Broad Molecular Ribbons of Nanometer Size Composed of Biphenyl Units

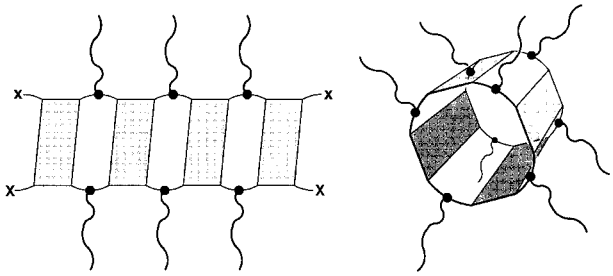
Wolfgang Boomgaarden,[a] Fritz Vögtle,*[a] Martin Nieger,[b] and Heike Hupfer[b]

Abstract: The new tetrafunctionalized biphenyl key building blocks **16** and **39** led, for the first time, to the hitherto broadest molecular ribbons that contain biphenyl units in a transverse arrangement by iterative synthetic methods. The length and breadth of the molecular ribbons, as single chemical entities, are diversified. They can be used as cyclization precursors in the synthesis of long molecular tubes of type **2** with a large diameter. The solubility and the host–guest behavior (clathrate formation with benzene, dimethylformamide, and dichloromethane) of these nanometer-size molecular ribbons were optimized by the introduction of various side chains (benzenesulfonamide, 4-toluenesulfonamide, and 4-*tert*-butylbenzenesulfonamide groups) into the skeleton of the ribbons. New 14-, 15-, and 16-membered model ring systems (compounds **20a**, **22a**, and **24** respectively) were synthesized in order to examine the constitution of the 16-membered diaza[3.3]-phane **18a**. Nanometer-size tube-shaped molecules **7a**, **7b** and **8** were obtained by cyclization of tetrafunctionalized molecular ribbons with the biphenyl building block. The constitution and conformation of the molecular ribbons and belts were proven by NOE experiments and X-ray analyses.

Keywords: cyclophanes · iterative synthesis · macrocycles · nanostructures · sulfonamides

Introduction

The interest in synthetic molecules with a ribbon-, belt-, or tube-shape in the nanometer scale is well documented.[1] Tube-shaped molecules build up cavities and may thus be used as hosts to enclose specific guest molecules, for example in the development of chemoselective sensors or for size exclusion. The skeleton of molecular ribbons and tubes can lead, after derivatization with catalytically active groups, to synthetic catalysts (synzymes), having an outer sphere that sterically protects the reaction center from the kinetic movement of the solvent molecules, as in enzymes. Up to now, there are only a few approaches known to synthesize such channel-containing molecules,[2] mainly by iterative synthetic methods.[3–5] The use of complementary building blocks in an iterative synthesis minimizes the effort otherwise involved in building nanosized molecules. We have previously reported on a repetitive method, which gave satisfactory yields of molecular ribbons up to a length of nine fourfold-bridged benzene rings.[6] These molecular ribbons have already been used as cyclization precursors in the synthesis of molecular belts of variable diameter.[7] The goal of the work described here is to design and prepare molecular ribbons that are broader than the ones known so far, where the breadth usually was given by the diameter of *ortho*- or *meta*-connected benzene rings (Scheme 1).



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Scheme 1. Broader molecular ribbons **1** lead to longer molecular tubes **2**.

This concept leads to molecular ribbons **1** (and further on to molecular tubes **2**), in which both the length and breadth can be varied by use of appropriate building blocks. Wide ribbons generate long tubes when their termini are linked. On the other hand, the diameter of the tubes is related to the length of the ribbon precursors. Up to now, a broadening of molecular ribbons beyond the benzene diameter was unknown. This can be achieved, as shown here, by the exchange of benzene rings through biphenyl units, and later even by broader terphenyl units, connected in the 3,3′,5,5′ positions and ordered in a transverse fashion.

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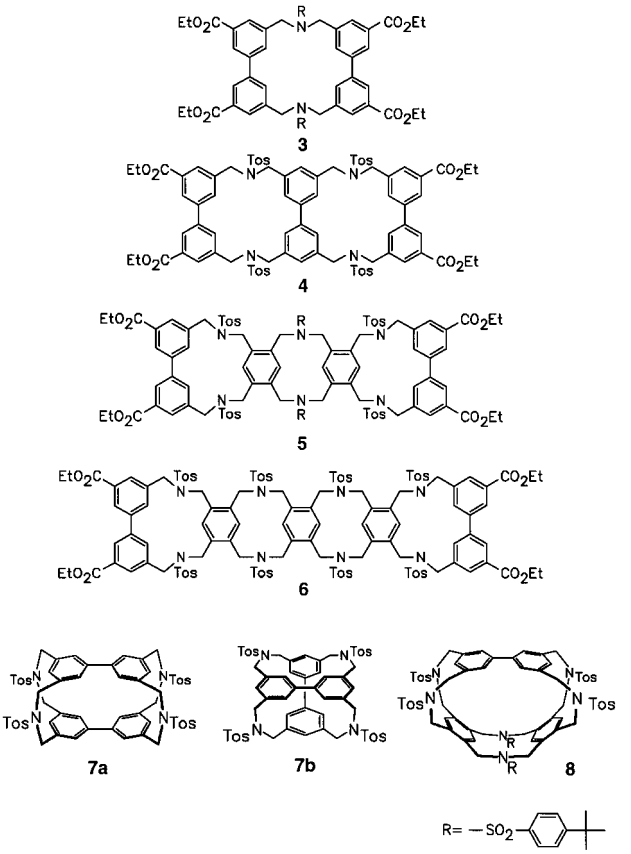
Results and Discussion

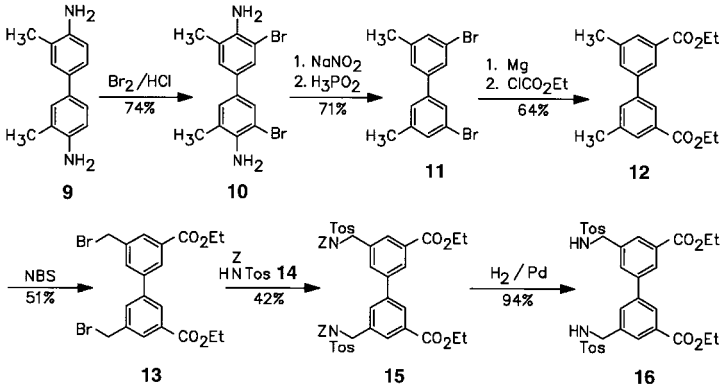
Synthetic overview: The basic concept of our synthesis is to cyclize di- or tetrafunctionalized building blocks to give ribbon-shaped macrooligocyclic phanes (Scheme 2). In this way we synthesised biphenylo⟨2⟩phane **3** by the cyclization of dibromide **13** with **27c** (see Scheme 9). Preparation of the key biphenyl building block **39** (see Scheme 8) and cyclization with **13** led to the first biphenylo⟨3⟩phane-type molecular ribbon **4** (see Scheme 10).[8] In addition we synthesized the new elongation block **16** (see Scheme 3) as a key compound in our iterative synthesis. The cyclization of **16** with tetrakis-(bromomethyl) cyclophanes **30** and **25** led to biphenylo⟨4⟩phane **5** and biphenylo⟨5⟩phane **6** (Scheme 7 and Scheme 6, respectively). Belt-shaped molecules were obtained by the cyclization of **39** with tetrakis(bromomethyl) building blocks **35** and **30** yielding biphenylo-beltane-type molecules (pseudo-beltanes)[9] **7a**, **7b** and **8** (see Scheme 11 and Scheme 12, respectively).



Scheme 2. Synthesized molecular ribbons **3**–**6** and pseudo-beltanes **7a**, **7b**, and **8**.

Abstract in German: *Mit den neuen vierfach funktionalisierten Schlüsselbausteinen **16** und **39** auf Biphenylbasis und durch Anwendung iterativer Synthesemethodik gelang die Darstellung der bisher breitesten molekularen Bänder, die erstmals die Breite querliegender Biphenyl-Einheiten aufweisen. Länge und Breite dieser strukturperfekten Bänder aus Diaza[3.3]-phan-Einheiten sind variierbar. Die Bänder können als Cyclisierungsbausteine zur Darstellung von verlängerten molekularen Röhren mit großem Durchmesser des Typs **2** dienen. Durch Einführung unterschiedlicher Seitenketten (Benzolsulfonamid-, 4-Toluolsulfonamid- und 4-tert-Butylbenzolsulfonamid-Gruppen) kann die Löslichkeit und das Wirt-Gast Verhalten (Clathratbildung mit Benzol, Dimethylformamid und Dichlormethan) dieser nanometergroßen molekularen Bänder und Röhren optimiert werden. Neue 14-, 15- und 16-gliedrige Modellringsysteme (Verbindungen **20a**, **22a** und **24**) wurden zur Konstitutionsaufklärung des Diaza[3.3]phans **18a** dargestellt. Nanometergroße rohrförmige Moleküle konnten durch Cyclisierung von vierfach funktionalisierten molekularen Bändern mit dem Biphenyl-Baustein erhalten werden. Die Konstitutionen und Konformationen der molekularen Bänder und Röhren wurden durch NOE-Experimente und Röntgenstrukturanalysen bestätigt.*

Key biphenyl elongation block 16: The hitherto unknown key biphenyl elongation block **16** was prepared by bromination of *ortho*-tolidine **9**,[10] followed by reduction of the amino groups,[11] and Grignard reaction with ethoxycarbonylchloride (Scheme 3). The double monobromination of **12** was achieved



Scheme 3. Preparation of the key biphenyl elongation block **16**.

with *N*-bromosuccinimide (NBS) in CH_2Cl_2.[12,13] Recrystallization from acetone removed monobrominated by-products; recrystallization from MeOH removed higher brominated by-products. The residual monobrominated by-products were brominated again with NBS to increase the overall yield. Suitable crystals for X-ray analysis were obtained by vapor diffusion of *n*-heptane into a solution of **13** in $CHCl_3$. The bromide was treated with benzyl *N*-tosylcarbamate **14**[14] to yield **15**. Hydrogenolytic separation of the benzyloxycarbonyl (Z)-group with palladium on carbon as catalyst gave the key elongation block **16**.

