Synthesis and an X-ray Structure of Soluble Phenylacetylene Macrocycles with Two Opposing Bipyridine Donor Sites

Oliver Henze, Dieter Lentz, and A. Dieter Schlüter*[a]

Abstract: The synthesis of the shape-persistent macrocycles **10a** and **10b** with two bipyridine units in opposing sides by Hagihara/Sonogashira cross-coupling chemistry of suitably functionalized building blocks is reported. X-ray analysis of single crystals of **10b** shows a layered structure with channels filled with solvent molecules and parts of the flexible chains, with which the cycle is decorated for solubility reasons.

Keywords: bipyridines · cross-coupling · heterocycles · macrocycles · modular chemistry · supramolecular chemistry

Introduction

We have recently reported on repetitive syntheses of oligophenylene rods and hexagons using a construction kit of orthogonally protected building blocks.[1] These building blocks can be variably connected to one another by Suzuki or Stille type cross-coupling chemistry; this enables us to prepare a variety of monodisperse compounds with sizes of up to a few nanometer at a reasonable quantity/effort relation.[2] We have now developed a related methodology to the synthesis of shape-persistent macrocycles with integral 2,2′-bipyridines (bipy)[3] and 2,2′:2,6″-terpyridine donor moieties[4] for subsequent metal complexation and supramolecular assembly. The present contribution describes the synthesis of the phenylacetylene macrocycles **10a** and **10b**, in which the final ring closure reaction uses the Sonogashira/Hagihara coupling reaction. The molecular structure of **10b** and its packing in the crystal was investigated by X-ray diffraction and will also be reported.

Results and Discussion

The targeted cycles **10a** and **10b** contain flexible chains for solubility reasons. These chains are designed to allow for their modification after the cycle's completion in order to be able to vary, for example, the aggregation behavior at minimum synthetic effort. Another built-in feature is the bipy units' free rotation; this allows for *endo* and *exo* complexation. Depending upon the metal, its oxidation state, and the counterion, this orientational option provides access to supramolecular aspects that span the whole range from metal-charged cylindrical aggregates[5] to metal coordination polymers.[6] The synthetic sequence used to give cycles **10a** and **10b** is delineated in Schemes 1–4, which contain a) the syntheses of the required phenylacetylene building blocks (Scheme 1), b) the replacement of the two bromo functions of the central bipyridine building block **5a** and **5b** (Scheme 2), c) the connection of the phenylacetylenes with **5a** and **b**, and d) the ring closure reaction. These or similar synthetic procedures have already been used by others.[7] Only a few strategic and preparative comments are therefore given here. Scheme 1: Compound **2** can be prepared with trimethylsilyl (TMS) or tri(isopropyl)silyl (TIPS) acetylene. Yields are comparably good (approx. 80%). The use of TIPS turned out to be somewhat superior as the purification of the respective product **2b** from remaining starting material is more facile than for **2a**.

Scheme 2: It has already been observed in similar cases that ring closure involving Pd-catalyzed cross-coupling reactions at arylbromides are inferior to the analogous aryliodides.[2] The same observation was made in context of the present work, in which cyclizations involving Sonogashira chemistry and arylbromides did not give cycles at all, whereas that with aryliodides was satisfactory. For this reason the bromo functions of the bipyridine building blocks **5a** and **5b** were converted into iodo functions. This was achieved by a short nucleophilic stannylation/iododestannylation sequence.[8] An alternative lithiation/silylation/iododesilylation sequence that proved successful in other cases could not be applied here because of the sensitivity of bipy towards BuLi. Scheme 3: The coupling between compounds **4** and **5** proceeded in high yields. In order to prevent tedious purification procedures, compounds **4a** and **4b** were used in an excess of approximately 30%.

Scheme 4: The ring closure reaction was done with components **7** and **9** under high dilution conditions (0.0015 M) in

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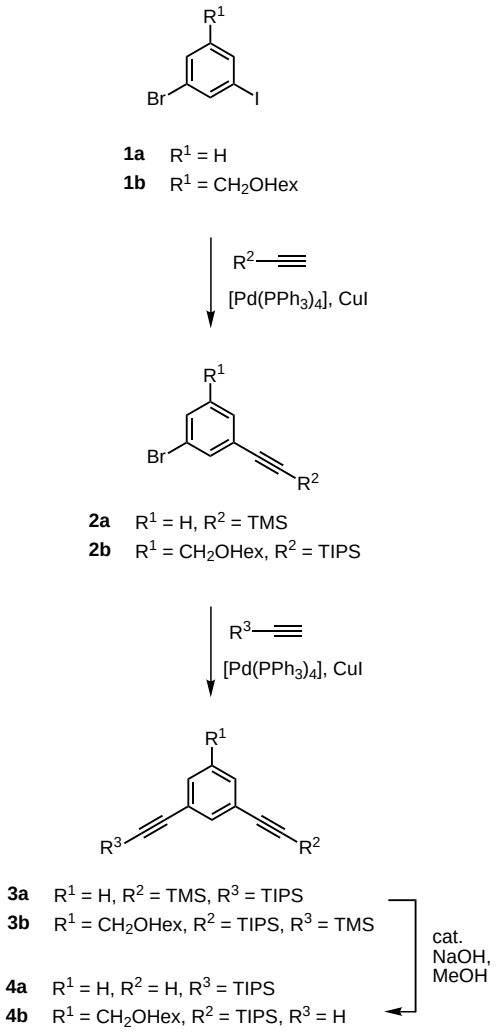
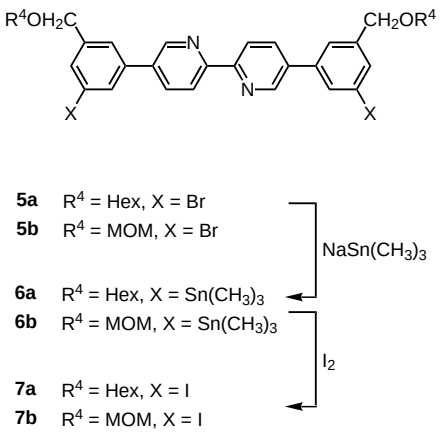
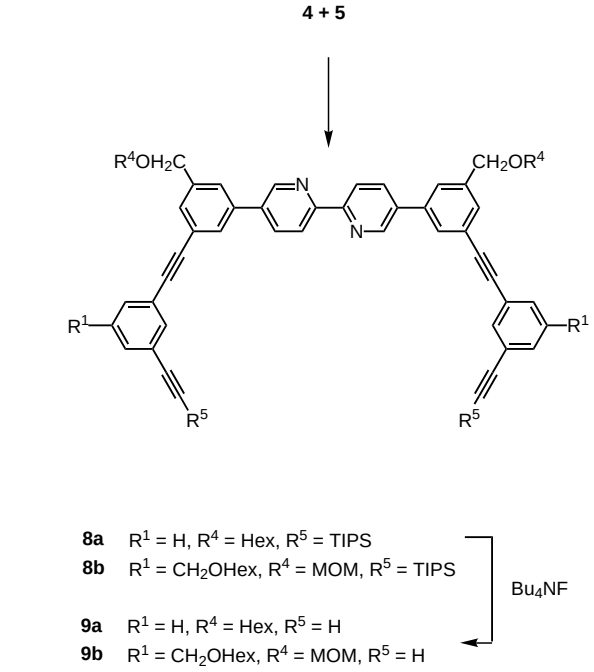


