

Supporting Information

Synthesis and Properties of a Triphenylene-Butadiynylene Macrocycle §

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§ Dedicated to Prof. Fred Wudl on the occasion of his 70th birthday.

Experimental section.

Synthesis. Solvents were dried, distilled and stored under Argon if necessary. Reagents were purchased at reagent grade from commercial sources and used without further purification. Unless otherwise stated, acid, base, and salt solutions are aqueous. All water- and/or air-sensitive reactions were carried out in preheated glassware under argon, using standard Schlenk-techniques. Thin-layer chromatography (TLC) was performed on aluminium plates pre-coated with silica gel and fluorescence indicator from Macherey-Nagel (Alugram SIL G/UV 0.25 mm). Column chromatography was performed with Merck silica gel 60 (230 ± 400 mesh). Radial chromatography was performed with Merck silica gel 60 PF254 containing CaSO₄. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AC 250 (¹H, 250 MHz) and Bruker AM 400 (¹H, 400 MHz; ¹³C, 100.6 MHz) spectrometers, respectively. Chemical shifts are reported as δ values (ppm) and referenced to residual ¹H or ¹³C signals in deuterated solvents. The MALDI-TOF measurements were carried out on a Bruker Daltronics autoflex TOF/TOF. The mass scale was calibrated with narrow-MWD polystyrene standards. DCTB was used as matrix in all cases. EI-MS data were obtained from a MS-50 by A.E.I. Melting points were measured with a Leica DMLB microscope. The resistive heating socket was controlled by a Leica LMW transformer and a Testo 925 digital thermometer. Gel permeation chromatography (GPC) measurements were carried out by using an Agilent Technologies instrument with a set of 4 columns (PSS, polystyrene, 8 mm * 300 mm, 10², 10³, 10⁵ and 10⁶ Å respectively) equipped with IsoPump G1310A, autosampler ALS G1329A, UV-detector VWD G1314B and refractive index (RI) detector RID G1362A, with THF (1 mL / min, HPLC grade, Fisher) as eluent. Universal calibration was performed with polystyrene standards (PSS Polymer Standards Service GmbH, Germany). Preparative recycling GPC was performed on a Shimadzu instrument equipped with a LC 20-AD pump, a DGU-20 A₃ degasser, a SIL-20 A HAT autosampler, a SPD-20 A UV-Vis detector, a CTO-20 AC column oven, a FRC-10 A fraction collector and FCV-20 AH₂ valves. A set of three GPC columns (PSS, polystyrene, 20mm * 300mm, 10³ Å) were used with THF (6 mL / min, HPLC grade, Fisher) as eluent. Light scattering experiments were carried out with an ALV/CGS 3 Compact Goniometer System connected to an ALV/LSE-5004 Light Scattering Electronics and Multiple Tau Digital Correlator.

Optical Spectroscopy. Absorption and photoluminescence (steady-state and time-resolved) spectroscopy of these compounds were carried out in dilute solutions (0.3 mg L⁻¹ concentration in CHCl₃). Fluorescence lifetimes were measured using a Hamamatsu streak camera with ~3 ps time resolution under excitation by a 80 MHz repetition rate, frequency-doubled Ti:Sapphire laser at 360 nm. PL quantum efficiencies (Φ) were determined relative to that of anthracene ($\Phi = 0.27$) by comparing the slopes of the respective I_{em} vs. A plots. I_{em} refers to total PL intensity, and is given by the area under the PL spectrum, when the sample is excited at λ_{ex} . A refers to the value of absorbance at λ_{ex} .

Computational methods. Semi-empirical methods (AM1, ZINDO) were used within the Gaussian program package⁵ as indicated in the text. The ground state geometry of truncated single and double bridged dimers was obtained, and we note that there was no appreciable difference in the central region of the molecules between these structures and those calculated for complete molecules. Vertical transition energies were calculated using ZINDO which were compared to absorption spectra. We determined the excited state structures using the first principles CIS method with a STO-3G basis set. The transition energies for these structures were again calculated with ZINDO and compared to the fluorescence spectra.

Details of calculated ground state geometries. There are significant differences in the triphenylene groups when one compares the single (**15**) and double (**1**) bridged dimers. In **15** the group is bent around a central axis, and in **1** both groups are twisted asymmetrically (Figure S1 comp). In the triphenylene groups of **1**, it is apparent that the biphenyl unit which borders the ring is planarized (Figure S1 comp (c)). This results in the hydrogen atoms within the double bridged dimer being 0.03 Å closer (bond length of 1.89 Å) than their equivalents on **15** (bond length of 1.92 Å).

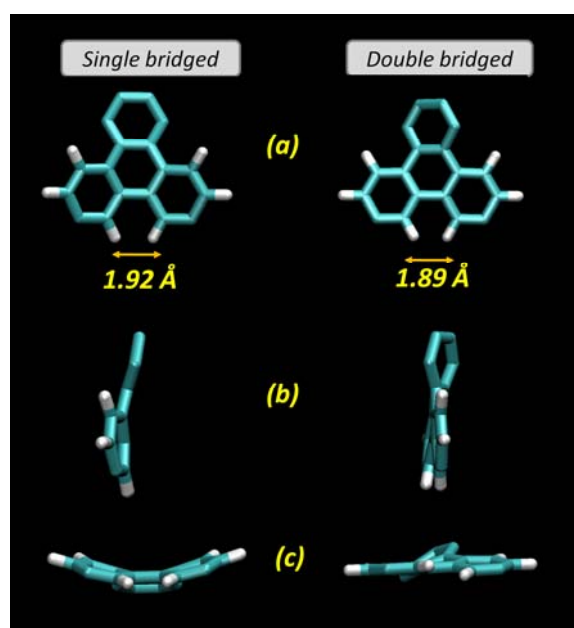


Fig. S1 Detail of the calculated ground state geometries showing the triphenylene groups taken from the open dimer **15** (single bridged) and macrocycle **1** (double bridged). (a) A front view; the distance between hydrogen atoms facing the ring and their single bridge equivalents are indicated. (b) A side view where (a) has been rotated 90° clockwise about a vertical axis passing through the centre of the group. (c) An under view where (a) has been rotated 90° anticlockwise about a horizontal axis passing through the centre of the group.

Calculated transition energies with oscillator strengths

Molecule	State	Energy [eV]	Oscillator Strength
15	1	3.4425	0.00
	2	3.5342	0.75
	6	3.8154	1.06
1	1	3.2973	0.00
	2	3.2999	0.01
	6	3.5524	2.17

Table S1 Energies of specific states and their oscillator strengths for the ground state corresponding to the absorption spectrum.

We note that the lowest energy states for both the open dimer and for the macrocycle do not have significant oscillator strengths and are therefore dark. Also, the lowest two energy states for the macrocycle are almost identical and can be attributed to Davydov splitting on account of the two weakly interacting acetylene bridges. If we consider the triple bonds on the

acetylene bridges which extend in the direction perpendicular (x) and parallel (y) to the bridge axis, practically no overlap of the p_x and p_y orbitals occurs in the single acetylene bridge with the lowest energy $p_y \rightarrow p_x$ transition being dark. There is no opportunity for intraband relaxation from the $p_x \rightarrow p_x$ bright state. The bending of the acetylene bridges in the macrocycle permits greater overlap of p_x and p_y and so the bright state can relax which probably determines the greater non-radiative decay rate as the molecule can undergo internal conversion (Kasha's rule) via an intraband transition to the dark state.

Small-angle x-ray scattering (SAXS). The small-angle scattering experiments were performed using a rotating anode device (Seifert, Ahrensburg) consisting of a Cu-anode, crossed Göbel mirrors, and an image plate detector (Fuji) at a sample-detector distance of 1.005 m. The whole beam area was evacuated and TESA® -film used as sample windows to detect the scattering intensity up to q -values of $q \approx 5 \text{ nm}^{-1}$. The samples were measured at a concentration of 10 g/L in cyclohexane at 25°C. The scattering of the solvent was used as the experimental background. q is the scattering vector given by $q = \frac{4\pi}{\lambda} \sin(\vartheta/2)$ where λ is the wavelength ($\lambda = 0.154 \text{ nm}$) and ϑ is the scattering angle.

Scanning probe microscopy. AFM experiments were carried out on samples prepared by drop casting **1** from two different solvents (chloroform and cyclohexane) at two different concentrations ($3.3 \times 10^{-5} \text{ M}$ and $1.7 \times 10^{-5} \text{ M}$) on highly oriented pyrolytic graphite (HOPG) and a silicon wafer. Here, we only present data on samples prepared on HOPG from both solvents (highest concentration), as this approach gives the most interesting results, namely 'fiber' formation. Especially the data obtained from deposition from cyclohexane are relevant. For each solvent, two solutions were prepared at different concentrations ($3.3 \times 10^{-5} \text{ M}$ and $1.7 \times 10^{-5} \text{ M}$). Then, a drop of the solution was applied to a freshly cleaved surface of HOPG which was put in a sealed chamber saturated by solvent. The system was then allowed to stabilize for at least 15 hours before measuring. STM samples were prepared by drop casting a 3 μL droplet of **1** in 1-phenyloctane at different concentrations (2×10^{-4} , 7×10^{-6} , $7 \times 10^{-8} \text{ M}$) onto the basal plane of a freshly cleaved piece of HOPG (GE Advanced Ceramics). The STM experiments were carried out using a PicoSPM (Agilent) at room temperature, in the constant-

current mode: the color coding in the STM graphs reflects differences in height. Pt/Ir STM tips were prepared by mechanical cutting from Pt/Ir wire (80%/20%, diameter 0.2 mm). For analysis purposes, the imaging of a molecular layer was immediately followed by recording the graphite lattice at a lower bias voltage, under otherwise identical experimental conditions. Drift effects were corrected for using Scanning Probe Image Processor (SPIP) software (Image Metrology ApS). To reduce noise, the images were filtered. The filtering procedure does not change the molecular features, yet enhances the visual presentation. **1** was dissolved in chloroform or cyclohexane at room temperature at a concentration of $3.3 \times 10^{-5} \text{ mol L}^{-1}$. Then, a drop of the solution was applied to a freshly cleaved surface of HOPG. The sample was put into a solvent-saturated chamber to slow down solvent evaporation for about 15 h. AFM experiments were carried out with a Digital Instruments Nanoscope IV scanning probe microscope system (Veeco Metrology, USA) at the air-solid interface in ambient conditions in tapping-mode with an E-type scanner. All AFM images presented here were flattened using the software to remove image artifacts due to vertical (Z) scanner drift, image bow, skips, etc. The image insets are Fourier transforms (2D-FFT).

Synthetic Details and Characterization

3,6-dibromo-9,10-phenanthrenequinone (4).¹ A mixture of 9,10-phenanthrenequinone **3** (12.6 g, 60.5 mmol) and bromine (19.9 g, 125 mmol) in nitrobenzene (150 mL) was stirred at 120 °C for 22 h. After cooling to rt, 75 mL 3 % aqueous NaHSO₃ solution was added and stirred. The crude product precipitated and was collected by filtration, washed with ice water and methanol. Purification was performed by recrystallization from acetic acid. The yellow-brownish needles were collected, washed with ice-water, methanol and dried (15.4 g, 42.1 mmol, 70 %). m.p.: 270-283 °C; ¹H NMR (250 MHz, CDCl₃): δ 8.10 (d, *J* = 1.8 Hz, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.65 (dd, *J* = 1.8 Hz, *J* = 8.4 Hz, 2 H); EI MS *m/z* (*M*⁺) calcd for C₁₄H₆Br₂O₂: 365.9; found: 365.9, 337.9 [*M*⁺-CO].

6,9-dibromophencyclone (5).¹ In a flask equipped with a condenser 3,6-dibromo-9,10-phenanthrenequinone **4** (3.47 g, 9.48 mmol) and 1,3-diphenylacetone (2.09 g, 9.95 mmol) were refluxed in MeOH (50 mL) under Argon. A solution of KOH (855 mg, 15.24 mmol) in MeOH (10 mL) was added dropwise to the refluxing suspension. After 30 min the reaction mixture was cooled in an ice bath. The greenish-yellow precipitate was collected, washed with ice-cold methanol and dried (4.09 g, 7.57 mmol, 80 %). The compound is hardly soluble in numerous common NMR solvents, but a satisfactory proton spectrum could be obtained in CD₂Cl₂ using a large number of scans (however, some unknown signals which arise from impurities are also observed); ¹H NMR (250 MHz, CD₂Cl₂) δ 7.93 (d, *J* = 2.0 Hz, 2 H); 7.46-7.32 (m, 12 H); 7.11 (dd, *J* = 1.9 Hz, *J* = 8.6 Hz, 2 H); m.p.: 260-270 °C; EI MS *m/z* (*M*⁺) calcd for C₂₉H₁₆Br₂O: 540.0; found: 540.0.

Bis-(4-methoxyphenyl)acetylene (6). A mixture of *p*-iodoanisole (1.63 g, 6.85 mmol), *p*-methoxyphenylacetylene (950 mg, 7.19 mmol), CuI (150 mg, 0.78 mmol), PPh₃ (300 mg, 1.14 mmol) and PdCl₂(PPh₃)₂ (300 mg, 0.42 mmol) in THF (20 mL) and piperidine (10 mL) was stirred at rt over night. The resulting suspension was diluted with dichloromethane, washed with water 10 % aqueous HOAc, water, 10 % aqueous NaOH and brine, and dried over MgSO₄. The solvent was removed in vacuum. Purification was performed by repeated chromatography on silica gel using petroleum ether / dichloromethane (2:1) as eluent followed by precipitation from dichloromethane / methanol. The product was obtained as a white solid (939 mg, 3.94 mmol, 58 %). ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.45 (d, *J* = 8.9 Hz,

¹ R.Callahan, K. Marshall, R. Rothchild, K. Rosmarion, *Chem. Educator*, 2001, **6**, 227.

4 H), 6.89 (d, $J = 8.9$ Hz, 4 H), 3.82 (s, 6 H); ^{13}C NMR (CD_2Cl_2 , 100 MHz): δ 159.91, 133.11, 115.94, 114.36, 88.16, 55.64; EI MS m/z (M^+) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2$: 238.1; found: 238.1.

7,10-Dibromo-2,3-bis-(4-methoxy-phenyl)-1,4-diphenyl-triphenylene (7). Under an Ar-atmosphere, 6,9-dibromophenylcyclohexane (**5**, 78 mg, 0.33 mmol) and bis-(4-methoxyphenyl)acetylene (**6**, 178 mg, 0.33 mmol) were suspended in diphenylether (3 mL) and heated up to 245 °C until the CO-formation stops (about 3h). After cooling to rt, the reaction mixture was chromatographed on silica gel using petroleum ether – dichloromethane (2:1) as eluent giving the product as a pale-yellow solid (133 mg, 0.18 mmol, 55 %). ^1H NMR (CD_2Cl_2 , 400 MHz): δ 8.48 (d, $J = 2.1$ Hz, 2 H), 7.40 (d, $J = 9.1$ Hz, 2 H), 7.18 – 7.09 (m, 8 H), 7.06 – 7.00 (m, 4 H), 6.61 (d, $J = 8.7$ Hz, 4 H), 6.47 (d, $J = 8.7$ Hz, 4 H), 3.66 (s, 6 H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 157.72, 142.88, 141.51, 137.93, 132.74, 132.69, 132.46, 132.34, 131.88, 130.63, 130.45, 129.25, 128.53, 126.76, 126.23, 120.99, 112.52, 55.30; EI MS m/z (M^+) calcd for $\text{C}_{44}\text{H}_{30}\text{Br}_2\text{O}_2$: 750.0; found: 750.0.

7,10-Dibromo-2,3-bis-(4-hydroxyphenyl)-1,4-diphenyl-triphenylene (8). 7,10-dibromo-2,3-bis-(4-methoxy-phenyl)-1,4-diphenyl-triphenylene (**7**, 319 mg, 0.43 mmol) was dissolved in dry dichloromethane (8 mL). After cooling to -78 °C, BBr_3 in dichloromethane (1M, 3.4 mL) was added dropwise. The reaction mixture was allowed to warm to rt over night and quenched with water. The organic layer was washed with water, saturated aqueous NaHCO_3 , water and brine, and dried over MgSO_4 . The solvent was removed in vacuum giving the product as a pale-greenish solid (308 mg, 0.43 mmol, 100 %). Due to its low solubility, **8** was used for the next step without further purification. ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.49 (d, $J = 2.2$ Hz, 2 H), 7.41 (d, $J = 9.1$ Hz, 2 H), 7.17 – 7.09 (m, 8 H), 7.05 – 7.01 (m, 4 H), 6.58 – 6.53 (m, 4 H), 6.43 – 6.38 (m, 4 H), 4.67 (bs, 2 H); EI MS m/z (M^+) calcd for $\text{C}_{42}\text{H}_{26}\text{Br}_2\text{O}_2$: 722.0; found: 722.0.

10. 7,10-Dibromo-2,3-bis-(4-hydroxyphenyl)-1,4-diphenyl-triphenylene (**8**, 308 mg, 0.43 mmol), 5-chloromethyl-1,2,3-tris-(hexadecyloxy)-benzene (**9**, 975 mg, 1.15 mmol) and K_2CO_3 (381 mg, 2.76 mmol) were stirred in dry dimethylformamide (20 mL) at 65 °C for 96 h. The reaction mixture was cooled to rt and diluted with dichloromethane. The organic layer was washed with water and brine, dried over MgSO_4 and evaporated. Purification was performed by chromatography on silica gel using petroleum ether – dichloromethane (1:1). The product was obtained as a yellow foam (871 mg, 0.37 mmol, 81 %). ^1H NMR (CD_2Cl_2 ,

400 MHz) δ 8.49 (d, $J = 2.1$ Hz, 2 H), 7.41 (d, $J = 9.1$ Hz, 2 H), 7.18 – 7.10 (m, 8 H), 7.06 – 7.01 (m, 4 H), 6.63 (d, $J = 8.8$ Hz, 4 H), 6.60 – 6.53 (m, 8 H), 4.79 (s, 4 H), 3.99 – 3.89 (m, 12 H), 1.85 – 1.67 (m, 12 H), 1.54 – 1.42 (m, 12 H), 1.37 – 1.25 (m, 144 H), 0.98 – 0.80 (m, 18 H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 156.94, 153.59, 142.88, 141.38, 138.01, 137.97, 133.07, 132.84, 132.49, 132.37, 132.33, 131.90, 130.71, 130.44, 129.29, 128.56, 126.78, 126.27, 121.05, 113.44, 106.28, 73.70, 70.45, 69.38, 32.34, 30.78, 30.19, 30.18, 30.14, 30.09, 30.05, 29.88, 29.78, 26.58, 23.10, 14.29; MS MALDI-TOF (POS, DCTB) m/z (M^+) calcd for $\text{C}_{152}\text{H}_{230}\text{Br}_2\text{O}_8$: 2344.6; found: 2344.8, 2368.8 ($\text{M}^+ + \text{Mg}$), 2384.8 ($\text{M}^+ + \text{Ca}$).

11. Under an Ar atmosphere, **10** (400 mg, 0.17 mmol), CuI (3 mg, 0.016 mmol), PPh_3 (6 mg, 0.023 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (6 mg, 0.008 mmol) were dissolved in THF / piperidine (7 mL each). Then CPDIPS-acetylene (106 mg, 0.51 mmol) was added and the solution was heated to 65 °C for 24 h. The reaction mixture was cooled to rt, diluted with diethylether / dichloromethane and washed with water, 10% aqueous AcOH solution, water, 10% aqueous NaOH solution, water, 25% aqueous NH_3 solution, water and brine, dried over MgSO_4 and evaporated. Purification was performed by chromatography on silica gel using petroleum ether – dichloromethane (1:3) as eluent. The product was obtained as an off-white solid (317 mg, 0.12 mmol, 72 %). ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.54 (d, $J = 1.6$ Hz, 2 H), 7.49 (d, $J = 8.7$ Hz, 2 H), 7.19 – 7.08 (m, 8 H), 7.04 – 7.02 (m, 4 H), 6.65 (d, $J = 8.8$ Hz, 4 H), 6.61 – 6.54 (m, 8 H), 4.80 (s, 4 H), 3.99 – 3.90 (m, 12 H), 2.44 (t, $J = 7.0$ Hz, 4 H), 1.94 – 1.68 (m, 16 H), 1.53 – 1.43 (m, 14 H), 1.41 – 1.22 (m, 150 H), 1.18 – 1.11 (m, 24 H), 0.92 – 0.84 (m, 18 H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 156.95, 153.59, 142.98, 141.46, 138.11, 138.01, 133.10, 132.86, 132.44, 132.34, 131.56, 131.27, 130.97, 130.15, 129.30, 128.48, 127.04, 126.72, 121.17, 120.13, 113.43, 108.09, 106.28, 90.91, 73.70, 70.46, 69.38, 32.34, 30.78, 30.19, 30.18, 30.14, 30.09, 30.05, 29.88, 29.78, 26.58, 23.10, 21.71, 21.10, 18.39, 18.15, 14.29, 12.17, 10.03; MS MALDI-TOF (POS, DCTB) m/z (M^+) calcd for $\text{C}_{176}\text{H}_{270}\text{N}_2\text{O}_8\text{Si}_2$: 2598.0; found: 2598.1, 2621.1 ($\text{M}^+ + \text{Na}$), 2662.1 ($\text{M}^+ + \text{Cu}$).

12. A solution of **11** (49 mg, 0.019 mmol) in THF (1 mL) was cooled to 0 °C. 17 μL of a TBAF solution (1 M in THF, containing 5% water) was added and the solution was warmed to rt. DC-monitoring (eluent: petroleum ether/dichloromethane 2:3) indicated that the reaction has finished already after 5 min. The reaction was diluted with water and diethyl ether. The organic layer was separated and washed with water and brine, dried over MgSO_4 , and evaporated. **12** was precipitated from dichloromethane/methanol as a white solid, collected

and dried (40 mg, 0.018 mmol, 94 %). ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.55 (d, $J = 1.6$ Hz, 2 H), 7.48 (d, $J = 8.7$ Hz, 2 H), 7.18 – 7.07 (m, 8 H), 7.06 – 7.02 (m, 4 H), 6.64 (d, $J = 8.7$ Hz, 4 H), 6.58 (s, 4 H), 6.56 (d, $J = 8.8$ Hz, 8 H), 4.79 (s, 4 H), 3.98 – 3.89 (m, 12 H), 3.20 (s, 2 H), 1.84 – 1.68 (m, 12 H), 1.54 – 1.42 (m, 12 H), 1.40 – 1.21 (m, 144 H), 0.91 – 0.85 (m, 18 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.41, 153.23, 142.43, 140.88, 137.84, 137.69, 132.60, 132.42, 131.99, 131.87, 131.23, 130.88, 130.52, 129.84, 128.80, 128.14, 127.12, 126.30, 119.82, 113.32, 106.08, 83.77, 77.71, 73.40, 70.06, 69.12, 31.93, 30.36, 29.76, 29.73, 29.68, 29.47, 29.37, 26.16, 22.69, 14.11; MS MALDI-TOF (POS, DCTB) m/z (M^+) calcd for $\text{C}_{156}\text{H}_{232}\text{O}_8$: 2234.8; found: 2234.7, 2273.8 ($\text{M}^+ + \text{K}$) 2257.9 ($\text{M}^+ + \text{Na}$), 3048.9 ($\text{M}^+ + 3*\text{DCTB} + 2*\text{Na}$).

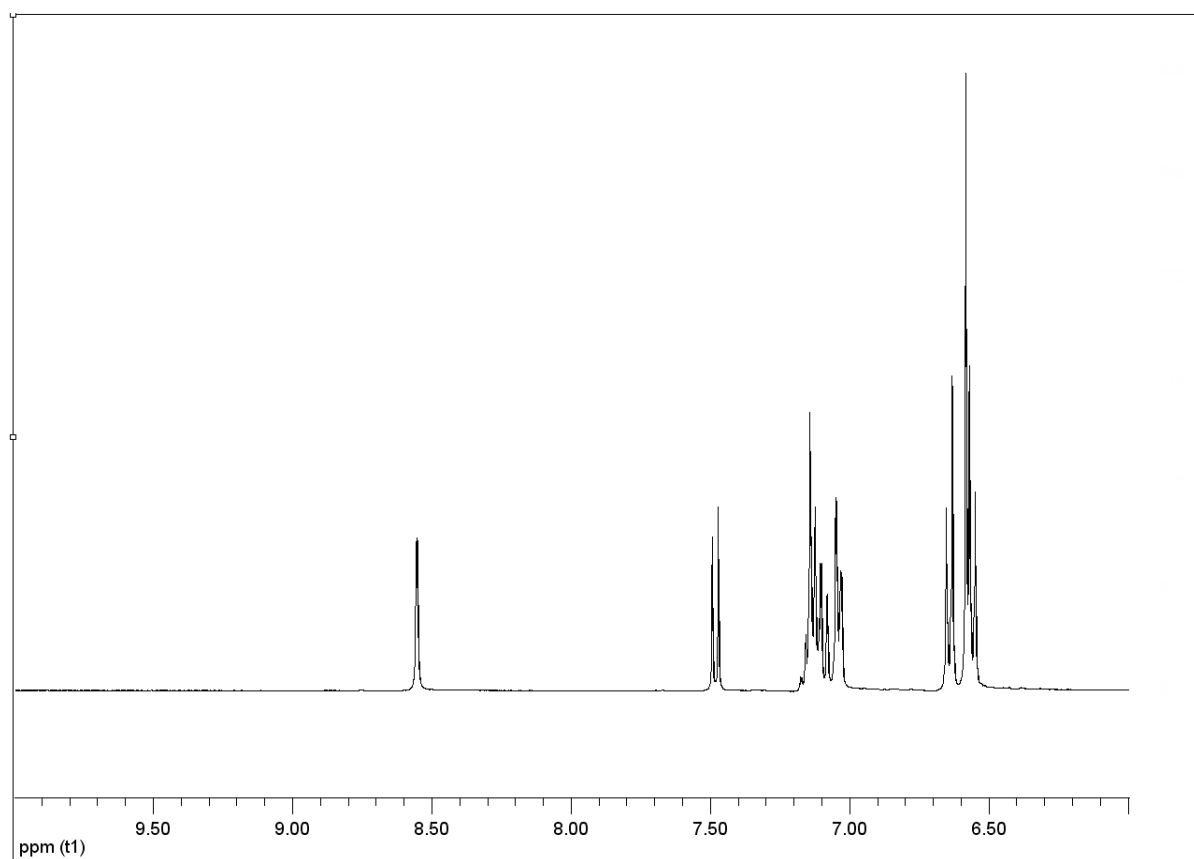


Fig. S2 Aromatic region of the ^1H -NMR spectrum of **12** (in CD_2Cl_2).

13. **11** (200 mg, 0.077 mmol) was dissolved in THF (4.6 mL), water (5%, 0.23 mL) was added and the solution was cooled to 0 °C. 69 μL of a TBAF solution (1 M in THF, containing 5% H_2O) was added and the mixture was stirred for 30 min at 0 °C and then at rt over night. The reaction was diluted with water and dichloromethane, washed with water and brine, dried over MgSO_4 and the solvent was removed in vacuum. Chromatography on silica gel using petroleum ether – dichloromethane (1:1) as eluent gave 97 mg (0.04 mmol, 52 %) of

13 as a white solid. ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.57 (d, $J = 1.4$ Hz, 1 H), 8.52 (d, $J = 1.4$ Hz, 1 H), 7.48 (d, $J = 8.7$ Hz, 1 H), 7.47 (d, $J = 8.7$ Hz, 1 H), 7.18 – 7.01 (m, 12 H), 6.64 (d, $J = 8.7$ Hz, 4 H), 6.58 (s, 4H), 6.56 (d, $J = 8.8$ Hz, 4 H), 4.80 (s, 4 H), 3.99 – 3.89 (m, 12 H), 3.21 (s, 1 H), 2.44 (t, $J = 7.0$ Hz, 2 H), 1.93 – 1.83 (m, 2 H), 1.83 – 1.67 (m, 14 H), 1.52 – 1.42 (m, 14 H), 1.40 – 1.21 (m, 144 H), 1.17 – 1.08 (m, 12 H), 0.92 – 0.82 (m, 18 H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 156.93, 153.58, 142.95, 142.90, 141.48, 141.45, 138.14, 138.11, 137.99, 133.08, 132.85, 132.41, 132.34, 131.72, 131.52, 131.29, 131.19, 130.97, 130.88, 130.18, 130.18, 130.16, 130.13, 129.23, 129.10, 128.47, 127.43, 127.11, 126.71, 121.20, 120.14, 113.41, 107.97, 106.26, 90.80, 83.92, 78.08, 78.07, 73.69, 70.44, 69.37, 32.32, 30.76, 30.17, 30.16, 30.12, 30.07, 30.04, 29.86, 29.76, 26.56, 23.08, 21.70, 21.10, 18.38, 18.14, 14.26, 12.15, 10.01; MS MALDI-TOF (POS, DCTB) m/z (M^+) calcd for $\text{C}_{166}\text{H}_{251}\text{NO}_8\text{Si}$: 2416.9; found: 2417 [M^+], 2440 ($\text{M}^+ + \text{Na}$), 2455 ($\text{M}^+ + \text{K}$), 2480 ($\text{M}^+ + \text{Cu}$).