Benzenobiphenylophanes: The reaction of bis(bromomethyl)biphenyl **13** with tetraamine **17** led to biphenylo⟨3⟩phane **18a** in a 29% yield (Scheme 4). Three constitutional isomers **18a–c** could have been formed in this reaction in principle but only one isomer was found. Owing to the lack of single crystals for X-ray analysis, we tried to solve the constitutional assignment by comparison with NMR spectra of suitable model compounds. Three aromatic protons (biphenyl) at $\delta =$ 6.46, 7.90, 7.97 and another aromatic proton (benzene) at $\delta =$ 7.64 were observed in the ^{1}H NMR spectrum of the obtained

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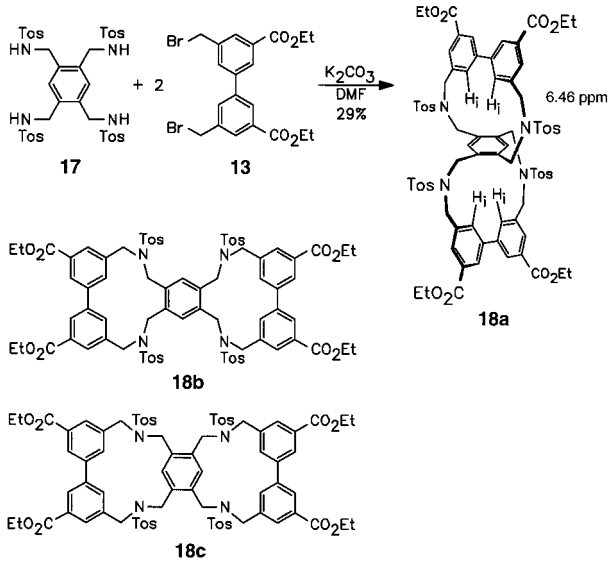
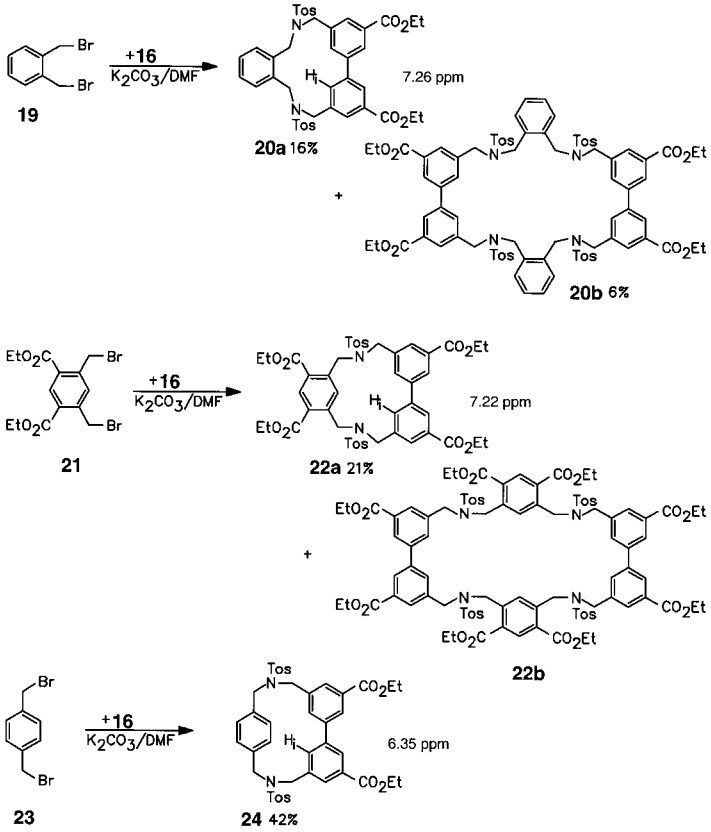


Scheme 4. Preparation of the benzenobiphenylo⟨3⟩phane **18a**; the chemical shift ($\delta = 6.46$) of the H_i protons indicates strong shielding.



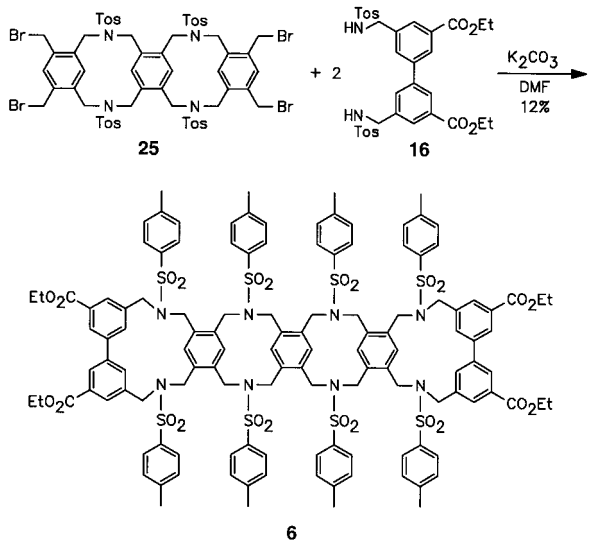
Scheme 5. Preparation of the new 14-, 15-, 16-, 28-, and 30-membered ring systems and NMR shifts of biphenyl H_i protons.

isomer **18a**. The signal at $\delta = 7.64$ was assigned to the two aromatic protons of the central benzene ring on account of the integration and by means of an H,H-COSY NMR spectrum, showing ^4J(H,H) coupling with the protons of the CH_2N bridges. The signal at $\delta = 6.46$ was assigned to the inner biphenyl protons (H_i), showing an upfield shift from about $\delta = 7.3$[15] to 6.46, caused by the anisotropy of the neighboring benzene ring.

We synthesized three model benzeno-biphenylo⟨2⟩phanes **20a**, **22a**, and **24**, containing 14-, 15- and 16-membered ring systems, respectively, in order to compare their NMR spectra with that of the isomer **18a** (Scheme 5). The ^{1}H NMR spectra of the *ortho*-substituted benzenobiphenylo⟨2⟩phane **18a** and of the *meta*-substituted benzenobiphenylo⟨2⟩phane **22a** showed no remarkable upfield shift of any of the biphenyl protons ($\delta = 7.26$, 7.79, 8.16 and $\delta = 7.22$, 7.62, 7.99, respectively). The upfield shift of the inner biphenyl proton was observed only in the ^{1}H NMR spectrum of the *para*-substituted benzenobiphenylo⟨2⟩phane **24** ($\delta = 6.35$, 7.78 and 7.94), which matched well with the NMR spectrum of the synthesized biphenylo⟨3⟩phane **18a** ($\delta = 6.46$, 7.90 and 7.97). We therefore assigned the constitution **18a** to the isolated biphenylo⟨3⟩phane. CPK models and molecular modeling calculations revealed that the inner biphenyl protons (H_i) lay directly above the anisotropy cone of the neighboring benzene ring. The constitution of this 15-membered ring system also agreed with the observed NOE effect between the inner biphenyl protons and the benzene protons; irradiating at $\delta = 7.64$ increased the signal intensity at $\delta = 6.46$. The signals of the NCH_2-bridging methylene protons contained information about the flexibility of these new macrocycles; sharp double doublets (coupling ^2J(H,H) = 15 Hz) indicated a rigid ring system, without interchange of the two geminal protons on the NMR-timescale. A flexible ring system would allow interchange between the geminal protons and consequently a singlet would be observed. Furthermore, the signals of the NCH_2-bridging methylene protons were solvent dependent: the ^{1}H NMR spectrum of **18a** in acetonitrile contained four sharp doublets, whereas in benzene two broad and two sharp doublets and in $CHCl_3$ two sharp doublets and two broad singlets were observed.

The ^{1}H NMR spectra of the *ortho*-substituted benzenobiphenylo⟨2⟩phane **20a** and of the *meta*-substituted benzenobiphenylo⟨2⟩phane **22a** showed a broad and a sharp singlet of the NCH_2-bridging methylene protons, indicating a conformationally restricted ring system. This ring tension could be responsible for the additional formation of the more flexible benzenobiphenylo⟨4⟩phane **20b** (6% yield). The NMR spectrum of **20b** showed two sharp singlets for the NCH_2-bridging methylene protons. Benzenobiphenylo⟨4⟩phane **22b** was only observed in the MALDI-TOF-spectrum. In contrast to **18a** the NCH_2-bridging methylene protons in the ^{1}H NMR spectrum of the *para*-substituted benzenobiphenylo⟨2⟩phane **24** appeared as two singlets, because no second ring was straining the molecule. The flexibility of **24** could be the reason for the rather high yield of this cyclization (39%). The twisted backbone of the benzenobiphenylo⟨3⟩phane **18a** is unfavorable for the synthesis of tube-shaped molecules. To avoid the formation of such twisted ribbons in further syntheses, we used cyclophanes as central units. The biphenyl elongation block **16** was treated with the known[6] tetrakis(bromomethyl)benzeno⟨3⟩phane **25** under high dilution conditions.

The benzenobiphenylo⟨5⟩phane **6** was obtained in a 12% yield. The broadening of the molecular ribbons did not lead to a change in the preferred conformation:[16] the all-*syn*



Scheme 6. Preparation of the molecular ribbon **6**.

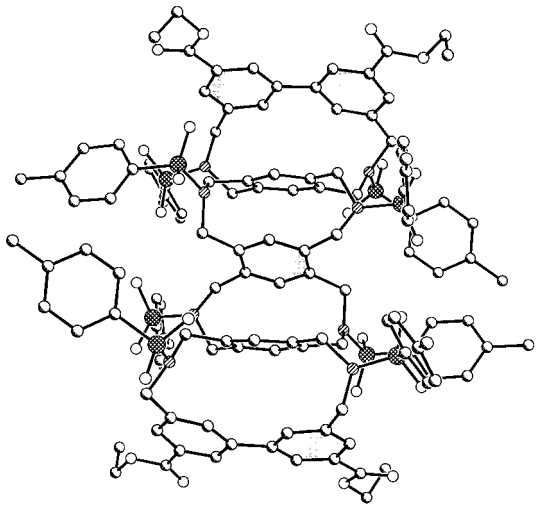


Figure 1. X-ray crystal structure of biphenylo⟨5⟩phane **6**.

conformation of the diaza[3.3]benzenophane subunits and of the diaza[3.3]benzeno-biphenylophane subunits led to a stacked structure. This structure was confirmed by ^{1}H NMR spectroscopy and by X-ray analysis. The aromatic protons in the skeleton of the molecular ribbon ($\delta = 6.11$, 6.42, 6.63, and 7.36) acted as a probe in the distinction between *syn* and *anti*-conformations:[17] low chemical shifts indicate an *anti*-conformation, because the magnetic anisotropy owing to the facing benzene rings caused internal hydrogens to exhibit an extensive upfield shift.[18] The chemical shifts of the inner aromatic protons in the skeleton were correlated with the length of the molecular ribbon: the chemical shifts moved to lower field with increasing length.[19] The molecular ribbon **6** is the hitherto longest biphenylophane. The distance of both biphenyls in *syn*-conformation is 1.4 nm. Crystals for X-ray analysis were obtained by recrystallization from DMF. The unit cell contained nine molecules of DMF, which are bound in a clathrate type structure (Figure 1).