Scheme 1.

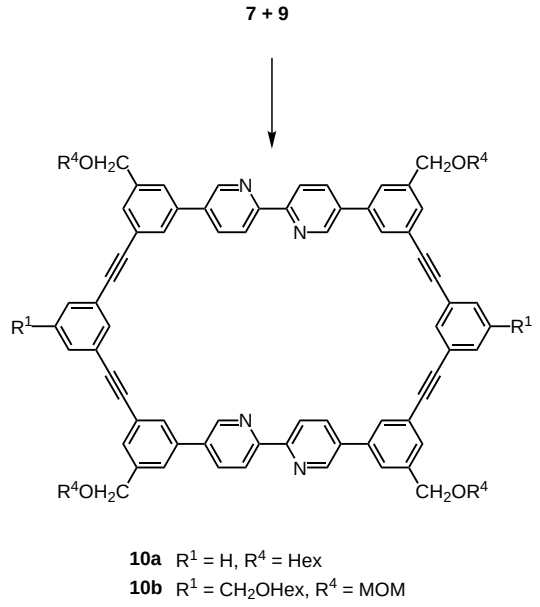


Scheme 2.

thick-walled glass vessels with a Rotaflo stopcock. The product mixture contained cycles **10a** and **10b**, the corresponding oligomers, whose nature was not investigated, and some insoluble material. The proportions between these components varied with reaction conditions. In the given concentration range approximately 60 % of the total mass was



Scheme 3.



Scheme 4.

soluble and 25 – 30 % was the macrocycle (39 – 47 % of soluble material). The macrocycles were isolated by preparative gel-permeation chromatography (GPC). Because of their symmetry the NMR spectra of **10a** and **10b** were simple. For **10b** single crystals were grown and the structure solved by X-ray diffraction. Cycles **10a** and **10b** differ from related macrocycles[9] by the fact that they combine both shape-persistency and the presence of two opposing and switchable bipy units. A recent review on phenylacetylene macrocycles is available.[10]

Suitable crystals of **10b** were obtained by slow diffusion of diethyl ether or ethanol into a chloroform solution. The X-ray structural analysis was done at $-100\,^{\circ}C$ and revealed that **10b**

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crystallizes with four molecules of chloroform per formula unit. Attempts to mount crystals of **10b** · 4 $CHCl_3$ at ambient temperature failed due to the loss of solvent molecules.[11]

Compound **10b** · 4 $CHCl_3$ crystallizes in the triclinic space group $P\bar{1}$ with half a molecule in the asymmetric unit. The ORTEP diagram of **10b** · 4 $CHCl_3$ shows the position of the four chloroform molecules (Figure 1a). The individual cycles form almost planar sheets. Major deviations from planarity are observed for the bipy subunits (C43-C44-C52-C53 28.4°, C21-C26-C32-C33 19.0°), which are themselves planar. Because of the difficulty to distinguish between carbon and nitrogen all ring atoms were refined as carbon in an early stage of refinement. The assignment of the bipy nitrogen atoms is based on bond lengths and thermal parameters. As observed in most sterically unrestricted bipy derivates,[12] the NCCN torsion angle is close to 180° (N2-C41-C35-N1 177.1°).

The largest distance across the hole inside the macrocycle, which is occupied by chloroform molecules, is between the acetylenic carbon atoms C58–C58A and is 1.720 nm. The nitrogen atoms N2 and N2A are separated by 1.039 nm. The shortest intermolecular distances of the solvent molecule are found between H1L and the oxygen atom O51 of the methoxymethoxymethyl side chains (H1L–O51 = 227.8 pm) and the nitrogen atom N2 of the bipy unit (H2L–N2 = 237.0 pm).

