Nanometre-Scale Molecular Ribbons

Stefan Breidenbach, Stefan Ohren and Fritz Vögtle*

Dedicated to Professor Heinz A. Staab on the occasion of his 70th birthday

Abstract: The longest molecular ribbons known to date (**3**–**10**), composed of a series of [3.3]metacyclophane units, have been synthesised by means of a repetitive synthetic strategy. These multiple ring systems with up to nine bridged benzene rings in a row are the longest structurally perfect cyclophane sequences known to date. The synthetic strategy comprises three steps: ester reduction to a tetrakis(hydroxymethyl) compound, derivatisation to the corresponding tetrakis(bromomethyl) derivative, and double cyclisation with the new key building block **14**, which was especially developed for this sequence. Single-crystal X-ray analyses (**3a**–**7a**) and ^{1}H NMR spectroscopy (**3**–**10**) show that, regardless of their length, these molecules adopt zigzag folded all-*syn* conformations. π-Stacks of nanometre dimensions are thus formed.

Keywords
cyclophanes · macrocyclisations · molecular ribbons · nanostructures · repetitive syntheses

Introduction

There is an increasing interest in nanoscale structures, since they exhibit novel properties as materials, largely as a consequence of their finite, small size. Chemists build structures from the atom up and should therefore be in a position to produce molecules that perfectly fit the size requirement for a given material. The aim is to tune structure–property relationships to give new materials with novel physical and chemical properties with applications in, for example, quantum electronics, chemoselective sensing, and information storage and processing.[1] In one branch of supramolecular chemistry,[2] architecturally impressive structures have been produced, such as belt-shaped arrangements of aromatic rings,[3] and molecular ribbons and tubes.[4]

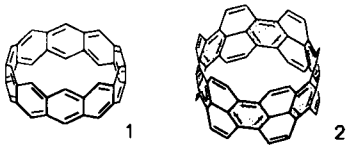

Fig. 1. Interesting synthetic targets.

Molecules such as **1** and **2** (Fig. 1) were put forward many years ago[5] as interesting molecules, and they remain a synthetic challenge to this day. An approach leading to structures of type **1** has been developed by several research groups, but no genuine cyclic polyacene has yet been prepared.[3]

One possible strategy for the synthesis of molecules of type **2** would be to form a molecular ribbon, which could then be macrocyclised by making use of four terminal functional groups.[6] In past publications we described a synthetic strategy that failed in the preparation of larger molecular ribbons.[7] We therefore evolved a new repetitive[8] synthetic strategy for the construction of molecular ribbons like **3a**–**10a**. A small part of this work has been published in a preliminarily communication.[9] Here we describe in detail the preparation of the cyclophanes containing 4–7 benzene rings (**5a**–**8a**, Fig. 2); in addition, the new cyclophanes with eight and nine repeating units (**9a** and **10a**, Fig. 2) are reported.

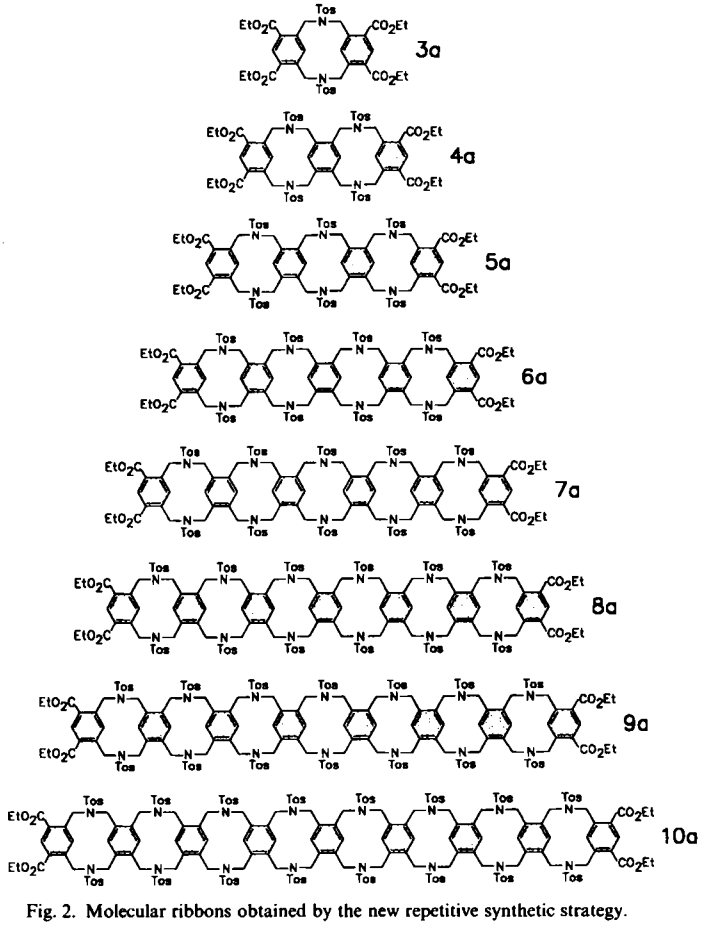

Fig. 2. Molecular ribbons obtained by the new repetitive synthetic strategy.

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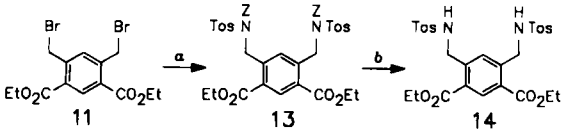
Results and Discussion

Synthesis: A possible strategy for the synthesis of long molecular ribbons involves the derivatisation of the four terminal ester functions (CO_2Et) in a [3.3]metacyclophane system such as **3a** to obtain four terminal aminomethyl groups (CH_2NHTos). Cyclisation with **11** would then yield a lengthened cyclophane. This approach gave only poor yields, and its extension to a preparative-scale synthesis did not seem to be feasible.