Remarkably, the structure of biphenylo⟨5⟩phane **6** contains an inversion center (space group ($P2_1/n$ (no. 14)). As a result the conformations of the bridges adopted the highly symmetrical order chair/boat – chair/boat – chair/boat – chair/boat. The mean angle of two benzene rings in the diaza[3.3]-metacyclophane subunits was 26° but depends on the conformation of the bridges (chair 24.8°; boat 27.9°). A slightly lower angle (mean 22.5°) was obtained between a benzene ring and a biphenyl in the diaza[3.3]benzenobiphenylophane subunits (chair 21.7°; boat 23.4°). The alternating chair – boat conformation leads to little distortion (max. 5°) in the second and in the fourth benzene ring of the skeleton, which are coplanar.[20] The central benzene ring is not distorted at all and is almost coplanar to the outer biphenyls. These are bent away from the neighboring benzene rings with the two benzene planes possessing an angle of 168° to each other.

Benzenobiphenylophanes with miscellaneous side chains: The solubility of **6** in common organic solvents ($CHCl_3$, CH_2Cl_2, benzene) was lower than that of **18a**. We tried to improve the solubility by introducing different side chains into the skeleton of the ribbons. Even small changes in the side chains can influence the secondary structure of molecular ribbons, similar to peptide chains. Derivatization of the side chains should also prove the general applicability of our iterative synthetic method on the way to nanometer-scale molecular ribbons and belts. We chose benzenesulfonamide and 4-*tert*-butylbenzenesulfonamide groups, connected to the CH_2-N-CH_2-bridges, as new side chains. Cyclization of diethyl 2,4-bis(bromomethyl)benzene-1,5-dicarboxylate (**26**) with the arylsulfonamide monosodium salts **27a – c** diluted in DMF[21] led to the diazametacyclophanes **28a – c** in a 23 – 28 % yield (Scheme 7).[22] These cyclophanes **28a – c** showed a conformationally restricted flexibility, which was indicated in the ^{1}H NMR spectrum through broad singlets of the NCH_2-bridging methylene protons. The mass spectra of **28a – c** showed characteristic fragmentations, depending of the arylsulfonamide side chains ($[M - X]^+$, X = 198, 155, 142). These compounds can be easily purified by vapor diffusion of EtOH into a $CHCl_3$ solution. The three-step iterative reaction sequence started with the lithium borohydride reduction of the four terminal ethyl ester groups of **28c** to give the tetrakis(hydroxymethyl) derivative **29**. Transformation with PBr_3 in $CHCl_3$ gave the tetrakis(bromomethyl) cyclophane **30**, which was then lengthened with the biphenyl elongation block **16**.

As anticipated, the solubility of **5** was increased compared to biphenylo⟨5⟩phane **6**, owing to the 4-*tert*-butylbenzenesulfonamide side chains. The MALDI-TOF spectrum showed two main fragmentations caused by the two different side chains; 4-*tert*-butylbenzenesulfonamide and tosylamide (mass difference = 198 and 155 atomic units, respectively).

Biphenyl building block 39: 3,3′,5,5′-Tetrakis(bromomethyl)-biphenyl (**35**) was obtained by Sandmeyer reaction of dimethyl-5-aminobenzene-1,3-dicarboxylate (**31**) with KI followed by Ullmann coupling with copper to yield **33** (Scheme 8).[23] The reduction of the four ester groups with $LiBH_4$/THF and bromination with PBr_3 were carried out

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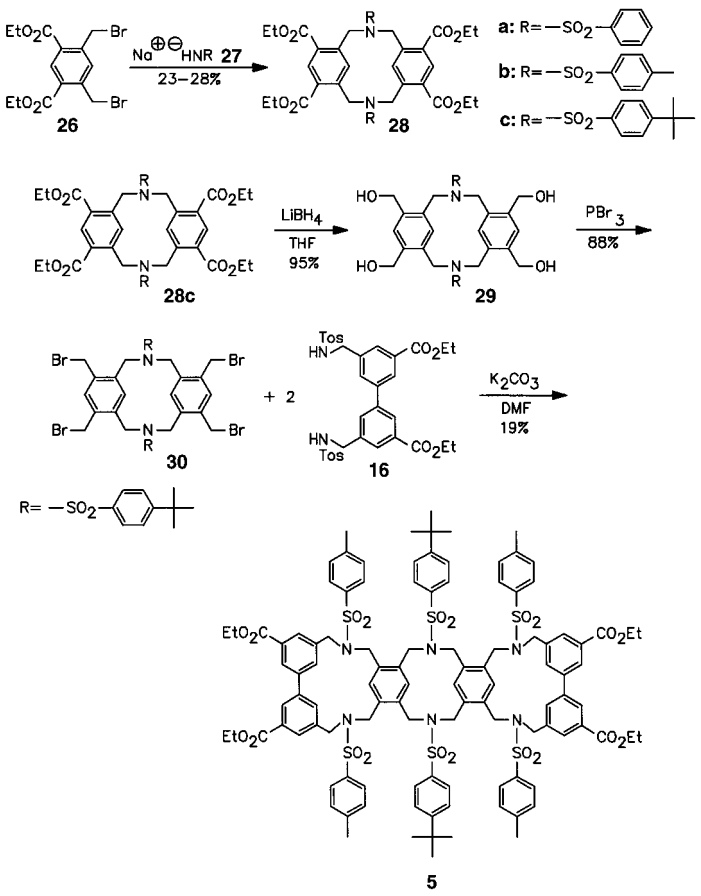
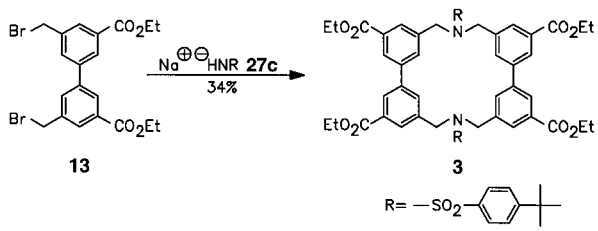


Scheme 7. The iterative reaction sequence leads to molecular ribbon **5**, containing 4-*tert*-butylbenzenesulfonamide and 4-toluenesulfonamide groups.

analogous to the method described above. Reaction of **34** with hydroiodic acid gave 3,3′,5,5′-tetrakis(iodomethyl)biphenyl (**36**) in 96% yield. This molecule contains four iodine atoms, which constitute better leaving groups and consequently increase the yield of further cyclizations. The tetrabromide **35** was treated with *N*-acetyl-4-toluenesulfonamide (**37**) to yield **38** at 87%. Deacetylation by heating with K_2CO_3 in MeOH/water under reflux gave **39** in a 81% yield.

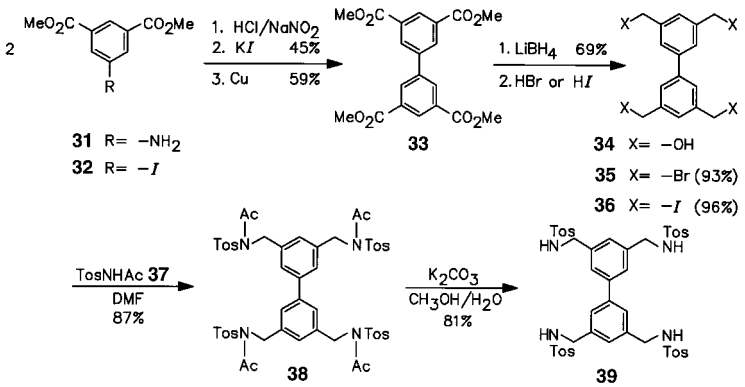
Biphenylophanes: The cyclization of **13** with 4-*tert*-butylbenzenesulfonamide monosodium salt **27c** in DMF under dilution conditions gave the diazabiphenylo⟨2⟩phane **3** in 34% yield (scheme 9). Single crystals of **3** for X-ray analysis were obtained by slow crystallization from benzene. Surprisingly the diazabiphenylo⟨2⟩phane **3** adopted an up to now unknown



Scheme 9. Preparation of the biphenylo⟨2⟩phane **3**.

conformation. It is neither the *syn* nor *anti* conformation of diaza[3.3]phanes, as the biphenyls lie one on top of the other. The CH_2-NR-CH_2-bridges are placed diagonally across from each other and consequently a tube- rather than a ribbon-shape is formed (Figure 2 left). The biphenyls are ordered in an interesting manner: the benzene rings in a biphenyl and the facing benzene rings form an angle of 24° to each other. This results in coplanarity of two benzene rings that lie diagonally across from each other and belong to different biphenyl units. The transannular distance of the arene units in [3.3]metacyclophanes was smaller than the calculated stacking distance of benzene dimers.[24] This leads to repulsion between the two π-electron systems, as a result of which the arenes change their geometry relative to each other: As a consequence, an angle of 24° was observed between the two benzene rings, and the interatomic distances are $C-C_{min} = 3.18$ Å and $C-C_{max} = 3.82$ Å between the two planes.

Both 4-*tert*-butylbenzenesulfonamide groups of **3** build up pockets in the solid state, in which two benzene molecules are enclosed. Short distances (278 pm) between a hydrogen of a methylene group and the center of the encapsulated benzene ring may indicate CH-π interactions.[25] van der Waals interactions may be assumed because some of the intermolecular distances are shorter than the sum of the van der Waals radii of the relevant atoms. Both carbonyl groups of each niche point towards the benzene hydrogen atoms. Short C=O···H–Ar contacts (247 and 269 pm) between the oxygen atom of the carbonyl group and the aromatic hydrogen atoms suggest that the ester groups form weak hydrogen bonds with benzene in the solid state.[26] The ^{1}H NMR spectrum of **3** shows one sharp singlet at $\delta = 4.39$ for the NCH_2-bridging methylene protons. The 18-membered ring system seems to be more flexible at room temperature than diazabenzenophanes (e.g. **28a–c**, **29**, and **30**) which possess a broad signal for these protons. Similar conformational behavior was observed in the ^{1}H NMR spec-



Scheme 8. Preparation of the biphenyl building blocks **35**, **36**, and **39**.