The quality of the structure determination suffers from a partial mobility of the chloroform molecules, which gives rise to high thermal parameters for the chlorine atoms. In addition the highest peaks in the difference Fourier map are located close to the chlorine atoms of intercalated solvent molecules. As it was not possible to find a reasonable disorder model for the chloroform molecules, corrected structure factors for a

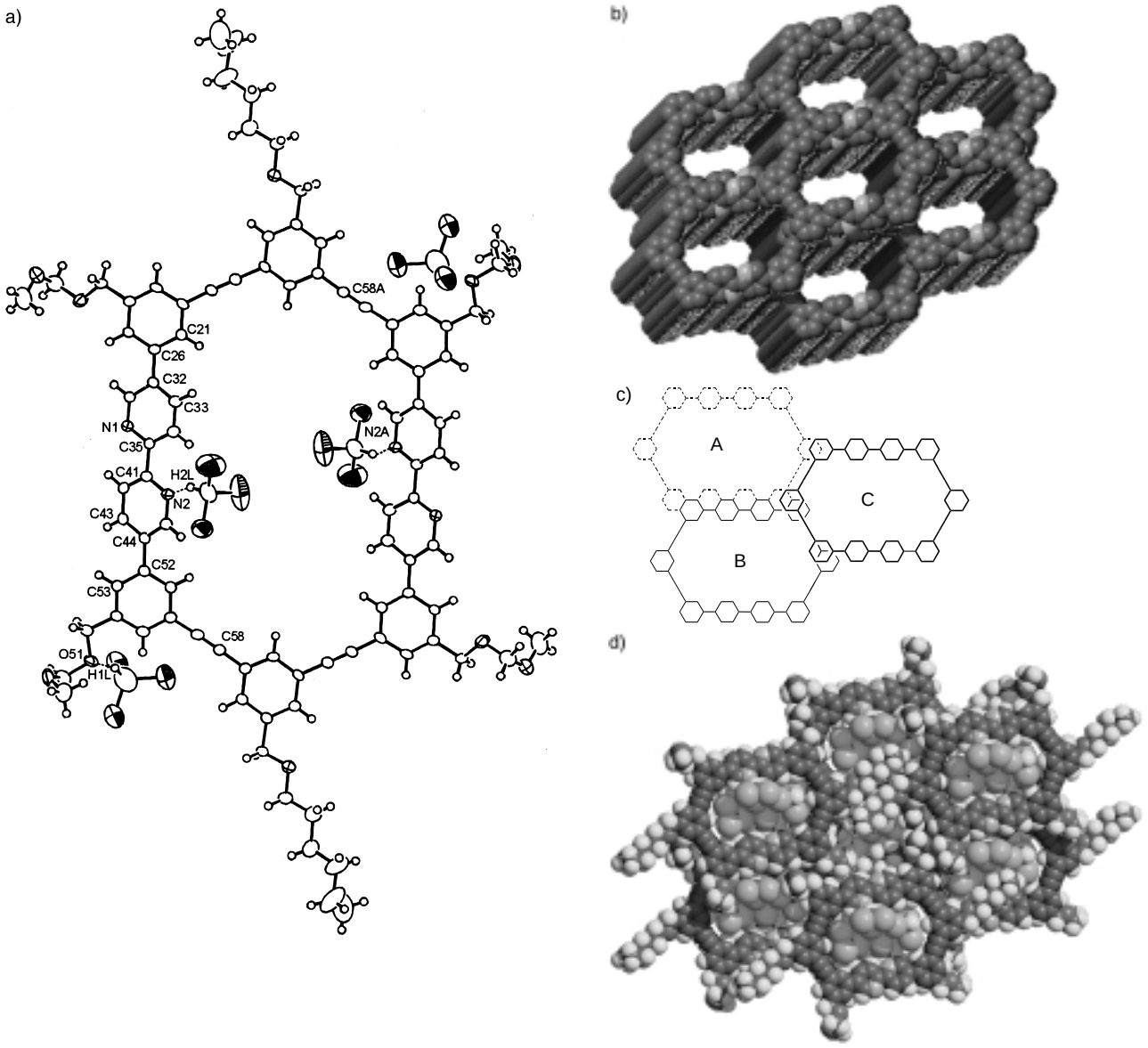

Figure 1. a) Molecular structure of macrocycle **10b** · 4 $CHCl_3$ (ORTEP[18]). b) Space-filling model (SCHAKAL[19]) of the packing of macrocycle **10b** · 4 $CHCl_3$. Side chains and solvent molecules are omitted to clarify the channels. c) Schematic representation of the macrocycles' packing. Double bonds are omitted and triple bonds drawn as straight lines for clarity. d) Space-filling model (SCHAKAL[19]) of the packing of **10b** · 4 $CHCl_3$ including solvent molecules and side chains.

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solvent-free model were calculated by using the "squeeze" option in the programm Platon. The space occupied by the four chloroform molecules is ~ 0.560 nm^3, which is about 25% of the total volume. By using the corrected structure factors the refinement comparison changes to $R1 = \sim 0.078$ from 0.136 in the model with the solvent molecules.

Similar to Moore's all hydrocarbon phenylacetylene macrocycles,[13] cycle **10b** forms a layered structure with channels (Figure 1b). The layers have an ABCABC sequence in which, if viewed along the *a* axis, every third layer lies directly on top of each other. The AA distance is 108.59 pm. Figure 1c shows the arrangement of three cycles of different layers A, B, and C when viewed along the crystallographic *a* axis. The cycles are slightly shifted against each other. A part of each chain is sandwiched into the empty space between consecutive sides of cycles, the remaining part reaches into the channel's interior void (Figure 1d).

Experimental Section

General: Compound **1a** was purchased from Aldrich or Acros. Compounds **1b**,[3a] **5a**,[3a] **5b**,[3a] and $NaSn(CH_3)_3$[8] were prepared according to literature. Compound **2a** is a known compound[14] but was here prepared following a different route. All other reagents were purchased from Aldrich or Acros and used without further purification.

General procedure for the coupling of terminal acetylenes and aryliodines and arylbromines: A heavy-walled flask was charged with the terminal acetylene, aryl iodide, $[Pd(PPh_3)_4]$ (0.02 equiv per coupling), CuI (0.02 equiv per coupling), and dry triethylamine. For some sequences, toluene was used as co-solvent owing to poor solubility of the reactants. The flask was then evacuated and flushed with nitrogen three times, and sealed with a Teflon screw cap, and the reaction mixture was stirred for 24 h at 60 °C (for iodo compounds) and 80 °C (for bromo compounds). Trimethylsilylethyne was added after evacuation because of its volatility. After completion, the solvent was removed and the reaction mixture was purified by column chromatography (silica gel).

1-Bromo-3-trimethylsilylethynylbenzene (2a): Compound **1a** (13 g, 44 mmol), trimethylsilylethyne (4.5 g, 46 mmol), triethylamine (60 mL). Yield: 8.7 g (78%) of **2a** as a colorless oil; R_f (hexane): 0.53; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.35$ (s, 9H; $Si(CH_3)_3$), 7.15 (dd, $^3J = 8$ Hz, 1H; phenyl-H), 7.37 (d, $^3J = 8$ Hz, 1H; phenyl-H), 7.41 (d, $^3J = 8$ Hz, 1H; phenyl-H), 7.60 (s, 1H; phenyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = -0.15$, 95.81, 103.26, 121.99, 125.07, 129.60, 130.34, 131.58, 134.65; MS (EI): *m*/*z* (%): 254 (22.6), 252 (22.4), 239 (100), 237 (99.3); HRMS: *m*/*z*: calcd 251.99699; found 251.99586.

1-Bromo-3-hexyloxymethyl-5-triisopropylsilylethynyl-benzene (2b): **1b** (28 g, 70 mmol), triisopropylsilylethyne (13 g, 73 mmol), triethylamine (200 mL). Yield: 29 g (94%) of **2b** as a colorless oil; R_f (ethyl acetate/hexane 1:20): 0.61; b.p. 215 °C (3×10^{-1} mbar); ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.88$ (t, 3H; CH_3), 1.13 (s, 21H; $Si(C_3H_7)_3$), 1.23–1.42 (m, 6H; γ-, δ-, ε-CH_2), 1.59 (m, 2H; β-CH_2), 3.46 (t, 2H; α-CH_2), 4.42 (s, 2H; benzyl-CH_2), 7.34 (s, 1H; phenyl-H), 7.44 (s, 1H; phenyl-H), 7.51 (s, 1H; phenyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 11.25$, 14.02, 18.62, 22.60, 25.82, 29.62, 31.64, 70.87, 71.56, 92.22, 105.30, 122.02, 125.35, 129.46, 130.37, 133.62, 140.99; MS (EI, 80 eV): *m*/*z* (%): 452 (8.1), 450 (7.7), 409 (100), 407 (94.7); HRMS: *m*/*z*: calcd 450.195356; found 450.19833.

1-Triisopropylsilylethynyl-3-trimethylsilylethynylbenzene (3a): Compound **2a** (17 g, 67 mmol), triisopropylsilylethyne (16 g, 87 mmol), triethylamine (120 mL). Yield: 22 g (92%) of **3a** as a colorless oil; R_f (hexane): 0.45; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.29$ (s, 9H; $Si(CH_3)_3$), 1.16 (s, 21H; $Si(C_3H_7)_3$), 7.25 (dd, $^3J = 8$ Hz, 1H; phenyl-H), 7.39–7.46 (m, 2H; phenyl-H), 7.61 (s, 1H; phenyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = -0.09$, 11.30, 18.66, 91.21, 94.78, 104.14, 106.09, 123.38, 123.76, 128.14, 131.65, 131.92, 135.32; MS (EI): *m*/*z* (%): 354 (13.4), 339 (5.99), 311 (100); HRMS: *m*/*z*: calcd 354.21969; found 354.21991.

1-Hexyloxymethyl-3-triisopropylsilylethynyl-5-trimethylsilylethynylbenzene (3b): Compound **2b** (4.8 g, 11 mmol), trimethylsilylethyne (2.1 g, 21 mmol), triethylamine (60 mL). Yield: 4.8 g (97%) of **3b** as a colorless oil; R_f (ethyl acetate/hexane 1:20): 0.59; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.24$ (s, 9H; $Si(CH_3)_3$), 0.89 (t, 3H; CH_3), 1.12 (s, 21H; $Si(C_3H_7)_3$), 1.24–1.42 (m, 6H; γ-, δ-, ε-CH_2), 1.60 (m, 2H; β-CH_2), 3.45 (t, 2H; α-CH_2), 4.41 (s, 2H; benzyl-CH_2), 7.39 (s, 2H; phenyl-H), 7.50 (s, 1H; phenyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = -0.13$, 11.27, 14.02, 18.63, 22.60, 25.84, 29.64, 31.65, 70.72, 71.87, 91.17, 94.75, 104.11, 106.03, 123.33, 123.77, 130.76, 130.95, 134.37, 139.13; MS (EI, 80 eV): *m*/*z* (%): 68 (7.5), 425 (100); HRMS: *m*/*z*: calcd 468.32437; found 468.32843.

1-Ethynyl-3-triisopropylsilylethynylbenzene (4a): A catalytic amount of 1M NaOH solution was added to a stirred solution of **3a** (3.6 g, 10 mmol) in a mixture of THF (60 mL) and methanol (60 mL). After complete consumption of the starting material, the reaction mixture was diluted with diethyl ether (100 mL) and brine (60 mL), and the phases were separated. The aqueous phase was washed with diethyl ether (50 mL) and the combined organic phases with brine (50 mL). The organic phase was dried over $MgSO_4$, the solvent removed, and the resulting oil was purified by column chromatography (silica gel, hexane) to give 2.7 g (94%) of **4a** as a colorless oil. R_f (hexane): 0.46; b.p. 115 °C (2×10^{-1} mbar); ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.17$ (s, 21H; $Si(C_3H_7)_3$), 3.10 (s, 1H; acetyl-H), 7.28 (dd, $^3J = 8$ Hz, 1H; phenyl-H), 7.45 (m, 2H; phenyl-H), 7.62 (s, 1H; phenyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 11.25$, 18.63, 77.72, 82.74, 91.51, 105.88, 122.30, 123.84, 128.25, 131.79, 132.22, 135.52; MS (EI, 80 eV): *m*/*z* (%): 282 (16.1), 239 (100); HRMS: *m*/*z*: calcd 282.18038; found 282.18457.