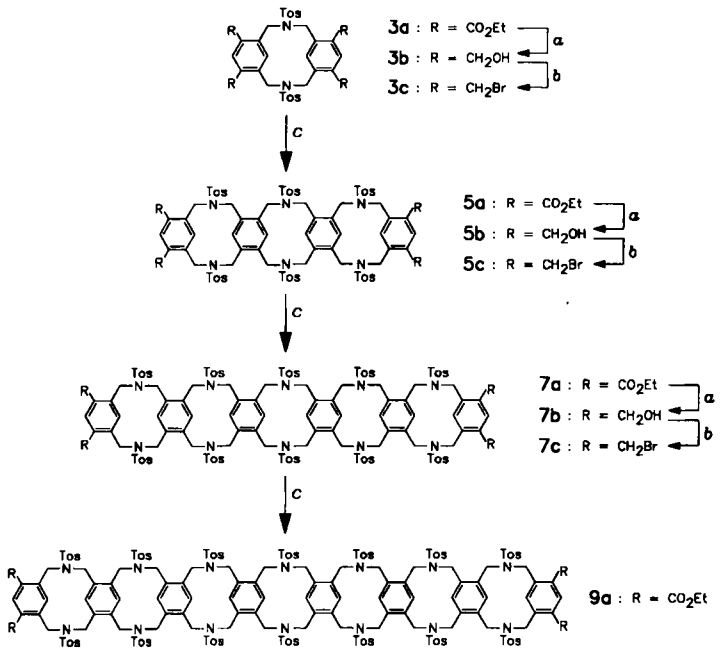
An alternative retrosynthetic approach is based on the formal reciprocal exchange of the reactive terminal groups in the two components (amine → bromide). This concept was used to develop our new repetitive strategy described below. The key compound of this reaction sequence is **14**, which can be obtained in two steps from the bromide **11** by the use of protecting groups. Thus, bromide **11** was treated with benzyl *N*-tosylcarbamate (**12**)[10] (i.e., tosylamine protected with a benzyloxycarbonyl (Z) group) to yield **13**. Hydrogenolysis with palladium on carbon as catalyst gave the key building block **14** (Scheme 1).



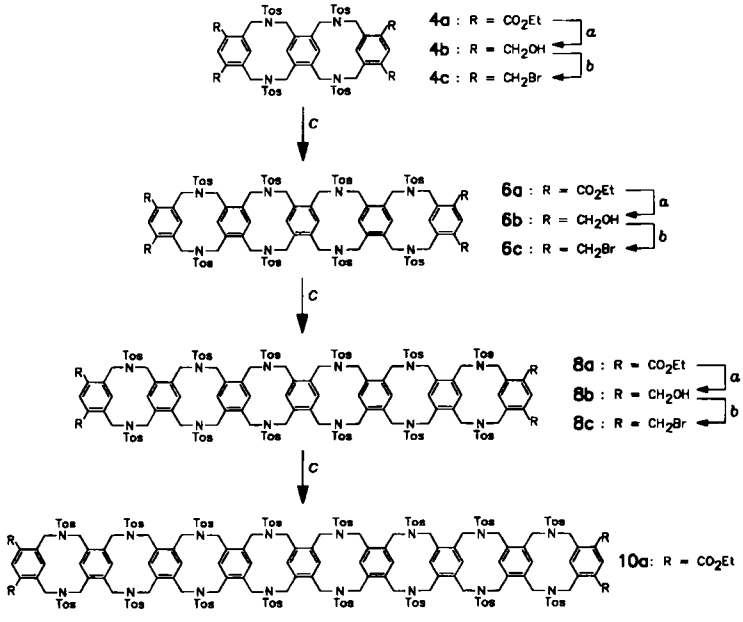
Scheme 1. Synthesis of the key compound **14**. Reagents and conditions: a) TosNHZ (**12**, Z = benzyloxycarbonyl) (2.4 equiv), K_2CO_3, DMF, RT, 72 h, 51%; b) 3.5 bar H_2, 10% Pd/C, $CHCl_3/CH_3OH$ (1:1), RT, 8 h, 98%.

The three-step repetitive reaction sequence (a–c in Scheme 2 and Scheme 3) starts with the nearly quantitative lithium borohydride reduction of the four terminal ethyl ester groups of **3a–8a** to give the tetrakis(hydroxymethyl) derivatives **3b–8b**. Their transformation with PBr_3 in $CHCl_3$ gave the corresponding tetrakis(bromomethyl) compounds **3c–8c**. The final step of this sequence is the cyclisation of **3c–8c** with two equivalents of **14**. This reaction was carried out with K_2CO_3 as base under high-dilution conditions,[11] that is, each solution of the reactants—bromide and **14**—was added dropwise to a stirred suspension of the base in DMF. Each reaction cycle led to the extension of the cyclophane by two benzene rings (e.g., **3a** → **5a**). The successive use of this three-step repetitive reaction cycle resulted in the successful production of yet longer molecular ribbons: starting with **3a** via **5a** and **7a** we obtained the benzeno<8>phane[12] **9a**. In an analogous manner the benzeno<9>phane **10a** was synthesised starting from **4a** via **6a** and **8a**.

The seven-, eight-, and nine-ring assemblies **8–10** represent the longest sequence of benzene rings connected in a cyclophane-



Scheme 2. Synthesis of molecular ribbon **9a**. Reagents and conditions: a) $LiBH_4$, THF, 6 h reflux, 96% (for all reductions). b) PBr_3, $CHCl_3$; 88% (**3b** → **3c**); 61% (**5b** → **5c**); 39% (**7b** → **7c**). c) **14** (2 equiv), K_2CO_3, DMF, RT, high-dilution conditions; 47% (**3c** → **5a**); 42% (**5c** → **7a**); 17% (**7c** → **9a**).



Scheme 3. Synthesis of molecular ribbon **10a**. Reagents and conditions: a) $LiBH_4$, THF, 6 h reflux, 96% (for all reduction reactions). b) PBr_3, $CHCl_3$; 86% (**4b** → **4c**); 73% (**6b** → **6c**); 42% (**8b** → **8c**). c) **14** (2 equiv), K_2CO_3, DMF, RT, high-dilution conditions; 36% (**4c** → **6a**); 50% (**6c** → **8a**); 14% (**8c** → **10a**).

Abstract in German: *Eine neue repetitive Synthesestrategie wurde entwickelt, mit der die Darstellung der molekularen Bänder 3–10 mit bis zu neun Benzoleinheiten gelang. Diese Verbindungen enthalten Diaza[3.3]metacyclophan-Einheiten und sind die längsten bisher bekannten strukturperfekten Cyclophane. Die verwendete Synthesestrategie basiert auf einer dreistufigen repetitiven Reaktionssequenz: Reduktion der vier terminalen Esterfunktionen zu Tetrakis(hydroxymethyl)-Gruppen, deren Umsetzung zu den entsprechenden Tetrakis(brommethyl)-Derivaten und die anschließende doppelte Cyclisierung mit dem neuen Schlüsselbaustein 14, der speziell für diese Reaktionsführung entwickelt wurde. Den Einkristall-Röntgenstrukturanalysen (von 3a–7a) und den ^{1}H-NMR-Spektren (von 3–10) zufolge wird unabhängig von der Länge der molekularen Bänder eine Mäanderstruktur gebildet. In den nanometergroßen π-Stapeln liegen die Benzolringe des Grundgerüsts in annähernd parallelen Ebenen übereinander. Die Ergebnisse von Rechnungen unterstützen die Annahme, daß dies hauptsächlich durch die energetisch günstige all-syn-Konformation des [3.3]Metacyclophan-Gerüsts hervorgerufen wird.*

type manner reported so far. Moreover, with this new procedure, the synthesis of even longer ribbons now seems feasible. Another advantage of the structures presented here is the good solubility of the ribbons **3a–10a**, independent of their length.