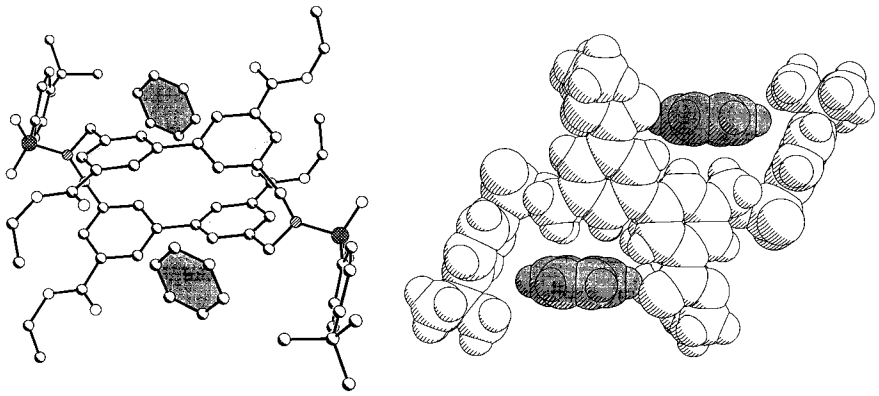
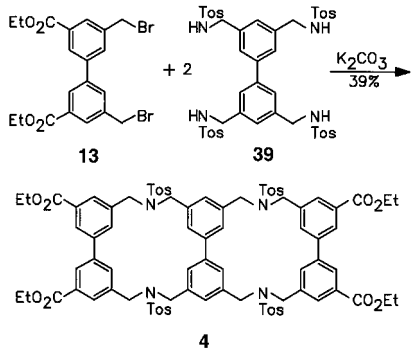


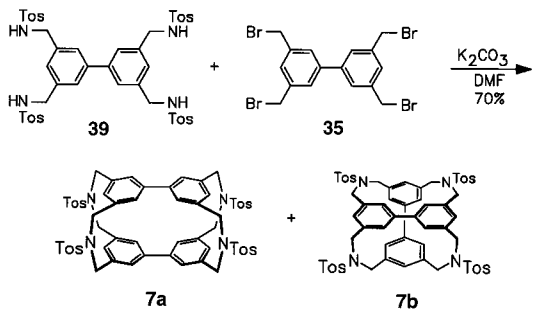
Figure 2. a) X-ray crystal structure of biphenylo⟨2⟩phane **3** enclosing benzene in both niches. b) Space-filling model of **3** enclosing benzene.

trum of biphenylo⟨3⟩phane **4** (two sharp singlets at $\delta = 4.02$ and 4.13). The biphenylo⟨3⟩phane **4** was synthesized by the cyclization of dibromide **13** with the new biphenyl building block **39** in a 39% yield. The possible isomer of **4** with the central biphenyl unit ordered crosswise was not detected (Scheme 10).



Scheme 10. Preparation of the biphenylo⟨3⟩phane **4**.

Biphenylo-pseudo-beltanes: The open ribbon structures can be used to synthesize macrocyclic tubes or belts of extended lengths. The cyclization of tetraamine **39** with tetrabromide **35** yielded the biphenylo-pseudo-beltanes **7a** and **7b** in a remarkable overall yield of 70% (Scheme 11). The separation



Scheme 11. Preparation of the biphenylo-pseudo-beltanes **7a** and **7b**.

of both isomers was difficult; chromatography afforded only an enrichment of the isomers. Separation was finally achieved through different solubility in DMF: the biphenylo-pseudo-beltane **7a** was less soluble than **7b**. The assignment to both isomers was achieved by ^{1}H NMR spectroscopy and X-ray analysis. The singlets at $\delta = 7.03$ and 7.10 in the ^{1}H NMR spectrum of **7a** were assigned to the biphenyl protons on account of the integration. The crossed isomer **7b** showed two singlets at $\delta = 6.71$ and 7.41. The signal at $\delta = 6.71$ was assigned to the inner biphenyl protons; it showed an upfield shift because the eight protons are positioned over the π-electron cloud of the other biphenyl ring. Single crystals of **7a** for X-ray analysis were obtained by slow vapor diffusion of ethyl acetate into a solution of the biphenylo-pseudo-beltane **7a** in $CHCl_3$ (Figure 3).

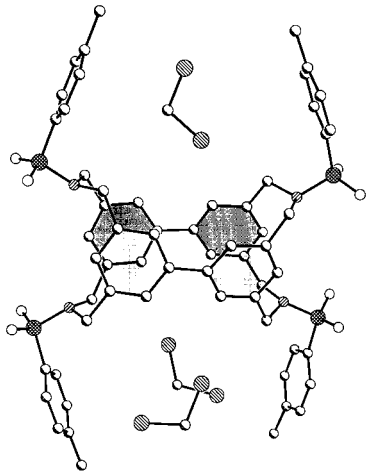


Figure 3. X-ray crystal structure of biphenylo-pseudo-beltane **7a** enclosing dichloromethane.

The shortest transannular distance between two biphenyl carbon atoms is 2.98 Å (Figure 3). As a result of the transannular π-π repulsion, both biphenyls are bent away from each other.[23] Consequently two benzene planes of a biphenyl form an angle of 168°. This is the same angle as observed in the X-ray analysis of biphenylo⟨5⟩phane **6**. Two facing benzene rings cannot form a favorable angle to each other (about 25°) because of the fourfold bridging. This results in an angle of only 15° between two facing benzene rings and consequently the methylene groups are bent out of the benzene plane by an angle of 14°. The tosyl groups of **7a** act as tweezers: the distance of two tosyl ring centers is roughly 1 nm; three CH_2Cl_2 molecules are bound (clathrated) in the cavities. Molecular tubes of larger diameters can be synthesized by using longer cyclization building blocks: The cyclization of the tetrabromide **30** with **39** gave biphenylo-pseudo-beltane **8** in a 26% yield (Scheme 12).

Only one isomer was found. The pseudo-beltane **8** was easily purified after preparation as it is only soluble in CH_2Cl_2

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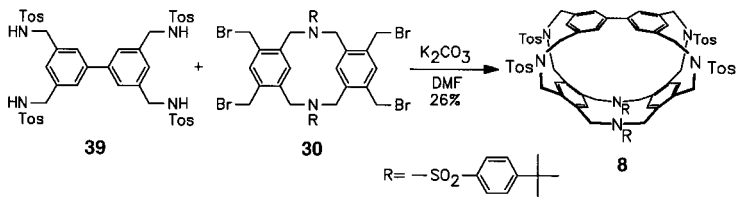

Scheme 12. Preparation of the biphenylo-pseudo-beltane **8**.

and DMF. An all-*syn* conformation of the arene units in the pseudo-beltane was assumed because the ^{1}H NMR spectrum showed no upfield shift of aromatic protons. We believe that the use of complementary building blocks, in this case a planar shape of **39** and concave shape of **30** (*syn* conformation in solution), has substantial influence on how successful the synthesis of molecular tubes will turn out.

Conclusion

An iterative synthesis method was successfully applied to newly designed biphenyl building blocks in combination with miscellaneous side chains to steer solubility. This yielded the most extended in terms of breadth large-diameter molecular ribbons and belts. These tetrafunctionalized ribbons are precursors for cyclizations to long belt-shaped molecules. The replacement of two bridges in molecular tubes by only one single bridge is not consistent with the usual beltane definition[8] as seen in the constitutional formula, but does not necessarily disturb the impression of a tube for the eye, as can be seen from space-filling models. Such structurally non-genuine tubes have been labeled pseudo-beltanes here due to their similar space-filling shape. NMR spectra and X-ray analyses have shown that the ribbons usually adopt a meander-type conformation. In future it should be possible to tune the conformation by modifying building blocks, allowing conformational design[27] of molecular ribbons. The use of even larger cyclization units will lead to beltanes with increasing diameter and length of the molecular tube. Incorporation of other building blocks (e.g. pyridines,[28] 4,4′-dihydroxybiphenyls) and their derivatization will produce functionalized molecular ribbons and belts and assemblies made from them.

Experimental Section

Materials and methods: Dry, freshly distilled solvents were used under anhydrous conditions unless otherwise noted. Tetrahydrofuran (THF) was distilled from $LiAlH_4$, trichloromethane ($CHCl_3$), and *N*,*N*-dimethylformamide (DMF) were dried over 4 Å molecular sieves. Yields refer to chromatographically and spectroscopically homogeneous materials. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60 F_{254}) using UV light ($\lambda = 254$ nm) as visualising agent. E. Merck TLC silica gel plates (2 mm, 60 F_{254}) were used for preparative layer chromatography. 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, Vienna, Austria) and are not corrected. Elemental analyses were performed by the Mikroanalytische Abteilung at the Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn. The ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AM-250 (250 MHz (^{1}H), 62.9 MHz (^{13}C)) or on a Bruker AM-400 (400 MHz (^{1}H), 100.6 MHz (^{13}C)) spectrometer and calibrated with the residual nondeuterated solvent as the internal reference. The NMR signals were assigned by the aid of HH-COSY and Dept 135 experiments when necessary. The spin-system of the *para*-substituted benzene-derivatives of the side chains, which constitute AA′XX′ spin system, were described as doublets, because the ^5J-coupling was not resolved. Mass spectra were recorded on an A. E. I. MS 50 operating in electron impact mode (EI-MS, HR = high-resolution), on a Kratos Concept 1 H (FAB) or on Micromass MALDI-TOF SpecE. The matrices used were 9-nitroanthracene, *m*-nitrobenzyl alcohol, and gentisic acid. Silver triflate was added in some cases to obtain molecule peaks of the silver adducts.

Diethyl 5,5′-bis[*N*-benzyloxycarbonyl-*N*-(4-tolylsulfonyl)aminomethyl]biphenyl-3,3′-dicarboxylate (**15**): A solution of dibromide **13** (1.65 g, 3.41 mmol), benzyl *N*-tosylcarbamate **14** (2.50 g, 8.20 mmol), and diisopropylethylamine (2.37 mL, 13.63 mmol) in DMF (150 mL) was stirred at room temperature for 72 h. The solvent was evaporated in vacuo and the remaining residue treated with CH_2Cl_2. The undissolved components were removed by filtration and the filtrate was washed with water, dried with Na_2SO_4, filtered, and concentrated in vacuo to give a yellowish oil, which was recrystallized from EtOH to give **15** (1.32 g; 42 %) as colorless crystals: M.p. 121 °C; $R_f = 0.74$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.45$ (t, $^3J(H,H) = 7$ Hz, 6H; CH_3), 2.28 (s, 6H; Tos-CH_3), 4.45 (q, $^3J(H,H) = 7$ Hz, 4H; OCH_2), 5.02 (s, 4H; CH_2), 5.10 (s, 4H; CH_2), 7.01–7.20 (m, 14H; Ar-H, Tos-H), 7.52 (d, $^3J(H,H) = 8$ Hz, 4H; Tos-H), 7.66 (s, 2H; Ar-H), 8.00 (s, 2H; Ar-H), 8.09 (s, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.41$ (CH_3), 21.61 (Tos-CH_3), 49.69 (NCH_2), 61.31 (OCH_2), 69.36 (OCH_2Ph), 127.20 (Ar-CH), 127.84 (Ar-CH), 128.44 (Ar-CH), 128.49 (Ar-CH), 128.51 (Ar-CH), 128.60 (Ar-CH), 129.33 (Ar-CH), 131.27 (Ar-CH), 131.61 (Ar-Cq), 134.30 (Ar-Cq), 136.02 (Ar-Cq), 138.12 (Ar-Cq), 140.57 (Ar-Cq), 144.74 (Ar-Cq), 152.35 (CO), 166.07 (CO); MS (FAB *m*-nitrobenzyl alcohol): *m/z* (%): 933.1 (17) $[M+H]^+$, 887.1 (81) $[M - OEt]^+$, 777.1 (12) $[M - Tos]^+$; $C_{50}H_{48}N_2O_{12}S_2$ (933.06).

