ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) FOR:

Modulating the self-assembly of rigid "clicked" dendrimers at the solid-liquid interface by tuning non-covalent interactions between side groups

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Table of Contents

1. General Methods

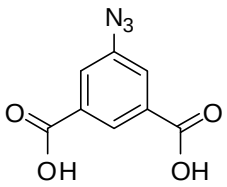
Chemicals. Solvents and starting materials were used as received. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled under an inert gas (Ar) atmosphere from sodium/benzophenone and CaH_2, respectively, prior to use and were prepared using previously published procedures. $Pd(PPh_3)_4$ was freshly prepared.[1] All reactions requiring inert gas were performed under an Ar-atmosphere. The Cu-catalyzed 1,3-dipolar cycloaddition reactions were performed in the dark under an Ar-atmosphere, using $CuSO_4 \cdot 5H_2O$ as copper source, solid sodium ascorbate as the in-situ reducing agent, and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)[2] as the supporting ligand. An aqueous ethylenediamine-tetraacetic acid disodium salt solution (EDTA) (16 g/L Na_2-EDTA), adjusted to 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, EA = ethyl acetate).

Spectroscopy. NMR spectra were recorded on a 300 MHz (75.6 MHz for ^{13}C) Bruker DPX 300 spectrometer or a 600 MHz Bruker Avance II spectrometer at 23 °C using residual protonated solvent signals as internal standard (^1H: $\delta(CHCl_3)$ = 7.28 ppm, $\delta(D_2O)$ = 4.79 ppm and ^{13}C: $\delta(CHCl_3)$ = 77.16 ppm). Assignments are based on chemical shifts (Ar is used as abbreviation for assigning aromatic phenyl as well as triazole moieties). Mass spectrometry was performed on Thermo LTQ FT instrument (ESI, ESI-HRMS; additives of mixtures of $MeOH/H_2O$ 75/25 + 0.5 % formic acid) and MSI Concept 1H (EI, 70 eV ionization) as well as on a QSTARXL Applied Biosystems ESI Q-TOF with a ISV of 950 V. UPLC measurements were performed with Waters Alliance systems consisting of a Waters Separations Module 2695, a Waters Diode Array detector 996 and a Waters Mass Detector ZQ 2000. (mixtures and gradient mixtures of acetoneitrile/water, flow = 0.6 ml/min) equipped with a 100 x 2.1 mm AQUITY HSST3 column (1.8 µm phenyl-hexyl material). Conditions are specified when describing the corresponding substances. Peak areas have been calculated from detection by UV between 200-400 nm (MaxPlot).

[1] D. R. Coulson, *Inorg. Syn.* **1971**, *13*, 121.
[2] T. R. Chan, R. Hilgraf, K. B. Sharpless, V. V. Fokin, *Org. Lett.* **2004**, *6*, 2853-2855.

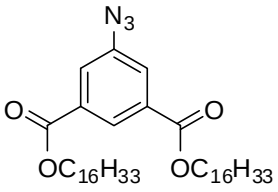
2. Synthesis

5-Azidoisophthalic acid **6.**[3]



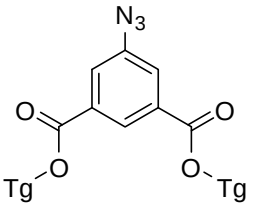
Compound **1** was prepared as described by *Yielding*.[3]

Bis(n-hexadecyl) 5-azidoisophthalate **7.**



5-Azidoisophthalic acid **6** (1.0 g, 5.52 mmol, 1 equiv.), 1-hexadecanol (2.66 g, 10.98 mmol, 1.99 equiv.), and DMAP (1.34 g, 11.04 mmol, 2 equiv.) were dissolved in 40 mL of CH_2Cl_2, cooled to 0 °C and EDC (4.23 g, 22.08 mmol, 4 equiv.) was added. The solution was allowed to warm up to rt and stirred for 24 h. Purification using column chromatography (PE/CH_2Cl_2 4/6) gave 2.8 g of the desired product as a colourless solid (76%). **TLC** (PE/CH_2Cl_2 4/6) R_f = 0.71.**^{1}H-NMR** (300 MHz, $CDCl_3$): **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.45(s, H, Ar*H*), 7.88 (s, 2H, Ar*H*), 4.39 (t, ^{3}J= 6.76 Hz, 4H, CO_2CH_2*),* 1.82-1.77 (m, 4H, CH_2), 1.45-1.27 (m, 52H, CH_2), 0.92 (t, ^{3}J = 6.55 Hz, 6H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.03 (-CO_2-), 141.10 (C_{Ar}), 132.65 (C_{Ar}), 126.83 (C_{Ar}), 123.88 (C_{Ar}), 65.87 (OCH_2), 31.93 (CH_2), 29.70 (CH_2), 29.59 (CH_2), 29.53 (CH_2), 29.37 (CH_2), 29.27 (CH_2), 28.64 (CH_2), 25.98 (CH_2), 22.70 (CH_2), 14.12 (CH_3).

Bis(3,6,9-trioxadecyl) 5-azidoisophthalate **8.**



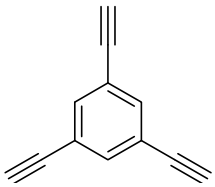
5-azidoisophthalic acid **6** (1.00 g, 5.52 mmol, 1 equiv.), triglyme (1.72 g, 10.98 mmol, 1.99 equiv.), and DMAP (1.34 g, 11.04 mmol, 2 equiv.) were dissolved in 40 mL CH_2Cl_2, cooled to 0°C and EDC (4.23 g, 22.08 mmol, 4 equiv.) was added. The solution was allowed to warm up to rt and stirred for 2 d. Purification using column chromatography (CH_2Cl_2/Acetone 9/1) gave 3.03 g of yellow oil (65%). TLC (CH_2Cl_2/Acetone 9/1) R_f = 0.41.**^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.44 (t, ^{3}J = 2.9 Hz 1H, Ar*H*), 7.86 (d, ^{2}J = 1.45 Hz 2H, Ar*H*), 4.51 – 4.48 (m, 4H, CO_2CH), 3.85 – 3.82 (m, 4H, CH_2), 3.71 – 3.61 (m, 12H, CH_2), 3.53 – 3.50 (m,

Tg= $(CH_2CH_2O)_3CH_3$

[3] W. E. White, Jr., K. L. Yielding, *Biochem. Biophys. Res. Comm.* **1973**, *52*, 1129.

4H, C*H*$_2$), 3.34 (s, 6H, OC*H*$_3$). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.86 (-*C*O$_2$-), 141.12 (*C*$_{Ar}$), 132.24 (*C*$_{Ar}$), 127.08 (*C*$_{Ar}$), 124.15 (*C*$_{Ar}$), 71.81 (*C*H$_2$), 70.64 (*C*H$_2$), 70.59 (*C*H$_2$), 70.54 (*C*H$_2$), 68.99 (*C*H$_2$), 64.69 (*C*H$_2$), 58.98 (O*C*H$_3$). **UPLC** R_t = 2.12 min, 99.8 % peak area. **HRMS** (ESI) *m/z* = 522.5010 (calcd 522.5012 for [M + Na^+]).

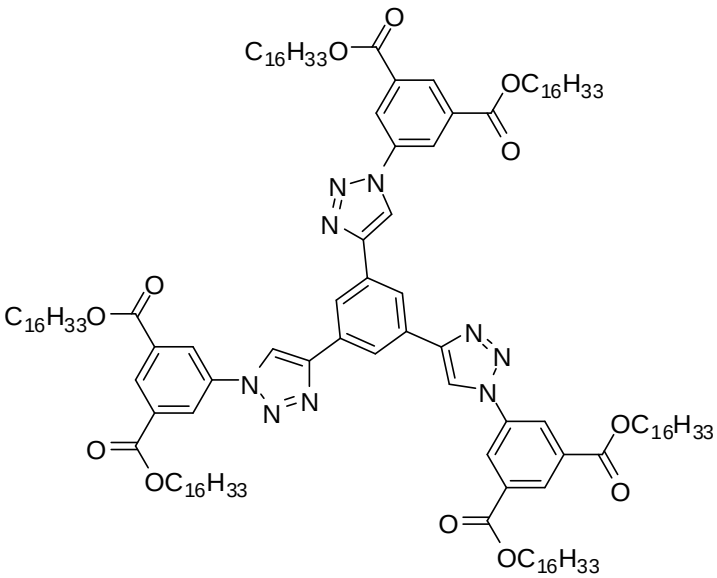
1,3,5-Triethynylbenzene **9.**[4]



Compound **9** was prepared as described by *Kijima.*[4]

Hexakis(n-hexahexadecyl) dendrimer **2.**

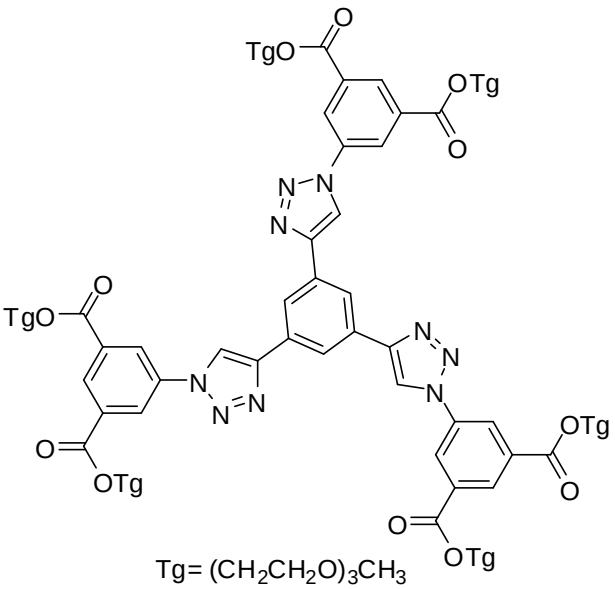
A three necked flask was charged with 1,3,5-triethynylbenzene **9** (541 mg, 3.6 mmol, 1 equiv.) and bis (*n*-hexadecyl) 5-azidoisophthalate **7** (7.79 g, 11.8 mmol, 3.3 equiv.), sodium ascorbate (214 mg, 1.08 mmol, 0.3 equiv.), TBTA (287 mg, 0.54 mmol, 0.15 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). $CuSO_4 \cdot 5H_2O$ was added (135 mg, 0.54 mmol, 0.15 equiv.) and the mixture was stirred for 2 d at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (PE/EA 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/EA 9/1) as



[4] N. Kobayashi, M. Kijima, *J .Mater. Chem*. **2007**, *17*, 4289.

colorless solid (6.5 g, 85%). **TLC** (PE/EA 9/1) R_f = 0.6.**^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.77 (m, 3H, Ar*H*), 8.70 (ss, 6H, Ar*H*), 8.62 (s, 3H, Ar*H*), 8.54 (s, 3H, Ar*H*), 4.44 (t, ^{3}J = 6.82 Hz, 12H, CO_2CH_2), 1.91-1.81 (m, 12H, CH_2), 1.48-1.25 (m, 156H, CH_3), 0.88 (t, ^{3}J = 6.91Hz, 18H, CH_3).**^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.56 (-CO_2-), 147.89 (C_{Ar}), 137.21 (C_{Ar}), 132.94 (C_{Ar}), 131.38 (C_{Ar}), 130.47 (C_{Ar}), 124.83 (C_{Ar}), 122.99 (C_{Ar}), 118.33 (C_{Ar}), 66.22 (OCH_2), 31.92 (CH_2), 29.64 (CH_2), 29.58 (CH_2), 29.37 (CH_2), 29.32 (CH_2), 28.69 (CH_2), 25.98 (CH_2), 22.69 (CH_2), 14.14 (CH_3). **MS** (EI, T = 37°C - 50 °C)**:** *m/z* = 2119.55 (calcd 2119.16 for [M + H$^+$]).