Conformational behaviour: The all-*syn* conformation of the diaza[3.3]metacyclophane subunits leads to a stacked structure[13] for all molecular ribbons in this series. This structure has been confirmed by ^{1}H NMR spectroscopy in solution (**3a–10a**) and by single-crystal X-ray analyses in the solid state (**3a–7a**).[7, 9] These data indicate that *syn* arrangements of the repeating units occur in each case such that the benzene rings align themselves on top of, and approximately parallel to, each other (Fig. 3). In this all-*syn* conformation the molecules **9a** and **10a** have lengths of approximately 2.4 and 2.7 nm, respectively.[14] The ability of the molecular ribbons to form a stacked structure of nanometre size in the solid state could be of importance in crystal engineering[15] and nanochemistry.[1]

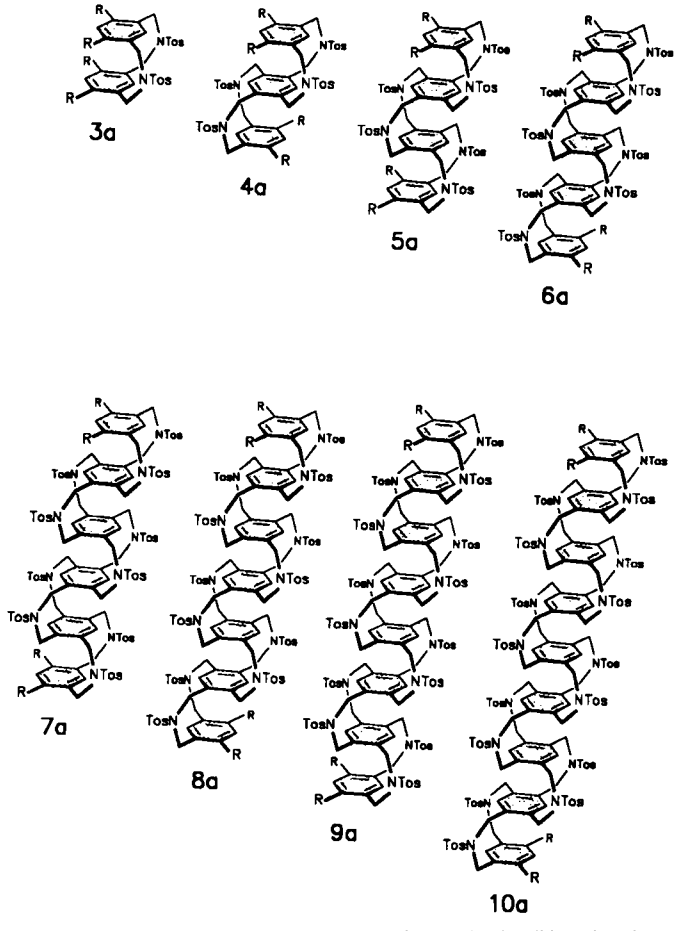


Fig. 3. Stacked structures (schematic drawing) of the molecular ribbons based on single-crystal X-ray analyses (**3a–7a**) and ^{1}H NMR spectroscopy (**3a–10a**) (R = CO_2Et).

Nomenclature suggestions: The long linear ribbon molecules lead to complicated and confusing names even in phane nomenclature.[16] We here propose a shorter and clearer system for naming the molecular ribbons. For example, **10a** according to conventional phane nomenclature is named 5,7,95,97-tetrakis-(ethoxycarbonyl)-2,11,20,29,32,41,44,53,56,65,68,77,80,89,92,101-hexadecakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,-53,56,65,68,77,80,89,92,101-hexadecaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<9>phane. As the components in the middle part of the molecules are listed repeatedly, we propose to put the repeating sequences in braces and use a multiplier to indicate the number of repititions. Moreover, the tosyl substituents and the nitrogen atoms can be combined, so that the numbering does not occur twice. According to this new convention **10a** has the shorter name of 5,7,95,97-tetrakis(ethoxycarbonyl)-2,11,20,29,32,41,44,53,56,65,68,77,80,89,92,101-hexadecakis[(*N*-4-tolylsulfonyl)aza][3.3](1,3)(1,3){[3.3](4,6)(1,3)}$_7$-benzeno<9>phane.

Conclusions

The synthetic strategy presented here demonstrates a general route to a new class of molecular ribbons. The repetitive reaction sequence yields oligomers of perfectly uniform structure, in contrast to polymerisation reactions which always result in a mixture of oligomers and polymers.

The tosyl groups can be replaced[17] by other substituents to initiate host/guest interactions. In addition, methods are known, and have already been demonstrated on shorter diaza[3.3]cyclophanes, for the extrusion of the nitrogen atoms[18] to yield the corresponding hydrocarbon ribbons. Other possible extensions of our versatile method include the use of other building blocks. For example, replacement of the benzene rings by biphenyl units would increase the breadth of ribbon molecules. The synthesis of even longer strings is feasible by repeated use of the three-step reaction cycle.

Experimental Section

General techniques: All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium benzophenone, trichloromethane ($CHCl_3$) and *N*,*N*-dimethylformamide (DMF) were dried over molecular sieve 4 Å. Yields refer to chromatographically and spectroscopically homogeneous materials.

Diethyl 2,4-bis(bromomethyl)benzene-1,5-dicarboxylate (**11**) [7a], benzyl *N*-(4-tolylsulfonyl)carbamate (**12**) [10], 5,7,14,16-tetrakis(ethoxycarbonyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]metacylophane (**3a**) [7a] and 5,7,23,25-tetrakis-(ethoxycarbonyl)-2,11,20,29-tetrakis(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3](1,3)-(1,3)[3.3](4,6)(1,3)benzeno<3>phane (**4a**) [7b] were prepared according to published procedures.

All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates ($60\ F_{254}$) with UV light (λ = 254 nm) as visualising agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for column chromatography. Melting points were determined on a Kofler microscope heater (Reichert, Wien, Austria) and are not corrected. Elemental analyses were performed in the microanalytical department at the Institut für Organische Chemie und Biochemie, University of Bonn. NMR spectra were recorded at ambient temperature on Bruker AM-250 or AM-400 instruments and calibrated with the residual undeuterated solvent as the internal reference. The following abbreviations were used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. Mass spectra were recorded on a Kratos Concept 1H (FAB) or a Kratos Kompact MALDI 3 (MALDI-TOF). The matrices used were *m*-nitrobenzyl alcohol or 9-nitroanthracene.