Diethyl 5,5′-bis[(4-tolylsulfonylamino)methyl]biphenyl-3,3′-dicarboxylate (**16**): A suspension of **15** (1.15 g, 1.23 mmol) and 10 % palladium on carbon (150 mg, 10 wt %) in $CHCl_3$/MeOH (1:1, 50 mL) was stirred for 8 h under H_2 atmosphere (3.5 bar) at room temperature. The suspension was filtered through Celite and the filtrate was evaporated in vacuo to give yellowish crystals. The crude crystals were recrystallized in MeOH to yield **16** (769 mg; 94 %) as a colorless substance: M.p. 146 °C; $R_f = 0.11$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.31$ (t, $^3J(H,H) = 7$ Hz, 6H; CH_3), 2.29 (s, 6H; Tos-CH_3), 4.11 (d, $^3J(H,H) = 6$ Hz, 4H; NCH_2) 4.30 (q, $^3J(H,H) = 7$ Hz, 4H; OCH_2), 5.63 (br, 2H; NH), 7.16 (d, $^3J(H,H) = 8$ Hz, 4H; Tos-H), 7.49 (s, 2H; Ar-H), 7.65 (d, $^3J(H,H) = 8$ Hz, 4H; Tos-H), 7.72 (s, 2H; Ar-H), 7.88 (s, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.36$ (CH_3), 21.51 (Tos-CH_3), 46.82 (NCH_2), 61.44 (OCH_2), 127.14, 127.32, 128.29, 129.77, 130.83, 131.20, 136.74, 137.62, 140.07, 143.60 (5Ar-Cq, 5Ar-CH), 166.12 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 773.2 (68) $[M+Ag]^+$, 704.1 (66) $[M+K]^+$, 687.4 (65) $[M+Na]^+$; $C_{34}H_{36}N_2O_8S_2$ (664.79): calcd C 61.43, H 5.46, N 4.21, S 9.65; found C 61.41, H 5.47, N 4.18, S 9.42.

6,12,30,36-Tetrakis(ethoxycarbonyl)-2,17,26,41-tetrakis(4-tolylsulfonyl)-2,17,26,41-tetraaza[3.3](3,3′)biphenylo(1,4)benzeno[3.3](2,5)benzeno-(3,3′)biphenylo⟨3⟩phane (**18a**): Diethyl 5,5′-bis(bromomethyl]biphenyl-3,3′-dicarboxylate (**13**) (166 mg, 0.343 mmol) and 1,2,4,5-tetrakis[(4-tolylsulfonylamino)methyl]benzene **17** (139 mg, 0.171 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with $CHCl_3$/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from ethyl acetate gave **18a** (72 mg; 29 %) as a colorless solid: M.p. 182 °C; $R_f = 0.46$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz,

$CDCl_3$): $\delta = 1.37$ (t, $^3J(H,H) = 7$ Hz, 12H; CH_3), 2.38 (s, 12H; Tos-CH_3), 3.67 (br, 4H; NCH), 4.07 (d, $^2J(H,H) = 15$ Hz, 4H; NCH), 4.20 (d, $^2J(H,H) = 15$ Hz, 4H; NCH) 4.26-4.51 (m, 12H; OCH_2, NCH), 6.46 (s, 4H; Ar-H), 7.31 (d, $^3J(H,H) = 8$ Hz, 8H; Tos-H), 7.62 (d, $^3J(H,H) = 8$ Hz, 8H; Tos-H), 7.64 (s, 2H; Ar-H), 7.90 (s, 4H; Ar-H), 7.97 (s, 4H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.41$ (CH_3), 21.62 (Tos-CH_3), 51.14 (NCH_2), 53.92 (NCH_2), 61.37 (OCH_2), 127.00 (Ar-CH), 127.48 (Ar-CH), 128.95 (Ar-CH), 129.88 (Ar-C_q), 130.28 (Ar-CH), 131.05 (Ar-C_q), 133.93 (Ar-CH), 134.14 (Ar-CH), 137.05 (Ar-C_q), 137.14 (Ar-C_q), 140.39 (Ar-C_q), 144.26 (Ar-C_q), 166.08 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 1493.4 (89) $[M+K]^+$, 1476.5 (100) $[M+Na]^+$; $C_{78}H_{78}N_4O_{16}S_4$ (1455.73): calcd for $C_{78}H_{78}N_4O_{16}S_4H_2O$: C 63.57, H 5.47, N 3.80, S 8.70; found C 63.84, H 5.46, N 3.55, S 8.94.

6,12-Bis(ethoxycarbonyl)-2,17-bis(4-tolylsulfonyl)-2,17-diaza[3.3](1,2)benzeno(3,3′)biphenylo⟨2⟩phane (20a) and 6,12,30,36-Tetrakis(ethoxycarbonyl)-2,17,26,41-tetrakis(4-tolylsulfonyl)-2,17,26,41-tetraaza[3.3.3.3](1,2)benzeno(3,3′)biphenylo(1,2)benzeno(3,3′)biphenylo⟨4⟩phane (20b): Diethyl 5,5′-bis[(4-tolylsulfonylamino)methyl]biphenyl-3,3′-dicarboxylate (**16**) (57 mg, 0.086 mmol) and 1,2-bis(bromomethyl)benzene (**19**) (23 mg, 0.086 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with $CHCl_3$/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by thin-layer chromatography gave **20b** (4 mg; 6%) and **20a** (10 mg; 16%) as colorless crystals: M.p. 211 °C; $R_f =$ 0.72 (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.42$ (t, $^3J(H,H) = 7$ Hz, 6H; CH_3), 2.43 (s, 6H; Tos-CH_3), 4.41 (q, $^3J(H,H) = 7$ Hz, 4H; OCH_2), 4.50 (s, 4H; NCH_2), 4.59 (s, 4H; NCH_2), 6.96 – 7.01 (m, 2H; Ar-H), 7.03 – 7.08 (m, 2H; Ar-H), 7.26 (s, 2H; Ar-H), 7.33 (d, $^3J(H,H) =$ 7 Hz, 4H; Tos-H), 7.75 (d, $^3J(H,H) = 7$ Hz, 4H; Tos-H), 7.79 (s, 2H; Ar-H), 8.16 (s, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.76$ (CH_3), 21.93 (Tos-CH_3), 48.58 (NCH_2), 50.67 (NCH_2), 61.72 (OCH_2), 125.14 (Ar-CH), 127.15 (Ar-CH), 127.91 (Ar-CH), 127.96 (Ar-CH), 128.33 (Ar-CH), 130.02 (Ar-CH), 131.86 (Ar-C_q), 132.76 (Ar-C_q), 135.36 (Ar-CH+Ar-C_q), 136.64 (Ar-C_q), 138.22 (Ar-C_q), 144.22 (Ar-C_q), 166.45 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 790.9 (100) $[M+Na]^+$, 768.7 (7) $[M+H]^+$; $C_{42}H_{42}N_2O_8S_2$ (766.92). **20b**: M.p. 172 °C; $R_f = 0.49$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.40$ (t, $^3J(H,H) = 7$ Hz, 12H; CH_3), 2.32 (s, 12H; Tos-CH_3) , 4.14 (s, 8H; NCH_2), 4.34 (s, 8H; NCH_2), 4.37 (q, $^3J(H,H) = 7$ Hz, 8H; OCH_2), 7.00 – 7.05 (m, 4H; Ar-H), 7.06 – 7.11 (m, 4H; Ar-H), 7.16 (s, 4H; Ar-H), 7.18 (d, $^3J(H,H) = 7$ Hz, 8H; Tos-H), 7.51 (s, 4H; Ar-H), 7.58 (d, $^3J(H,H) = 7$ Hz, 8H; Tos-H), 7.78 (s, 4H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.42$ (CH_3), 21.48 (Tos-CH_3), 50.54 (NCH_2), 51.86 (NCH_2), 61.22 (OCH_2), 126.89, 127.22, 128.08, 128.79, 129.32, 129.75, 130.79, 130.93, 133.98, 136.07, 136.98, 139.50, 143.47 (7Ar-CH+6 Ar-C_q), 165.88 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 1572.1 (19) $[M+K]^+$, 1556.1 (100) $[M+Na]^+$, 1379.2 (22) $[M-Tos]^+$; $C_{84}H_{84}N_4O_{16}S_4$ (1533.84).

6,12,20,22-Tetrakis(ethoxycarbonyl)-2,17-bis(4-tolylsulfonyl)-2,17-diaza[3.3](1,3)benzeno(3,3′)biphenylo⟨2⟩phane (22a): Diethyl 5,5′-bis[(4-tolylsulfonylamino)methyl]biphenyl-3,3′-dicarboxylate (**16**) (57 mg, 0.086 mmol) and diethyl 2,4-bis(bromomethyl)benzene-1,5-dicarboxylate (**21**) (35 mg, 0.086 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with $CHCl_3$/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by thin-layer chromatography gave **22a** (16 mg; 21%) as colorless crystals: M.p. 68 °C; $R_f = 0.31$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.15$ (t, $^3J(H,H) = 7$ Hz, 6H; CH_3), 1.33 (t, $^3J(H,H) = 7$ Hz, 6H; CH_3), 2.31 (s, 6H; Tos-CH_3), 4.06 (q, $^3J(H,H) = 7$ Hz, 4H; OCH_2), 4.31 (q, $^3J(H,H) = 7$ Hz, 4H; OCH_2), 4.57 (br, 4H; NCH_2), 4.92 (s, 4H; NCH_2), 7.22 (s, 2H; Ar-H), 7.29 (d, $^3J(H,H) =$ 7 Hz, 4H; Tos-H), 7.62 (s, 2H; Ar-H), 7.86 (s, 1H; Ar-H), 7.87 (d, $^3J(H,H) =$ 7 Hz, 4H; Tos-H), 7.99 (s, 2H; Ar-H), 8.73 (s, 1H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.01$ (CH_3), 14.40 (CH_3), 21.56 (Tos-CH_3), 49.13 (NCH_2), 53.81 (NCH_2), 61.22 (OCH_2), 61.48 (OCH_2), 125.04 (Ar-CH), 127.04 (Ar-CH), 127.85 (Ar-CH), 128.85 (Ar-C_q), 130.05 (Ar-CH), 130.84 (Ar-C_q), 131.17 (Ar-CH), 132.58 (Ar-CH), 135.32 (Ar-CH), 135.38 (Ar-C_q), 137.49 (Ar-C_q), 138.20 (Ar-C_q), 143.92 (Ar-C_q), 143.97 (Ar-C_q), 165.84 (CO), 166.28 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 949.5 (19) $[M+K]^+$, 934.5 (100) $[M+Na]^+$, 911.5 (65) $[M+H]^+$, 758.83 (16) $[M-Tos]^+$; $C_{48}H_{50}N_2O_{12}S_2$ (911.05).