1-Ethynyl-3-hexyloxymethyl-5-triisopropylsilylethynylbenzene (4b): The light yellow oil **4b** (3.2 g, 87%) was obtained from **3b** (4.4 g, 9.4 mmol) by using the procedure described for **4a**. R_f (ethyl acetate/hexane 1:20): 0.51; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.88$ (t, 3H; CH_3), 1.11 (s, 21 H $Si(C_3H_7)_3$), 1.23–1.39 (m, 6H; γ-, δ-, ε-CH_2), 1.60 (m, 2H; β-CH_2), 3.06 (s, 1H; acetyl-H), 3.44 (t, 2H; α-CH_2), 4.41 (s, 2H; benzyl-CH_2), 7.40 (s, 1H; phenyl-H), 7.42 (s, 1H; phenyl-H), 7.51 (s, 1H; phenyl-H); ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta = 11.21$, 14.03, 18.60, 22.60, 25.81, 29.62, 31.64, 70.74, 71.77, 77.64, 82.70, 91.41, 105.83, 122.29, 123.85, 130.83, 131.22, 134.56, 139.24; MS (EI, 80 eV): *m*/*z* (%): 396 (11.4) 353 (100); elemental analysis calcd (%) for $C_{26}H_{40}OSi$ (396.691): C 78.72, H 10.16; found C 78.30, H 9.78.

5,5′-Bis-(3-hexyloxymethyl-5-trimethylstannyl-phenyl)-[2,2′]bipyridinyl (6a): A suspension of **5a** (3.5 g, 5 mmol) in DME (20 mL) was added over a period of 20 min to a solution of $NaSn(CH_3)_3$ in DME (40 mL), prepared as described in literature from Na (2.5 g) and $ClSn(CH_3)_3$ (12 g, 60 mmol). After stirring for 20 h at RT, the solvent was removed under reduced pressure, and the residual material was purified by chromatography over silica gel (ethyl acetate/hexane 1:6) to give 3.1 g (71%) of **6a** as colorless crystals. R_f (ethyl acetate/hexane 1:6): 0.20; m.p 107 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.37$ (s, 18H; $Sn(CH_3)_3$), 0.89 (t, 6H; CH_3), 1.21–1.45 (m, 12H; γ-, δ-, ε-CH_2), 1.64 (m, 4H; β-CH_2), 3.56 (t, 4H; α-CH_2), 4.61 (s, 4H; benzyl-CH_2), 7.52 (s, 2H; phenyl-H), 7.60 (s, 2H; phenyl-H), 7.69 (s, 2H; phenyl-H), 8.05 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H; pyridyl-H), 8.52 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.94 (s, $^4J = 2$ Hz, 2H; pyridyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = -9.49$, 14.00, 22.55, 25.86, 29.68, 31.62, 70.71, 72.73, 120.75, 126.32, 133.42, 134.71, 135.21, 136.62, 137.18, 138.82, 143.46, 147.72, 154.54; MS (EI): *m*/*z* (%): 862 (23.0), 847 (100); elemental analysis calcd (%) for $C_{42}H_{60}N_2O_2Sn_2$ (862.334): C 58.50, H 7.01, N 3.25; found C 58.27, H 6.83, N 3.06.

5,5′-Bis-[3-(methoxymethoxy-methyl)-5-trimethylstannyl-phenyl]-[2,2′]bipyridinyl (6b): White crystals of **6b** (1.9 g, 75%) were obtained from **5b** (2.0 g, 3.3 mmol, dissolved in 30 mL DME) by using the procedure described for **6a**. $NaSn(CH_3)_3$ was prepared from Na (1.9 g) and $ClSn(CH_3)_3$ (7.8 g, mmol) in DME (20 mL). R_f (ethyl acetate/hexane 1:3): 0.49; m.p. 96 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.37$ (s, 18H; $Sn(CH_3)_3$), 3.49 (s, 6H; CH_3), 4.69 (s, 4H; CH_2), 4.78 (s, 4H; CH_2), 7.52 (s, 2H; phenyl-H), 7.61 (s, 2H; phenyl-H), 7.70 (s, 2H; phenyl-H), 8.07 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H; pyridyl-H), 8.54 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.95 (d, $^4J = 2$ Hz, 2H; pyridyl-H,); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = -9.44$, 55.38, 69.16, 95.83, 120.80, 126.61, 133.40, 134.98, 135.29, 136.58, 137.30, 138.00, 143.72, 147.76, 154.59; MS (EI, 80 eV): *m*/*z* (%): 782 (35.4), 707 (100); elemental analysis calcd (%) for $C_{34}H_{44}N_2O_4Sn_2$ (782.116): C 52.21, H 5.67, N 3.58; found C 52.21, H 5.50, N 3.51.

5,5′-Bis-(3-hexyloxymethyl-5-iodo-phenyl)-[2,2′]bipyridinyl (7a): I_2 (1.8 g, 7.2 mmol) over a period of 15 min at RT to a solution of **6a** (3.1 g,