Diethyl 2,4-bis[*N*-benzyloxycarbonyl-*N*-(4-tolylsulfonyl)aminomethyl]benzene-1,5-dicarboxylate (13): A suspension of **11** [7a] (2.04 g, 5.0 mmol), **12** [10] (3.66 g, 12.0 mmol) and K_2CO_3 (5.53 g, 40.0 mmol) in DMF (300 mL) was stirred at room temperature for 72 h. The solvent was evaporated in vacuo, and the remaining residue treated with dichloromethane. The undissolved components were removed by filtration, and the filtrate was washed with water, dried (Na_2SO_4), filtered, and concentrated in vacuo to give a crude oil, which was recrystallised from methanol to give 2.18 g (51%) of **13** as colourless crystals: M.p. 152 °C; R_f = 0.51 (silica, $CHCl_3$:acetone 100:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.42 (t, ^3J = 7 Hz, 6H; CH_2CH_3), 2.38 (s, 6H; Tos-CH_3), 4.40 (q, ^3J = 7 Hz, 4H; OCH_2CH_3), 5.15 (s, 4H; OCH_2), 5.55 (s, 4H; NCH_2), 7.12–7.31 (m, 10H; ArH), 7.14 (d, ^3J = 8 Hz, 4H; Tos-H), 7.67 (d, ^3J = 8 Hz, 4H; Tos-H), 7.89 (s, 1H; ArH), 8.63 (s, 1H; ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.35 ($2CH_2CH_3$), 21.66 (2Tos-CH_3), 49.49 ($2NCH_2$), 61.39 ($2OCH_2CH_3$), 69.46 ($2OCH_2Ph$), 125.77 (CH), 127.11 (2Cq),

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128.31 (2CH), 128.36 (4CH), 128.45 (4CH), 128.66 (4CH), 129.29 (4CH), 133.66 (CH), 134.86 (2Cq), 136.45 (2Cq), 144.17 (2Cq), 144.45 (2Cq), 152.25 (2CO), 166.07 (2CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 857.2 (42) $[M+H]^+$, 811.2 (10) $[M-OEt]^+$, 701.2 (16) $[M-Tos]^+$; $C_{44}H_{44}N_2O_{12}S_2$ (856.96): calcd C 61.67, H 5.18, N 3.27; found C 61.21, H 5.36, N 3.42.

Diethyl 2,4-bis[(4-tolylsulfonylamino)methyl]benzene-1,5-dicarboxylate (14): A suspension of **13** (4.28 g, 5.0 mmol) and 10% palladium on carbon (428 mg, 10 wt%) in $CHCl_3$/methanol (1:1, 200 mL) was stirred for 8 h under a hydrogen atmosphere (3.5 bar) at room temperature. The suspension was filtered through Celite and the filtrate evaporated in vacuo to give a yellowy oil. Purification by column chromatography (silica, $CHCl_3$:acetone, 20:1) gave 2.94 g (98%) of **14** as colourless crystals: M.p. 126 °C; $R_f = 0.33$ (silica, $CHCl_3$:acetone 20:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.36$ (t, $^3J = 7$ Hz, 6H; CH_2CH_3), 2.36 (s, 6H; Tos-CH_3), 4.28 (d, $^3J = 7$ Hz, 4H; NCH_2), 4.34 (q, $^3J = 7$ Hz, 4H; OCH_2CH_3), 5.87 (t, $^3J = 7$ Hz, 2H; NH), 7.20 (d, $^3J = 8$ Hz, 4H; Tos-H), 7.28 (s, 1H; ArH), 7.65 (d, $^3J = 8$ Hz, 4H; Tos-H), 8.34 (s, 1H; ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 14.25$ ($2CH_2CH_3$), 21.50 (2 Tos-CH_3), 46.10 ($2NCH_2$), 61.88 ($2OCH_2CH_3$), 127.04 (4CH), 128.49 (2Cq), 129.67 (4CH), 133.61 (CH), 133.72 (CH), 137.47 (2Cq), 142.74 (2Cq), 143.31 (2Cq), 166.13 (2CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 589.2 (74) $[M+H]^+$, 543.1 (28) $[M-OEt]^+$, 433.1 (42) $[M-Tos]^+$; $C_{28}H_{32}N_2O_8S_2$ (588.69): calcd C 57.13, H 5.48, N 4.76; found C 56.88, H 5.54, N 4.89.

General procedure for ester reduction of 3a–8a and transformation into the corresponding tetrakis(bromomethyl) compounds 3c–8c: A stirred supension of the tetraester (**3a–8a**) and lithium borohydride in dry THF was refluxed for 6 h. The cooled mixture was evaporated in vacuo. Water (100 mL) was added to the remaining residue, and the suspension obtained was stirred for 30 min at room temperature to dissolve the inorganic salts while the corresponding tetraalcohols remained undissolved. The tetraalcohols **3b–8b** were filtered, washed with water, and dried in vacuo at 50 °C. The alcohols were used without further purification.
PBr_3 was added over 2 h to a stirred suspension of the tetraalcohol (**3b–8b**) in dry $CHCl_3$. The mixture was then stirred and heated for a period, which is given below. The cooled mixture was poured into ice-water and stirred for 1 h. The organic layer was separated, washed three times with $NaHCO_3$ solution, dried (Na_2SO_4), filtered, and evaporated in vacuo. The crude tetrabromides **3c–8c** were purified by column chromatography on silica gel. The eluents are given below.

5,7,14,16-Tetrakis(hydroxymethyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]metacyclophane (3b): **3a** (5.10 g, 6.1 mmol), $LiBH_4$ (1.9 g, 87 mmol), THF (300 mL). Yield: 3.91 g (96%) of **3b** as a colourless substance. Analytical data correspond to those published in the literature [7a].

5,7,14,16-Tetrakis(bromomethyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3]metacyclophane (3c): **3b** (3.91 g, 5.86 mmol), PBr_3 (15 mL, 155 mmol), $CHCl_3$ (300 mL), 110 h RT. Recrystallisation from benzene gave 4.72 g (88%) of **3c** as colourless crystals. Analytical data correspond to those published in the literature [7a].

5,7,23,25-Tetrakis(hydroxymethyl)-2,11,20,29-tetrakis-(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)-benzeno<3>phane (4b): Ester **4a** (650 mg, 0.50 mmol), $LiBH_4$ (270 mg, 12.4 mmol), THF (100 mL). Yield: 545 mg (96%) of **4b** as a colourless substance. Analytical data correspond to those published in the literature [7b].

5,7,23,25-Tetrakis(bromomethyl)-2,11,20,29-tetrakis-(4-tolylsulfonyl)-2,11,20,29-tetraaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)-benzeno<3>phane (4c): Alcohol **4b** (545 mg, 0.48 mmol), PBr_3 (6 mL, 62 mmol), $CHCl_3$ (200 mL), 12 h reflux. Eluent: dichloromethane. Yield: 572 mg (86%) of **4c** as a colourless substance. $R_f = 0.33$ (silica, dichloromethane). Analytical data correspond to those published in the literature [7b].