6,12-Bis(ethoxycarbonyl)-2,17-bis(4-tolylsulfonyl)-2,17-diaza[3.3](1,4)benzeno(3,3′)biphenylo⟨2⟩phane (24): Diethyl 5,5′-bis[(4-tolylsulfonylamino)methyl]biphenyl-3,3′-dicarboxylate (**16**) (57 mg, 0.086 mmol) and 1,4-bis(bromomethyl)benzene (**23**) (23 mg, 0.086 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with $CHCl_3$/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude solid was suspended in EtOH to induce crystallization. The colorless crystals were filtered off and dried in vacuo to yield **24** (28 mg; 42%): M.p. 289 °C; $R_f = 0.54$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.35$ (t, $^3J(H,H) = 7$ Hz, 6H; CH_3), 2.39 (s, 6H; Tos-CH_3), 4.23 (s, 4H; NCH_2), 4.30 (s, 4H; NCH_2), 4.33 (q, $^3J(H,H) = 7$ Hz, 4H; OCH_2), 6.35 (s, 2H; Ar-H), 7.27 (s, 4H; Ar-H), 7.28 (d, $^3J(H,H) = 7$ Hz, 4H; Tos-H), 7.70 (d, $^3J(H,H) = 7$ Hz, 4H; Tos-H), 7.78 (s, 2H; Ar-H), 7.94 (s, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.42$ (CH_3), 21.60 (Tos-CH_3), 54.32 (NCH_2), 55.23 (NCH_2), 61.27 (OCH_2), 127.17 (Ar-CH), 127.54 (Ar-CH), 128.31 (Ar-CH), 129.96 (2 Ar-CH), 130.81 (Ar-C_q), 132.38 (Ar-CH), 135.34 (Ar-C_q), 137.55 (Ar-C_q), 137.64 (Ar-C_q), 140.39 (Ar-C_q), 143.92 (Ar-C_q), 166.25 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 805.3 (100) $[M+K]^+$, 789.3 (96) $[M+Na]^+$, 767.3 (19) $[M+H]^+$; $C_{42}H_{42}N_2O_8S_2$ (766.92).

6,12,54,60-Tetrakis(ethoxycarbonyl)-2,17,26,35,38,47,50,65-oktakis(4-tolylsulfonyl)-2,17,26,35,38,47,50,65-oktaaza[3.3](3,3′)biphenylo(1,3)benzeno[3.3](4,6)benzeno(1,3)benzeno[3.3](4,6)benzeno(1,3)benzeno[3.3](4,6)benzeno(3,3′)biphenylo⟨5⟩phane (6): Diethyl 5,5′-bis[(4-tolylsulfonylamino)methyl]biphenyl-3,3′-dicarboxylate (**16**) (57 mg, 0.086 mmol) and tetrabromide **25** (60 mg, 0.043 mmol) were separately dissolved in DMF (25 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (20 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with CH_2Cl_2/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by thin-layer chromatography and recrystallization from benzene gave **6** (12 mg; 12%) as colorless crystals: M.p. > 280 °C; $R_f = 0.78$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 1.40$ (t, $^3J(H,H) = 7$ Hz, 12H; CH_3), 2.37 (s, 24H; Tos-CH_3), 3.34-5.22 (br, 40H; CH_2), 6.11 (s, 2H; Ar-H), 6.42 (s, 2H; Ar-H), 6.63 (s, 2H; Ar-H), 7.36 (s, 4H; Ar-H), 7.59 (d, $^3J(H,H) = 7$ Hz, 16H; Tos-H), 7.77 (d, $^3J(H,H) = 7$ Hz, 16H; Tos-H), 7.91 (s, 4H; Ar-H), 8.07 (s, 4H; Ar-H); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 2431.3 (28) $[M+K]^+$, 2415.3 (100) $[M+Na]^+$, 2238.3 (22) $[M-Tos]^+$; $C_{126}H_{126}N_8O_{24}S_8$ (2392.91).

5,7,14,16-Tetrakis(ethoxycarbonyl)-2,11-bis(benzenesulfonyl)-2,11-diaza[3.3]metacyclophane (28a): A solution of dibromide **26** (6.18 g, 20 mmol), dissolved in DMF (60 mL) was added within 1 h to a suspension of benzenesulfonamide monosodium salt **27a** (3.58 g, 20 mmol) in DMF (400 mL) under an argon atmosphere at 80 °C. Additional benzenesulfonamide monosodium salt **27a** (3.58 g, 20 mmol) was added to the reaction mixture, which was then heated for a further 4 h. The solvent was evaporated in vacuo and the remaining residue treated with CH_2Cl_2. The undissolved components were removed by filtration and the filtrate was washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from ethyl ester gave **28a** (2.08 g; 27%) as colorless crystals: M.p. 281 °C; $R_f = 0.14$ (silica, $CHCl_3$/acetone, 100:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.30$ (t, $^3J(H,H) = 7$ Hz, 12H; CH_3), 4.23 (q, $^3J(H,H) = 7$ Hz, 8H; OCH_2) 4.86 (br, 8H; NCH_2), 7.64 (m, 6H; Ar-H), 7.89 (s, 2H; Ar-H), 7.97 – 8.07 (m, 4H; Ar-H), 8.27 (s, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.21$ (CH_3), 50.62 (NCH_2), 61.37 (OCH_2), 127.50 (Ar-CH), 127.97 (Ar-C_q), 129.62 (Ar-CH), 131.74 (Ar-CH), 133.00 (Ar-CH), 135.92 (Ar-CH), 139.22 (Ar-C_q), 140.97 (Ar-C_q), 165.86 (CO); MS

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(FAB *m*-nitrobenzyl alcohol): *m/z* (%): 829.2 (8) $[M+Na]^+$, 807.2 (100) $[M+H]^+$, 665.2 (68) $[M-SO_2C_6H_5]^+$; $C_{40}H_{42}N_2O_{12}S_2$ (758.86).

5,7,14,16-Tetrakis(ethoxycarbonyl)-2,11-bis(4-*tert*-butylbenzenesulfonyl)-2,11-diaza[3.3]metacyclophane (**28c**): A solution of **26** (4.08 g, 10 mmol), dissolved in DMF (30 mL) was added within 1 h to a suspension of 4-*tert*-butylbenzenesulfonamide monosodium salt (**27c**) (2.35 g, 10 mmol) in DMF (200 mL) under an argon atmosphere at 80 °C. Additional 4-*tert*-butylbenzenesulfonamide monosodium salt (**27c**) (2.35 g, 10 mmol) was added to the reaction mixture which was then heated for a further 4 h. The solvent was evaporated in vacuo and the remaining residue treated with CH_2Cl_2. The undissolved components were removed by filtration and the filtrate was washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from ethyl ester gave **28c** (1.18 g; 26%) as colorless crystals: M.p. 231 °C; $R_f = 0.30$ (silica, $CHCl_3$/acetone, 100:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.29$ (t, $^3J(H,H) = 7$ Hz, 12H; CH_3), 1.37 (s, 18H; CH_3), 4.23 (q, $^3J(H,H) = 7$ Hz, 8H; OCH_2) 4.86 (br, 8H; NCH_2), 7.62 (d, $^3J(H,H) = 8$ Hz, 4H; Ar-H), 7.89 (s, 2H; Ar-H), 7.93 (d, $^3J(H,H) = 8$ Hz, 4H; Ar-H), 8.31 (s, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.17$ (CH_3), 31.15 (CH_3), 35.23 (C_q), 50.62 (NCH_2), 61.31 (OCH_2), 126.58 (Ar-CH), 127.28 (Ar-CH), 127.86 (Ar-C_q), 131.66 (Ar-CH), 136.04 (Ar-CH), 136.25 (Ar-C_q), 141.15 (Ar-C_q), 156.53 (Ar-C_q), 165.88 (CO); MS (FAB *m*-nitrobenzyl alcohol): *m/z* (%): 941.4 (11) $[M+Na]^+$, 919.4 (43) $[M+H]^+$, 721.3 (46) $[M-SO_2C_6H_4C(CH_3)_3]^+$; $C_{48}H_{58}N_2O_{12}S_2$ (919.11): calcd C 62.73, H 6.36, N 3.05; found C 62.90, H 6.38, N 2.85.

5,7,14,16-Tetrakis(hydroxymethyl)-2,11-bis(4-*tert*-butylbenzenesulfonyl)-2,11-diaza[3.3] metacyclophane (**29**): A stirred suspension of tetraester **28c** (688 mg, 0.75 mmol) and lithium borohydride (245 mg, 11.23 mmol) in dry THF (40 mL) 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 tetraalcohol remained undissolved. The tetraalcohol was filtered, washed with water, and dried in vacuo at 50 °C to give **29** (536 mg, (95%): M.p. 282 °C; ^{1}H NMR (400 MHz, DMSO): $\delta = 1.37$ (s, 18H; CH_3), 4.40 (br, 16H; CH_2), 4.83 (t, $^3J(H,H) = 5$ Hz, 4H; OH), 6.95 (s, 2H; Ar-H), 7.34 (s, 2H; Ar-H), 7.73 (d, $^3J(H,H) = 8$ Hz, 4H; Ar-H), 7.90 (d, $^3J(H,H) = 8$ Hz, 4H; Ar-H); ^{13}C NMR (100 MHz, DMSO): $\delta = 30.89$ (CH_3), 35.01 (C_q), 51.63 (NCH_2), 60.14 (OCH_2), 125.66, 126.54, 127.24, 129.83, 135.06, 138.33, 139.15, 156.11 (4Ar-Cq, 4Ar-CH); MS (FAB *m*-nitrobenzyl alcohol): *m/z* (%): 773.4 (100) $[M+Na]^+$, 751.4 (48) $[M+H]^+$, 733.4 (41) $[M-H_2O]^+$, 715.4 (41) $[M-2H_2O]^+$, 553.3 (33) $[M-SO_2C_6H_4C(CH_3)_3]^+$; $C_{40}H_{50}N_2O_8S_2$ (750.97).

5,7,14,16-Tetrakis(bromomethyl)-2,11-bis(4-*tert*-butylbenzenesulfonyl)-2,11-diaza[3.3]metacyclophane (**30**): PBr_3 (3 mL, 31 mmol) was added over 2 h to a stirred suspension of the tetraalcohol **29** (503 mg, 0.67 mmol) in dry $CHCl_3$ (50 mL). The mixture was then stirred and heated for 8 h. 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 with Na_2SO_4, filtered, and evaporated in vacuo. Recrystallization from toluene gave **30** (588 mg; 88%) as colorless crystals: M.p. 243 °C; $R_f = 0.53$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.41$ (s, 18H; CH_3), 4.46 (br, 16H; CH_2), 6.95 (s, 2H; Ar-H), 7.35 (s, 2H; Ar-H), 7.66 (d, $^3J(H,H) = 8$ Hz, 4H; Ar-H), 7.87 (d, $^3J(H,H) = 8$ Hz, 4H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.94$ (CH_2Br), 31.19 (CH_3), 35.40 (C_q), 52.01 (NCH_2), 125.37, 126.76, 127.37, 128.30, 129.11, 132.78, 133.03, 137.94 (4Ar-Cq, 4Ar-CH); MS (FAB *m*-nitrobenzyl alcohol): *m/z* (%): 1003.0 (74) $[M+H]^+$, 923.0 (100) $[M+H-Br]^+$; $C_{40}H_{46}Br_4N_2O_4S_2$ (1002.55): calcd C 47.92, H 4.62, N 2.79, S 6.40; found C 48.17, H 4.76, N 2.70, S 6.21.