3.6 mmol) in $CHCl_3$ (120 mL). After stirring for 2 h, a saturated solution of KF (30 mL) was added. The resulting mixture was made alkaline with potassium carbonate and the phases were separated. The aqueous phase was washed with $CHCl_3$ (2 × 50 mL) and the combined organic phases were washed with a saturated solution of KF (50 mL) and then with a saturated sodium thiosulfate solution (50 mL). The organic phase was dried over $MgSO_4$, the solvent removed, and the resulting oil was purified by chromatography over silica gel (ethyl acetate/hexane 1:3) to give 2.7 g (95%) of **7a** as white crystals. R_f (ethyl acetate/hexane 1:3): 0.56; m.p. 112 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.90$ (t, 6H; CH_3), 1.22 – 1.45 (m, 12H; γ-, δ-, ε-CH_2), 1.58 – 1.70 (m, 4H; β-CH_2), 3.52 (t, 4H; α-CH_2), 4.54 (s, 4H; benzyl-CH_2), 7.60 (s, 2H; phenyl-H), 7.78 (s, 2H; phenyl-H), 7.92 (s, 2H; phenyl-H), 8.00 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H; pyridyl-H), 8.51 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.90 (d, $^4J = 2$ Hz, 2H; pyridyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 14.04$, 22.60, 25.85, 29.67, 31.64, 71.01, 71.73, 95.02, 121.00, 125.36, 134.96, 135.23, 136.01, 139.70, 141.87, 147.57, 154.95; MS (EI, 80 eV): *m*/*z* (%): 788 (100), 688 (32.3), 561 (26.6); elemental analysis calcd (%) for $C_{36}H_{42}I_2N_2O_2$ (788.544): C 54.83, H 5.37, N 3.55; found C 54.86, H 5.36, N 3.25.

5,5′-Bis-[3-iodo-5-(methoxymethoxy-methyl)phenyl]-[2,2′]bipyridinyl (7b): White crystals of **7b** (1.2 g, 83%) were obtained from **6b** (1.6 g, 2.1 mmol, dissolved in 70 mL $CHCl_3$ and I_2 (1.1 g, 4.1 mmol) by using the procedure described for **6a**. R_f (ethyl acetate/hexane 1:1): 0.36; m.p. 142 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.41$ (s, 6H; CH_3), 4.60 (s, 4H; CH_2), 4.73 (s, 4H; CH_2), 7.56 (s, 2H; phenyl-H), 7.72 (s, 2H; phenyl- H), 7.88 (s, 2H; phenyl- H), 7.94 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H; pyridyl-H), 8.47 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.84 (d, $^4J = 2$ Hz, 2H; pyridyl-H); ^{13}C NMR ($CDCl_3$, 126 MHz): $\delta = 55.49$, 68.03, 95.00, 95.91, 120.96, 125.50, 134.80, 135.08, 135.15, 136.11, 139.71, 141.02, 147.51, 154.92; MS (EI, 70 eV): *m*/*z* (%): 708 (100), 662 (4.4), 648 (17.7); elemental analysis calcd (%) for $C_{28}H_{26}I_2N_2O_4$ (708.326): C 47.48, H 3.70, N 3.95; found C 47.37, H 3.65, N 3.69.

5,5′-Bis-[3-hexyloxymethyl-5-(3-triisopropylsilylethynyl-phenylethynyl)-phenyl]-[2,2]bipyridinyl (8a): Coupling of **4a** (2.1 g, 7.5 mmol) and **5a** (2.0 g, 2.9 mmol) in a mixture of triethylamine (30 mL) and toluene (10 mL) by using the general procedure gave 2.3 g (88%) of **8a** as a light yellow oil. R_f (ethyl acetate/hexane 1:3): 0.69; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.91$ (t, 6H; CH_3), 1.17 (s, 42H; Si(C_3H_7)$_3$), 1.21 – 1.48 (m, 12H; γ-, δ-, ε-CH_2), 1.66 (m, 4H; β-CH_2), 3.54 (t, 4H; α-CH_2), 4.59 (s, 4H; benzyl-CH_2), 7.32 (dd, $^3J = 8$ Hz, 2H; phenyl-H), 7.41 – 7.51 (m, 4H; phenyl-H), 7.55 (s, 2H; phenyl-H), 7.59 (s, 2H; phenyl-H), 7.70 (s, 2H; phenyl-H), 7.72 (s, 2H; phenyl-H), 8.01 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H; pyridyl-H), 8.52 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.91 (d, $^4J = 2$ Hz, 2H; pyridyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 11.20$, 14.02, 18.58, 22.58, 25.84, 29.66, 31.63, 70.85, 72.11, 89.05, 89.46, 91.36, 105.98, 120.90, 123.15, 123.84, 125.98, 128.28, 129.09, 130.17, 131.27, 131.79, 135.02, 135.42, 137.88, 140.08, 147.53, 154.79; MS (EI, 80 eV): *m*/*z* (%): 1096 (3.3) 1053 (100), 659 (18.9), 531 (58.5); HRMS: *m*/*z* calcd for $[M - C_3H_7]^+$ 1053.61496; found 1053.61780.

5,5′-Bis-[3-(3-hexyloxymethyl-5-triisopropylsilylethynyl-phenylethynyl)-5-(methoxymethoxy-methyl)-phenyl]-[2,2′]bipyridinyl (8b): Coupling of **4b** (2.1 g, 7.5 mmol) and **5b** (2.0 g, 2.9 mmol) in a mixture of triethylamine (30 mL) and toluene (5 mL) by using the general procedure gave 2.8 g (88%) of **8b** as a light yellow oil. R_f (ethyl acetate/hexane 1:3): 0.36; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.90$ (t, 6H; CH_3), 1.14 (s, 42H; Si(C_3H_7)$_3$), 1.23 – 1.42 (m, 12H; γ-, δ-, ε-CH_2), 1.62 (m, 4H; β-CH_2), 3.48 (s, 6H; CH_3), 3.49 (t, 4H; α-CH_2), 4.48 (s, 4H; CH_2), 4.69 (s, 4H; CH_2), 4.77 (s, 4H; CH_2), 7.43 (s, 2H; phenyl-H), 7.49 (s, 2H; phenyl-H), 7.59 (s, 2H; phenyl-H), 7.61 (s, 2H; phenyl-H), 7.62 (s, 2H; phenyl-H), 7.75 (s, 2H; phenyl-H), 8.06 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H; pyridyl-H), 8.55 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.95 (d, $^4J = 2$ Hz, 2H; pyridyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 11.24$, 14.01, 18.62, 22.58, 25.80, 29.63, 31.63, 55.46, 68.48, 70.77, 71.86, 89.26, 91.39, 95.88, 105.99, 121.00, 123.15, 123.93, 124.07, 126.28, 129.36, 130.39, 130.91, 134.11, 135.22, 135.49, 138.08, 139.33, 147.62, 154.91; MS (FAB): *m*/*z* (%): 1247 (4.0); elemental analysis calcd (%) for $C_{80}H_{104}N_2O_6Si_2$ (1245.892): C 77.12, H 8.41, N 2.25; found C 77.06, H 8.33, N 2.10.