5,7,35,37-Tetrakis(hydroxymethyl)-2,11,20,29,32,41-hexakis-(4-tolylsulfonyl)-2,11,20,29,32,41-hexaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)-benzeno<4>phane (5b): **5a** (2.06 g, 1.16 mmol), $LiBH_4$ (1.9 g, 87 mmol), THF (380 mL). Yield: 1.79 g (96%) of **5b** as a colourless substance. M.p. 206 °C; $R_f = 0.41$ (silica, $CHCl_3$:methanol 10:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.45$ (s, 6H; Tos-CH_3), 2.47 (s, 12H; Tos-CH_3), 2.9–5.3 (br, 32H; $ArCH_2$), 6.37 (s, 2H; ArH), 6.61 (s, 2H; ArH), 6.69 (s, 2H; ArH), 6.89 (s, 2H; ArH), 7.29–7.49 (br, 12H; Tos-H), 7.65–7.88 (br, 12H; Tos-H); MS (FAB nitrobenzyl alcohol): *m/z* (%): 1603.3 (<1) $[M+H]^+$, 1448.3 (1) $[M-Tos]^+$; $C_{82}H_{86}N_6O_{16}S_6$ (1603.97)·$3H_2O$: calcd C 59.40, H 5.59, N 5.07; found C 59.10, H 5.13, N 5.12.

5,7,35,37-Tetrakis(bromomethyl)-2,11,20,29,32,41-hexakis(4-tolylsulfonyl)-2,11,20,29,32,41-hexaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<4>phane (5c): **5b** (1.79 g, 1.12 mmol), PBr_3 (12 mL, 124 mmol), $CHCl_3$ (300 mL), 18 h RT, 4 h reflux. Eluent: $CHCl_3$:acetone 20:1. Yield: 1.26 g (61%) of **5c** as a colourless substance. M.p. 199 °C; $R_f = 0.44$ ($CHCl_3$:acetone 20:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.47$ (s, 12H; Tos-CH_3), 2.49 (s, 6H; Tos-CH_3), 2.8–5.3 (br, 32H; $ArCH_2$), 6.38 (s, 2H; ArH), 6.77 (s, 2H; ArH), 6.80 (s, 2H; ArH), 6.99 (s, 2H; ArH), 7.33–7.51 (br, 12H; Tos-H), 7.61–7.77 (br, 4H; Tos-H), 7.82 (d, $^3J = 8$ Hz, 8H; Tos-H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 21.70$ (2 Tos-CH_3), 21.74 (4 Tos-CH_3), 29.38 ($4CH_2Br$), 49.44 (br, $ArCH_2N$), 53.51 (br, $ArCH_2N$), 127.23 (CH), 127.56 (CH), 130.35 (CH), 131.62 (Cq), 132.43 (CH), 133.16 (br, Cq), 136.39 (CH), 136.58 (CH), 144.06 (br, Cq); MS (FAB nitrobenzyl alcohol): *m/z* (%): 1879.1 (40) $[M+Na]^+$, 1855.0 (45) $[M+H]^+$, 1701.0 (41) $[M-Tos]^+$; $C_{82}H_{82}Br_4N_6O_{12}S_6$ (1855.56)·$3H_2O$: calcd C 51.58, H 4.64, N 4.40; found C 51.57, H 4.38, N 4.67.

5,7,47,49-Tetrakis(hydroxymethyl)-2,11,20,29,32,41,44,53-octakis-(4-tolylsulfonyl)-2,11,20,29,32,41,44,53-octaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<5>phane (6b): **6a** (950 mg, 0.424 mmol), $LiBH_4$ (600 mg, 27.27 mmol), THF (150 mL). Yield: 844 mg (96%) of **6b** as a colourless substance. M.p. >300 °C; $R_f = 0.34$ (silica, $CHCl_3$:methanol 10:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.48$ (s, 24H; Tos-CH_3), 3.75 (t, $^3J = 5$ Hz, 4H; OH); 4.0–5.3 (br, 40H; $ArCH_2$), 6.23 (s, 2H; ArH), 6.26 (s, 2H; ArH), 6.53 (s, 2H; ArH), 6.71 (s, 2H; ArH), 6.89 (s, 2H; ArH), 7.42 (d, $^3J = 8$ Hz, 16H; Tos-H), 7.74 (d, $^3J = 8$ Hz, 16H; Tos-H); MS (FAB nitrobenzyl alcohol): *m/z* (%): 2078.6 (100) $[M+Li]^+$, 1917.6 (90) $[M-Tos]^+$; $C_{106}H_{110}N_8O_{20}S_8$ (2072.56).

5,7,47,49-Tetrakis(bromomethyl)-2,11,20,29,32,41,44,53-octakis-(4-tolylsulfonyl)-2,11,20,29,32,41,44,53-octaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<5>phane (6c): **6b** (194 mg, 0.093 mmol), PBr_3 (20 mL, 207 mmol), $CHCl_3$ (300 mL), 12 h reflux. Eluent: CH_2Cl_2:acetone 20:1. Yield: 159 mg (73%) of **6c** as a colourless substance. M.p. >300 °C; $R_f = 0.53$ (CH_2Cl_2:acetone 15:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.48$ (s, 24H; Tos-CH_3), 3.8–5.0 (br, 40H; $ArCH_2$), 6.22 (s, 2H; ArH), 6.30 (s, 2H; ArH), 6.56 (s, 2H; ArH), 6.77 (s, 2H; ArH), 6.83 (s, 2H; ArH), 7.41 (d, $^3J = 8$ Hz, 16H; Tos-H), 7.75 (d, $^3J = 8$ Hz, 16H; Tos-H); MS (FAB nitrobenzyl alcohol): *m/z* (%): 2325.0 (100) $[M+H]^+$, 2167.0 (69) $[M-Tos]^+$; $C_{106}H_{106}Br_4N_8O_{16}S_8$ (2324.05)·$2CH_2Cl_2$: calcd C 52.01, H 4.45, N 4.49; found C 52.00, H 4.46, N 4.68.

5,7,59,61-Tetrakis(hydroxymethyl)-2,11,20,29,32,41,44,53,56,65-decakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65-decaaza-[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)-[3.3](4,6)(1,3)benzeno<6>phane (7b): **7a** (364 mg, 0.13 mmol), $LiBH_4$ (800 mg, 36.7 mmol), THF (200 mL). Yield: 327 mg (96%) of **7b** as a colourless substance. M.p. 247 °C; $R_f = 0.38$ (silica, $CHCl_3$:methanol 10:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.47$ (s, 30H; Tos-CH_3), 2.8–5.3 (br, 48H; $ArCH_2$), 6.09 (s, 2H; ArH), 6.10 (s, 2H; ArH), 6.20 (s, 2H; ArH), 6.49 (s, 2H; ArH), 6.70 (s, 2H; ArH), 6.87 (s, 2H; ArH), 7.41 (d, br, 20H; Tos-H), 7.74 (d, br, 20H; Tos-H); MS (FAB nitrobenzyl alcohol): *m/z* (%): 2563.8 (1) $[M+Na]^+$, 2407.8 (<1) $[M+Na-Tos]^+$, 2253.7 (<1) $[M+Na-2Tos]^+$, 2096.7 (<1) $[M+Na-3Tos]^+$; $C_{130}H_{134}N_{10}O_{24}S_{10}$ (2541.14).