6,12,42,48-Tetrakis(ethoxycarbonyl)-26,35-bis(4-*tert*-butylbenzenesulfonyl)-2,17,38,53-tetrakis(4-tolylsulfonyl)-2,17,26,35,38,53-hexaaza[3.3]-(3,3′)biphenylo(1,3)benzeno[3.3](4,6)benzeno(1,3)benzeno[3.3](4,6)benzeno(3,3′)biphenylo⟨4⟩phane (**5**): Diethyl 5,5′-bis[(4-tolylsulfonylamino)-methyl]biphenyl-3,3′-dicarboxylate (**16**) (100 mg, 0.150 mmol) and tetrabromide **30** (75 mg, 0.075 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with CH_2Cl_2/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by thin-layer chromatography and recrystallization from acetonitrile gave **5** (29 mg; 19%) as colorless crystals: M.p. 197–199 °C; $R_f = 0.71$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 1.31$ (s, 18H; CH_3), 1.35 (t, $^3J(H,H) = 7$ Hz, 12H; CH_3), 2.41 (s, 12H; Tos-CH_3), 3.80–5.25 (br, 24H; NCH_2), 4.37 (q, $^3J(H,H) = 7$ Hz, 8H; OCH_2), 6.07 (s, 2H; Ar-H), 6.96 (s, 4H; Ar-H), 7.33-7.47 (m, 10H; Tos-H+Ar-H), 7.50–7.64 (m, 8H; Ar-H), 7.85 (s, 4H; Ar-H), 7.90 (s, 4H; Ar-H), 7.94 (d, $^3J(H,H) = 8$ Hz, 8H; Tos-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.42$ (CH_3), 21.58 (Tos-CH_3) 31.09 (CH_3), 35.28 (C_q), 48.18 (NCH_2), 54.29 (NCH_2), 54.62 (NCH_2), 61.34 (OCH_2), 125.04, 125.17, 126.69 (br), 127.51 (br.), 130.19 (br), 130.91, 131.40, 131.91 (br), 132.18, 133.43, 135.76, 136.44, 136.73, 137.29, 143.77, 144.05, 156.73, (9 Ar-CH+9 Ar-C_q), 166.15 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 2048.1 (21) $[M+K]^+$, 2030.2 (100) $[M+Na]^+$, 1875.3 (8) $[M+Na-Tos]^+$, 1813.2 (6) $[M-SO_2C_6H_4C(CH_3)_3]^+$; $C_{108}H_{114}N_6O_{20}S_6$ (2008.48).

Dimethyl 5-iodo-benzene-1,3-dicarboxylate (**32**): A solution of sodium nitrite (17.25 g, 0.25 mmol) in water (300 mL) was added to a suspension of dimethyl 5-amino-benzene-1,3-dicarboxylate (**31**) (52.30 g, 0.25 mol) in hydrochloric acid (150 mL, 20%) at −5 °C. Toluene (400 mL) and then a solution of potassium iodide (84.00 g, 0.50 mol) in water (200 mL) was slowly added to the suspension. Following the addition, the suspension was stirred for a further 12 h at room temperature and afterwards heated for 1 h under reflux. The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from methanol gave **32** (35.73 g, 45%) as colorless crystals: M.p. 104 °C; $R_f = 0.53$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.85$ (s, 6H; CH_3), 8.26 (s, 2H; Ar-H), 8.73 (s, 1H; Ar-H); MS 50 (210 °C, 70 eV, 300 mA): *m/z* (%): 320 (83) $[M]^+$, 289 (100) $[M-CH_3O]^+$; HR-EI: calcd 319.9556, found 319.9551; $C_{10}H_9IO_4$ (320.08).

3,3′,5,5′-Tetrakis(methoxycarbonyl)biphenyl (**33**): A mixture of **32** (15.00 g, 0.05 mol) and copper powder (15 g, 0.24 mol) was heated slowly to 220 °C. After 2 h the temperature was increased to 250 °C and maintained for 1 h. The solid was extracted three times with $CHCl_3$, dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was suspended in acetone, filtered off, and dried. Compound **33** (5.32 g; 59%) was obtained as a colorless solid: M.p. 213 °C; $R_f = 0.43$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.97$ (s, 12H; CH_3), 8.48 (s, 4H; Ar-H), 8.70 (s, 2H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 52.65$ (CH_3), 130.28 (Ar-Cq), 131.58 (Ar-CH), 132.34 (Ar-CH), 139.89 (Ar-Cq); MS 50 (210 °C, 70 eV, 300 mA): *m/z* (%): 386 (86) $[M]^+$, 355 (100) $[M-CH_3O]^+$; HR-EI: calcd 386.0991, found 386.0992; $C_{20}H_{18}O_8$ (386.36).

3,3′,5,5′-Tetrakis(iodomethyl)biphenyl (**36**): A stirred suspension of 3,3′5,5′-tetrakis(hydroxymethyl)biphenyl (**34**) (220 mg, 0.80 mmol) and hydriodic acid (30 mL, 57%) was refluxed for 2 h. The precipitate was filtered off, washed three times with water, and dried in vacuo. Recrystallization from CH_2Cl_2 gave **36** (547 mg, 96%) as colorless crystals: M.p. 218–220 °C; $R_f = 0.76$ (silica, $CHCl_3$/acetone, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.48$ (s, 8H; CH_2), 7.39 (s, 2H; Ar-H), 7.43 (s, 4H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 4.60$ (CH_2I), 127.22, 127.63, 128.54, 140.84 (2Ar-Cq, 2Ar-CH); MS 50 (210 °C, 70 eV, 300 mA): *m/z* (%): 713.3 (10) $[M]^+$, 586.6 (100) $[M-I]^+$, 459.8 (31) $[M-2I]^+$, 332.9 (25) $[M-3I]^+$, 206.1 (32) $[M-4I]^+$; $C_{16}H_{14}I_4$ (713.91).

3,3′,5,5′-Tetrakis[(*N*-acetyl-*N*-(4-tolylsulfonyl)-amino)methyl]biphenyl (**38**): A solution of tetrabromide **35** (1.80 g, 3.42 mmol) dissolved in DMF (30 mL) was added within 2 h to a suspension of *N*-acetyl-4-toluenesulfonamide **37** (3.65 g, 17.10 mmol) and K_2CO_3 (4.73 g, 34.2 mmol) in DMF (50 mL) under an argon atmosphere at 80 °C. The mixture was stirred for a further 18 h. The solvent was evaporated in vacuo and the remaining residue treated with CH_2Cl_2. The undissolved components were removed by filtration and the filtrate was washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from acetone gave **38** (3.12 g, 87%) as colorless crystals: M.p. 138 °C; $R_f = 0.53$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.34$ (s, 12H; CH_3), 2.38 (s, 12H; CH_3), 5.11 (s, 8H; NCH_2), 7.29 (d, $^3J(H,H) = 8$ Hz, 8H; Tos-H), 7.34 (s, 2H; Ar-H), 7.36 (s, 4H; Ar-H), 7.66 (d, $^3J(H,H) = 8$ Hz, 8H; Tos-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.60$ (Tos-CH_3), 24.99 (CO-CH_3), 49.27 (NCH_2), 125.74, 126.21, 127.73, 129.91, 136.42, 137.69, 141.09, 145.06 (4 Ar-C_q, 4 Ar-CH), 170.36 (CO); MS (FAB *m*-nitrobenzyl alcohol): *m/z* (%): 1093.3 (18) $[M+K]^+$, 1055.4 (61) $[M+H]^+$; 899.3 (72) $[M-Tos]^+$; $C_{52}H_{54}N_4S_4O_{12}$(1055.26).

3,3′,5,5′-Tetrakis[(4-tolylsulfonylamino)methyl]biphenyl (**39**): A suspension of **38** (2.81, 2.66 mmol) and K_2CO_3 (6.91, 50 mmol) in MeOH/water (150 mL, 20:1) was heated for 2 h under reflux. The solvent was evaporated in vacuo and the remaining residue was washed with water (100 mL). The crude product was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 10:1) to give **39** (1.90 g, 81 %) as colorless crystals: M.p. 181 °C; $R_f = 0.33$ (silica, $CHCl_3$/MeOH, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 2.33 (s, 12H; CH_3), 3.91 (d, ^3J(H,H) = 6 Hz, 8H; NCH_2), 6.15 (t, ^3J(H,H) = 6 Hz, 4H; NH), 6.90 (s, 2H; Ar-H), 7.17 (s, 4H; Ar-H), 7.23 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H), 7.80 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.55$ (Tos-CH_3), 46.89 (NCH_2), 126.00, 127.34, 127.39, 129.80, 136.63, 137.03, 140.18, 143.50 (4 Ar-C_q, 4 Ar-CH); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 924.8 (13) $[M+K]^+$, 909.1 (70) $[M+Na]^+$; elemental analysis calcd for $C_{44}H_{46}N_4O_8S_4$ (887.11): C 59.57, H 5.23, N 6.32, S 14.46; found C 59.07, H 5.20, N 6.13, S 14.43.

6,12,21,27-Tetrakis(ethoxycarbonyl)-2,17-bis(4-*tert*-butylbenzenesulfonyl)-2,17-diaza [3.3](3,3′)(3,3′)biphenylo⟨2⟩phane (**3**): A solution of dibromide **13** (97 mg, 0.20 mmol), dissolved in DMF (50 mL) was added within 1 h to a suspension of 4-*tert*-butylbenzenesulfonamide monosodium salt (**27c**) (47 mg, 0.20 mmol) in DMF (50 mL) under an argon atmosphere at 80 °C. Additional 4-*tert*-butylbenzenesulfonamide monosodium salt (**27c**) (47 mg, 0.20 mmol) was added to the reaction mixture, which was then heated for a further 4 h. The solvent was evaporated in vacuo and the remaining residue treated with CH_2Cl_2. The undissolved components were removed by filtration and the filtrate was washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by preparative layer chromatography (silica, $CHCl_3$/acetone, 10:1) and recrystallization from benzene gave **3** (36 mg, 34 %) as a colorless substance: M.p. 249 °C; $R_f = 0.41$ (silica, $CHCl_3$/acetone, 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.38$ (s, 18H; CH_3), 1.40 (t, ^3J(H,H) = 7 Hz, 12H; CH_3), 4.35 (q, ^3J(H,H) = 7 Hz, 8H; OCH_2), 4.39 (s, 8H; NCH_2), 7.34 (s, 4H; Ar-H), 7.63 (d, ^3J(H,H) = 9 Hz, 4H; Ar-H), 7.65 (s, 4H; Ar-H), 7.74 (s, 4H; Ar-H), 7.88 (d, ^3J(H,H) = 9 Hz, 4H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.36$ (CH_3), 31.11 (CH_3), 35.29 (C_q), 53.91 (NCH_2), 61.21 (OCH_2), 126.57 (Ar-CH), 127.23 (Ar-CH), 127.36 (Ar-CH), 129.01 (Ar-CH), 131.02 (Ar-C_q), 131.88 (Ar-CH), 135.32 (Ar-C_q), 136.93 (Ar-C_q), 139.62 (Ar-C_q), 156.97 (Ar-C_q), 165.66 (CO); MS (FAB *m*-nitrobenzyl alcohol): *m/z* (%): 1109.2 (21) $[M+K]^+$, 1093.3 (100) $[M+Na]^+$, 1071.12 (27) $[M+H]^+$; $C_{60}H_{66}N_2O_{12}S_2$ (1071.31).