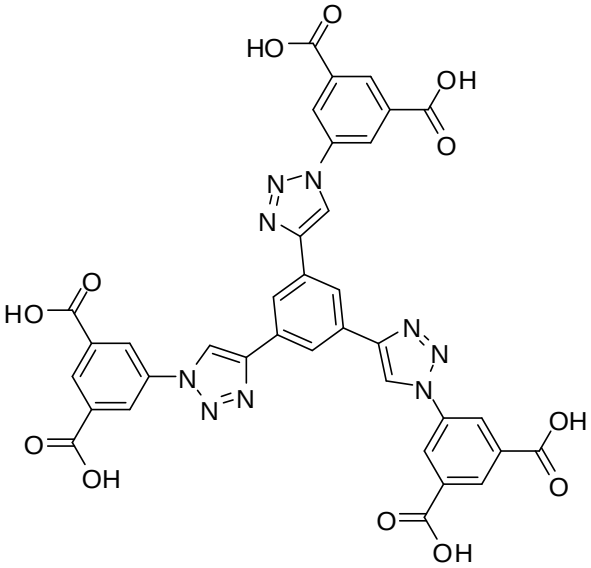
Hexakis(triglyme) dendrimer **10.**



A three necked flask was charged with 1,3,5-triethynylbenzene (811 mg, 5.40 mmol, 1 equiv.) and bis(3,6,9-trioxadecyl) 5-azido-isophthalate **8** (8.90 g, 17.82 mmol, 3.3 equiv.), sodium ascorbate (321 mg, 1.62 mmol, 0.3 equiv.), TBTA (430 mg, 0.81 mmol, 0.15 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). An aqueous stock solution of $CuSO_4$ was added (0.81 mmol, 0.81 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. After the acetylene starting material was consumed indicated by TLC monitoring (CH_2Cl_2/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 (CH_2Cl_2/Acetone 5/5) as yellow oil (679 mg, 75.3%). **TLC** (CH_2Cl_2/Acetone 5/5) R_f = 0.25.**^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.80 (s, 3H, Ar*H*), 8.73-8.71 (m, 9H, Ar*H*), 8.52 (s, 3H, Ar*H*), 4.58-4.55 (m, 12H, CO_2CH_2), 3.93-3.90 (m, 12H, CH_2), 3.78-3.49 (m, 48H, CH_2), 3.30 (s, 18H, OCH_3).**^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.34 (-CO_2-), 147.60 (C_{Ar}), 137.18 (C_{Ar}), 132.20 (C_{Ar}), 131.20 (C_{Ar}), 130.01 (C_{Ar}), 124.51

(C_{Ar}), 122.41 (C_{Ar}), 118.92 (C_{Ar}), 71.77 (CH_2), 70.64 (CH_2), 70.56 (CH_2), 70.45(CH_2), 68.89 (CH_2), 64.89 (CH_2), 58.77 (OCH_3). **UPLC** R_t = 5.30, 98.81% peak area**. HRMS** (ESI) *m/z* = 1648.7115 (calcd 1648.7057 for [M + H^+])

Hexakis(acid) dendrimer **1.**



A one necked flask was charged with hexakis(triglyme) dendrimer **10** (0.84 g, 0.51 mmol, 1 equiv.), 40 mL of a mixture of H_2O/EtOH 1/2 and 0.315 mg of KOH (5.61 mmol, 11 equiv.). The reaction mixture was stirred for 4 h at 78 °C and after consumption of starting material **6** indicated by TLC monitoring. EtOH was evaporated and the aqueous layer was acidified with 1N HCl to pH 2, filtration, washed with water and removal of the solvent *in vacuo* the title compound was obtained as colorless solid (354 mg, 90%) which was used for characterization without further purification. **^{1}H-NMR** (300 MHz, D_2O): δ (ppm) = 9.81 (s, 3H, Ar*H*), 8.74 - 8.73 (ss, 6H, Ar*H*), 8.67 (s, 3H, Ar*H*), 8.56 (s, 3H, Ar*H*). **^{13}C-NMR** (75 MHz, D_2O): δ (ppm) = 166.11 (-CO_2-), 149.38 (C_{Ar}), 138.95 (C_{Ar}), 133.97 (C_{Ar}), 132.98 (C_{Ar}), 131.78 (C_{Ar}), 126.28 (C_{Ar}), 124.19 (C_{Ar}), 120.69 (C_{Ar}).

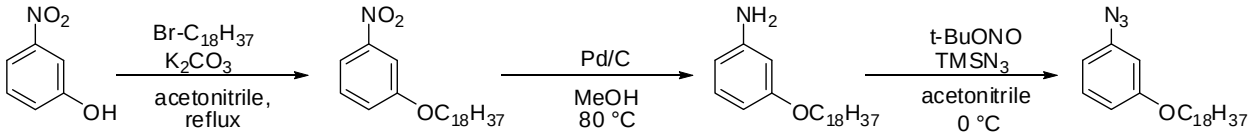
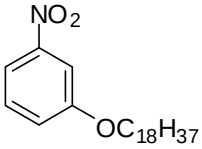


Figure S1. Synthesis scheme of 1-azido-3-(n-octadecyloxy) benzene **13**.

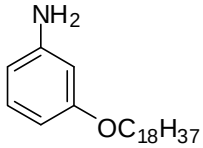
1-Nitro-3-(n-octadecyloxy) benzene **11.**



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

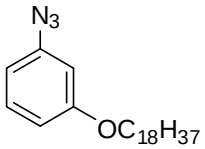
evacuating under stirring and flushing with argon (4 cycles). The suspension was stirred at 80 °C over night and after TLC monitoring the yellow solution was transferred into a separation funnel and diluted with EtOAc. The organic phase was washed with sat. aq. $NaHCO_3$ solution (3 x), water (3 x) and brine (1 x). After drying over $MgSO_4$ and filtration the solvent was removed *in vacuo*. Purification by column chromatography (PE/EA 25/1) gave 11.3 g (96.2%) of the title compound as pale yellow solid. **TLC** (PE/EA 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, OC*H*$_2$), 1.85-1.78(m, 2H, OCH_2CH_2), 1.50-1.27 (m, 30H, C*H*$_2$), 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 220–380 nm, ret. time 26.85 min.): 97.6 area %.

3-(n-Octadecyloxy) aniline **12.**



In a one necked flask 6.0 g (15.32 mmol) of 1-nitro-3-(n-octadecyloxy) benzene **11** 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/EA 25/1) gave 5.2 g (93.8%) of a colourless solid. TLC (PE/EA 25/1) $R_f = 0.42$. ^{1}H-NMR (300 MHz, CDCl3): 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, OC*H*$_2$), 2.93 (br s, 2H, Ar-N*H*$_2$), 1.78-1.73 (m, 2H, OCH_2CH_2), 1.49-1.27 (m, 30H, C*H*$_2$), 0.89 (t, ^{3}J = 6.51 Hz, 3H, CH_2CH_3). ^{13}C-NMR (75 MHz, CDCl3): 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 **13.**



In a round-bottomed flask 1.08 g (3 mmol, 1 equiv.) of 3-(*n*-octadecyloxy) aniline **12** 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 (PE) 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 %.

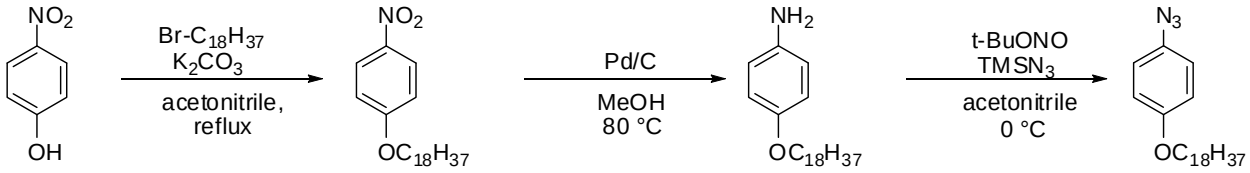
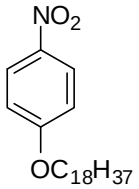


Figure S2. Synthesis scheme of 1-azido-4-(octadecyloxy) benzene **16.**

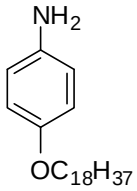
1-Nitro-4-(n-octadecyloxy) benzene ***14***.



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 EA. 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*.

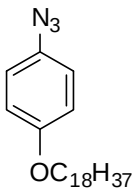
Purification by column chromatography (PE/EA 25/1) gave 11.51 g (98%) of the title compound as pale yellow solid. **TLC** (PE/EA 25/1) $R_f = 0.53$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.23-8.18 (m, ^3J = 2.18, 2H, Ar*H*), 6.98-6.92 (m, 2H, Ar*H*), 4.08 (t, ^3J = 6.53 Hz, 2H, OCH_2), 1.86-1.79 (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 **15.**



In a one necked flask 6.0 g (15.32 mmol) of 1-nitro-4-(n-octadecyloxy) benzene **14** 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/EA 25/1) gave 5.4 g (97%) of a colourless solid. TLC (PE/EA 25/1) $R_f = 0.45$. ^{1}H-NMR (300 MHz, CDCl3): 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, CDCl3): 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 **16.**

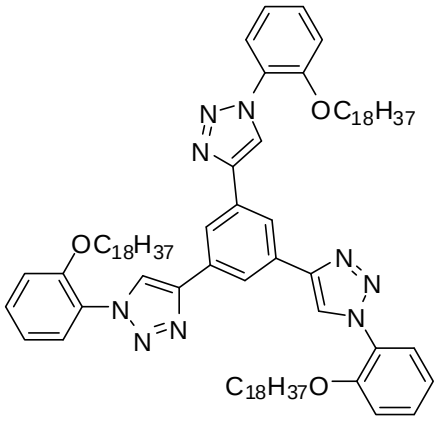


In a round-bottomed flask 1.08 g (3 mmol, 1 equiv.) of 4-(*n*-octadecyloxy) aniline **15** was dissolved in 6 mL of acetonitrile and cooled to 0 °C in an ice bath. To this stirred mixture were added 0.46 g (4.5 mmol, 1.5 equiv.) of t-BuONO followed by 0.41 g (3.6 mmol, 1.2 equiv.) $TMSN_3$ dropwise. 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 (PE) 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$_2$CH_2), 1.49-1.28 (m, 30H, CH_2), 0.93 (t, ^3J = 6.41 Hz, 3H, CH$_2$CH_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$_2$CH$_3$). **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 of the tris(octadecyloxy) dendrimers ***3-5***

Tris(ortho-octadecyloxy) dendrimer **3.**

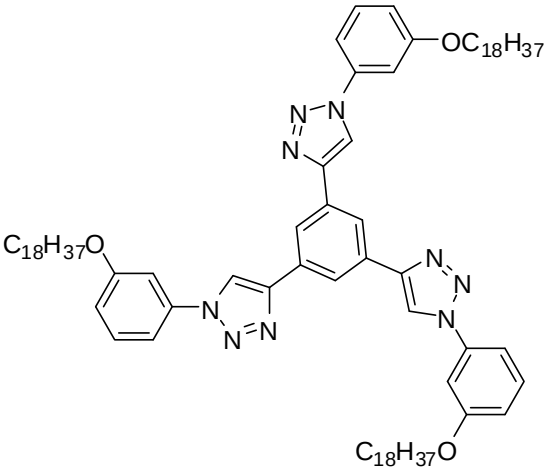


A three necked flask was charged with 1,3,5-triethynylbenzene **9** (300 mg, 2 mmol, 1 equiv.) and 1-azido-2-**(***n*-octadecyloxy) benzene[5] (2.55 g, 6.6 mmol, 3.3 equiv.), sodium ascorbate (119 mg, 0.60 mmol, 0.3 equiv.), TBTA (159 mg, 0.30 mmol, 0.15 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). $CuSO_4 \cdot 5H_2O$ was added (75 mg, 0.30 mmol, 0.15 equiv.) and the mixture was stirred for 2 d at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (PE/EA 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/EA 9/1) as colorless solid (2.49 g, 95%). **TLC** (PE/EA 9/1) $R_f = 0.58$.**^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.61 (s, 3H, Ar*H*), 8.53 (s, 3H, Ar*H*), 7.90-7.86 (dd, 3H, Ar*H*), 7.48-7.42 (m, 3H, Ar*H*), 7.17-7.12 (m, 6H, Ar*H*), 4.14 (t, ^3J = 5.95 Hz, 6H, OCH_2), 1.88-1.79 (m, 6H, CH_2), 1.47-1.16 (m, 90H, CH_2), 0.89 (t, ^3J = 6.01 Hz, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 150.67 (C_{Ar}), 146.64 (C_{Ar}), 132.04 (C_{Ar}), 130.07 (C_{Ar}), 126.55 (C_{Ar}), 125.43 (C_{Ar}), 122.44 (C_{Ar}), 121.05

[5] L. Piot, R. M. Meudtner, T. El Malah, S. Hecht, P. Samorì, *Chem. Eur. J.* **2009**, *15*, 4788.