5,5′-Bis-[3-(3-ethynyl-phenylethynyl)-5-hexyloxymethyl-phenyl]-[2,2′]bipyridinyl (9a): Tetrabutylammonium fluoride trihydrate (1.1 g, 3.5 mmol) was added to a stirred solution of **8a** (1.9 g, 1.7 mmol) in THF (40 mL). After complete consumption of the starting material (1 h), the reaction mixture was diluted with diethyl ether (100 mL) and water (80 mL), and the phases were separated. The aqueous phase was washed with diethyl ether (50 mL), and the combined organic phases were washed with with water (50 mL). The organic phase was dried over $MgSO_4$, the solvent removed, and the resulting residue purified by recrystallization from ethyl acetate/hexane (1:6) to give 1.26 g (92%) of **9a** as white solid. R_f (ethyl acetate/hexane 1:3): 0.46; m.p. 92 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.87$ (t, 6H; CH_3), 1.17 – 1.42 (m, 12H; γ-, δ-, ε-CH_2), 1.63 (m, 4H; β-CH_2), 3.10 (s, 2H; acetyl-H), 3.50 (t, 4H; α-CH_2), 4.56 (s, 4H; benzyl-CH_2), 7.29 (dd, $^3J = 8$ Hz, 2H; phenyl-H), 7.43 (d, $^3J = 8$ Hz, 2H; phenyl-H), 7.50 (d, $^3J = 8$ Hz, 2H; phenyl-H), 7.55 (s, 2H; phenyl-H), 7.59 (s, 2H; phenyl-H), 7.69 (s, 2H; phenyl-H), 7.71 (s, 2H; phenyl-H), 8.00 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 2H; pyridyl-H), 8.50 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.91 (d, $^4J = 2$ Hz, 2H; pyridyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 14.02$, 22.59, 25.85, 29.68, 31.64, 70.91, 72.13, 77.91, 82.67, 88.88, 89.63, 120.97, 122.49, 123.33, 126.11, 128.43, 129.15, 130.22, 131.82, 131.91, 135.09, 135.15, 135.48, 137.94, 140.13, 147.57, 154.83; MS (EI, 80 eV): *m*/*z* (%): 784 (50.7) 684 (85.8), 546 (44.8), 446 (100); elemental analysis calcd (%) for $C_{56}H_{52}N_2O_2$ (785.044): C 85.68, H 6.67, N 3.57; found C 85.56, H 6.86, N 3.37.

5,5′-Bis-[3-(3-ethynyl-5-hexyloxymethyl-phenylethynyl)-5-(methoxymethoxy-methyl)-phenyl]-[2,2′]bipyridinyl (9b): Compound **9b** (670 mg, 92%) was obtained from a solution of **8b** (960 mg, 0.77 mmol) in THF (30 mL) and tetrabutylammonium fluoride trihydrate (0.58 g, 1.9 mmol) by using the procedure described for **9a**. R_f (ethyl acetate/hexane 1:1): 0.39; m.p. 62 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.86$ (t, 6H; CH_3), 1.19 – 1.41 (m, 12H; γ-, δ-, ε-CH_2), 1.58 (m, 4H; β-CH_2), 3.11 (s, 2H; acetyl-H), 3.44 (s, 6H; CH_3), 3.45 (t, 4H; α-CH_2), 4.41 (s, 4H; CH_2), 4.63 (s, 4H; CH_2), 4.73 (s, 4H; CH_2), 7.40 (s, 2H; phenyl-H), 7.59 (s, 2H; phenyl-H), 7.52 (s, 2H; phenyl-H), 7.58 (s, 2H; phenyl-H), 7.59 (s, 2H; phenyl-H), 7.69 (s, 2H; phenyl-H), 7.98 (dd, $^3J = 8$ Hz, ^{4}J = 2 Hz, 2H; pyridyl-H), 8.49 (d, $^3J = 8$ Hz, 2H; pyridyl-H), 8.89 (d, $^4J = 2$ Hz, 2H; pyridyl-H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 13.94$, 22.48, 25.69, 25.52, 31.52, 55.30, 68.29, 70.67, 71.58, 77.67, 82.61, 88.96, 89.36, 95.71, 120.83, 122.40, 123.17, 123.80, 126.10, 129.12, 130.23, 130.65, 130.78, 133.93, 134.95, 135.16, 137.84, 139.20, 139.42, 147.39, 154.68; MS (FAB): *m*/*z* (%): 933 (34.3); elemental analysis calcd (%) for $C_{62}H_{64}N_2O_6$ (933.202): C 79.80, H 6.91, N 3.00; found C 79.40, H 6.99, N 2.94.