6,12,36,42-Tetrakis(ethoxycarbonyl)-2,17,32,47-tetrakis(4-tolylsulfonyl)-2,17,32,47-tetraaza[3.3](3,3′)(3,3′)[3.3](5,5′)(3,3′)biphenylo⟨3⟩phane (**4**): Diethyl 5,5′-bis(bromomethyl]biphenyl-3,3′-dicarboxylate (**13**) (100 mg, 0.207 mmol) and 3,3′5,5′-tetrakis[(4-tolylsulfonylamino)methyl]biphenyl (**39**) (92 mg, 0.103 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with $CHCl_3$/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by thin-layer chromatography gave **4** (62 mg, 39 %) as colorless crystals: M.p. 173 °C; $R_f = 0.44$ (silica, $CHCl_3$/acetone 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.27$ (t, ^3J(H,H) = 7 Hz, 12H; CH_3), 2.41 (s, 12H; Tos-CH_3), 4.02 (s, 8H; NCH_2), 4.13 (s, 8H; NCH_2), 4.23 (q, ^3J(H,H) = 7 Hz, 8H; OCH_2), 6.70 (s, 2H; Ar-H), 6.76 (s, 4H; Ar-H), 7.17 (s, 4H; Ar-H), 7.36 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H), 7.60 (s, 4H; Ar-H) 7.75 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H), 7.76 (s, 4H; Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.35$ (CH_3), 21.62 (Tos-CH_3), 52.12 (NCH_2), 52.56 (NCH_2), 61.29 (OCH_2), 127.06, 127.22, 127.37, 128.60, 129.00, 130.15, 131.21, 131.87, 135.95, 136.45, 137.04, 139.05, 139.50, 144.00 (7Ar-C_q, 7Ar-CH), 165.86 (CO); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 1569.3 (53) $[M+K]^+$, 1554.2 (100) $[M+Na]^+$; $C_{84}H_{82}N_4O_{16}S_4$ (1531.83).

2,17,26,35-Tetrakis(4-tolylsulfonyl)-2,17,26,35-tetraaza[3.3.3.3](3,3′)(3,3′)-biphenylo(5,5′)(5,5′)biphenylo⟨2⟩phane (7a) and 2,11,26,35-Tetrakis(4-tolylsulfonyl)-2,11,26,35-tetraaza[3.3.3.3](3,3′)(3,5)biphenylo(3′,5′)(5,5′)biphenylo⟨2⟩phane (**7b**): 3,3′5,5′-Tetrakis(bromomethyl)biphenyl (**35**) (53 mg, 0.10 mmol) and 3,3′5,5′-tetrakis[(4-tolylsulfonylamino)methyl]biphenyl (**39**) (89 mg, 0.10 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue was extracted with CH_2Cl_2. Purification by thin-layer chromatography gave **7a–b** (76 mg, 70 %) as a mixture of both isomers. The mixture was treated with DMF to dissolve isomer **7b**. The residue was filtered off and dried in vacuo to yield **7a** (33 mg, 30 %) as a colorless substance. The filtrate was evaporated in vacuo to yield **7b** (43 mg, 40 %) as a colorless substance. **7a**: M.p. > 300 °C; $R_f = 0.72$ (silica, $CHCl_3$/acetone 50:1); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 2.42$ (s, 12H; Tos-CH_3), 4.47-5.38 (br, 16H; NCH_2), 7.03 (s, 4H; Ar-H), 7.10 (s, 8H; Ar-H), 7.39 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H), 7.76 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 1127.5 (100) $[M+K]^+$, 1112.5 (98) $[M+Na]^+$, 1089.5 (21) $[M+H]^+$; $C_{60}H_{56}N_4O_8S_4$ (1089.37). **7b**: M.p. 155 °C; $R_f = 0.72$ (silica, $CHCl_3$/acetone 50:1); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 2.38$ (s, 12H; Tos-CH_3), 3.77-4.55 (br, 16H; NCH_2), 6.71 (s, 8H; Ar-H), 7.41 (s, 4H; Ar-H), 7.45 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H), 7.86 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H); ^{13}C NMR (100 MHz, DMF): $\delta = 21.32$ (Tos-CH_3), 55.27 (NCH_2), 128.26 (Ar-CH), 129.53 (Ar-CH), 130.84 (Ar-CH), 132.22 (Ar-CH), 133.01 (Ar-C_q), 136.19 (Ar-C_q), 137.23 (Ar-C_q), 144.45 (Ar-C_q); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 1127.3 (36) $[M+K]^+$, 1112.3 (100) $[M+Na]^+$, 1089.3 (34) $[M+H]^+$, 972.3 (4) $[M+K-Tos]^+$, 957.3 (18) $[M+Na-Tos]^+$, 934.3 (9) $[M+H-Tos]^+$; $C_{60}H_{56}N_4O_8S_4$ (1089.37).

29,38-Bis(4-*tert*-butylbenzenesulfonyl)-2,17,26,41-tetrakis(4-tolylsulfonyl)-2,17,26,29,38,41-hexaaza[3.3](3,5)biphenylo(1,3)benzeno[3.3](4,6)benzeno(1,3)benzeno[3.3](4,6)benzeno(3′,5′)biphenylo⟨3⟩phane (**8**): Tetrabromide **30** (100 mg, 0.10 mmol) and 3,3′5,5′-tetrakis[(4-tolylsulfonylamino)-methyl]biphenyl (**39**) (89 mg, 0.10 mmol) were separately dissolved in DMF (50 mL). Both solutions were added simultaneously by means of a perfusor over 8 h to a suspension of K_2CO_3 (100 mg, 0.72 mmol) in DMF (50 mL) at room temperature under an argon atmosphere. Following the addition, stirring was maintained for a further 12 h. The solvent was evaporated in vacuo and the residue treated with CH_2Cl_2/water (100 mL, 1:1). The organic layer was separated, washed three times with water, dried with Na_2SO_4, filtered, concentrated in vacuo, and purified by thin-layer chromatography. The solid was suspended in benzene and filtered to yield 41 mg (26 %) **8** as colourless substance: M.p. 222–224 °C; $R_f = 0.39$ (silica, $CHCl_3$/acetone 50:1); ^{1}H NMR (400 MHz, DMF): $\delta = 1.18$ (s, 18H; CH_3), 2.36 (s, 12H; Tos-CH_3), 3.09-5.18 (br, 24H; NCH_2), 7.31 (s, 4H; Ar-H), 7.44 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H), 7.47-7.52 (m, 8H; Ar-H), 7.71 (d, ^3J(H,H) = 8 Hz, 4H; Ar-H), 7.80 (d, ^3J(H,H) = 8 Hz, 8H; Tos-H), 7.88 (s, 2H; Ar-H); MALDI-TOF-MS, (9-nitroanthracene): *m/z* (%): 1604.0 (14) $[M+K]^+$, 1587.9 (57) $[M+Na]^+$, 1565.9 (100) $[M+H]^+$, 1410.9 (17) $[M-Tos]^+$, 1369.9 (37) $[M-SO_2C_6H_4C(CH_3)_3]^+$; $C_{84}H_{88}N_6O_{12}S_6$ (1566.02).

X-ray crystallographic data: Table 1 gives details of the structures of **3**, **6**, and **7a** . The structures were solved by direct methods (SHELXS-97).[29] The non-hydrogen atoms were refined anisotropically, H atoms were refined by using a riding model (full-matrix least-squares refinement on F^2 (SHELXL-93)).[30] In **6** one DMF molecule is disordered. Crystallographic data (excluding structure factors) for the structures **3**, **6**, **7a**, **13** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101490. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 1. Crystallographic data, structure solution and refinement of **3**, **6,** and **7a**.

Compound	**6**	**7a**	**3**
formula	$C_{126}H_{126}N_8O_{24}S_8 \cdot 8\,DMF$	$C_{60}H_{56}N_4O_8S_4 \cdot 3\,CH_2Cl_2$	$C_{60}H_{66}N_2O_{12}S_2 \cdot 2\,C_6H_6$
M_r	2977.6	1344.1	1227.5
dimensions [mm]	$0.10 \times 0.20 \times 0.30$	$0.05 \times 0.10 \times 0.15$	$0.23 \times 0.35 \times 0.45$
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	16.7090(4)	16.7508(9)	10.2068(3)
b [Å]	16.6596(2)	23.1611(17)	13.6082(3)
c [Å]	27.2399(5)	17.3134(9)	13.8057(4)
α [°]			63.495(2)
β [°]	105.376(1)	111.759(3)	69.250(2)
γ [°]			72.121(2)
V [Å^3]	7311.2(2)	6238.4(7)	1579.10(7)
Z	2	4	1
ρ [g cm^{-3}]	1.35	1.43	1.29
μ [mm^{-1}]	0.204	0.468	0.150
F(000)	3156	2792	652
diffractometer	Nonius-CCD	Nonius-CCD	Nonius-CCD
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
λ [Å]	0.71073	0.71073	0.71073
T [K]	123(2)	123(2)	123(2)
$2\theta_{max.}$ [°]	50	50	56.5
	$-19 \le h \le 19$	$-19 \le h \le 19$	$-3 \le h \le 13$
	$-19 \le k \le 19$	$-27 \le h \le 27$	$-18 \le h \le 18$
	$-32 \le h \le 32$	$-20 \le h \le 20$	$-16 \le h \le 16$
no. Of measured data	70996	56858	24619
no. Of unique data	11823	9739	5847
no. Of obs. Data for ($I > 2\sigma(I)$)	8016	5185	4972
R_{int}	0.041	0.089	0.022
refinement on	F^2	F^2	F^2
no. of parameters/ restraints	930/88	770/0	397/0
R [for $F > \sigma(F)$]	0.038	0.044	0.034
$wR2$ (all data)	0.098	0.107	0.095
max/min difference peak [e Å^3]	0.609/ − 0.569	0.401/ − 0.427	0.253/ − 0.365

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