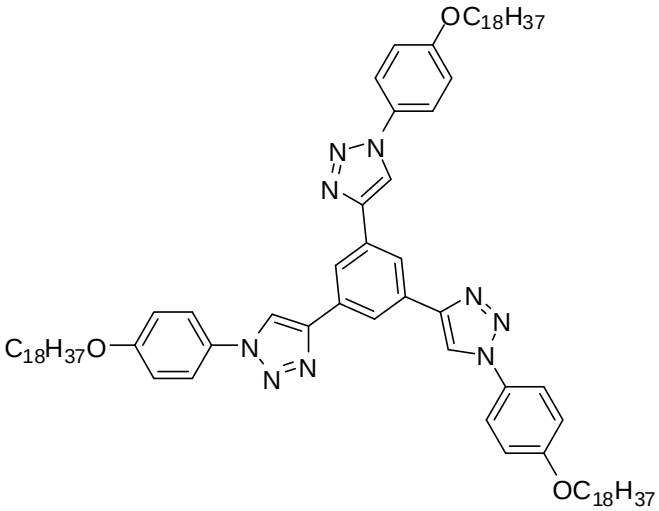
(C_{Ar}), 113.39 (C_{Ar}), 69.31 (OCH_2), 31.94 (CH_2), 29.72 (CH_2), 29.69 (CH_2), 29.60 (CH_2), 29.56 (CH_2), 29.39 (CH_2), 29.30 (CH_2), 29.00 (CH_2), 26.04 (CH_2), 22.70 (CH_2), 14.14 (CH_3). **MS** (EI, T = 37°C - 50 °C)**:** *m/z* = 1314.20 (calcd 1313.99 for [M + H^+]).

Tris(meta-octadecyloxy) dendrimer **4.**



A three necked flask was charged with 1,3,5-triethynylbenzene **9** (74 mg, 0.49 mmol, 1 equiv.) and 1-azido-3-(*n*-octadecyloxy) benzene **13** (626 mg, 1.61 mmol , 3.3 equiv.), sodium ascorbate (29 mg, 0.15 mmol, 0.3 equiv.), TBTA (39 mg, 0.07 mmol, 0.15 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). $CuSO_4 \cdot 5H_2O$ was added (18 mg, 0.07 mmol, 0.15 equiv.) and the mixture was stirred for 2 d at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (PE/EA 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/EA 9/1) as colorless solid (591 mg, 95%). **TLC** (PE/EA 9/1) R_f = 0.55. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.26 (s, 6H, Ar*H*), 7.36-7.25 (m, 9H, Ar*H*), 6.90-6.87 (m, 3H, Ar*H*), 3.98 (t, ^{3}J = 5.93 Hz, 6H, OCH_2), 1.86-1.76 (m, 6H, CH_2), 1.49-1.27 (m, 90H, CH_2), 0.88 (t, ^{3}J = 6.69 Hz, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 160.07 (C_{Ar}), 147.25 (C_{Ar}), 137.73 (C_{Ar}), 131.31 (C_{Ar}), 130.33 (C_{Ar}), 122.28 (C_{Ar}), 118.12 (C_{Ar}), 115.13 (C_{Ar}), 111.74 (C_{Ar}), 106.00 (C_{Ar}), 68.41 (OCH_2), 31.95 (CH_2), 29.75 (CH_2), 29.70 (CH_2), 29.51 (CH_2), 29.40 (CH_2), 29.25 (CH_2), 26.08 (CH_2), 22.71 (CH_2), 14.13 (CH_3). **MS** (EI, T = 37°C - 50 °C)**:** *m/z* = 1314.18 (calcd 1313.99 for [M + H^+]).

Tris(para-octadecyloxy) dendrimer **5.**



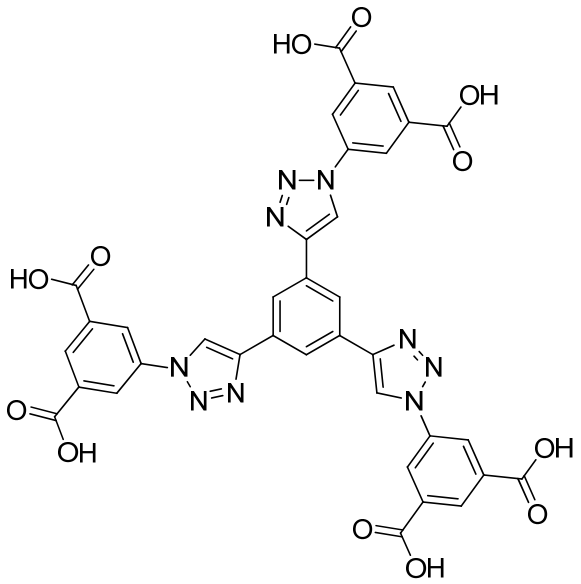
A three necked flask was charged with 1,3,5-triethynylbenzene **9** (150 mg, 1 mmol, 1 equiv.) and 1-azido-4-(*n*-octadecyloxy) benzene **16** (1.28 g, 3.3 mmol , 3.3 equiv.), sodium ascorbate (59 mg, 0.3 mmol, 0.3 equiv.), TBTA (80 mg, 0.15 mmol, 0.15 equiv.) and a solvent mixture of H_2O/^{tert}BuOH/CH_2Cl_2 (1/2/8). The flask was evacuated and flushed with argon repeatedly (3 cycles). $CuSO_4 \cdot 5H_2O$ was added (37 mg, 0.15 mmol, 0.15 equiv.) and the mixture was stirred for 2 d at rt in the dark. After the acetylene starting material was consumed indicated by TLC monitoring (PE/EA 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/EA 9/1) as colorless solid (1.26 g, 96%). **TLC** (PE/EA 9/1) $R_f = 0.56$. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.34 (s, 3H, Ar*H*), 8.25 (s, 3H, Ar*H*), 7.66 (d, ^{2}J = 8.97 Hz, 6H, Ar*H*), 6.99 (d, ^{2}J = 9.06 Hz, 6H, Ar*H*), 3.96 (t, ^{3}J = 6.59 Hz, 6H, OCH_2), 1.82-1.75 (m, 6H, CH_2), 1.48-1.28 (m, 90H, CH_2), 0.89 (t, ^{3}J = 6.70 Hz, 9H, CH_3). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 159.33 (C_{Ar}), 147.28 (C_{Ar}), 131.55 (C_{Ar}), 130.12 (C_{Ar}), 122.29 (C_{Ar}), 121.76 (C_{Ar}), 118.35 (C_{Ar}), 115.17 (C_{Ar}), 68.42 (OCH_2), 31.95 (CH_2), 29.74 (CH_2), 29.69 (CH_2), 29.65 (CH_2), 29.49 (CH_2), 29.39 (CH_2), 29.24 (CH_2), 26.06 (CH_2), 22.71 (CH_2), 14.14 (CH_3). **MS** (EI, T = 37°C - 50 °C)**:** *m/z* = 1314.19 (calcd 1313.99 for [M + H^+]).

3. STM Investigations

STM measurements were performed using a Veeco scanning tunneling microscope (multimode Nanoscope III, Veeco) at the interface between highly oriented pyrolitic graphite (HOPG) and a supernatant solution. 2 mM solutions of investigated molecules were applied to the basal plane of the surface. For STM measurements the substrates were glued on a magnetic disk and an electric contact is made with silver paint (Aldrich Chemicals). The STM tips were mechanically cut from a Pt/Ir wire (90/10, diameter 0.25 mm). The raw STM data were processed through the application of background flattening and the drift was corrected using the underlying graphite lattice as a reference. The latter lattice was visualized by lowering the bias voltage to 20 mV and raising the current to 65 pA. All of the models were minimized with Chem3D at the MM2 level and subsequently rendered with QuteMol[6]. The molecules were dissolved in 1-phenyloctane with an approximate concentration of 2 mM, and diluted to the concentrations 200 μM and 20 μM respectively. However, STM investigation of diluted solutions, i.e. 200 μM and 20 μM did not produced any meaningful results. All molecules were visualized by STM only upon the use 1-phenyloctane; investigations using different solvents, i.e. 1,2,4-trichlorobenzene, 1-heptanoic acid and tetradecane, did not produced any ordered monolayer.

[6] M. Tarini, P. Cignoni, C. Montani, *Leee T Vis Comput Gr* **2006**, *12*, 1237.

*Self-assembly of Hexakis(acid) dendrimer **1**.*



Scanning tunneling microscopy (STM) was used to probe the self-assembly behavior of **1** at the solution-graphite interface. A drop of a highly concentrated solution in 1-phenyloctane was applied to the graphite surface. Figure S3 shows STM current images of the obtained physisorbed monolayer featuring a monocrystalline structure only one hundreds of square nanometers large crystalline domain was observed over tens of minutes. These domains exhibit a unit cell: a = (3.12 ± 0.2) nm, b = (5.51 ± 0.2) nm, α = (87 ± 2)° leading to an area A = (17.16 ± 1.26) nm^2, where each unit cell contains four molecules **1** (Figure S3b). We could not determine unambiguously the orientation of triazole nitrogens, thus we were unable to ascribe the packing of molecule **1** to neither the p3m1, p6, nor p6m space group. Our model suggests a p6 packing whereas the experimental data provides evidence for a higher symmetry within the packing, in line with a plane group p6m.