5,7,59,61-Tetrakis(bromomethyl)-2,11,20,29,32,41,44,53,56,65-decakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65-decaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<6>phane (7c): **7b** (327 mg, 0.13 mmol), PBr_3 (5 mL, 52 mmol), $CHCl_3$ (180 mL), 18 h RT, 4 h reflux. Eluent: $CHCl_3$:acetone 30:1. Yield: 140 mg (39%) of **7c** as a colourless substance. M.p. 224 °C; $R_f = 0.22$ ($CHCl_3$:acetone 30:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.47$ (s, 30H; Tos-CH_3), 2.7–5.2 (br, 48H; $ArCH_2$), 6.10 (s, 2H; ArH), 6.14 (s, 2H; ArH), 6.23 (s, 2H; ArH), 6.63 (s, 2H; ArH), 6.76 (s, 2H; ArH), 6.88 (s, 2H; ArH), 7.32–7.48 (3d, 20H; Tos-H), 7.58–7.85 (2d, 12H; Tos-H), 7.77 (d, $^3J = 8$ Hz, 8H; Tos-H); ^{13}C NMR (62.89 MHz, CD_2Cl_2): $\delta = 21.63$ (Tos-CH_3), 21.66 (Tos-CH_3), 29.81 (CH_2Br), 49.45 (br, $ArCH_2N$), 127.50 (br, CH), 130.47 (CH), 131.63 (Cq), 132.42 (CH), 133.74 (br, Cq), 136.02 (CH), 136.15 (CH), 136.64 (CH), 144.42 (br, Cq); MS (FAB nitrobenzyl alcohol): *m/z* (%): 2815.3 (17) $[M+Na]^+$, 2793.2 (100) $[M+H]^+$, 2637.2 (99) $[M-Tos]^+$; $C_{130}H_{130}Br_4N_{10}O_{20}S_{10}$ (2792.73).

5,7,71,73-Tetrakis(hydroxymethyl)-2,11,20,29,32,41,44,53,56,65,68,77-dodecakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65,68,77-dodecaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<7>phane (8b): **8a** (193 mg, 0.061 mmol), $LiBH_4$ (540 mg, 24.80 mmol), THF (60 mL). Yield: 176 mg (96%) of **8b** as a colourless substance. M.p. >300 °C; $R_f = 0.21$ (silica, $CHCl_3$:methanol 10:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.48$ (s, 36H; Tos-CH_3), 3.73 (t, $^3J = 5$ Hz, 4H; OH); 3.8–5.3 (br, 56H; $ArCH_2$), 5.91 (s, 2H; ArH), 5.98 (s, 2H; ArH), 6.04 (s, 2H; ArH), 6.47 (s, 2H; ArH), 6.68 (s, 2H; ArH), 6.86 (s, 2H; ArH), 7.03 (s, 2H; ArH), 7.24–7.48 (br, 24H; Tos-H), 7.59–7.88 (br, 24H; Tos-H); MS (FAB nitrobenzyl alcohol): *m/z* (%): 3140.9 (100) $[M+Cs]^+$, 2988.4 (79) $[M+Cs-Tos]^+$; $C_{154}H_{158}N_{12}O_{28}S_{12}$ (3009.73).

5,7,71,73-Tetrakis(bromomethyl)-2,11,20,29,32,41,44,53,56,65,68,77-dodecakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65,68,77-dodecaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<7>phane (8c): **8b** (180 mg, 0.060 mmol), PBr_3 (10 mL, 104 mmol), $CHCl_3$ (100 mL), 12 h reflux. Eluent: $CHCl_3$:acetone 15:1. Yield: 83 mg (42%) of **8c** as a colourless substance. M.p. >300 °C; $R_f = 0.43$ ($CHCl_3$:acetone 15:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.47$ (s, 36H; Tos-CH_3), 3.5–5.2 (br, 56H; $ArCH_2$), 6.05 (s, 4H; ArH), 6.07 (s, 2H; ArH), 6.21 (s, 2H; ArH), 6.61 (s, 2H; ArH), 6.76 (s, 2H; ArH), 6.86 (s, 2H; ArH), 7.40 (d, $^3J = 8$ Hz, 24H; Tos-H), 7.76 (d, $^3J = 8$ Hz, 24H; Tos-H); MS (FAB nitrobenzyl alcohol): *m/z* (%): 3263.5 (46) $[M+H]^+$, 3105.3 (100) $[M-Tos]^+$; $C_{154}H_{154}Br_4N_{12}O_{24}S_{12}$ (3261.32).

General procedure for the cyclisation of 14 with tetrakis(bromomethyl) compounds 3c–8c to give molecular ribbons 5a–10a: The tetrakis(bromomethyl) compound (**3c–8c**) and the key building block **14** were each dissolved in 50 mL of DMF. This solutions were added dropwise and simultaneously over a period of 50 h to a stirred suspension of K_2CO_3 in DMF. The mixture was then stirred for a further 12 h. The solvent was evaporated in vacuo, and the residue treated with $CHCl_3$/water (400 mL, 1:1). The organic layer was separated, washed three times with brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude tetraesters **5a–10a** were purified by column chromatography on silica gel. The eluents are given below.

5,7,35,37-Tetrakis(ethoxycarbonyl)-2,11,20,29,32,41-hexakis-(4-tolylsulfonyl)-2,11,20,29,32,41-hexaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<4>phane (5a, cf. [7b]): Solutions: **3c** (1.25 g, 1.36 mmol) in DMF (50 mL), **14** (1.60 g, 2.72 mmol) in DMF (50 mL). Suspension: K_2CO_3 (3.00 g, 21.7 mmol) in DMF (200 mL). Eluent: CH_2Cl_2:ethyl acetate 10:1. Yield: 1.13 g (47%) of **5a** as colourless cyrstals. M.p. 275 °C; $R_f = 0.28$ (silica, CH_2Cl_2:ethyl acetate 10:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.30$ (t, $^3J = 7$ Hz, 12H; CH_2CH_3), 2.47 (s, 12H; Tos-CH_3), 2.48 (s, 6H; Tos-CH_3), 3.6–5.0 (br, 24H; $ArCH_2N$), 4.29 (q, $^3J = 7$ Hz, 8H; OCH_2CH_3), 6.31 (s, 2H; ArH), 6.76 (s, 2H; ArH), 7.28 (s, 2H; ArH), 7.39 (d, $^3J = 8$ Hz, 4H; Tos-H), 7.41 (d, $^3J = 8$ Hz, 8H; Tos-H), 7.53 (s, 2H; ArH), 7.71 (d, $^3J = 8$ Hz, 4H; Tos-H), 7.85 (d, $^3J = 8$ Hz, 8H; Tos-H); ^{13}C NMR (62.89 MHz, CD_2Cl_2): $\delta = 14.17$ (CH_2CH_3), 21.57 (Tos-CH_3), 21.63 (Tos-CH_3), 51.12 (br, $ArCH_2N$), 61.86 (OCH_2CH_3), 127.44 (CH), 127.69 (CH), 129.01 (Cq), 130.26 (CH), 130.47 (CH), 131.13 (CH), 131.61 (Cq), 132.99 (Cq), 134.71 (Cq), 135.53 (Cq), 135.99 (CH), 136.35 (CH), 136.47 (CH), 139.11 (Cq), 144.36 (Cq), 144.44 (Cq), 166.55 (CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 1904.2 (100) $[M+Cs]^+$, 1772.3 (35) $[M+H]^+$, 1616.3 (39) $[M - Tos]^+$, 1461.3 (11) $[M - 2Tos]^+$; $C_{90}H_{94}N_6O_{20}S_6$ (1772.12)·DMF: calcd *C* 60.54, H 5.52, N 5.31; found C 60.64, H 5.22, N 5.52.

5,7,47,49-Tetrakis(ethoxycarbonyl)-2,11,20,29,32,41,44,53-octakis-(4-tolylsulfonyl)-2,11,20,29,32,41,44,53-octaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<5>phane (6a): Solutions: **4c** (1.04 g, 0.75 mmol) in DMF (50 mL), **14** (0.89 g, 1.52 mmol) in DMF (50 mL). Suspension: K_2CO_3 (4.18 g, 30.0 mmol) in DMF (400 mL). Eluent: $CHCl_3$:acetone 15:1. Yield: 1.22 g (36%) of **6a** as colourless cyrstals. M.p. > 300 °C; $R_f = 0.45$ (silica, $CHCl_3$:acetone 15:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.28$ (t, $^3J = 7$ Hz, 12H; CH_2CH_3), 2.47 (s, 12H; Tos-CH_3), 2.48 (s, 12H; Tos-CH_3), 3.5–5.1 (br, 32H; $ArCH_2N$), 4.27 (q, $^3J = 7$ Hz, 8H; OCH_2CH_3), 6.17 (s, 2H; ArH), 6.26 (s, 2H; ArH), 6.72 (s, 2H; ArH), 7.31 (s, 2H; ArH), 7.36 (d, $^3J = 8$ Hz, 8H; Tos-H), 7.38 (d, $^3J = 8$ Hz, 8H; Tos-H), 7.54 (s, 2H; ArH), 7.76 (d, $^3J = 8$ Hz, 8H; Tos-H), 7.79 (d, $^3J = 8$ Hz, 8H; Tos-H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 14.15$ (CH_2CH_3), 21.64 (Tos-CH_3), 50.57 (br, $ArCH_2N$), 61.52 (OCH_2CH_3), 127.39 (CH), 127.57 (CH), 130.15 (CH), 130.22 (CH), 131.17 (CH), 132.09 (Cq), 135.17 (CH), 135.79 (CH), 136.02 (CH), 136.64 (CH), 138.78 (Cq), 143.77 (Cq), 166.15 (CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 2262.6 (37) $[M+Na]^+$, 2240.7 (78) $[M+H]^+$, 2085.6 (100) $[M - Tos]^+$, 1929.6 (22) $[M - 2Tos]^+$; MS (MALDI-TOF 9-nitroanthracene): *m/z* (%): 2278.5 (71) $[M+K]^+$, 2242.2 (44) $[M+H]^+$, 2085.8 (70) $[M - Tos]^+$: $C_{114}H_{118}N_8O_{24}S_8$ (2240.71)·2 H_2O: calcd C 60.14, H 5.40, N 4.92; found *C* 59.88, H 5.48, N 5.06.

5,7,59,61-Tetrakis(ethoxycarbonyl)-2,11,20,29,32,41,44,53,56,65-decakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65-decaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<6>phane (7a): Solutions: **5c** (500 mg, 0.27 mmol) in DMF (50 mL), **14** (317 mg, 0.54 mmol) in DMF (50 mL). Suspension: K_2CO_3 (1.00 g, 7.2 mmol) in DMF (200 mL). Eluent: CH_2Cl_2:acetone 20:1. Yield: 306 mg (42%) of **7a** as colourless cyrstals. M.p. > 300 °C; $R_f = 0.52$ (silica, CH_2Cl_2:acetone 20:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (t, $^3J = 7$ Hz, 12H; CH_2CH_3), 2.47 (s, 30H; Tos-CH_3), 3.4–5.1 (br, 40H; $ArCH_2N$), 4.27 (q, $^3J = 7$ Hz, 8H; OCH_2CH_3), 6.04 (s, 2H; ArH), 6.08 (s, 2H; ArH), 6.22 (s, 2H; ArH), 6.69 (s, 2H; ArH), 7.27 (s, 2H; ArH), 7.36 (d, $^3J = 8$ Hz, 8H; Tos-H), 7.38 (d, $^3J = 8$ Hz, 8H; Tos-H), 7.39 (d, $^3J = 8$ Hz, 4H; Tos-H), 7.53 (s, 2H; ArH), 7.70 (d, $^3J = 8$ Hz, 8H; Tos-H), 7.80 (d, $^3J = 8$ Hz, 12H; Tos-H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 14.19$ (CH_2CH_3), 21.71 (Tos-CH_3), 50.26 (br, $ArCH_2N$), 53.87 (br, $ArCH_2N$), 61.57 (OCH_2CH_3), 127.43 (CH), 127.61 (CH), 129.05 (br, Cq), 130.16 (CH), 130.27 (CH), 131.22 (CH), 132.11 (br, Cq), 133.8–136.7 (br, CH, Cq), 135.59 (CH), 136.02 (CH), 137.07 (CH), 138.86 (br, Cq), 143.78 (br, Cq), 166.24 (CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 2731.6 (26) $[M+Na]^+$, 2709.5 (73) $[M+H]^+$, 2553.6 (100) $[M - Tos]^+$, 2398.5 (40) $[M - 2Tos]^+$, 2243.5 (14) $[M - 3Tos]^+$; $C_{138}H_{142}N_{10}O_{28}S_{10}$ (2709.29)·3 CH_2Cl_2: calcd C 57.14, H 5.03, N 4.73; found C 57.47, H 5.06, N 4.58.

5,7,71,73-Tetrakis(ethoxycarbonyl)-2,11,20,29,32,41,44,53,56,65,68,77-dodecakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65,68,77-dodecaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<7>phane (8a): Solutions: **6c** (600 mg, 0.26 mmol) in DMF (50 mL), **14** (304 mg, 0.52 mmol) in DMF (50 mL). Suspension: K_2CO_3 (1.5 g, 11.0 mmol) in DMF (250 mL). Eluent: $CHCl_3$:acetone 15:1. Yield: 413 mg (50%) of **8a** as colourless cyrstals. M.p. > 300 °C; $R_f = 0.35$ (silica, $CHCl_3$:acetone 15:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (t, $^3J = 7$ Hz, 12H; CH_2CH_3), 2.47 (s, 36H; Tos-CH_3), 3.5–5.1 (br, 48H; $ArCH_2N$), 4.27 (q, $^3J = 7$ Hz, 8H; OCH_2CH_3), 5.96 (s, 2H; ArH), 5.99 (s, 2H; ArH), 6.05 (s, 2H; ArH), 6.22 (s, 2H; ArH), 6.68 (s, 2H; ArH), 7.24 (s, 2H; ArH), 7.38 (d, $^3J = 8$ Hz, 24H; Tos-H), 7.53 (s, 2H; ArH), 7.80 (d, $^3J = 8$ Hz, 24H; Tos-H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 14.17$ (CH_2CH_3), 21.69 (Tos-CH_3), 47.0–58.0 (br, $ArCH_2N$), 61.57 (OCH_2CH_3), 126.93 (Cq), 127.45 (CH), 127.55 (CH), 128.20 (Cq), 129.59 (CH), 129.94 (CH), 130.16 (Cq), 130.24 (CH), 131.22 (Cq), 135.07 (Cq), 135.26 (Cq), 135.69 (Cq), 136.00 (CH), 136.96 (CH), 138.83 (CH), 143.74 (Cq), 166.20 (CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 3178.7 (95) $[M+H]^+$, 3022.6 (100) $[M - Tos]^+$, 2867.6 (50) $[M - 2Tos]^+$; MS (MALDI-TOF 9-nitroanthracene): *m/z* (%): 3217.4 (52) $[M+K]^+$, 3179.6 (44) $[M+H]^+$, 3024.3 (74) $[M - Tos]^+$; $C_{162}H_{166}N_{12}O_{32}S_{12}$ (3177.88)·H_2O: calcd *C* 60.88, H 5.30, N 5.26; found C 60.15, H 5.56, N 4.87.

5,7,83,85-Tetrakis(ethoxycarbonyl)-2,11,20,29,32,41,44,53,56,65,68,77,80,89-tetradecakis(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65,68,77,80,89-tetradecaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<8>phane (9a): Solutions: **7c** (115.8 mg, 0.042 mmol) in DMF (50 mL), **14** (48.9 mg, 0.084 mmol) in DMF (50 mL). Suspension: K_2CO_3 (250 mg, 1.8 mmol) in DMF (200 mL). Eluent: $CHCl_3$:acetone 20:1. Yield: 25.7 mg (17%) of **9a** as colourless cyrstals. M.p. > 300 °C; $R_f = 0.09$ (silica, $CHCl_3$:acetone 20:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.26$ (t, $^3J = 7$ Hz, 12H; CH_2CH_3), 2.46 (s, 42H; Tos-CH_3), 3.4–5.1 (br, 56H; $ArCH_2N$), 4.26 (q, $^3J = 7$ Hz, 8H; OCH_2CH_3), 5.90 (s, 2H; ArH), 5.92 (s, 2H; ArH), 5.95 (s, 2H; ArH), 6.06 (s, 2H; ArH), 6.24 (s, 2H; ArH), 6.66 (s, 2H; ArH), 7.30–7.45 (m, 28H; Tos-H), 7.38 (s, 2H; ArH), 7.52 (s, 2H; ArH), 7.60–7.85 (m, 28H; Tos-H); ^{13}C NMR (62.89 MHz, CD_2Cl_2): $\delta = 14.18$ (CH_2CH_3), 21.66 (Tos-CH_3), 49.83 (br, $ArCH_2N$), 61.84 (OCH_2CH_3), 127.66 (CH), 128.42 (CH), 129.5–132.0 (br), 130.10 (CH), 130.44 (CH), 131.17 (CH), 135.84 (br), 144.28 (br, Cq), 166.36 (CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 3671.3 (100) $[M+Na]^+$, 3647.2 (58) $[M+H]^+$, 3514.3 (37) $[M+Na - Tos]^+$, 3490.7 (43) $[M - Tos]^+$; $C_{186}H_{190}N_{14}O_{36}S_{14}$ (3646.46).

5,7,95,97-Tetrakis(ethoxycarbonyl)-2,11,20,29,32,41,44,53,56,65,68,77,80,89,92,101-hexadecakis-(4-tolylsulfonyl)-2,11,20,29,32,41,44,53,56,65,68,77,80,89,92,101-hexadecaaza[3.3](1,3)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)[3.3](4,6)(1,3)benzeno<9>phane (10a): Solutions: **8c** (106 mg, 0.032 mmol) in DMF (50 mL), **14** (38 mg, 0.064 mmol) in DMF (50 mL). Suspension: K_2CO_3 (1.0 g, 7.1 mmol) in DMF (250 mL). Eluent: $CHCl_3$:acetone 20:1. Yield: 18 mg (14%) of **10a** as colourless cyrstals. M.p. > 300 °C; $R_f = 0.32$ (silica, $CHCl_3$:acetone 20:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.28$ (t, $^3J = 7$ Hz, 12H; CH_2CH_3), 2.46 (s, 48H; Tos-CH_3), 3.2–5.2 (br, 64H; $ArCH_2N$), 4.25 (q, $^3J = 7$ Hz, 8H; OCH_2CH_3), 5.83 (s, 2H; ArH), 5.87 (s, 2H; ArH), 5.91 (s, 2H; ArH), 6.09 (s, 2H; ArH), 6.26 (s, 2H; ArH), 6.57 (s, 2H; ArH), 6.65 (s, 2H; ArH), 7.36 (s, 2H; ArH), 7.38 (d, $^3J = 8$ Hz, 32H; Tos-H), 7.51 (s, 2H; ArH), 7.80 (d, $^3J = 8$ Hz, 32H; Tos-H); ^{13}C NMR (62.89 MHz, $CDCl_3$): $\delta = 14.20$ (CH_2CH_3), 21.73 (Tos-CH_3), 49.48 (br, $ArCH_2N$), 61.62 (OCH_2CH_3), 127.1–127.9 (br, CH), 130.28 (CH), 130.5–131.8 (br), 134.6–136.7 (br, CH), 143.2–144.4 (br, Cq), 166.23 (CO); MS (FAB nitrobenzyl alcohol): *m/z* (%): 4113.4 (<1) $[M+H]^+$, 3960.2 (<1) $[M - Tos]^+$; MS (MALDI-TOF 9-nitroanthracene): *m/z* (%): 4118.1 (79) $[M+H]^+$, 3960.1 (100) $[M - Tos]^+$; $C_{210}H_{214}N_{16}O_{40}S_{16}$ (4115.05).

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