Ar}), 139.97 (O_2NC_{Ar}), 133.94 (HC_{Ar}), 125.49 (HC_{Ar}), 119.95 (HC_{Ar}), 114.39 (HC_{Ar}), 69.62 (OCH_2), 31.93 (CH_2), 29.71 (CH_2), 29.67 (CH_2), 29.59 (CH_2), 29.53 (CH_2), 29.38 (CH_2), 29.29 (CH_2), 28.95 (CH_2), 25.84 (CH_2), 22.70 (CH_2), 14.12 (CH_3). **HRMS** (ESI) *m/z* = 392.3251 (calcd 392.3165 for $[M + H^+]$). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 26 min.): 98.6 area %.

2-(*n*-Octadecyloxy)aniline 2a.

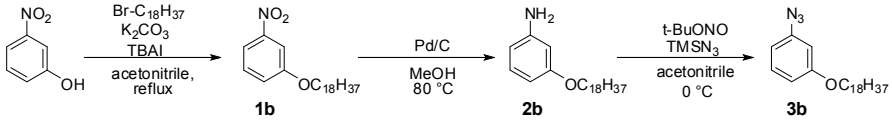


In a one necked flask 6.0 g (15.32 mmol) of 1-nitro-2-(*n*-octadecyloxy)benzene were dissolved in 50 mL of MeOH, 600 mg Pd on charcoal (10 wt%) were added, the stirred mixture was degassed at rt *in vacuo* and flushed with H_2 (3 cycles). After stirring for 24 h at 60 °C in H_2 atmosphere (2 bar) the mixture was filtered through a celite pad and the solvent removed *in vacuo*. Purification by column chromatography (PE/EtOAc 25/1) gave 5.4 g (97%) of a colorless solid. **TLC** (PE/EtOAc 25/1) R_f = 0.47. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.80-6.77 (m, 4H, Ar*H*), 4.00 (t, ^{3}J = 6.54 Hz, 2H, OC*H*$_2$), 2.91 (br s, 2H, Ar-N*H*$_2$), 1.85-1.80 (m, 2H, OCH$_2$C*H*$_2$), 1.50-1.28 (m, 30H, C*H*$_2$), 0.90 (t, ^{3}J = 6.43 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 146.77 (O*C*$_{Ar}$), 136.29 (H$_2$N*C*$_{Ar}$), 120.90 (H*C*$_{Ar}$), 118.44 (H*C*$_{Ar}$), 115.01 (H*C*$_{Ar}$), 111.42 (H*C*$_{Ar}$), 68.22 (O*C*H$_2$), 31.97 (*C*H$_2$), 29.74 (*C*H$_2$), 29.66 (*C*H$_2$), 29.64 (*C*H$_2$), 29.48 (*C*H$_2$), 29.41 (*C*H$_2$), 26.19 (*C*H$_2$), 22.73 (*C*H$_2$), 14.16 (*C*H$_3$). **HRMS** (ESI) *m/z* = 362.3537 (calcd 362.3423 for [M$^+$]). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 24.38 min.): 97.8 area %.

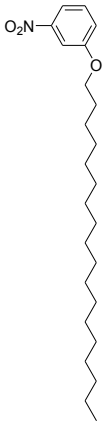
1-Azido-2-(*n*-octadecyloxy)benzene 3a.

In a round-bottomed flask 1.08 g (3 mmol, 1 equiv.) of 2-(*n*-octadecyloxy)aniline was dissolved in 6 mL of acetonitrile and cooled to 0 °C using an ice bath. To this stirred mixture were added 0.46 g (4.5 mmol, 1.5 equiv.) of t-BuONO followed by 0.41 g (3.6 mmol, 1.2 equiv.) TMS-N_3 dropwise. The resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under *vacuo* and the crude product was purified by column chromatography (PE) to give 0.8 g (69%) of a brown solid. **TLC** (PE) R_f = 0.47. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.09-7.06 (m, 1H, Ar*H*), 7.00-6.89 (m, 3H, Ar*H*), 4.03 (t, ^{3}J = 6.56 Hz, 2H, OCH_2), 1.90-1.81 (m, 2H, OCH_2CH_2), 1.53-1.29 (m, 30H, CH_2), 0.91 (t, ^{3}J = 6.26 Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 151.94 (OC_{Ar}), 128.28 (N_3C_{Ar}), 125.56 (HC_{Ar}), 121.01 (HC_{Ar}), 120.72 (HC_{Ar}), 112.81 (HC_{Ar}), 69.03 (OCH_2), 31.95 (CH_2), 29.73 (CH_2), 29.69 (CH_2), 29.61 (CH_2), 29.59 (CH_2), 29.39 (CH_2), 29.37 (CH_2), 29.07 (CH_2), 26.04 (CH_2), 22.72 (CH_2), 14.14 (CH_2CH_3). **MS** (ESI) *m/z* = 388.19 (calcd 388.33 for [M + H^+]).**HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 27.85 min.): 98.3 area %.

Synthesis scheme of 1-azido-3-(n-octadecyloxy)benzene 3b



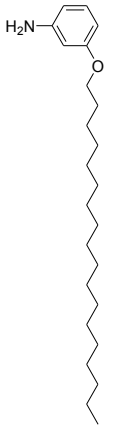
1-Nitro-3-(*n*-octadecyloxy)benzene 1b.



In a 3-necked flask equipped with a condenser 4.17 g (30.0 mmol, 1 equiv.) of 3-nitrophenol, 10.31 g (30.0 mmol, 1 equiv.) of 1-bromooctadecane, 10.36 g (75 mmol, 2.5 equiv.) of potassium carbonate, 0.39 g (1.5 mmol, 0.05 equiv.) of 18-crown-6 and 0.55 g (1.5 mmol, 0.05 equiv.) of tetrabutylammonium iodide (TBAI) were suspended in 600 mL of acetonitrile and the mixture was degassed at rt by evacuating under stirring and flushing with argon (4 cycles). The suspension was stirred at 80 °C over night and after TLC monitoring the yellow solution was transferred into a separation funnel and diluted with EtOAc. The organic phase was washed with sat. aq. $NaHCO_3$ solution (3 x), water (3 x) and brine (1 x). After drying over $MgSO_4$ and filtration the solvent was removed *in vacuo*. Purification by column chromatography (PE/EtOAc 25/1) gave 11.3 g (96.2%) of the title compound as pale yellow solid. **TLC** (PE/EtOAc 25/1) R_f = 0.60. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.83-7.80

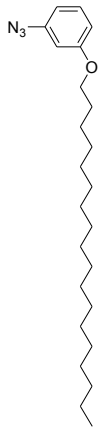
(m, 1H, Ar*H*), 7.73 (t, ^{3}J = 8.22 Hz, 1H, Ar*H*), 7.42 (t, ^{3}J = 6.52 Hz, 1H, Ar*H*), 7.24-7.20 (m, 1H, Ar*H*), 4.04 (t, ^{3}J = 6.42 Hz, 2H, OCH_2), 1.85-1.78(m, 2H, OCH_2CH_2), 1.50-1.27 (m, 30H, CH_2), 0.89 (t, ^{3}J = 6.44 Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 159.69 (OC_{Ar}), 149.19 (O_2NC_{Ar}), 129.82 (HC_{Ar}), 121.67 (HC_{Ar}), 115.49 (HC_{Ar}), 108.64 (HC_{Ar}), 68.73 (OCH_2), 31.93 (CH_2), 29.71 (CH_2), 29.67 (CH_2), 29.59 (CH_2), 29.55 (CH_2), 29.37 (CH_2), 29.34 (CH_2), 29.01 (CH_2), 25.95 (CH_2), 22.70 (CH_2), 14.13 (CH_3). **MS** (ESI) *m/z* = 391.36 (calcd 391.31 for [M$^+$]). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 26.85 min.): 97.6 area %.

3-(*n*-Octadecyloxy)aniline 2b.