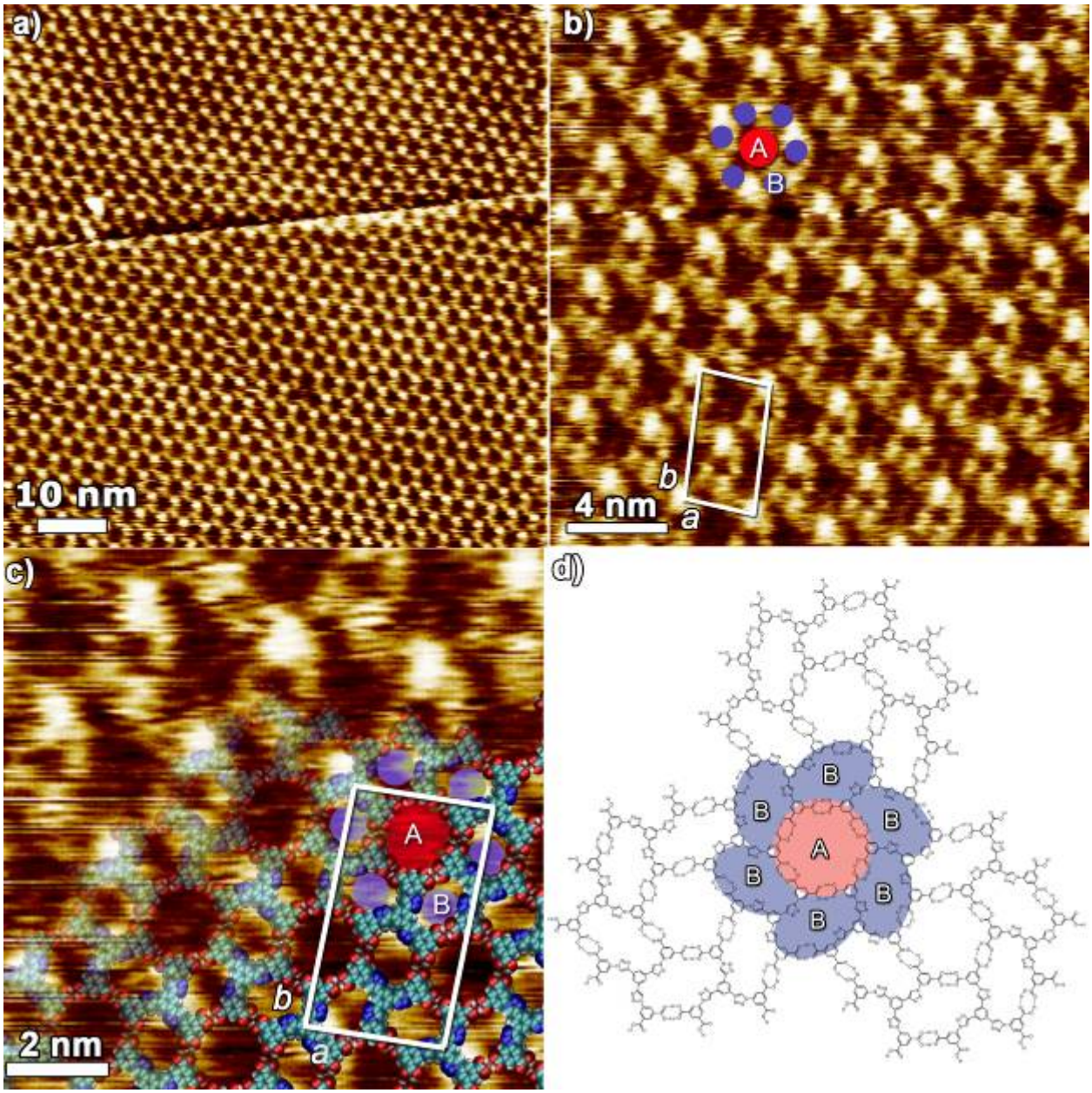


Figure S3. a) Large scale STM current image of **1** at the solid-liquid interface; b) small scale STM height image. c) Proposed CPK model of the **1**; (a, b, c) Tunneling parameters: Average tunneling current (I_t) = 18pA, tip bias voltage (V_t) = 600 mV, d) chemical representation of the proposed packing motif. In green Highlight of the 48 atoms perimeter central pore **A**, resulting from 6 di-hapto O-H···O H-bonding, and in blue the 42 atoms "smaller" pores **B**.

Contrast differences between molecules

The contrast differences (Fig. S3a,b,c) between molecules along the fast-scan direction can be ascribed to the following effects: i) scanning artifacts, e.g. trace-retrace or double tip effects; ii) defects of the molecular packing on the surface or impurities in the material; iii) different number of molecules in a stack filling the tunneling gap between the tip and substrate (e.g. A-

B multilayers); iv) different conformation of the molecules; v) different positions of the molecules in the tip-substrate gap; vi) Moiré pattern.

The points (i-iii) can be readily excluded: The acquisition of different images from different experiments, recorded at different angles, ruled out scenario i); the number of defects in freshly cleaved HOPG is orders of magnitude smaller, and the fact that the materials have been proven by ^{1}H NMR as analytically pure, also rules out hypothesis ii); iii) can easily be excluded observing the vacancy in Fig. S3a); scenarios iv) and v) can be rejected since the core of molecule **1** is fully planar as proven by DFT calculations. In fact Moiré effect between the self-assembled monolayer and the underlying substrate is the most probable explanation. In an attempt to further prove hypothesis vi), epitaxial registration according to Hooks et al. [7] has been computed. Molecule **1** exhibits a Moiré pattern with a measured azimuthal rotation of the overlayer of 18.3 ± 2°, as measured from the principal lattice vectors, and a registry between the two lattices at a length scale of approximately 4.5 nm; the calculated matrix elements (p=13.0, q=10.6, r=-8.0, s=-18.2) are within the experimental agreement with a point-on-line Coincidence-IA. In Fig. S4a the different position of the TPTB core respect the underlying lattice is highlighted. To simplify the observation of the contrast, Figures S4b and S4c show the proposed model on the top of the standard HOPG Moiré pattern as depicted in different scales.

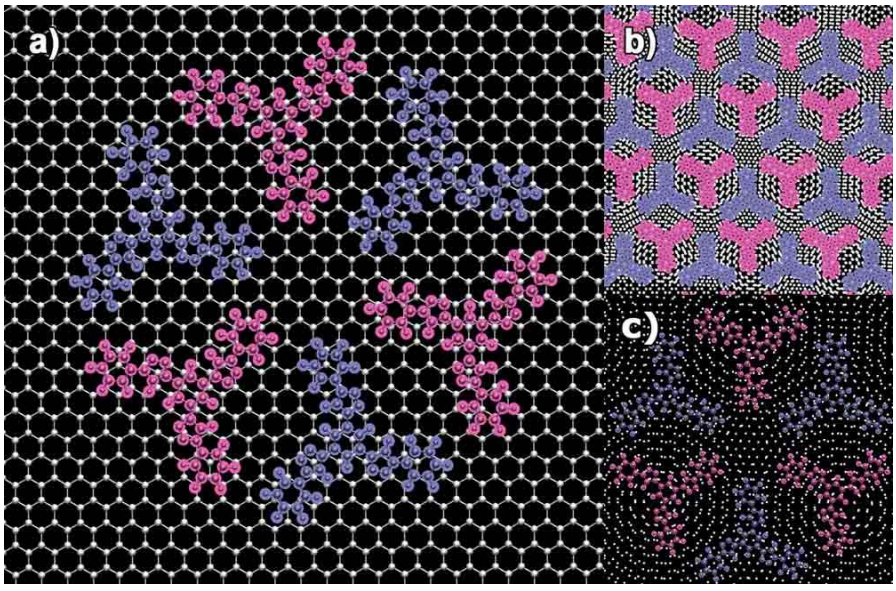


Figure S4. a) Model highlighting the different positions respect to the substrate of the TPTB core in the proposed model purple and pink molecules differs by the number of staggered/eclipsed atoms. b,c) illustrative

[7] 1. M. D. Ward, D. E. Hooks and T. Fritz, Adv Mater, 2001, 13, 227-241.

superposition of the proposed lattice on a model graphene sheet, simplifying contrast differences due to moiré effect.

Tiling topology determination

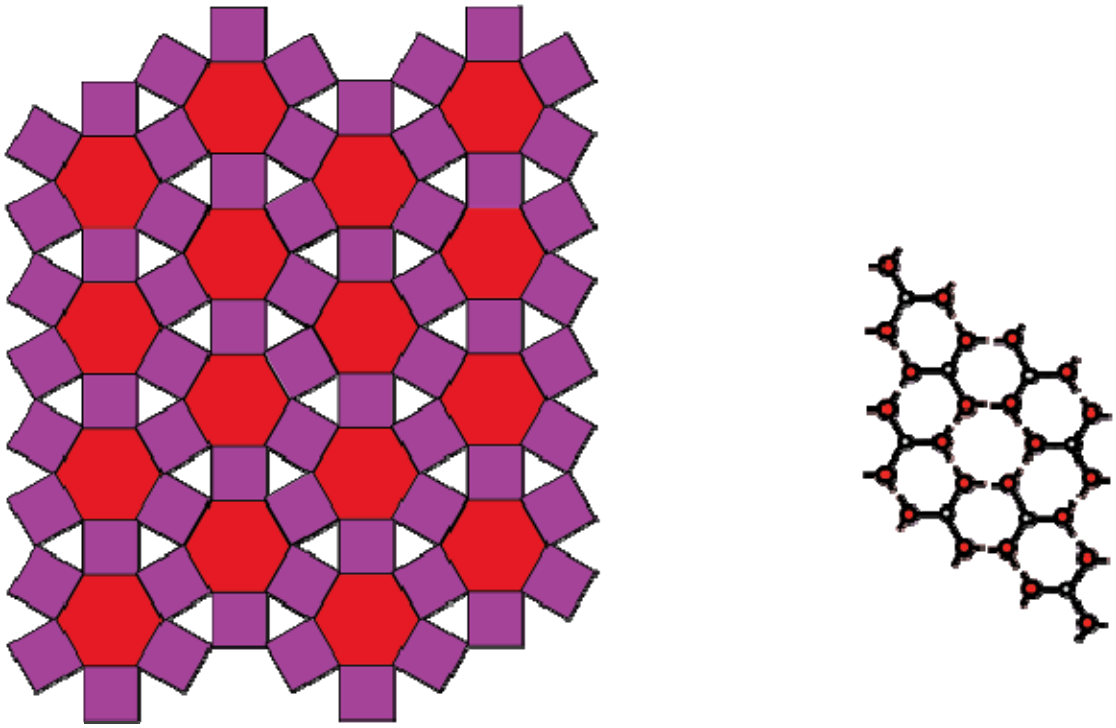


Figure S5. a) Rhombitrihexagonal tiling; b) superposition of a simplified molecular model. The red highlighted nodes are the "isophthalic" rings.

Considering the isophthalic moieties as "nodes", the structure is topologically equivalent to the semi-regular rhombitrihexagonal tiling: Each isophthalic node is connected to one molecule (the triangles), two B pores (the squares) and one A pore (the hexagons). Correspondingly, each node contacts one triangle (the molecule), two squares (B pores) (as they involves 4 nodes, are topologically squares) and one hexagon (A pores - six nodes). Schlafli symbol is $t_{0.2}\{3,6\}$.

Pore size determination

The sizes of the pores have been calculated using SPIP software via automatic procedure of pixel counting, on different STM images. The values are in good agreement to the ones calculated by the estimated molecular van der Waals volume projected onto the surface and to the experimental results (17.16 ± 1.26 nm^2).