Macrocycle (10a): A solution of **7a** (810 mg, 1.1 mmol) and **9a** (820 mg, 1.1 mmol) in triethylamine (360 mL) and toluene (360 mL) was carefully degassed. After addition of tetrakistriphenylphosphine palladium(0) (48 mg, 0.04 equiv) and copper(I) iodide (8 mg, 0.04 equiv), this mixture was stirred under nitrogen at 60 °C for 4 d and then at 95 °C for 24 h. After cooling, the orange suspension was treated with a solution of KCN (300 mg) in water (100 mL) which resulted in a color change to white. The mixture was then filtered and the insoluble residue (brown-orange) was washed with toluene (2 × 50 mL). The phases were separated, the aqueous one was washed with toluene (50 mL) and the combined organic phases were washed with water (100 mL). The organic phase was dried over $MgSO_4$, and the solvent was removed. Purification of the residue by preparative GPC gave 383 mg (28%) of cycle **10a**. The melting behavior of **10a** is presently under investigation. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.85$ (t, 12H; CH_3), 1.16 – 1.46 (m, 24H; γ-, δ-, ε-CH_2), 1.62 (m, 8H; β-CH_2), 3.50 (t, 8H; α-CH_2), 4.49 (s, 8H; benzyl-CH_2), 7.26 (dd, $^3J = 8$ Hz, 2H; phenyl-H), 7.41 (m, 8H; phenyl-H), 7.46 (s, 4H; phenyl-H), 7.60 (s, 4H; phenyl-H), 7.68 (s, 2H; phenyl-H), 7.89 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 4H; pyridyl-H), 8.39 (d, $^3J = 8$ Hz, 4H; pyridyl-H), 8.80 (d, $^4J = 2$ Hz, 4H; pyridyl-H); 13C NMR ($CDCl_3$, 63 MHz): $\delta = 14.06$, 22.63, 25.91, 29.74, 31.70, 70.93, 72.23, 89.11, 89.73, 120.91, 123.44, 123.85, 125.59, 128.44, 129.18, 129.86, 131.07, 134.80, 134.91, 135.24, 137.53, 139.94, 147.31, 154.70; MS (FAB): *m*/*z* (%): 1318 (26.1), 1317 (21.7), 1319 (24.8); elemental analysis calcd (%) for $C_{92}H_{92}N_4O_4$ (1317.772): C 83.85, H 7.04, N 4.25; found C 83.52, H 7.37, N 3.88.

Macrocycle (10b): The procedure was analogous to the one described for **10a**. Compound **9b** (670 mg, 0.72 mmol), compound **7b** (510 mg, 0.72 mmol), triethylamine (250 mL), toluene (250 mL), tetrakistriphenylphosphine palladium(0) (33 mg, 0.04 equiv), and copper(I) iodide (5.5 mg, 0.04 equiv). Yield: 250 mg (25%). The melting behavior of **10a** is presently under investigation. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.90$ (t, 6H; CH_3, $^3J = 8$ Hz), 1.32 (m, 8H; γ-, δ-CH_2), 1.40 (m, 4H; ε-CH_2), 1.66 (m, 4H; β-CH_2), 3.46 (s, 12H; CH_3), 3.51 (t, $^3J = 8$ Hz, 4H; α-CH_2), 4.50 (s, 4H; benzyl-CH_2), 4.68 (s, 8H; CH_2), 4.78 (s, 8H; CH_2), 7.49 (s, 4H; phenyl-H), 7.55 (s, 4H; phenyl-H), 7.61 (s, 4H; phenyl-H), 7.75 (s, 6H; phenyl-H), 8.09 (d, $^3J = 8$ Hz, 4H; pyridyl-H), 8.56 (br s, 4H; pyridyl-H), 8.96 (br s, 4H;

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pyridyl-H); 13C NMR ($CDCl_3$, 63 MHz): $\delta = 13.98$, 22.54, 25.77, 29.60, 31.60, 55.35, 68.33, 70.75, 71.82, 89.01, 89.29, 95.70, 120.64, 123.16, 123.64, 125.23, 128.82, 129.75, 129.90, 133.90, 134.18, 134.37, 136.96, 138.64, 139.06, 146.78, 154.14; MS (FAB): *m/z* (%): 1386 (4.3), 1387 (5.2), 1388 (4.2).

X-ray structure analysis: Crystals of **10b** suitable for X-ray structure analysis were obtained by slow diffusion of diethyl ether into a solution of **10b** in chloroform. A prismatic crystal ($0.8 \times 0.5 \times 0.4$ mm) was mounted on top of a glass fibre at $-150\,^{\circ}C$ and brought into the cold gas stream of a Bruker-AXS SMART CCD diffractometer. To avoid loss of intercalated solvent the data collection was performed at $-100\,^{\circ}C$. A total of 1800 frames were collected [$Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, a scan width of 0.3° in ω and exposure time of 20 s per frame, detector–crystal distance 4.00 cm] and integrated with Bruker Saint software package using a wide-frame integration algorithm.[15] Triclinic, space group $P\bar{1}$, $a = 10.8587(4)$, $b = 14.1781(5)$, $c = 16.2292(6)$ Å, $\alpha = 76504(1)$, $\beta = 89.246(1)$, $\gamma = 68.151(1)^{\circ}$, $V = 2247.53(14)$ Å^3, $Z = 1$, $2\theta_{max} = 49.42^{\circ}$, 7543 crystallographically unique reflections [5858 observed with $I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full matrix least squares in full-matrix against F^2, non-H atoms anisotropic.[16] The hydrogen atoms were included with geometrically calculated positions and refined with a "riding model". 541 parameters, $R1 = 0.136$, w$R2 = 0.439$, GOF = 1.987. The highest residual electron density of 1.99 e Å^{-3} is located 1.75 Å from the carbon atom of the chloroform molecule C2L, indicating that one solvent molecule is disordered. In addition all chlorine atoms of the intercalated chloroform molecules exhibit large temperature factors. Furthermore, there is some evidence for a disorder of one oxygen atom of the MOM side chain. These findings explain the unsatisfying *R* values of the structure determination. To get an impression of the effects of the intercalated solvent molecules an *hkl* file corrected for the electron density within the solvent accessible area (560 Å^3, 25% of the cell volume) was created by using the program PLATON.[17] Refinement of the remaining atoms by full-matrix least squares on F^2 converged at $R1 = 0.078$ for 5592 reflections with $F_o > 4\sigma(F_o)$, w$R2 = 0.264$, GOF = 1.145 for all 7543 data and 469 refined parameters.

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