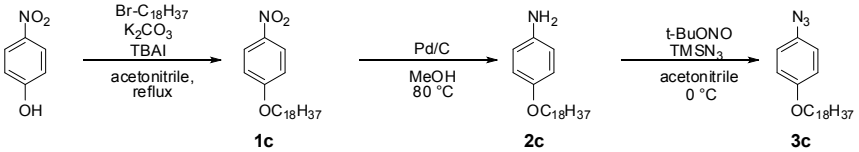
In a one necked flask 6.0 g (15.32 mmol) of 1-nitro-3-(*n*-octadecyloxy)benzene were dissolved in 50 mL of MeOH, 600 mg Pd on charcoal (10 wt%) were added, the stirred mixture was degassed at rt *in vacuo* and flushed with H_2 (3 cycles). After stirring for 24 h at 60 °C in H_2 atmosphere (2 bar) the mixture was filtered through a celite pad and the solvent removed *in vacuo*. Purification by column chromatography (PE/EtOAc 25/1) gave 5.2 g (93.8%) of a colourless solid. **TLC** (PE/EtOAc 25/1) R_f = 0.42. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.04 (t, ^{3}J = 7.97 Hz, 1H, Ar*H*), 6.34-6.25 (m, 3H, Ar*H*) 3.91 (t, ^{3}J = 6.58 Hz, 2H, OCH_2), , 2.93 (br s, 2H, Ar-NH_2), 1.78-1.73 (m, 2H, OCH_2CH_2), 1.49-1.27 (m, 30H, CH_2), 0.89 (t, ^{3}J = 6.51 Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 160.29 (OC_{Ar}), 147.61 (H_2NC_{Ar}), 130.01 (HC_{Ar}), 107.78 (HC_{Ar}), 104.67 (HC_{Ar}), 101.72 (HC_{Ar}), 67.78 (OCH_2), 31.93 (CH_2), 29.71 (CH_2), 29.62 (CH_2), 29.43 (CH_2), 29.38 (CH_2), 29.32 (CH_2), 26.08 (CH_2), 24.20 (CH_2), 22.70 (CH_2), 19.76 (CH_2), 14.13 (CH_3). **MS** (ESI) *m/z* = 362.40 (calcd 362.34 for [M + H$^+$]). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 16.62 min.): 98.1 area %.

1-Azido-3-(*n*-octadecyloxy)benzene 3b.



In a round-bottomed flask 1.08 g (3 mmol, 1 equiv.) of 3-(*n*-octadecyloxy)aniline was dissolved in 6 mL of acetonitrile and cooled to 0 °C in an ice bath. To this stirred mixture were added 0.46 g (4.5 mmol, 1.5 equiv.) of t-BuONO followed by 0.41 g (3.6 mmol, 1.2 equiv.) $TMSN_3$ dropwise. The resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under *vacuo* and the crude product was purified by column chromatography (petroleum) to give 0.74 g (64.2%) of a brown solid. **TLC** (PE) $R_f = 0.50$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.25-7.23 (m, 1H, Ar*H*), 6.71-6.62 (m, 2H, Ar*H*), 6.56 (t, ^3J = 2.22 Hz 1H, Ar*H*), 3.95 (t, ^3J = 6.54 Hz, 2H, OCH_2), 1.84-1.74 (m, 2H, OCH_2CH_2), 1.48-1.27 (m, 30H, CH_2), 0.90 (t, ^3J = 6.26 Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 160.37 (OC_{Ar}), 141.17 (N_3C_{Ar}), 130.37 (HC_{Ar}), 111.17 (HC_{Ar}), 111.08 (HC_{Ar}), 105.44 (HC_{Ar}), 68.14 (OCH_2), 31.95 (CH_2), 29.73 (CH_2), 29.69 (CH_2), 29.62 (CH_2), 29.59 (CH_2), 29.40 (CH_2), 29.19 (CH_2), 26.03 (CH_2), 22.72 (CH_2), 14.15 (CH_2CH_3). **MS** (ESI) *m/z* = 410.37 (calcd 410.31 for $[M + Na^+]$). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 22.53 min.): 97.1 area %.

Synthesis scheme of 1-azido-4-(octadecyloxy)benzene 3c



1-Nitro-4-(*n*-octadecyloxy)benzene 1c.

In a 3-necked flask equipped with a condenser 4.17 g (30.0 mmol, 1 equiv.) of 4-nitrophenol, 10.31 g (30.0 mmol, 1 equiv.) of 1-bromooctadecane, 10.36 g (75 mmol, 2.5 equiv.) of potassium carbonate, 0.39 g (1.5 mmol, 0.05 equiv.) of 18-crown-6 and 0.55 g (1.5 mmol, 0.05 equiv.) of tetrabutylammonium iodide (TBAI) were suspended in 600 mL of acetonitrile and the mixture was degassed at rt by evacuating under stirring and flushing with argon (4 cycles). The suspension was stirred at 80 °C over night and after TLC monitoring the yellow solution was transferred into a separation funnel and diluted with EtOAc. The organic phase was washed with sat. aq. $NaHCO_3$ solution (3 x), water (3 x) and brine (1 x). After drying over $MgSO_4$ and filtration the

solvent was removed *in vacuo*. Purification by column chromatography (PE/EtOAc 25/1) gave 11.51 g (98%) of the title compound as pale yellow solid. **TLC** (PE/EtOAc 25/1) $R_f = 0.53$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.23-8.18 (m, $^3J = 2.18$, 2H, Ar*H*), 6.98-6.92 (m, 2H, Ar*H*), 4.08 (t, ^3J = 6.53 Hz, 2H, OCH_2), 1.86-1.79 (m, 2H, OCH_2CH_2), 1.50-1.27 (m, 30H, CH_2), 0.89 (t, ^3J = 6.41 Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.26 (OC_{Ar}), 141.28 (O_2NC_{Ar}), 125.89 (HC_{Ar}), 114.38 (HC_{Ar}), 68.89 (OCH_2), 31.93 (CH_2), 29.71 (CH_2), 29.68 (CH_2), 29.58 (CH_2), 29.54 (CH_2), 29.37 (CH_2), 29.32 (CH_2), 28.97 (CH_2), 25.91 (CH_2), 22.70 (CH_2), 14.12 (CH_3). **MS** (ESI) *m/z* = 391.28 (calcd 391.31 for [M^+]). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 26.71 min.): 98 area %.

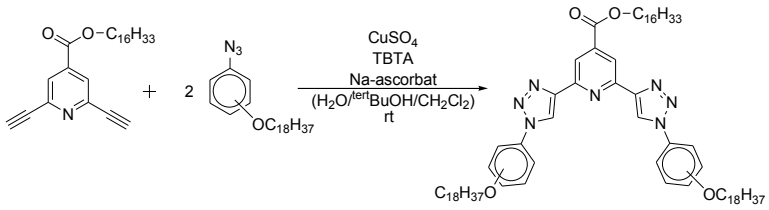
4-(*n*-Octadecyloxy)aniline 2c.

In a one necked flask 6.0 g (15.32 mmol) of 1-nitro-4-(*n*-octadecyloxy)benzene were dissolved in 50 mL of MeOH, 600 mg Pd on charcoal (10 wt%) were added, the stirred mixture was degassed at rt *in vacuo* and flushed with H_2 (3 cycles). After stirring for 24 h at 60 °C in H_2 atmosphere (2 bar) the mixture was filtered through a celite pad and the solvent removed *in vacuo*. Purification by column chromatography (PE/EtOAc 25/1) gave 5.4 g (97%) of a colourless solid. **TLC** (PE/EtOAc 25/1) $R_f = 0.45$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.78-6.74 (m, 2H, Ar*H*), 6.68-6.64 (m, 2H, Ar*H*), 3.89 (t, $^3J = 6.61$ Hz, 2H, OCH_2), 2.94 (br s, 2H, Ar-NH_2), 1.80-1.71 (m, 2H, OCH_2CH_2), 1.47-1.28 (m, 30H, CH_2), 0.90 (t, $^3J = 6.44$ Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 152.36 (OC_{Ar}), 139.74 (H_2NC_{Ar}), 116.44 (HC_{Ar}), 115.65 (HC_{Ar}), 68.70 (OCH_2), 31.94 (CH_2), 29.72 (CH_2), 29.63 (CH_2), 29.45 (CH_2), 29.39 (CH_2), 26.08 (CH_2), 22.71 (CH_2), 14.14 (CH_3). **MS** (ESI) *m/z* = 362.44 (calcd 362.34 for [M^+]). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 11.82 min.): 98.8 area %.

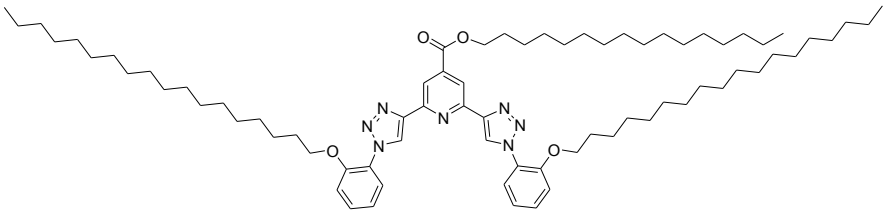
1-Azido-4-(*n*-octadecyloxy)benzene 3c.

In a round-bottomed flask 1.08 g (3 mmol, 1 equiv.) of 4-(*n*-octadecyloxy)aniline was dissolved in 6 mL of acetonitrile and cooled to 0 °C in an ice bath. To this stirred mixture were added 0.46 g (4.5 mmol, 1.5 equiv.) of t-BuONO followed by 0.41 g (3.6 mmol, 1.2 equiv.) $TMSN_3$ dropwise. The resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under *vacuo* and the crude product was purified by column chromatography (petroleum) to give 0.81 g (70%) of a brown solid. **TLC** (PE) $R_f = 0.41$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.98-6.88 (m, 4H, Ar*H*), 3.94 (t, $^3J = 6.57$ Hz, 2H, OCH_2), 1.84-1.74 (m, 2H, OCH_2CH_2), 1.49-1.28 (m, 30H, CH_2), 0.93 (t, $^3J = 6.41$ Hz, 3H, CH_2CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 156.56 (OC_{Ar}), 132.06 (N_3C_{Ar}), 119.93 (HC_{Ar}), 115.70 (HC_{Ar}), 68.40 (OCH_2), 31.95 (CH_2), 29.69 (CH_2), 29.62 (CH_2), 29.59 (CH_2), 29.40 (CH_2), 29.26 (CH_2), 26.03 (CH_2), 22.72 (CH_2), 14.14 (CH_2CH_3). **HPLC** (Luna Phenyl-Hexyl 3 um 2 x 150, acetonitrile/water 8/2, det. UV 220 nm - 380 nm, ret. time 21.59 min.): 97.9 area %.

Synthesis scheme for click reactions affording the G-1 dendrons.



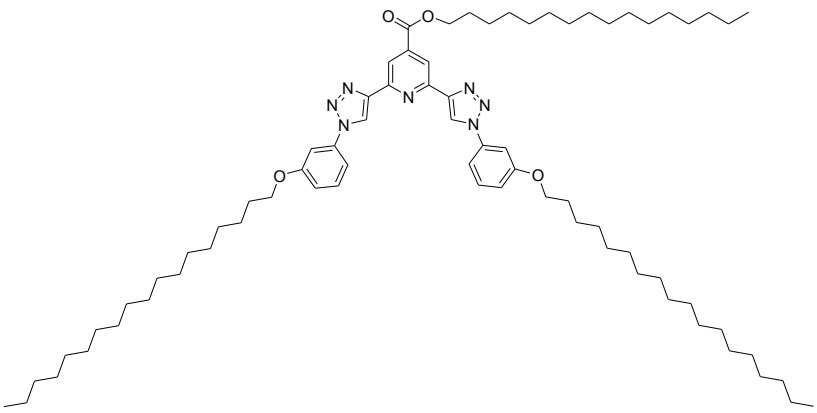
Hexadecyl 2,6-bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)isonicotinate G-1_a.



A three necked flask was charged with 600 mg of 2,6-diethynyl-4-(*n* -hexadecyl-oxycarbonyl) pyridine (1.51 mmol, 1 equiv.) and 1.35 g of 1-azido-2-(octadecyloxy)benzene (3.48 mmol, 2.3 equiv.), 60 mg of sodium ascorbate (0.30 mmol, 0.2 equiv.), 80 mg of TBTA (0.152 mmol, 0.10 equiv.) and 30 mL of a solvent mixture composed by H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). An aqueous stock solution of $CuSO_4$ was added (0.152 mmol, 0.10 equiv.; stock solution: 10 mg $CuSO_4$ per 0.3 mL of water) and the mixture was stirred for 3 d at rt in the dark. In case of an appearing precipitate additional CH_2Cl_2 was added. After

the acetylene starting material was consumed indicated by TLC monitoring (PE/EtOAc 8/2) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2 (3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (PE/EtOAc 8/2) as yellow solid (1.72 g, 97%). **TLC** (PE/EtOAc 8/2) $R_f = 0.51$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.76 (s, 2H, Ar*H*), 8.74 (s, 2H, Ar*H*), 7.87 (dd, ^{3}J = 6.22, ^{4}J = 1.6 Hz, 2H, Ar*H*), 7.47-7.41 (m, 2H, Ar*H),* 7.16-7.10 (m, 4H, Ar*H),* 4.44 (t, ^{3}J = 6.84 Hz, 2H, CO_2CH_2), 4.08 (t, ^{3}J = 6.51 Hz, 4H, OCH_2), 1.89-1.72 (m, 6H, CH_2), 1.49-1.06 (m, 86H, CH_2), 0.89 (t, ^{3}J = 6.19 Hz, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.15 (-CO_2-), 151.18 (OC_{Ar}), 150.80 (OC_{Ar}), 147.36 (C_{Ar}), 139.75 (C_{Ar}), 130.26 (C_{Ar}), 126.46 (C_{Ar}), 125.51 (C_{Ar}), 124.61 (C_{Ar}), 121.17 (C_{Ar}), 118.59 (C_{Ar}), 113.42 (C_{Ar}), 69.24 (OCH_2), 66.10 (OCH_2), 31.93 (CH_2), 29.72 (CH_2), 29.68 (CH_2), 29.62 (CH_2), 29.56 (CH_2), 29.52 (CH_2), 29.44 (CH_2), 29.41 (CH_2), 29.38 (CH_2), 29.17 (CH_2), 28.96 (CH_2), 28.70 (CH_2), 26.0 (CH_2), 25.93 (CH_2), 22.70 (CH_2), 14.12 (CH_3). **Elemental analysis** calcd (%) for $C_{74}H_{119}N_7O_4$: *C* 75.91, *H* 10.24, *N* 8.37; found *C* 75.75, *H* 10.07, *N* 8.34. **MS** (EI, T = 37°C - 50 °C)**:** 1170.9 (calcd 1170.9395 for [M + H^+]).

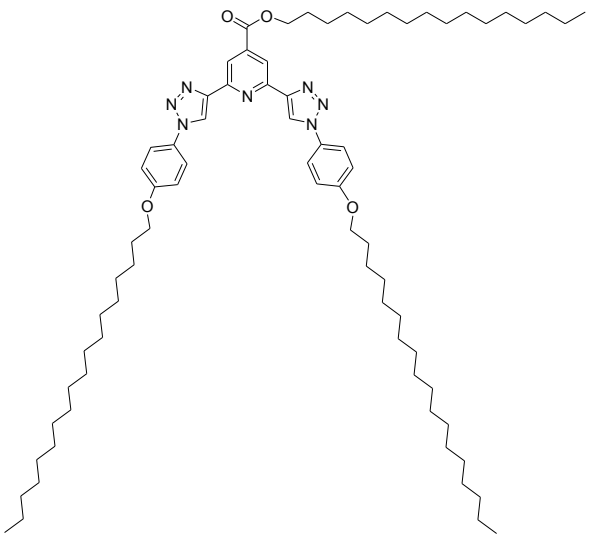
Hexadecyl 2,6-bis(1-(3-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)isonicotinate G-1_b.



A three necked flask was charged with 600 mg of 2,6-diethynyl 4-(n-hexadecyl-oxycarbonyl) pyridine (1.51 mmol, 1 equiv.) and 1.35 g of 1-azido-2-(octadecyloxy)benzene (3.48 mmol, 2.3 equiv.), 60 mg of sodium ascorbate (0.30 mmol, 0.2 equiv.), 80 mg of TBTA (0.152 mmol, 0.10 equiv.) and 30 mL of a solvent mixture composed by H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). An aqueous stock solution of $CuSO_4$ was added (0.152 mmol, 0.10 equiv.; stock solution: 10 mg $CuSO_4$ per 0.3 mL of water) and the mixture was stirred for 3 d at rt in the dark. In case of an appearing precipitate additional CH_2Cl_2 was added. After the acetylene starting material was consumed indicated by

TLC monitoring (PE/EtOAc 8/2) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2 (3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (PE/EtOAc 8/2) as yellow solid (1.68 g, 95%). **TLC** (PE/EtOAc 8/2) $R_f = 0.44$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.79 (s, 2H, Ar*H*), 8.77 (s, 2H, Ar*H*), 7.50-7.39 (m, 6H, Ar*H*), 7.04-7.01 (m, 2H, Ar*H),* 4.45 (t, ^{3}J = 6.75 Hz, 2H, CO_2CH_2), 4.08 (t, ^{3}J = 6.53 Hz, 4H, OCH_2), 1.88-1.81 (m, 6H, CH_2), 1.51-1.27 (m, 86H, CH_2), 0.89 (t, ^{3}J = 6.23 Hz, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.90 (-CO_2-), 160.21 (OC_{Ar}), 150.77 (OC_{Ar}), 148.19 (C_{Ar}), 139.83 (C_{Ar}), 137.82 (C_{Ar}), 130.51 (C_{Ar}), 120.48 (C_{Ar}), 118.95 (C_{Ar}), 115.14 (C_{Ar}), 112.11 (C_{Ar}), 106.84 (C_{Ar}), 68.50 (OCH_2), 66.20 (OCH_2), 31.94 (CH_2), 29.72 (CH_2), 29.65 (CH_2), 29.62 (CH_2), 29.56 (CH_2), 29.43 (CH_2), 29.38 (CH_2), 29.33 (CH_2), 29.19 (CH_2), 28.65 (CH_2), 26.04 (CH_2), 25.99 (CH_2), 22.70 (CH_2), 14.13 (CH_3). **Elemental analysis** calcd (%) for $C_{74}H_{119}N_7O_4$: *C* 75.91, *H* 10.24, *N* 8.37; found *C* 75.91, *H* 10.46, *N* 8.30. **HRMS** (EI): *m/z*= 1170.9396 (calcd 1170.9395 for [M + H^+]).

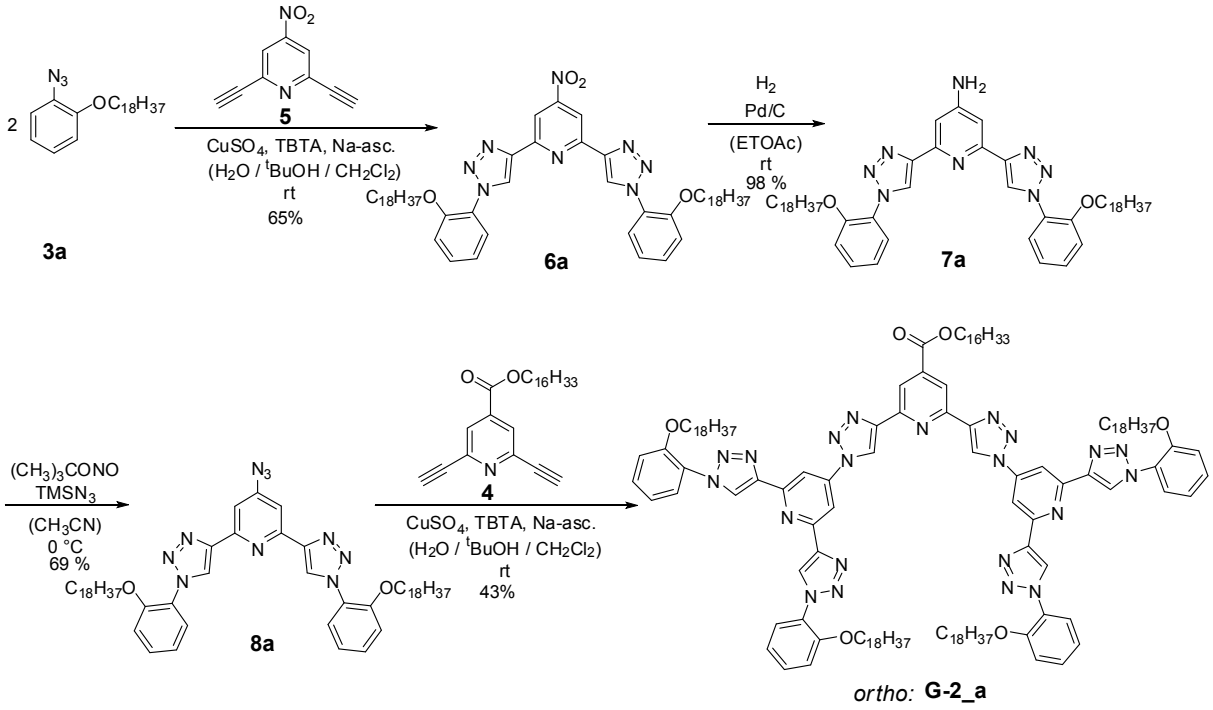
Hexadecyl 2,6-bis(1-(4-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)isonicotinate G-1_c.



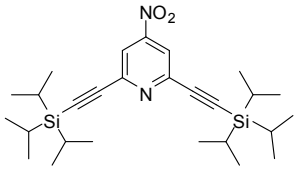
A three necked flask was charged with 600 mg of 2,6-diethynyl 4-(hexadecyloxycarbonyl) pyridine (1.51 mmol, 1 equiv.) and 1.35 g of 1-azido-2-(octadecyloxy)benzene (3.48 mmol, 2.3 equiv.), 60 mg of sodium ascorbate (0.30 mmol, 0.2 equiv.), 80 mg of TBTA (0.152 mmol, 0.10 equiv.) and a 30 mL of a solvent mixture composed by H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). An aqueous stock solution of $CuSO_4$ was added (0.152 mmol, 0.10 equiv.; stock solution: 10 mg $CuSO_4$ per 0.3 mL of water) and the mixture was stirred for 3 d at rt in the dark. In case of an appearing precipitate additional CH_2Cl_2 was added. After the acetylene starting material was consumed indicated by TLC monitoring (PE/EtOAc 8/2) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2

(3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (PE/EtOAc 8/2) as yellow solid (1.66 g, 94%). **TLC** (PE/EtOAc 8/2) $R_f = 0.55$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.70 (s, 2H, Ar*H*), 8.59 (s, 2H, Ar*H*), 7.74 (d, ^{3}J = 8.91, 4H, Ar*H*), 7.06 (d, ^{3}J = 9.0, 4H, Ar*H*), 4.42 (t, ^{3}J = 6.79 Hz, 2H, CO_2CH_2), 4.03 (t, ^{3}J = 6.53 Hz, 4H, OCH_2), 1.88-1.79 (m, 6H, CH_2), 1.50-1.27 (m, 86H, CH_2), 0.91-0.87 (m, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.97 (-CO_2-), 159.61 (OC_{Ar}), 150.88 (OC_{Ar}), 148.07 (C_{Ar}), 139.89 (C_{Ar}), 130.11 (C_{Ar}), 122.12 (C_{Ar}), 120.61 (C_{Ar}), 118.89 (C_{Ar}), 115.31 (C_{Ar}), 68.50 (OCH_2), 66.21 (OCH_2), 31.93 (CH_2), 29.71 (CH_2), 29.63 (CH_2), 29.60 (CH_2), 29.55 (CH_2), 29.42 (CH_2), 29.38 (CH_2), 29.32 (CH_2), 29.19 (CH_2), 28.65 (CH_2), 26.03 (CH_2), 25.98 (CH_2), 22.70 (CH_2), 14.13 (CH_3). **Elemental analysis:** calcd (%) for $C_{74}H_{119}N_7O_4$: *C* 75.91, *H* 10.24, *N* 8.37; found *C* 75.94, *H* 10.30, *N* 8.31. **HRMS** (EI): *m/z*= 1192.9216 (calcd 1192.9225 for [M + Na^+]).

Synthesis scheme for click reactions affording the dendrons G-2_a.

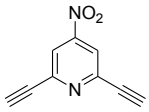


4-Nitro-2,6-bis((triisopropylsilyl)ethynyl)pyridine.



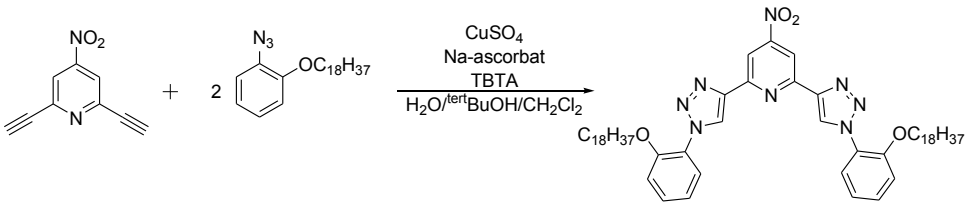
In a dry three necked flask equipped with a condenser 2.81 g of 2,6-dibromo-4-nitropyridine (10 mmol, 1 equiv.), copper iodide (38 mg, 0.2 mmol, 0.02 equiv.), and triphenylphosphine (131 mg, 0.5 mmol, 0.05 equiv.) were suspended in 30 mL of a mixture of dry toluene/TEA (3/1). The solution was degassed at rt by evacuating and flushing with argon (4 cycles), freeze degassed (1 x) and tetrakistriphenylphosphine palladium (231 mg, 0.2 mmol, 0.02 equiv.) was added under argon atmosphere. After freeze degassing (1 x) TIPS-acetylene (6.73 mL, ρ = 0.813 g/mL, 30 mmol, 3 equiv.) was added in the counterflow of argon using a syringe. The reaction mixture was stirred at 70 °C for 2 d. After consumption of all starting material **3** indicated by TLC monitoring (PE/DCM 9:1) the solvent was removed *in vacuo*. Purification by column chromatography (PE/DCM 9:1) gave (4.12 g, 85%) of the title compound as a yellow oil. **TLC** (PE/EtOAc 99/1) R_f = 0.5. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.03 (s, 2H, Ar*H*), 1.19 – 1.16(m, 42H, SiC*H*, SiCHC*H*$_3$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 153.70 (C_{Ar}), 145.82 (C_{Ar}), 119.20 (C_{Ar}), 103.74 (C≡*C*), 96.58 (C≡*C*), 18.61 (SiCH*C*H$_3$), 11.19 (Si*C*H). **UPLC** R_t = 2.89, 100 % peak area. **HRMS** (ESI) *m/z* = 485.3014 (calcd 485.3020 for [M + H$^+$]).

2,6-Diethynyl-4-nitropyridine 5.



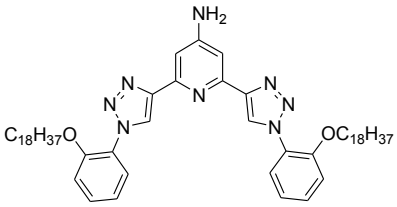
3.87 g of 4-nitro-2,6-bis((triisopropylsilyl)ethynyl)pyridine (8.0 mmol, 1 equiv.) were dissolved in 15 mL of THF and the mixture was cooled down to 0 °C. To the rapidly stirred reaction mixture was added a solution of TBAF in THF (6.27 mL, 1 M solution, 3 equiv.) slowly via a syringe and while stirring for 10 min the mixture was allowed to reach rt. The mixture was filtered through a short silica plug using THF and the solvent was removed *in vacuo*. Purification by column chromatography (DCM) gave 1.24 g of a colorless solid (90%). **TLC** (DCM) R_f = 0.48. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.12 (s, 2H, Ar*H*), 3.28 (s, 2H, C≡C*H*). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 153.96 (-*C*O_2-), 144.99 (C_{Ar}), 119.60 (C_{Ar}), 80.86 (C≡*C*), 80.60 (C≡*C*H), **UPLC** R_t = 0.49, 100 % peak area. **HRMS** (ESI) *m/z* = 173.0376 (calcd 173.0351 for [M + H$^+$]).

4-Nitro-2,6-bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridine 6a.



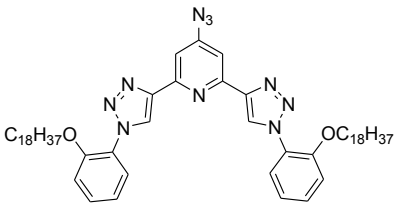
A three necked flask was charged with 2,6-diethynyl-4-nitropyridine (172 mg, 1.0 mmol , 1 equiv.) and 1-azido-2-(octadecyloxy)benzene (0.85 g, 2.3 mmol, 2.3 equiv.), sodium ascorbate (40 mg, 0.2 mmol, 0.2 equiv .), TBTA (53 mg, 0.1 mmol, 0.1 equiv.) and a solvent mixture of $H_2O/^{tert}BuOH/CH_2Cl_2$ (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). And $CuSO_4$ $5H_2O$ was added (25 mg, 0.1 mmol, 0.1 equiv.) and the mixture was stirred 24 h at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (PE/EtOAc 9/1) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2 (3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (PE/EtOAc 9/1) as yellow solid (616 mg, 65%). **TLC** (PE/EtOAc 9/1) $R_f = 0.51$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.83 (s, 2H, Ar*H*), 8.75 (s, 2H, Ar*H*), 7.84 – 7.82 (dd, ^3J = 7.87 Hz, ^4J = 1.6 Hz, 2H, Ar*H*), 7.45 - 7.40 (m, 2H, Ar*H*), 7.13 - 7.08 (m, 4H, Ar*H*), 4.06 (t, J^3 = 6.5 Hz, 4H, OCH_2), 1.75 - 1.71 (m, 4H, CH_2), 1.36 - 1.01 (m, 60H, CH_2), 0.87 - 0.83 (m, 6H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 155.65 (NO_2C_{Ar}), 153.13 (C_{Ar}), 150.73 (C_{Ar}), 146.35 (C_{Ar}), 130.52 (C_{Ar}), 126.19 (C_{Ar}), 125.45 (C_{Ar}), 125.06 (C_{Ar}), 121.25 (C_{Ar}), 113.43 (C_{Ar}), 111.57 (C_{Ar}), 69.26 (OCH_2), 31.94 (CH_2), 29.71 (CH_2), 29.68 (CH_2), 29.66 (CH_2), 29.63 (CH_2), 29.53 (CH_2), 29.44 (CH_2), 29.38 (CH_2), 28.18 (CH_2), 28.97 (CH_2), 25.97 (CH_2), 22.71 (CH_2), 14.14 (CH_3). **UPLC** R_t = 4.04, 99.6 % peak area. **HRMS** (ESI) *m/z* = 947.6855 (calcd 947.6850 for $[M + H^+]$). **Elemental analysis:** calcd (%) for $C_{57}H_{86}N_8O_4$: *C* 72.27, *H* 9.15, *N* 11.83; found *C* 72.26, *H* 9.16, *N* 11.84

2,6-Bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridin-4-amine 7a.



In a one necked flask was charged with 4-nitro-2,6-bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridine (616 mg , 0.65 mmol) were dissolved in 20 mL of EtOAc, 61 mg Pd on charcoal (10% wt) were added, the stirred mixture was degassed at rt in vacuo and flushed with H_2 (3 cycles). After stirring for 6 h at rt in H_2 atmosphere (2 bar) the mixture was filtered through a celite pad and the solvent removed *in vacuo*. (PE/EtOAc 7/3) gave white solid (395 mg, 98%) of a. **TLC** (PE/EtOAc 7/3) $R_f = 0.52$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.67 (br s, 2H, Ar*H*), 7.83 – 7.8 (ss, 2H, Ar*H*), 7.56 (s, 2H, Ar*H*), 7.45 – 7.39 (m, 2H, Ar*H*), 7.14 - 7.08 (m, 4H, Ar*H*), 4.57 (br s, 2H, Ar-N*H*$_2$), 4.06 (t, J^3 = 6.58 Hz, 4H, OC*H*$_2$), 1.80 - 1.71 (m, 4H, C*H*$_2$), 1.39 - 1.09 (m, 60H, C*H*$_2$), 0.89 (t, ^{3}J = 6.63 Hz, 6H, C*H*$_3$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 150.93 (*C*$_{Ar}$), 130.14 (*C*$_{Ar}$), 126.61 (*C*$_{Ar}$) 125.59 (*C*$_{Ar}$), 124.31 (*C*$_{Ar}$), 121.06 (*C*$_{Ar}$), 113.39 (*C*$_{Ar}$), 101.19 (*C*$_{Ar}$), 69.20 (O*C*H$_2$), 31.94 (*C*H$_2$), 29.73 (*C*H$_2$), 29.69 (*C*H$_2$), 29.66 (*C*H$_2$), 29.56 (*C*H$_2$), 29.48 (*C*H$_2$), 29.44 (*C*H$_2$), 29.38 (*C*H$_2$), 28.19 (*C*H$_2$), 28.93 (*C*H$_2$), 25.89 (*C*H$_2$), 22.70 (*C*H$_2$), 14.14 (*C*H$_3$). **UPLC** R_t = 5.60, 99.6 % peak area. **Elemental analysis:** calcd (%) for $C_{57}H_{88}N_8O_2$: *C* 74.63, *H* 9.67, *N* 12.21; found *C* 74.61, *H* 9.68, *N* 12.22.

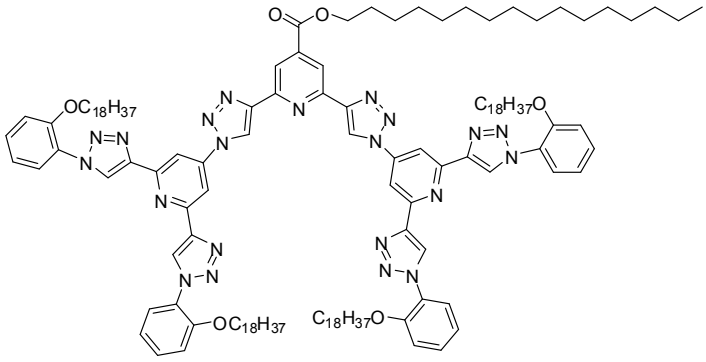
4-Azido-2,6-bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridine 8a.



In a round-bottomed flask (1.96 g, 2.14 mmol, 1 equiv.) of 2,6-bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridin-4-amine was dissolved in 15 mL of acetonitrile and cooled to 0°C in an ice bath. To this stirred mixture were added (0.38 g, 3.2 mmol, 1.5 equiv.) of t-BuONO followed by (0.33 g, 2.5 mmol, 1.2 equiv.) $TMSN_3$ dropwise. The resulting solution was stirred at rt for 1 h. The reaction mixture was concentrated under *vacuo* and the crude product was purified by column chromatography (petroleum) to give yellow oil (1.39 g, 69%) **TLC** (PE) $R_f = 0.47$. . **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.74 (s, 2H, Ar*H*), 7.79 – 7.75 (m, 4H, Ar*H*), 7.38 – 7.32 (m, 2H, Ar*H*), 7.07 – 7.0 (m, 4H, Ar*H*), 3.96 (t, J^3 = 6.53 Hz, 4H, OC*H*$_2$), 1.72 - 1.63 (m, 4H, C*H*$_2$), 1.27 – 0.99 (m, 60H, C*H*$_2$), 0.86 – 0.82 (m, 6H, C*H*$_3$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 151.75 (*C*$_{Ar}$), 150.52 (*C*$_{Ar}$), 150.33 (*C*$_{Ar}$) 147.06 (*C*$_{Ar}$), 130.16 (*C*$_{Ar}$), 126.19 (*C*$_{Ar}$), 125.26

(C_{Ar}), 124.63 (C_{Ar}), 121.0 (C_{Ar}), 113.24 (C_{Ar}), 109.18 (C_{Ar}), 69.14 (OCH_2), 31.93 (CH_2), 29.73 (CH_2), 29.69 (CH_2), 29.64 (CH_2), 29.55 (CH_2), 29.44 (CH_2), 29.39 (CH_2), 29.20 (CH_2), 28.92 (CH_2), 25.90 (CH_2), 22.69 (CH_2), 14.10 (CH_3). **UPLC** R_t = 4.43, 100 % peak area. **HRMS** (ESI) *m/z* = 943.7053 (calcd 943.7013 for [M + H^+]).

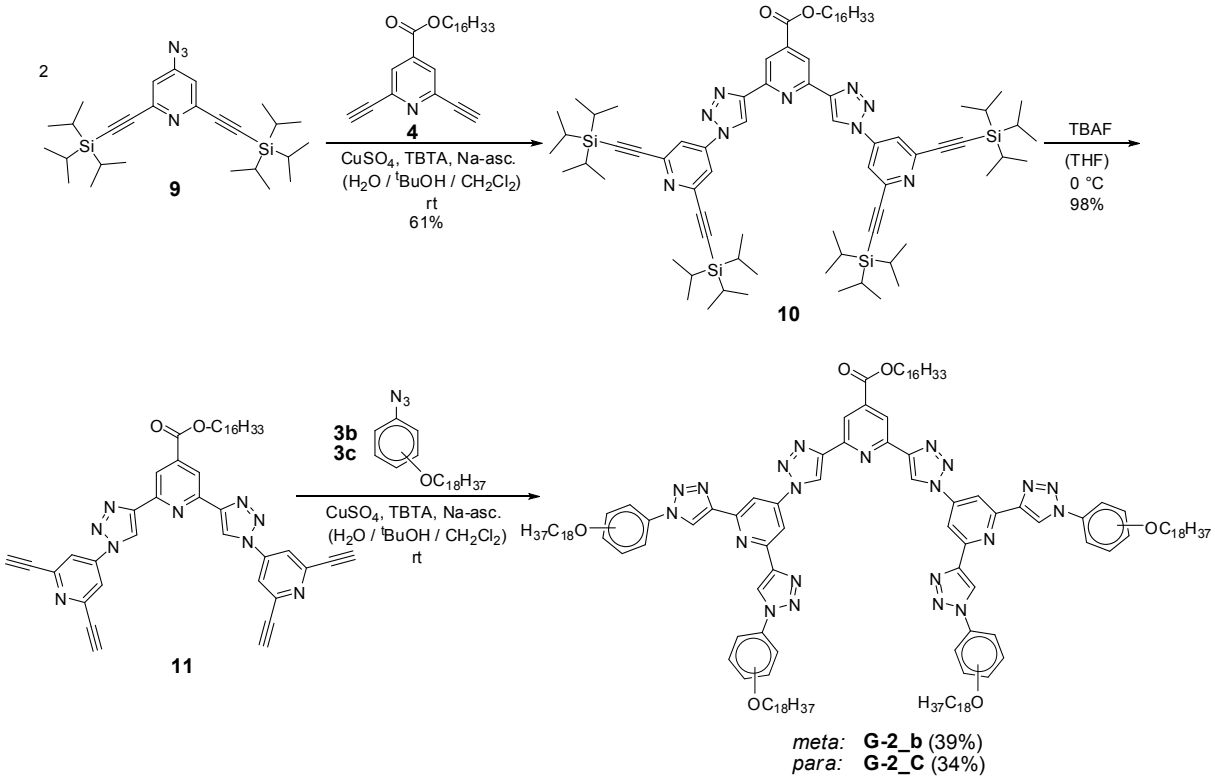
Hexadecyl 2,6-bis(1-(2,6-bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)-1H-1,2,3-triazol-4-yl)isonicotinate G-2_a.



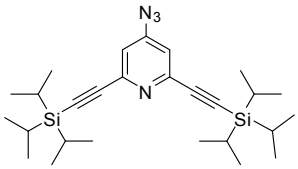
A three necked flask was charged with 2,6-diethynyl 4-(hexadecyloxycarbonyl) pyridine (369 mg, 0.93 mmol , 1 equiv.) and 4-azido-2,6-bis(1-(2-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridine (2.02 g, 2.14 mmol, 2.3 equiv.), sodium ascorbate (37 mg, 0.18 mmol, 0.2 equiv .), TBTA (49 mg, 0.09 mmol, 0.1 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). And $CuSO_4$ $5H_2O$ was added (23 mg, 0.09 mmol, 0.1 equiv.) and the mixture was stirred 3d at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (DCM/MeOH 1:2%) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2 (3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (DCM/MeOH 1:2%) as beige solid (915 mg, 43%). **TLC** (DCM/MeOH 1:2%) R_f = 0.27. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 9.20 - 911 (m, 2H, Ar*H*), 8.90 – 8.80 (m, 10H, Ar*H*), 7.88 – 7.85 (m, 4H, Ar*H*), 7.46 – 7.41 (m, 4H, Ar*H*), 7.13 – 7.09 (m, 8H, Ar*H*), 4.48 (t, ^{3}J = 6.85 Hz, 2H, CO_2CH_2), 4.12 -4.10 (ss, 8H, OCH_2), 1.91 – 1.78 (m, 10H, CH_2), 1.51 – 1.07 (br m, 146H, CH_2), 0.89 – 0.85 (m, 15H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 151.84 (-CO_2-), 150.68 (C_{Ar}), 150.51 (C_{Ar}), 148.90 (C_{Ar}), 146.02 (C_{Ar}), 145.10 (C_{Ar}), 140.10 (C_{Ar}), 130.40 (C_{Ar}), 130.29 (C_{Ar}), 126.21 (C_{Ar}), 125.39 (C_{Ar}), 121.07 (C_{Ar}), 119.48 (C_{Ar}), 116.46 (C_{Ar}), 113.30 (C_{Ar}), 109.99 (C_{Ar}), 109.55 (C_{Ar}), 69.29 (OCH_2), 66.32 (OCH_2), 31.91 (CH_2), 29.70 (CH_2), 29.66 (CH_2), 29.56

(CH_2), 29.47 (CH_2), 29.36 (CH_2), 29.20 (CH_2), 28.93 (CH_2), 26.01 (CH_2), 25.94 (CH_2), 22.69 (CH_2), 14.12 (CH_3). **MS** (ESI-QTOF [THF/DMF/KBr] and MALDI-TOF, [dithranole/KTFA] *m/z* = 2319.90 (calcd 2319.63 for [M] + K^+)). **Elemental analysis:** calcd (%) for $C_{140}H_{209}N_{21}O_6$: *C* 73.68, *H* 9.23, *N* 12.89; found *C* 73.67, *H* 9.22, *N* 12.88.

Synthesis scheme for click reactions affording the dendrons G-2_b,c.

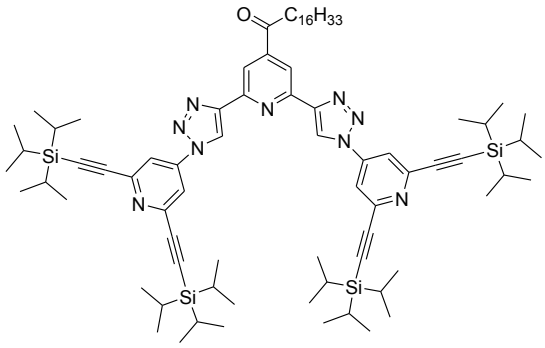


4-Azido-2,6-bis((triisopropylsilyl)ethynyl)pyridine 9.



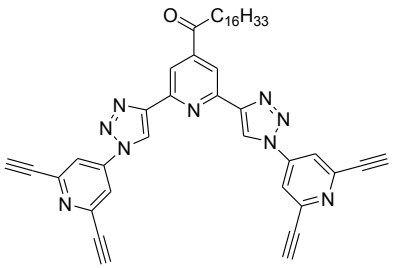
4-Nitro-2,6-bis((triisopropylsilyl)ethynyl)pyridine (698 mg, 1.4 mmol, 1 equiv.) was dissolved in 15 mL acetonitrile and solution of NaN_3 (936 mg, 14.4 mmol, 10 equiv.) in 5 mL of water was added into the reaction mixture and stirred at 80°C for 4 d .The reaction mixture was poured on water and extracted with ethyl acetate (3 x), and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* as yellow oil (260 mg, 38%). yellow oil. **TLC** (PE/EtOAc 99/1) $R_f = 0.45$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.03 (s, 2H, Ar*H*), 1.18 – 1.13(m, 42H, SiC*H*, SiCHCH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 148.92 (C_{Ar}), 144.87 (C_{Ar}), 117.34 (C_{Ar}), 104.71 (C≡*C*), 93.44 (C≡*C*), 18.63 (SiCH*C*H_3), 11.23 (Si*C*H). **UPLC** R_t = 2.85, 99.8 % peak area. **HRMS** (ESI) *m/z* = 481.3145. (calcd 481.3183 for [M + H^+]).

1-(2,6-bis(1-(2,6-bis((triisopropylsilyl)ethynyl)pyridin-4-yl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)heptadecan-1-one 10.



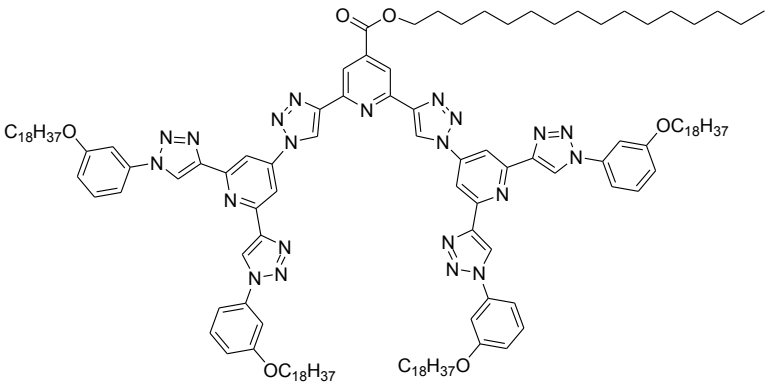
A three necked flask was charged with 2,6-diethynyl 4-(hexadecyloxycarbonyl) pyridine (2.67 g, 6.75 mmol , 1 equiv.) and 4-azido-2,6-bis((triisopropylsilyl)ethynyl)pyridine (6.49 g, 13.5 mmol, 2 equiv.), sodium ascorbate (535 mg, 2.7 mmol, 0.4 equiv .), TBTA (716 mg, 1.35 mmol, 0.2 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). And $CuSO_4$ $5H_2O$ was added (337 mg, 1.35 mmol, 0.2 equiv.) and the mixture was stirred 3 h at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (DCM/Acetone 5/5) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2 (3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (PE/DCM 1/1) as yellow oil (5.60 g, 61%). **TLC** (PE/DCM 1/1) $R_f = 0.50$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 9.17 (br, 2H, Ar*H*), 8.78 (s, 2H, Ar*H*), 8.06 (s, 4H, Ar*H*), 4.46 (t, J^3 = 6.76 Hz, 2H, OCH_2), 1.89 – 1.82 (m, , 2H, CH_2), 1.52 - 1.26 (m, 84H, CH_2), 1.07 – 1.06 (ss, 84H, SiC*H*, SiCHCH_3), 0.90 – 0.86 (m, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.78 (-*C*O_2-), 150.36 (C_{Ar}), 149.05 (C_{Ar}), 145.37 (C_{Ar}), 143.62 (C_{Ar}), 140.03 (C_{Ar}), 119.79 (C_{Ar}), 116.71 (C_{Ar}), 104.07 (C≡*C*), 95.24 (C≡*C*), 66.37 (O*C*H_2), 31.92 (*C*H_2), 29.69 (*C*H_2), 29.66 (*C*H_2), 29.62 (*C*H_2), 29.36 (*C*H_2), 28.65 (*C*H_2), 25.97 (*C*H_2), 22.69 (*C*H_2), 18.54 (SiCH*C*H_3), 14.11 (*C*H_3), 12.27 (Si*C*H). **MS** (EI, T = 37°C - 50 °C)**:** *m/z* = 1340.89 (calcd 1340.91 for [M + H^+]).

1-(2,6-bis(1-(2,6-diethynylpyridin-4-yl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)heptadecan-1-one 11.



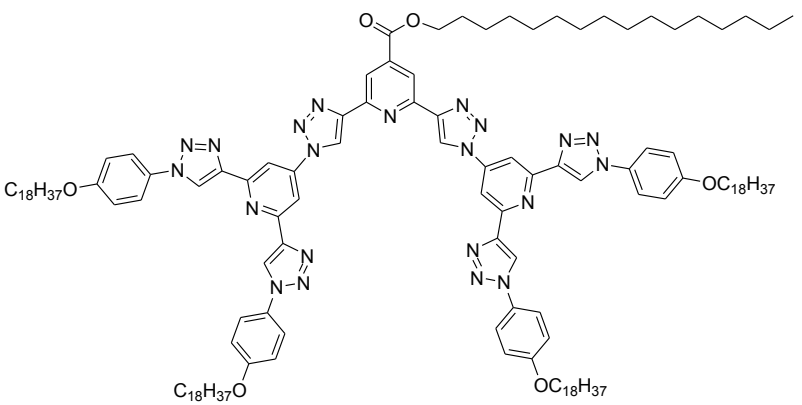
1-(2,6-bis(1-(2,6-bis((triisopropylsilyl)ethynyl)pyridin-4-yl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)heptadecan-1-one (5 g, 3.7 mmol, 1 equiv.) were dissolved in 100 mL of THF and the mixture was cooled down to 0 °C. To the rapidly stirred reaction mixture was added a solution of TBAF in THF (5.2 mL, 1 M solution, 4 equiv.) slowly via a syringe and while stirring for 10 min the mixture was allowed to reach rt. The mixture was filtered through a short silica plug using THF and the solvent was removed *in vacuo*. Purification by column chromatography (PE + 7% EtOAc) gave beige solid (2.65 g, 98%). **TLC** (PE/EtOAc 97/3) R_f = 0.48. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 9.29 (s, 2H, Ar*H*), 8.64 (s, 2H, Ar*H*), 8.17 (s, 4H, Ar*H*), 4.45 (t, J^3 = 6.77 Hz, 2H, OCH_2), 3.61 (s, 4H, C≡C*H*), 1.97 – 1.89 (m, 2H, CH_2), 1.54 - 1.41 (m, 26H, CH_2), 0.93 – 0.89 (m, 3H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.01 (-*C*O_2-), 150.72 (C_{Ar}), 148.59 (C_{Ar}), 144.62 (C_{Ar}), 143.74 (C_{Ar}), 140.12 (C_{Ar}), 120.88 (C_{Ar}), 118.42 (C_{Ar}), 116.45 (C_{Ar}), 81.73 (C≡*C*), 79.59 (C≡*C*H), 66.71 (O*C*H_2), 31.89 (*C*H_2), 29.68 (*C*H_2), 29.63 (*C*H_2), 29.56 (*C*H_2), 29.33 (*C*H_2), 28.58 (*C*H_2), 27.0 (*C*H_2), 25.93 (*C*H_2), 24.87 (*C*H_2), 24.61 (*C*H_2), 24.34 (*C*H_2), 24.07 (*C*H_2), 23.80 (*C*H_2), 22.58 (*C*H_2), 22.03 (*C*H_2), 17.34 (*C*H_2), 13.47 (*C*H_3). **MS** (EI, T = 37°C - 50 °C)**:** *m/z* = 716.37 (calcd 716.38 for [M + H^+])

Hexadecyl 2,6-bis(1-(2,6-bis(1-(3-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)-1H-1,2,3-triazol-4-yl)isonicotinate G-2_b.



A three necked flask was charged with 1-(2,6-bis(1-(2,6-diethynylpyridin-4-yl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)heptadecan-1-one (644 mg, 0.9 mmol , 1 equiv.) and 1-azido-3-(octadecyloxy)benzene (1.5 g, 3.8 mmol, 4.3 equiv.), sodium ascorbate (71 mg, 0.36 mmol, 0.4 equiv .), TBTA (96 mg, 0.18 mmol, 0.2 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). And $CuSO_4$ $5H_2O$ was added (45 mg, 0.18 mmol, 0.2 equiv.) and the mixture was stirred 3 d at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (DCM/MeOH 1:2%) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2 (3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (DCM/MeOH 1:2%) as beige solid (800 mg, 39%). **TLC** (PE/EtOAc 7/3) R_f = 0.36. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.98 (br s, 2H, Ar*H*), 8.76 – 8.45 (br m, 10H, Ar*H*), 7.89 (br s, 2H, Ar*H*), 7.27 – 7.12 (br m, 10H, Ar*H*), 6.89 - 6.83 (br m, 4H, Ar*H*), 4.39 (s, 2H, CO_2CH_2), 3.91 (s, 8H, OCH_2), 1.78 (s, 10H, CH_2), 1.44 – 1.27 (br m, 146H, CH_2), 0.89 (t, ^{3}J = 6.22 Hz, 15H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.49 (-CO_2-), 160.05 (C_{Ar}), 159.96 (C_{Ar}), 152.10 (C_{Ar}), 151.38 (C_{Ar}), 150.02 (C_{Ar}), 148.61 (C_{Ar}), 146.96 (C_{Ar}), 143.74 (C_{Ar}), 137.22 (C_{Ar}), 130.23 (C_{Ar}), 120.59 (C_{Ar}), 114.98 (C_{Ar}), 111.65 (C_{Ar}), 110.01 (C_{Ar}), 108.60 (C_{Ar}), 105.91 (C_{Ar}), 68.40 (OCH_2), 66.17 (OCH_2), 31.94 (CH_2), 29.75 (CH_2), 29.69 (CH_2), 29.56 (CH_2), 29.48 (CH_2), 29.39 (CH_2), 29.25 (CH_2), 29.18 (CH_2), 26.09 (CH_2), 26.03 (CH_2), 22.70 (CH_2), 14.13 (CH_3). **MS** (ESI-QTOF [THF/DMF/KBr] and MALDI-TOF, [dithranole/KTFA] *m/z* = 2319.90 (calcd 2319.63 for [M] + K^+)). **Elemental analysis:** calcd (%) for $C_{140}H_{209}N_{21}O_6$: *C* 73.68, *H* 9.23, *N* 12.89; found *C* 73.67, *H* 9.22, *N* 12.90.

Hexadecyl 2,6-bis(1-(2,6-bis(1-(4-(octadecyloxy)phenyl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)-1H-1,2,3-triazol-4-yl)isonicotinate G-2_c.



A three necked flask was charged with 1-(2,6-bis(1-(2,6-bis((triisopropylsilyl) ethynyl)pyridin-4-yl)-1H-1,2,3-triazol-4-yl)pyridin-4-yl)heptadecan-1-one (644 mg, 0.9 mmol, 1 equiv.) and 1-azido-4-(octadecyloxy)benzene (1.5 g, 3.8 mmol, 4.3 equiv.), sodium ascorbate (71 mg, 0.36 mmol, 0.4 equiv .), TBTA (96 mg, 0.18 mmol, 0.2 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). And $CuSO_4$ $5H_2O$ was added (45 mg, 0.18 mmol, 0.2 equiv.) and the mixture was stirred 3 h at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (DCM/MeOH 1:2%) the mixture was diluted with CH_2Cl_2 and transferred into a separation funnel. The organic phase was washed with aqueous Na_2-EDTA solution (1 x), the aqueous phase was extracted with CH_2Cl_2 (3 x), and afterwards the combined organic phases were washed again with aqueous Na_2-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over $MgSO_4$, filtration, and removal of the solvent *in vacuo* the title compound was obtained by column chromatography (DCM/MeOH 1:2%) as beige solid (700 mg, 34%). **TLC** (DCM/MeOH 1:2%) $R_f = 0.31$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.94 – 8.89 (br m, 2H, Ar*H*), 8.64 – 8.20 (br m, 10H, Ar*H*), 7.75 – 7.45 (m, 8H, Ar*H*), 6.96 – 6.84 (m, 8H, Ar*H*), 4.37 – (br m, 2H, CO_2CH_2), 3.96 (s, 8H, OCH_2), 1.82 (s, 10H, CH_2), 1.30 – 1.27 (br m, 146H, CH_2), 0.93 – 0.87 (m, 15H, CH_3).**^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.63 (-CO_2-), 159.13 (C_{Ar}), 151.65 (C_{Ar}), 150.81 (C_{Ar}), 149.81 (C_{Ar}), 148.57 (C_{Ar}), 146.52 (C_{Ar}), 143.49 (C_{Ar}), 139.36 (C_{Ar}), 129.50 (C_{Ar}), 121.56 (C_{Ar}), 115.05 (C_{Ar}), 114.79 (C_{Ar}), 109.99 (C_{Ar}), 108.39 (C_{Ar}), 68.38 (OCH_2), 66.06 (OCH_2), 31.98 (CH_2), 31.94 (CH_2), 29.83 (CH_2), 29.80 (CH_2), 29.75 (CH_2), 29.52 (CH_2), 29.47 (CH_2), 29.43 (CH_2), 29.39 (CH_2), 26.21 (CH_2), 26.07 (CH_2), 22.73 (CH_2), 22.71 (CH_2), 14.15 (CH_3).). **MS** (ESI-QTOF [THF/DMF/KBr] and MALDI-TOF, [dithranole/KTFA] *m/z* = 2319.90 (calcd 2319.63 for [M] + K^+)). **Elemental analysis:** calcd (%) for $C_{140}H_{209}N_{21}O_6$: *C* 73.68, *H* 9.23, *N* 12.89; found *C* 73.69, *H* 9.22, *N* 12.88.

Copies of Spectral Data (^{1}H-NMR, ^{13}C-NMR) of Dendrons G-1_a-c and G-2_a-c