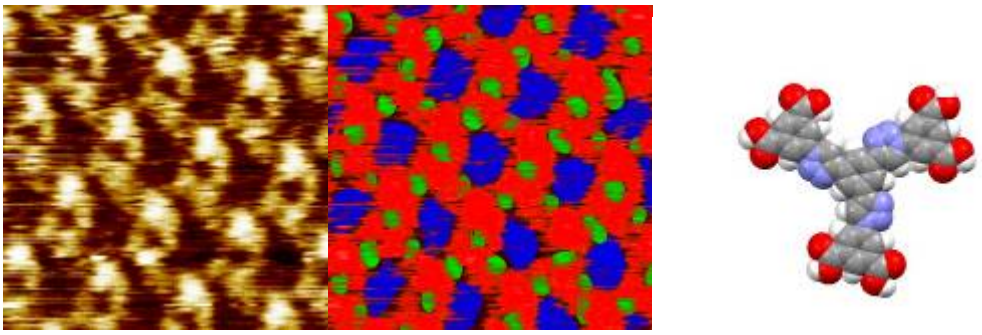
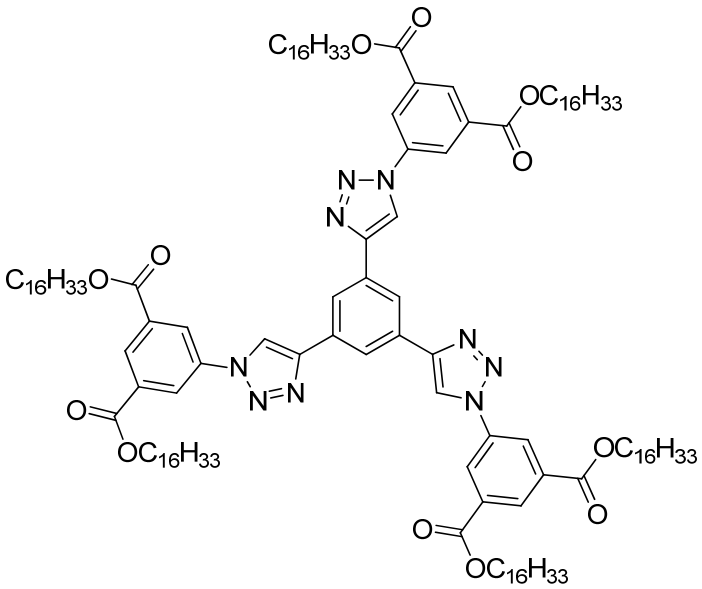


Figure S6. a) as an example we show a zoom into the STM image of 2D crystal of molecule **1** on HOPG (11x11nm); b) the colored domains are those whose area have been estimated trough an automatic procedure of pixel counting; c) estimated projection of the molecular van der Waals volume onto the surface (AvdW)

Table S1. Calculated pore parameters.

	Calculated area	Surface Pore A	Surface Pore B	Surface per mol.
Pixel counting	17.2±2.5	1.54±0.29	0.54 ± 0.20	2.73±0.46
AvdW	17.36	1.55	0.65	2.75

*Self-assembly of Hexakis(n-hexahexadecyl) dendrimer **2**.*



Scanning tunneling microscopy (STM) was used to probe the self-assembly behavior of the Hexakis(*n*-hexahexadecyl) dendrimer **2** at the solution-graphite interface. A drop of a 1 mM solution in 1-phenyloctane was applied to the graphite surface. Figure S6 shows STM current images of the obtained physisorbed monolayer featuring a crystalline structure, which consists of hundreds of square nanometers large crystalline domains that are stable over several minutes. These domains exhibit a unit cell: $a = b = (4.15 \pm 0.2)$ nm, $\alpha = (45 \pm 3)°$ leading to an area $A = (12.17 \pm 0.72)$ nm^2, where each unit cell contains two molecules **2** (Fig. S6b), featuring an Inter-Lamellae distance of 1.60 ±0.17nm.

Study of this system at different concentrations, i.e. at 60µM, 600µM, and 1 mM in 1-phenyloctane, revealed always the same self-assembled structure.

Compound **2** was found to self-assemble into lamellar structure at the solid-liquid interface. Within the lamella the molecules are physisorbed flat on the surface. One can easily see, especially on the STM height image (Fig. S6b), molecules forming “head-to-head” and also “tail-to-tail” type of dimers. The entire supramolecular architecture is stabilized by interdigitated alkyl side chains from adjacent **5** molecules. Only four out of six -$C_{16}H_{33}$ alkyl side chains per molecule are nicely visible on STM images. However taking into account their dynamic nature and the area of the unit cell, it is more likely that all of them are physisorbed at the HOPG surface.

The orientation of the molecule within the packing could not be unambiguously established, thus the space group could not be unequivocally determined. According to our model molecule **2** should belong to plane group cm.

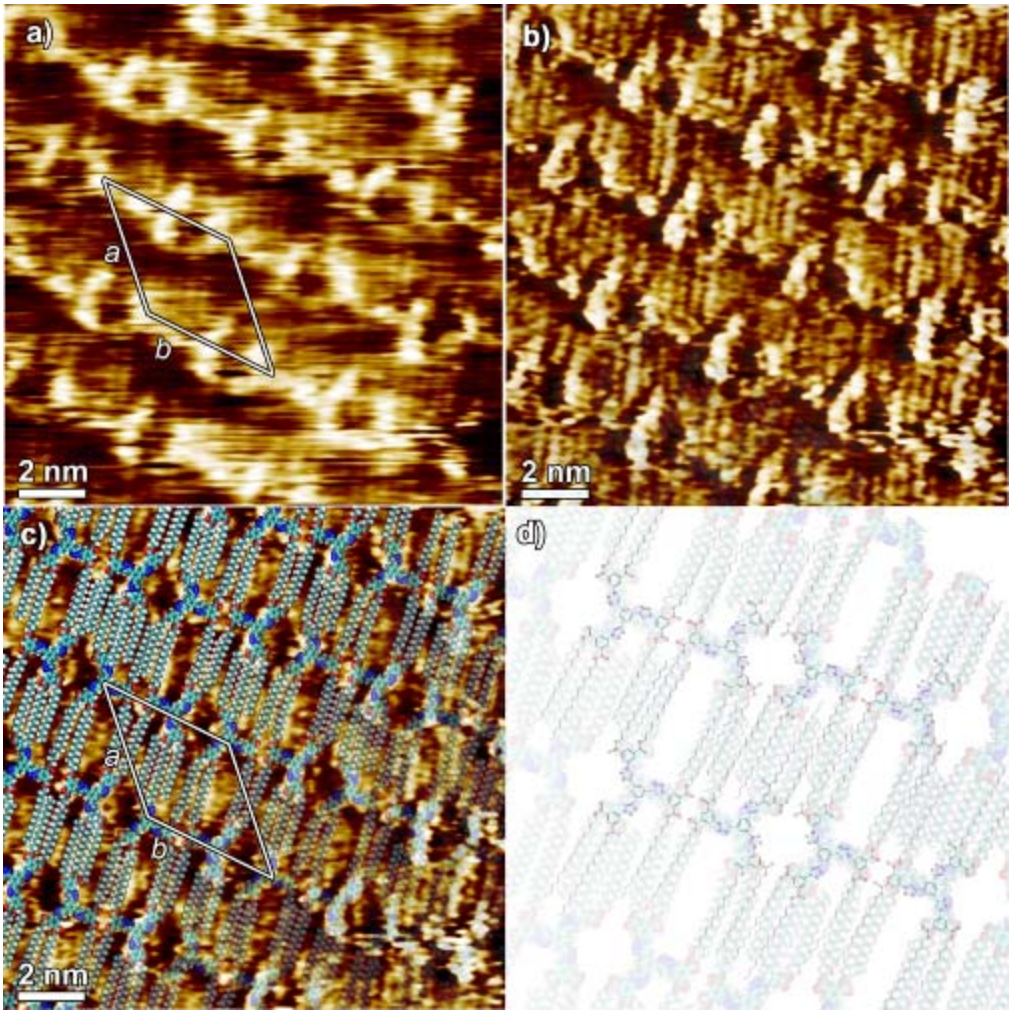
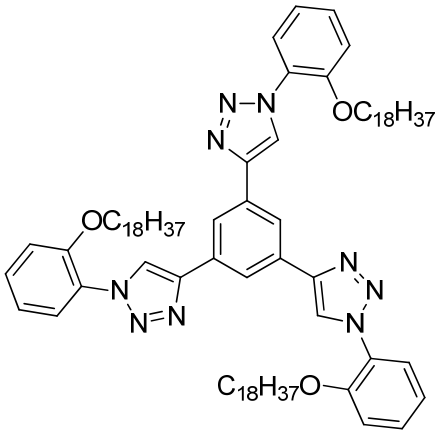


Figure S7. a) Small height image of the monolayer of **2** self assembled at the solid liquid interface, b) small scale STM current image of **2** at the solid-liquid interface; c) Proposed CPK model of the TPTB**2**. Tunneling parameters: Average tunneling current (I_t) = 15pA, tip bias voltage (V_t) = 300 mV. d) chemical rapresentationo of the model.

*Self-assembly of Tris(ortho-octadecyloxy) dendrimer **3**.*



Scanning tunneling microscopy (STM) was used to probe the self-assembly behavior of **3** at the solution-graphite interface. A drop of a 2mM solution in 1-phenyloctane was applied to the graphite surface. Figure S7 shows STM height images of the obtained physisorbed monolayer featuring a crystalline structure, which consists of hundreds of square nanometers large polycrystalline structures that are stable over several minutes. These domains exhibit a unit cell: a = (3.68 ± 0.2) nm, b = (3.70 ± 0.2) nm, α = (58 ± 3)° leading to an area A = (11.58 ± 0.67) nm^2, where each unit cell contains two molecules **3** (Fig. S7b). Plane Group p6.

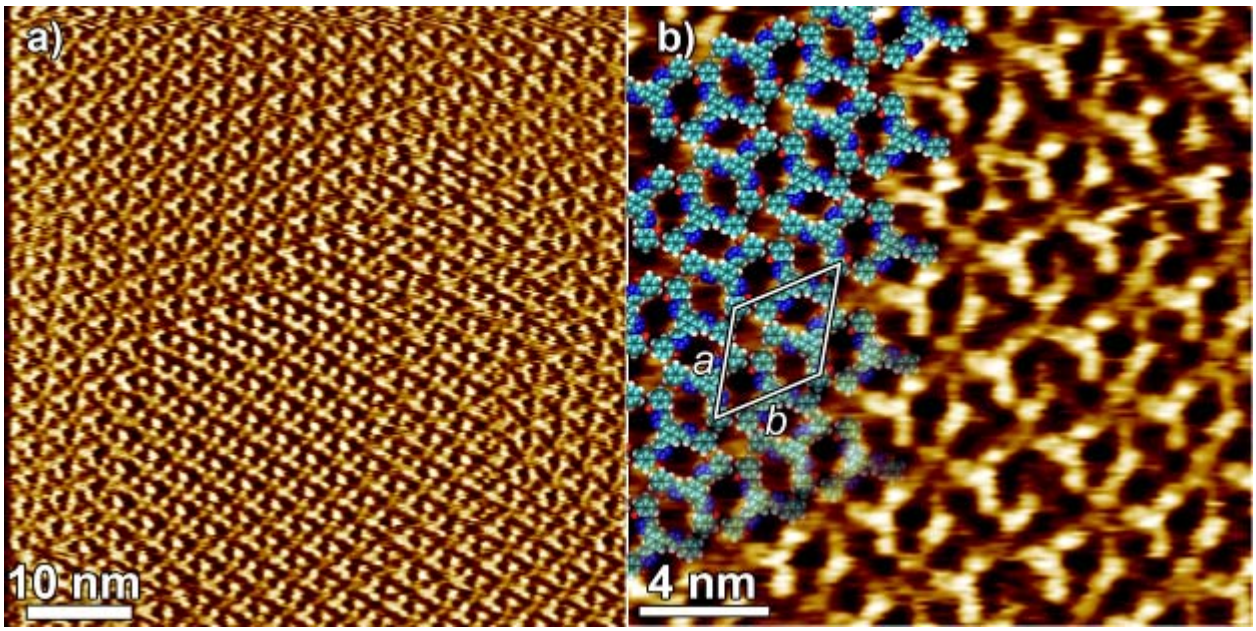
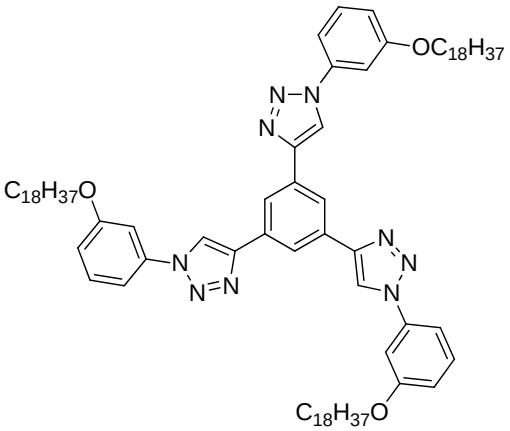