14. 13 (111 mg, 0.046 mmol) was dissolved in dry dichloromethane (5 mL). After adding CuCl (4.6 mg, 0.046 mmol) and TMEDA (6 mg, 0.046 mmol) a slight airflow was passed through the solution for about 4 h at rt. The airflow was stopped and the reaction mixture stirred at rt for another 24 h. The reaction mixture was diluted with diethyl ether, washed with water and brine, dried over MgSO_4 and the solvent was removed in vacuum. After purification by chromatography on silica gel using petroleum ether – dichloromethane (1:1) as eluent, the product was obtained as a yellow solid (100 mg, 0.021 mmol, 91 %). ^1H (CD_2Cl_2 , 400 MHz) δ 8.64 (d, $J = 1.4$ Hz, 2 H), 8.54 (d, $J = 1.4$ Hz, 2 H), 7.52 (d, $J = 8.8$ Hz, 2 H), 7.49 (d, $J = 8.8$ Hz, 2 H), 7.22 – 7.02 (m, 24 H), 6.66 (d, $J = 8.5$ Hz, 8 H), 6.59 (s, 8 H), 6.57 (d, $J = 8.8$ Hz, 8 H), 4.81 (s, 8 H), 4.00 – 3.90 (m, 24 H), 2.45 (t, $J = 7.0$ Hz, 4 H), 1.95 – 1.85 (m, 4 H), 1.85 – 1.68 (m, 28 H), 1.54 – 1.43 (m, 28 H), 1.42 – 1.21 (m, 288 H), 1.19 – 1.11 (m, 24 H), 0.93 – 0.84 (m, 36 H); ^{13}C (CD_2Cl_2 , 100 MHz) δ 157.04, 153.67, 142.99, 142.92, 141.77, 141.61, 138.32, 138.24, 138.08, 133.13, 133.11, 132.93, 132.50, 132.41, 132.25, 131.65, 131.53, 131.23, 131.17, 130.85, 130.38, 129.42, 129.36, 128.61, 128.58, 128.17, 127.24, 126.88, 126.83, 121.37, 120.21, 119.64, 113.53, 108.03, 106.35, 90.96, 82.62, 74.87, 73.77, 70.53, 69.45, 32.41, 30.85, 30.27, 30.25, 30.22, 30.17, 30.13, 29.96, 29.85, 26.65, 23.17, 21.80, 21.18, 18.50, 18.25, 14.36, 12.24, 10.08; MS MALDI-TOF (POS, DCTB) m/z (M^+) calcd for $\text{C}_{332}\text{H}_{500}\text{N}_2\text{O}_{16}\text{Si}_2$: 4830.8; found: 4831.3, 4854.5 ($\text{M}^+ + \text{Na}$), 4896.0 ($\text{M}^+ + \text{Cu}$), 5644.3 ($\text{M}^+ + 3*\text{DCTB}$).

15. 14 (95 mg, 0.02 mmol) was dissolved in THF (1 mL), 500 μ L TBAF-solution (1 M in THF) were added and the mixture was stirred at rt for 1 h. The solution was diluted with diethyl ether, washed with water and brine and dried over $MgSO_4$. After removal of the solvent the product was purified by radial chromatography on silica gel using petroleum ether / dichloromethane (1:1) as eluent giving **15** as a yellow solid (84 mg, 0.019 mmol, 95 %). 1H NMR (CD_2Cl_2 , 400 MHz) δ 8.61 (d, $J = 1.1$ Hz, 2 H), 8.56 (d, $J = 1.2$ Hz, 2 H), 7.51 (d, $J = 8.3$ Hz, 2 H), 7.49 (d, $J = 8.4$ Hz, 2 H), 7.19 – 7.09 (m, 16 H), 7.08 – 7.02 (m, 8 H), 6.68 – 6.62 (m, 8 H), 6.61 – 6.53 (m, 16 H), 4.80 (s, 8 H), 3.98 – 3.90 (m, 24 H), 3.21 (s, 2 H), 1.84 – 1.68 (m, 24 H), 1.53 – 1.43 (m, 24 H), 1.41 – 1.22 (m, 288 H), 0.95 – 0.83 (m, 36 H); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 156.97, 153.59, 142.86, 141.70, 141.57, 138.26, 138.20, 138.01, 133.05, 132.86, 132.42, 132.34, 132.15, 131.75, 131.38, 131.19, 131.03, 130.81, 130.30, 129.27, 129.23, 128.52, 128.12, 127.52, 126.82, 126.77, 120.32, 119.66, 113.45, 106.28, 83.81, 82.45, 78.20, 74.86, 73.70, 70.46, 69.38, 32.34, 30.78, 30.20, 30.18, 30.15, 30.10, 30.06, 29.89, 29.78, 26.58, 23.10, 14.29; MS MALDI-TOF (POS, DCTB) m/z (M^+) calcd for $C_{312}H_{462}O_{16}$: 4469.0; found: 4470.2, 4493.3 ($M^+ + Na$), 4533.7 ($M^+ + Na + K$), 5283.0 ($M^+ + 3 \cdot DCTB$).

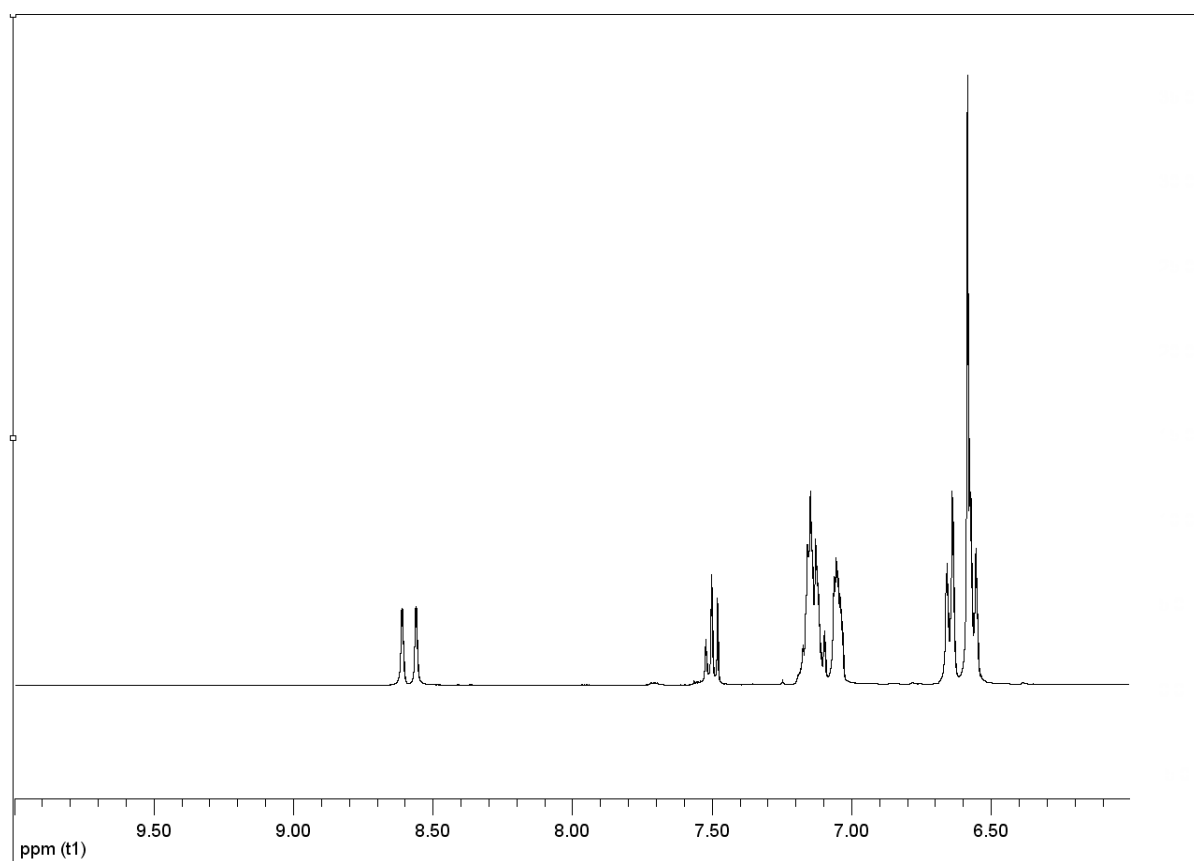


Fig. S3 Aromatic region of the 1H -NMR spectrum of **15** (in CD_2Cl_2).

Macrocycle 1.

A. From 12: A solution of **12** (60 mg, 0.027 mmol) in pyridine (30 mL) was slowly added (96 h) to a suspension of CuCl (267 mg, 2.7 mmol) and CuCl₂ (54 mg, 0.4 mmol) in pyridine (50 mL) at 35 °C. After completion of the addition the mixture was stirred another 24 h at 35 °C. The reaction mixture was diluted with diethyl ether, washed with water, NH₃ aq., water, HCl aq., sat. NaHCO₃ aq. and brine, dried over MgSO₄ and the solvent was evaporated in vacuum. The crude product was analysed by analytical GPC. Purification was performed by preparative recycling GPC (31 mg, 0.007 mmol, 53 %). Analysis see below.

B. From 15: A solution of **15** (84 mg, 0.019 mmol) in pyridine (20 mL) was slowly added (96 h) to a suspension of CuCl (260 mg, 2.6 mmol) and CuCl₂ (52 mg, 0.38 mmol) in pyridine (20 mL) at rt. After completion of the addition the mixture was stirred another 24 h at rt. The mixture was diluted with toluene, the organic layer was separated and washed with water, 25% aqueous NH₃ solution, water, 10% aqueous HOAc solution, water, 10% aqueous NaOH solution, water and brine. After drying over MgSO₄ the solvent was removed in vacuum. Purification was performed by filtration over silica gel (eluent petroleum ether / dichloromethane 1:1) and finally by radial chromatography on silica gel (eluent: petroleum ether / dichloromethane 1:1). The product was obtained as a faint yellow solid (66 mg, 0.015 mmol, 79 %) by precipitation from chloroform / methanol. ¹H NMR (CD₂Cl₂, 400 MHz) δ 9.27 (d, *J* = 1.4 Hz, 4 H), 7.41 (d, *J* = 8.8 Hz, 4 H), 7.20 – 7.12 (m, 12 H), 7.10 – 7.04 (m, 8 H), 6.89 (dd, *J* = 1.5 Hz, *J* = 8.9 Hz, 4 H), 6.64 (d, *J* = 8.7 Hz, 8 H), 6.58 (s, 8 H), 6.55 (d, *J* = 8.8 Hz, 8 H), 4.79 (s, 8 H), 3.98 – 3.89 (m, 24 H), 1.84 – 1.67 (m, 24 H), 1.52 – 1.42 (m, 24 H), 1.39 – 1.25 (m, 288 H), 0.91 – 0.84 (m, 36 H); ¹³C NMR (CD₂Cl₂, 125 MHz) δ 156.88, 153.55, 142.96, 141.86, 138.81, 137.92, 133.43, 133.04, 132.78, 132.30, 132.27, 131.96, 131.32, 130.83, 130.32, 128.55, 126.81, 124.77, 120.29, 113.36, 106.20, 90.08, 78.10, 73.67, 70.41, 69.32, 32.31, 30.74, 30.16, 30.15, 30.11, 30.06, 30.02, 29.84, 29.75, 26.54, 23.07, 14.26; MS MALDI-TOF (POS, DCTB) *m/z* (M⁺) calcd for C₃₁₂H₄₆₀O₁₆: 4466.5; found: 4466.6, 4717.0 (M⁺ + DCTB).

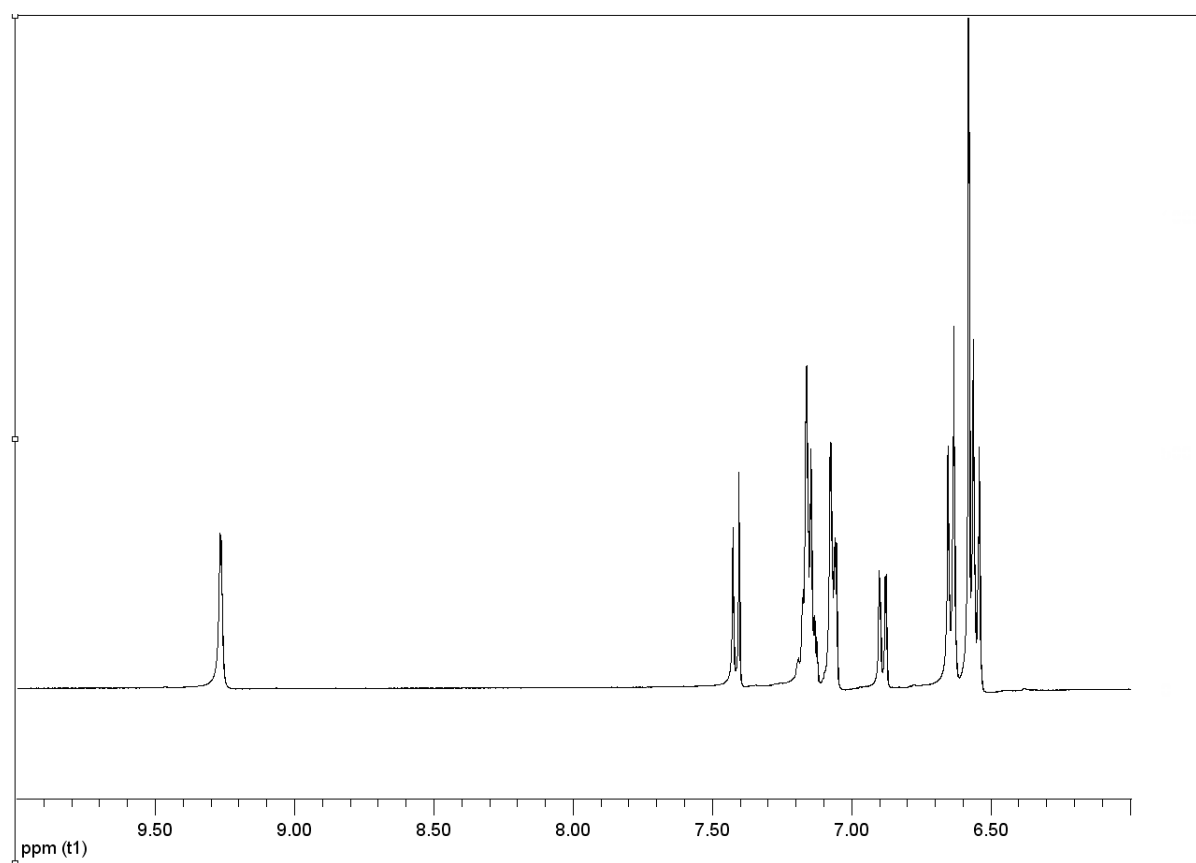


Fig. S4 Aromatic region of the $^1\text{H-NMR}$ spectrum of **1** (in CD_2Cl_2).

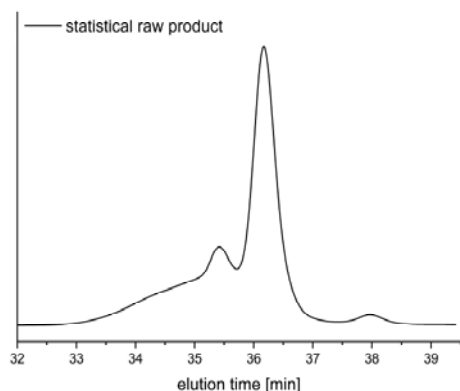


Fig. S5 Elution diagram (analytical GPC) of the raw product from the statistical cyclization reaction.

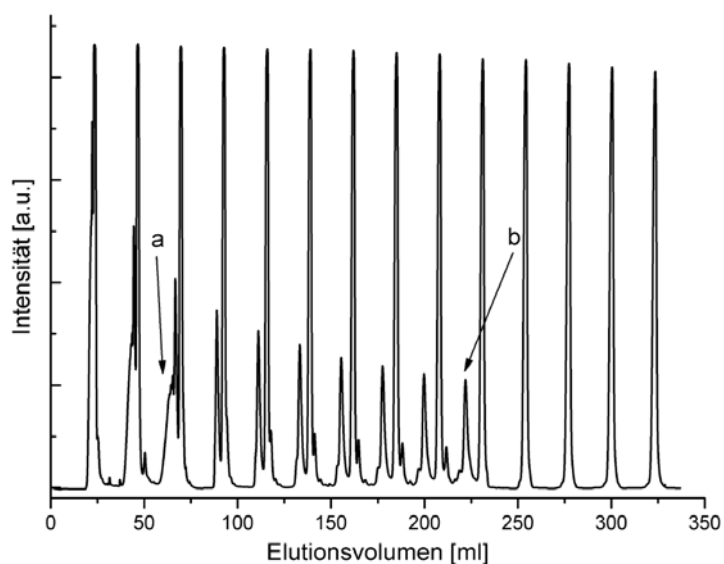


Fig. S6 Elution diagram of the recycling GPC separation; a) removal of the polymeric fraction; b) removal of the cyclotrimer fraction.

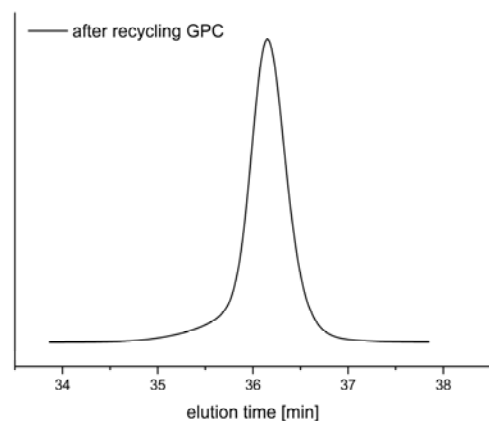


Fig. S7 Elution diagram (analytical GPC) of macrocycle **1** separated by recycling GPC.