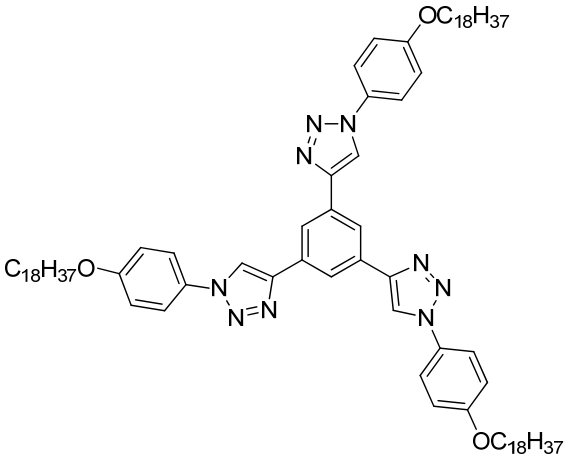
Figure S8. a) Large scale STM current image of **3** at the solid-liquid interface; b) small scale STM current image and proposed CPK model of the **3**. Tunneling parameters: Average tunneling current (I_t) = 15pA, tip bias voltage (V_t) = 900 mV.

Self-assembly of:

tris(meta-octadecyloxy) dendrimer ***4***



tris(para-octadecyloxy) dendrimer ***5***



Scanning tunneling microscopy (STM) was used to probe the self-assembly behavior of **4** (Figure S8a/b) and **5** (Figure S8c/d) at the solution-graphite interface. A drop of a 2 mM solution in 1-phenyloctane was applied to the graphite surface. Figure S8 shows STM height images of the obtained physisorbed monolayer featuring a crystalline lamellar structure, which consists of hundreds of square nanometers large polycrystalline structures that are stable over several minutes. In the case of **4**, These domains exhibit a unit cell: a = (4.36 ± 0.2) nm, b = (3.77 ± 0.2) nm, α = (63 ± 3)° leading to an area A = (15.63 ± 0.85) nm^2, where each unit cell contains two molecules **4** (Figure S8b), featuring an Inter-Lamellae distance of 1.60±0.16 nm.

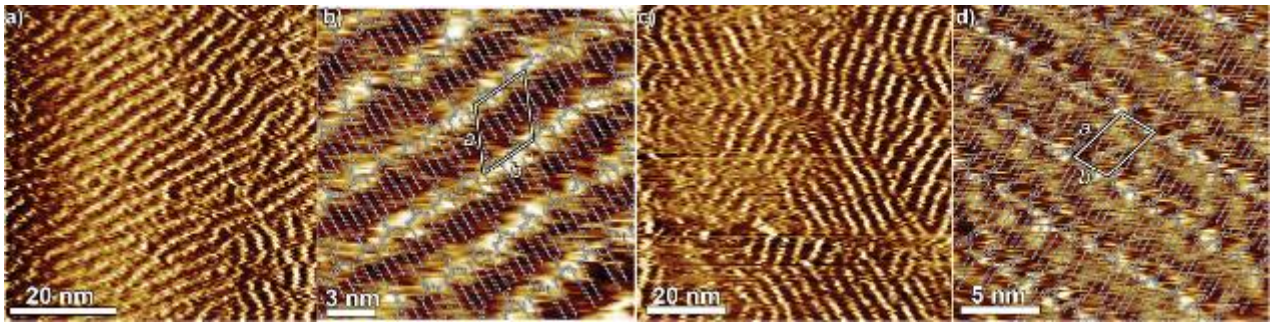


Figure S9. a) Large scale STM current image of **4** at the solid-liquid interface; b) Small scale STM current image and proposed CPK model of the **4**. Tunneling parameters: Average tunneling current (I_t) = 15pA, tip bias voltage (V_t) = 860 mV. c) Large scale STM current image of **5** at the solid-liquid interface; d) Small scale STM current image and proposed CPK model of the **5**. Tunneling parameters: Average tunneling current (I_t) = 15pA, tip bias voltage (V_t) = 860 mV.

In the case of **5**, These domains exhibit a unit cell: a = (4.36 ± 0.2) nm, b = (3.52 ± 0.2) nm, α = (72 ± 3)° leading to an area A = (14.59 ± 0.85) nm^2, where each unit cell contains two molecules **5** (Figure S6d) featuring an Inter-Lamellae distance of 1.53 ± 0.20.

Typical STM images of **4** and **5** are shown in Figure S8. As strikingly evident from the image, the two regioisomers **4** and **5** were observed to form unstable lamellar structures. At first sight, nanoscale phase segregation between the conjugated and the aliphatic parts of the molecules becomes apparent. The orientation of the molecules **4** and **5** could not be established; therefore the space group of their packing could be only identified from the modeling, suggesting a plane group cm.

4. Density Functional Theory

The molecular geometries of TPBTs have been minimized with Chem3D at the MM2 level and fully optimized using the density functional theory (DFT) with restricted Becke three-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP). The standard 6-311G(d,p) basis set was used in all calculations. Literature analysis shows that the geometries, relative stabilities, and frequencies of the structures calculated at the B3LYP/6-311G(d,p) level are in good accord with experimental data.

DFT techniques were used to probe the geometrical preferences of the **TPTB** molecules at room temperature (in vacuum). Investigated structure of **TPTB** slightly differs from the ones previously investigated with Scanning Tunneling Microscopy. We decided to remove long alkyl chains since they shouldn't affect the geometrical preferences of cores. Also the number of atoms (especially number of hetero-atoms) is a crucial point in all *ab initio* calculations. The time of calculation is proportional to the number of atoms in the investigated structure. Figure S7 shows the relaxed structure of **TPTB** after B3LYP computation. As shown in the Figure S7b the core of the molecule is almost perfectly flat. Terminal phenyl rings are slightly bended in respect with the core. However, as was already shown with STM measurements, the phenyl rings can rotate in the presence of substrate surface and the molecule can adopt fully planar conformation.

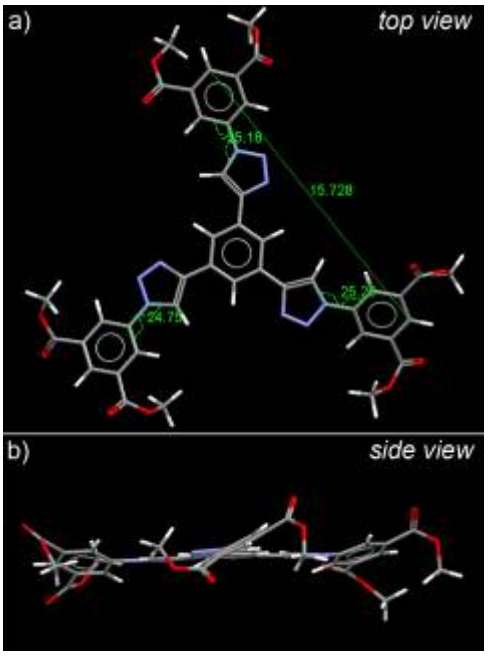
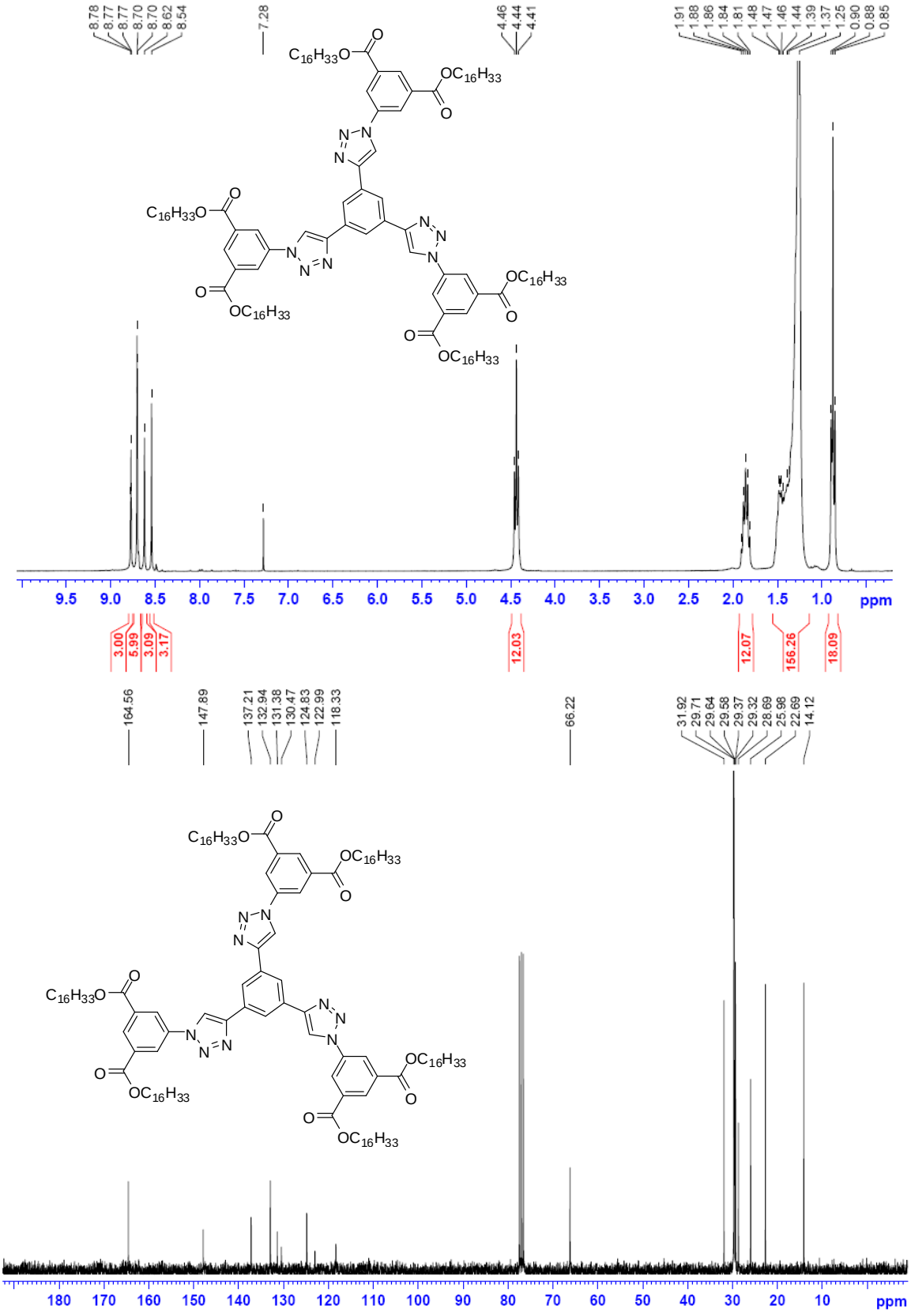
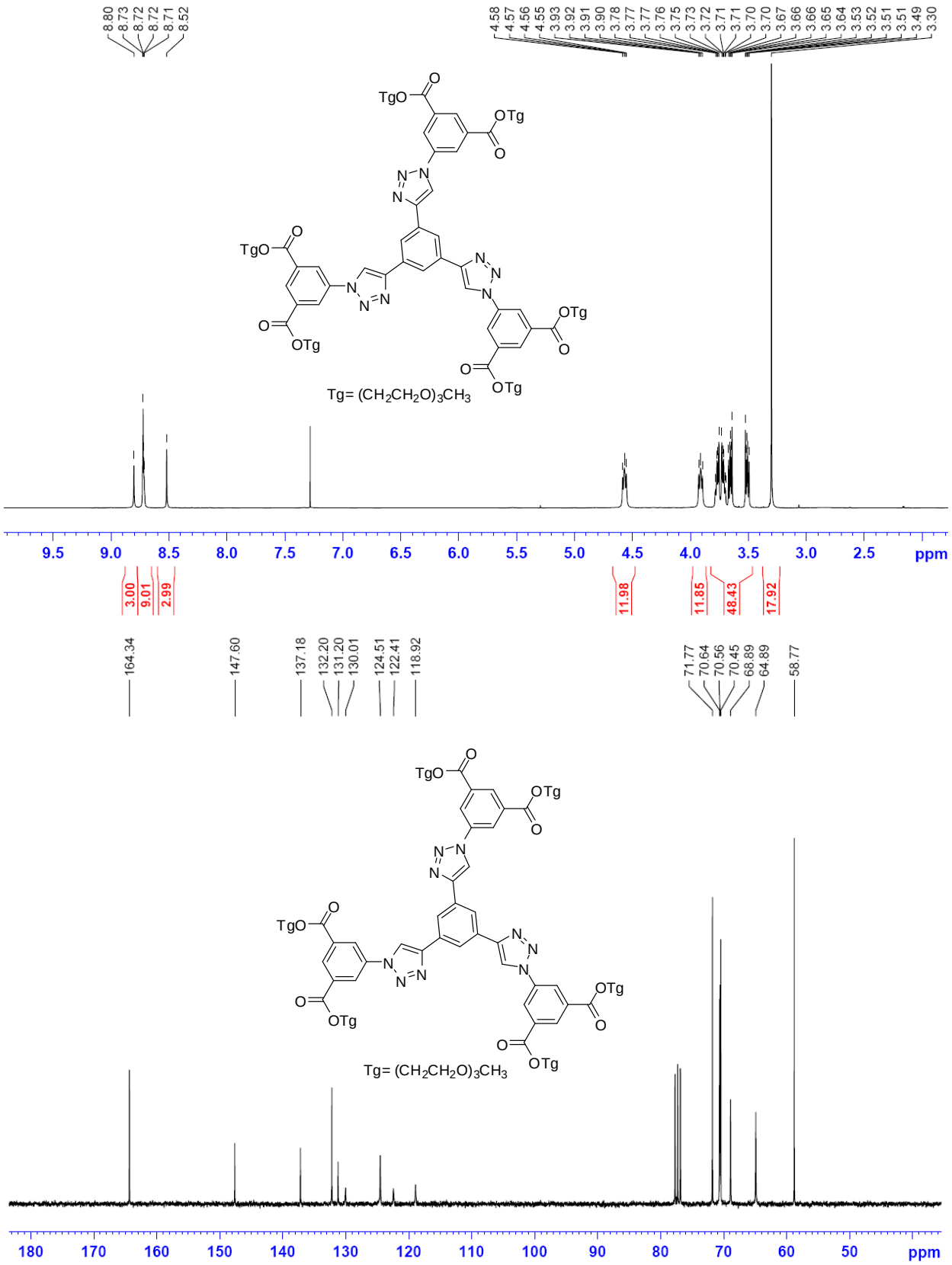


Figure S10. Molecular structures of a hexakis(methyloxy) dendrimer after B3LYP relaxation. Distances are given in Å.

5. Copies of Spectral Data (^{1}H-NMR, ^{13}C-NMR) of Dendrimers

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8.72
8.72
8.71
8.52
4.58
4.57
4.56
4.55
3.93
3.92
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3.90
3.78
3.77
3.77
3.76
3.75
3.73
3.72
3.71
3.71
3.70
3.70
3.67
3.66
3.66
3.65
3.64
3.53
3.52
3.51
3.51
3.49
3.30
TgO
OTg
O
N
N
N
TgO
O
OTg
O
N
N
N
N
N
N
OTg
O
O
OTg
O
OTg
Tg= (CH2CH2O)3CH3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
3.00
9.01
2.99
11.98
11.85
48.43
17.92
164.34
147.60
137.18
132.20
131.20
130.01
124.51
122.41
118.92
71.77
70.64
70.56
70.45
68.89
64.89
58.77
TgO
OTg
O
N
N
N
TgO
O
OTg
O
N
N
N
N
N
N
OTg
O
O
OTg
O
OTg
Tg= (CH2CH2O)3CH3
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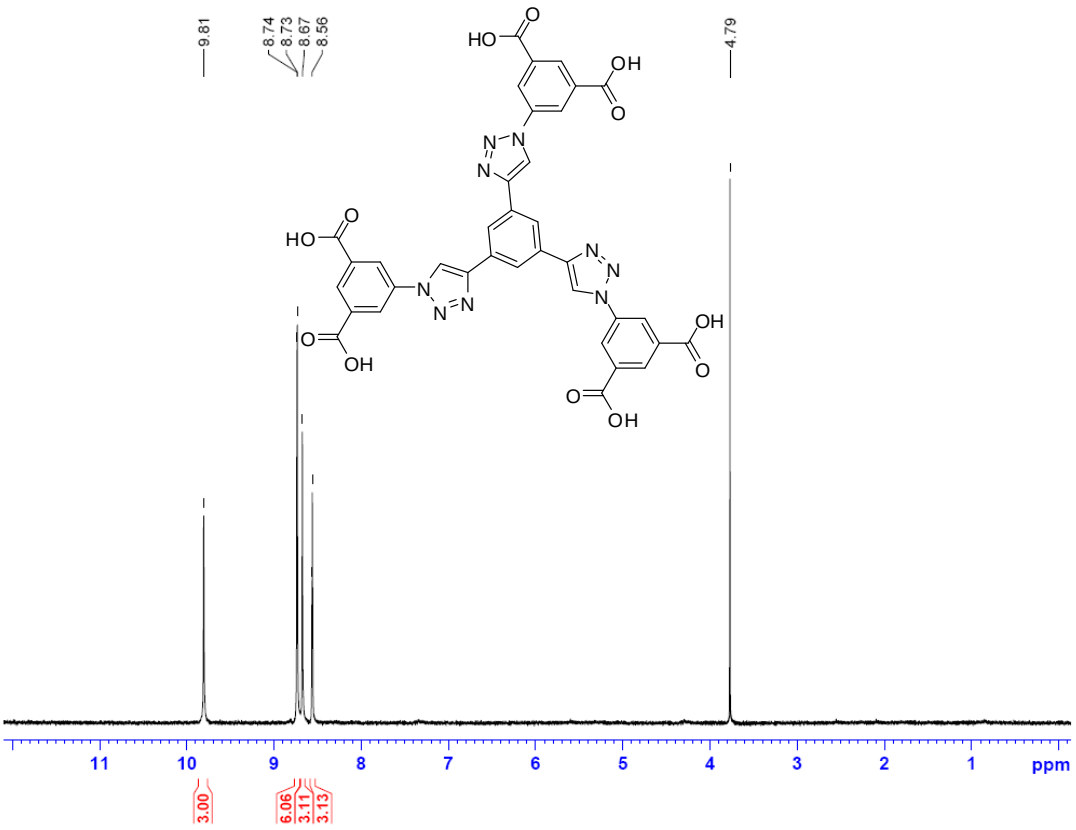
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm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8.74
8.73
8.67
8.56
4.79
HO
OH
O
N
11
10
9
8
7
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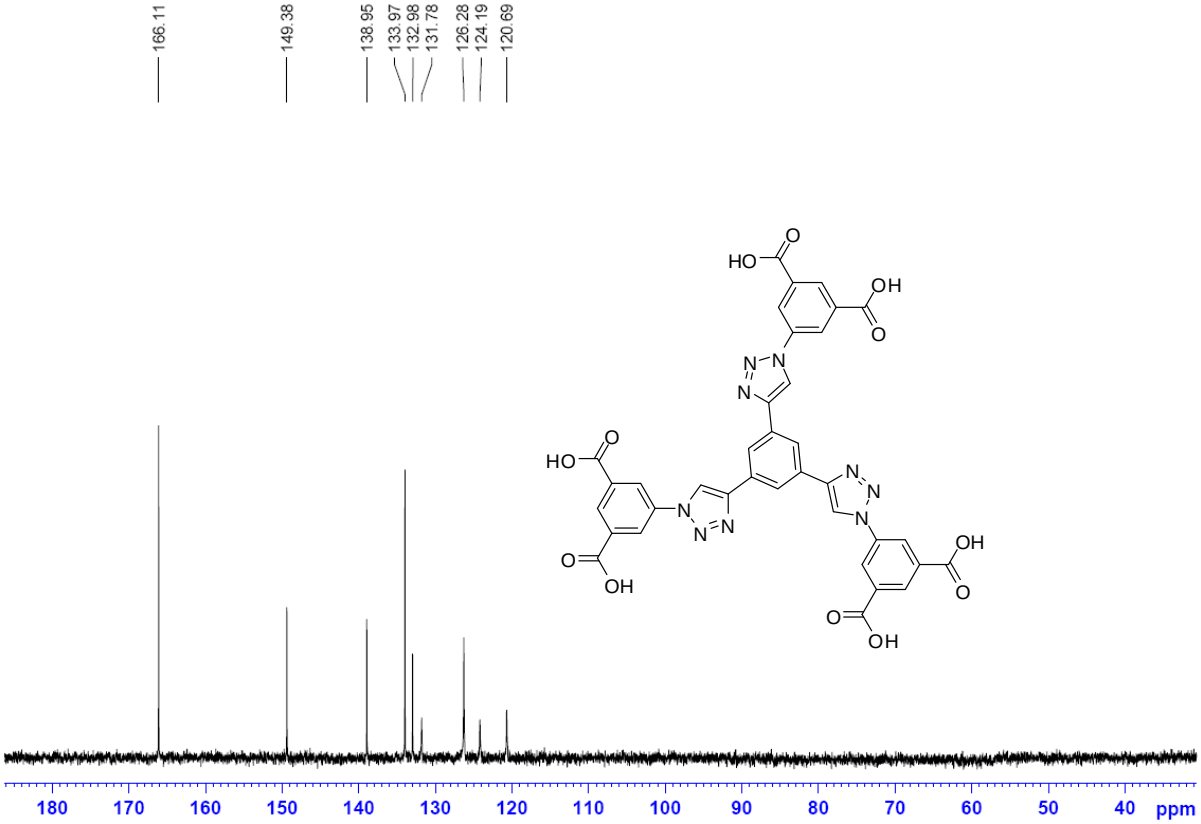
2
1
ppm
3.00
6.06
3.11
3.13


166.11
149.38
138.95
133.97
132.98
131.78
126.28
124.19
120.69
HO
OH
O
N
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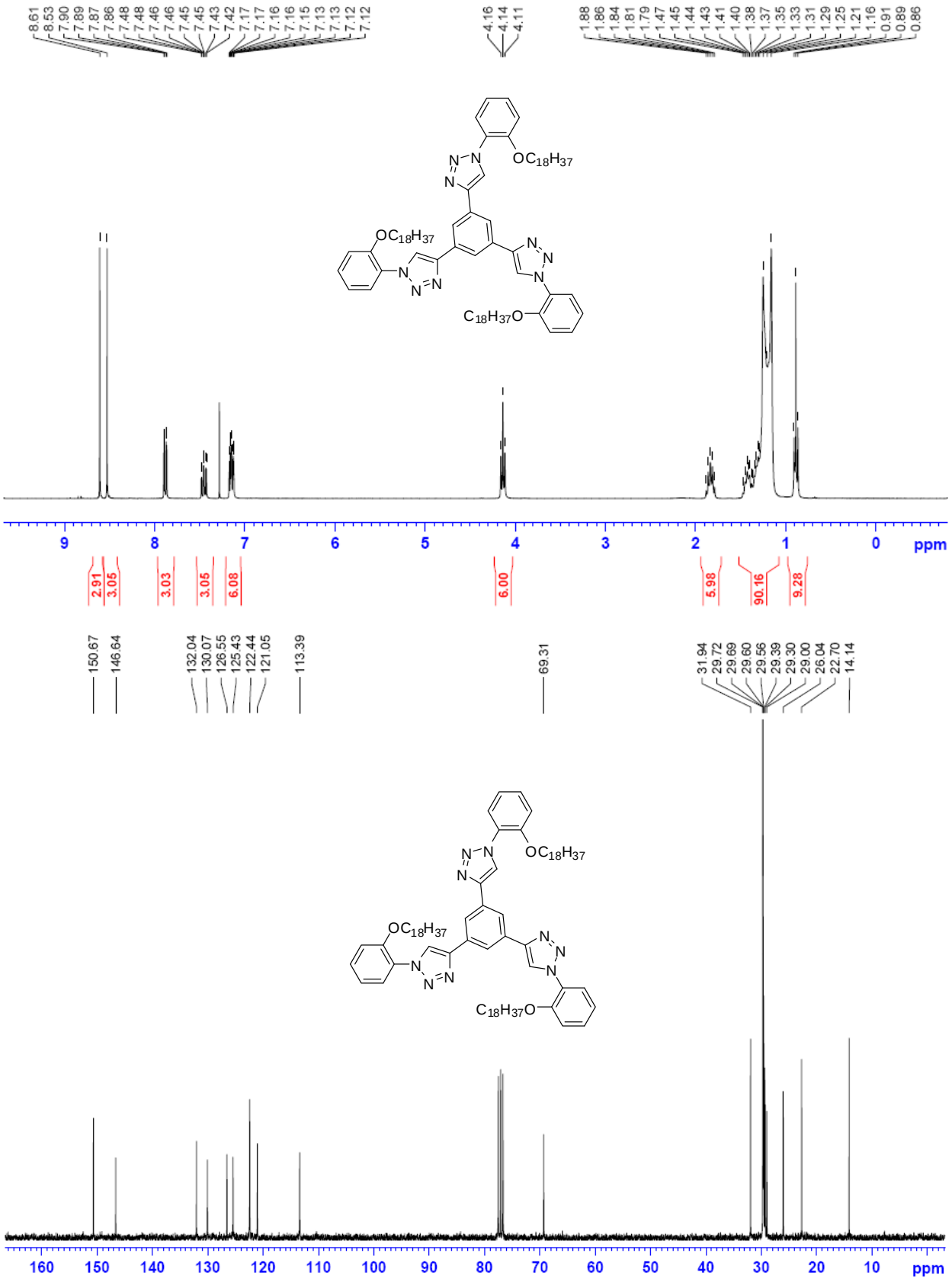
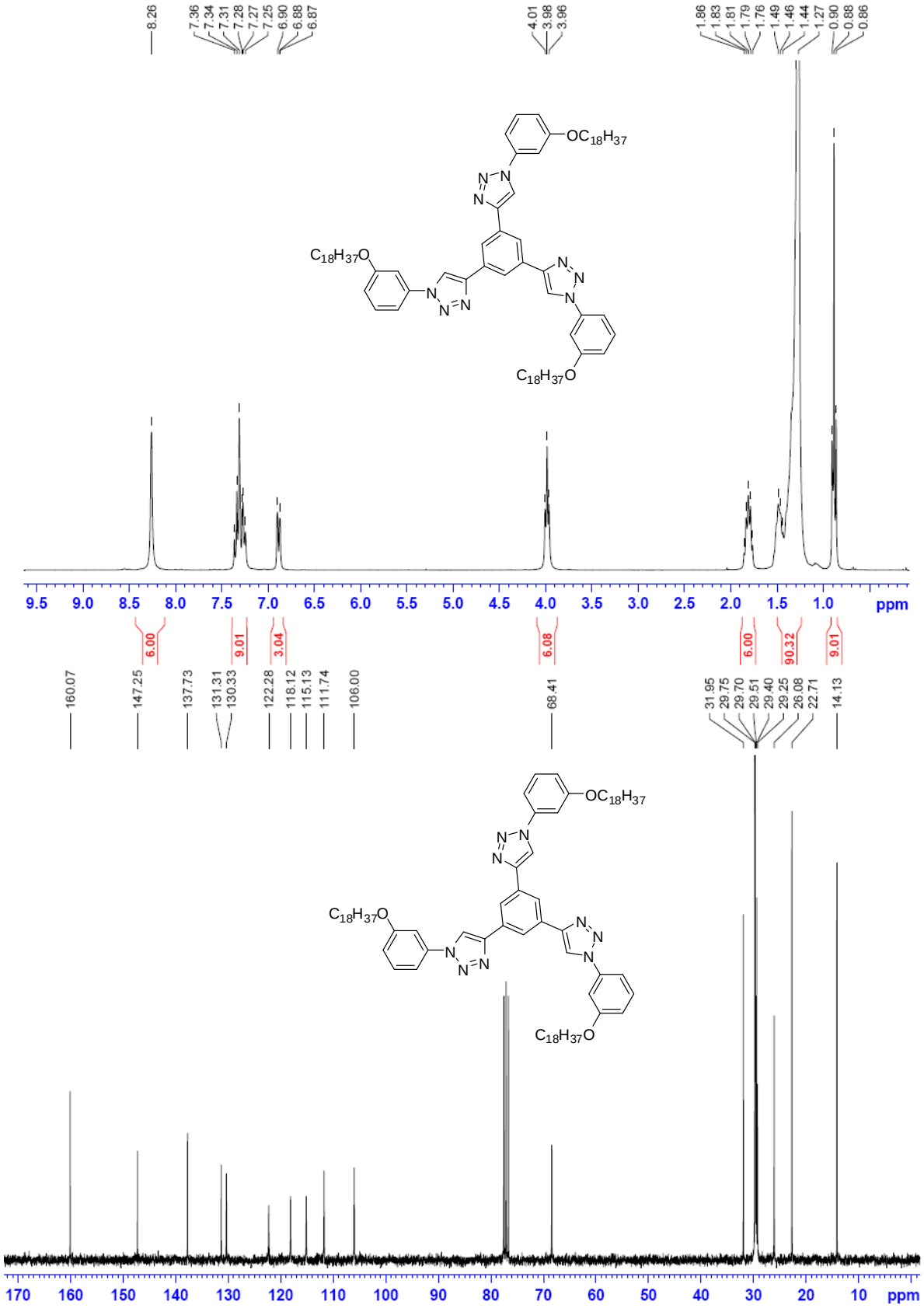
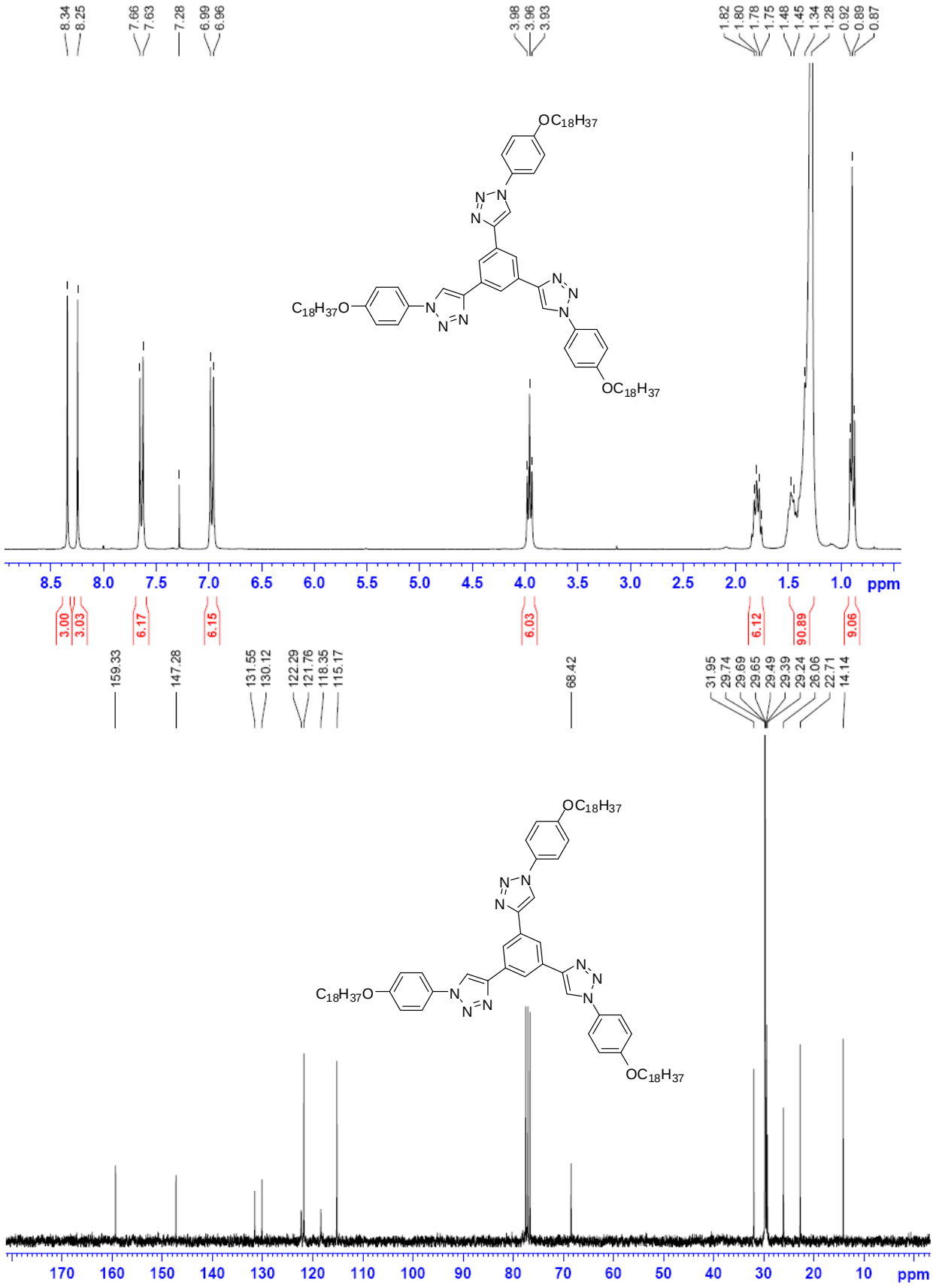
120
110
100
90
80
70
60
50
40
ppm






8.34
8.25
7.66
7.63
7.28
6.99
6.96
3.98
3.96
3.93
1.82
1.80
1.78
1.75
1.48
1.45
1.34
1.28
0.92
0.89
0.87
OC18H37
C18H37O
OC18H37
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.00
3.03
6.17
6.15
6.03
6.12
90.89
9.06
159.33
147.28
131.55
130.12
122.29
121.76
118.35
115.17
68.42
31.95
29.74
29.69
29.65
29.49
29.39
29.24
26.06
22.71
14.14
OC18H37
C18H37O
OC18H37
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm