Pd-catalyzed amination of dibromobiphenyls in the synthesis of macrocycles comprising two biphenyl and two polyamine moieties

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Dedicated to Prof. Usein M. Dzhemilev on the occasion of his 65th anniversary

DOI: http://dx.doi.org/10.3998/ark.5550190.0012.807

Abstract

Two approaches to the synthesis of polyazamacrocycles containing two biphenyl and two polyamine moieties are described. The first route comprises the synthesis of N,N'-bis(bromobiphenyl) substituted di- and poly-amines by the reactions of 2.2'- or 3,3'-dibromobiphenyls with corresponding di- and polyamines followed by the reaction with a second molecule of the amine. The second approach includes the synthesis of bis(polyamine) substituted biphenyls by the reactions of 4,4'- or 3,3'-dibromobiphenyls with four equivalents of di- and poly-amines with subsequent reaction of these in situ prepared intermediates with dibromobiphenyls. The yields of target macrocycles obtained according to two routes are compared and the advantage of the approach via bis(polyamine) substituted biphenyls in the majority of cases is established. Side products, when formed in all reactions, were analyzed.

Keywords: Amination, macrocycles, Pd catalysis, polyamines, dibromobiphenyls

Introduction

Macrocycles containing biphenyl units are of constant interest due to their interesting coordination possibilities which arise from the combination of flexible and tunable polyoxa- and polyaza-cycles with a rigid non-planar aryl moiety. Many cyclic polyethers were formed starting from 2,2'-dihydroxybiphenyl,1-3 their coordination with organic cations like tert-butylammonium was studied,4 as well as the transport of Li, Na, K cations4,5 and of Hg(CF3)26,7 through a liquid membrane. In such macrocycles one or two polyoxaethylene chains were attached to one biphenyl unit. Molecular structures of various 2,2'-biphenyl-based crown ethers and their
coordination with anions have been studied.\textsuperscript{8,9} Polyoxadiaminomacrocycles were also synthesized on the basis of 2,2'-disubstituted biphenyl and their coordination with primary alkylammonium salts, including chiral compounds, was investigated.\textsuperscript{10} Polyazamacrocycles with 3, 4 and 8 nitrogen atoms were studied for binding Cu\textsuperscript{2+}, Zn\textsuperscript{2+} and [PdCl\textsubscript{4}]\textsuperscript{2-} ions.\textsuperscript{11} Macrocycles of cryptand type with N and S atoms have been shown to form complexes with Cu(I) and Ag(I).\textsuperscript{12} Biphenyl-containing macro lactams have been tested as colorimetric sensors for nitrophenolate anions,\textsuperscript{13} and fluorescent and electrochemical sensors were elaborated on the basis of the macrocycles containing 2,2'-biphenyls substituted with amino groups in positions 4 and 4'.\textsuperscript{14} Recently more sophisticated macrocycles like peptide-biphenyl hybrid\textsuperscript{15} and hemispherand macrocycle\textsuperscript{16} with bi- and quaterphenyl moieties have been reported. Cyclic triamides\textsuperscript{17} as well as cyclic Schiff bases (trianglimines)\textsuperscript{18,19} are known, usually comprised of three 3,3'- or 4,4'-disubstituted biphenyls. Among them the most interesting are chiral nonracemic molecules with 1,2-diamino cyclohexane and 4,4'- and 3,4'-biphenyl fragments.\textsuperscript{20} Atropoisomeric biphosphine ligands were synthesized by functionalizing macrocycles constructed on the basis of 3,3'-biphenyls, and tested in the asymmetric hydrogenation of alkenes.\textsuperscript{21} π-Electron donor\textsuperscript{22} and acceptor\textsuperscript{23} macrocyclic systems with 4,4'-biphenyls were reported, the first being tested as hosts for fused aromatic systems. There are some unusual macrocycles with long rigid units which combine two 4,4'-biphenyl fragments with four triple bonds linked through sulfur atoms which possess interesting electronic properties.\textsuperscript{24} The majority of known macrocycles based on biphenyls were synthesized using non-catalytic approaches which are often multistep procedures, however, in some cases one-step formation of macrocycles can be achieved, e.g. for the synthesis of aromatic tetrasulfonate 2,2'-biphenyl-based macrocycles.\textsuperscript{25} In some approaches biphenyl fragment was built using Pd-catalyzed coupling of two benzene moieties at the step of macrocyclization, as it was in the case of the compound with diazacrown, dipeptide and biphenyl fragments.\textsuperscript{26} Palladium catalysis was also employed for the synthesis of an unusual macrobicycle where anomalously bent 4,4'-biphenyl is incorporated into calix[4]amide.\textsuperscript{27} Another example of the application of the catalytic method for the synthesis of biphenyl-based macrocycles is zirconocene-mediated macrocyclization which afforded strained cyclophanes with two 4,4'-biphenyls.\textsuperscript{28} It was mentioned that biphenyls were incorporated in some biologically active macrocycles, e.g. tricyclic glucopipeptides of vancomycin group.\textsuperscript{29} All these data envisage biphenyl-based macrocycles as valuable compounds with numerous applications.

Recently we have shown the possibility to synthesize earlier unknown family of polyazamacrocycles with C(sp\textsuperscript{2}-N) bonds by the Pd-catalyzed amination reaction of 4,4'- and 3,3'-dibromobiphenyls with di- and polya mines.\textsuperscript{30,31} Macrocycles based on 3,3'-disubstituted biphenyl were obtained in rather high yields up to 40%, whereas macrocycles containing 4,4'-disubstituted biphenyl were formed only with the longest diamines and in tiny yields not exceeding 10% due to geometrical factors. In all cases the formation of cyclic dimers and oligomers was noted, and in many reactions these compounds were isolated in pure state. We decided to reveal the reaction paths according to which these symmetrical macrocycles
containing two biphenyl and two polyamine units (cyclic dimers) may be formed, to elaborate particular methods for their synthesis because these molecules are of the utmost interest due to their versatile coordination properties, to find out scope and limitations of tested approaches and their dependence on the nature of starting compounds.

**Results and Discussion**

At first the synthesis of cyclodimers via intermediate $N,N'$-bis(bromobiphenyl) substituted polyamines was studied. For the first experiments with 4,4′-dibromobiphenyl 1 we chose 1,3-propanediamine 2a, dioxadiamine 2b, trioxadiamine 2c, and tetraamine 2d as model polyamines. The reactions were run with 2.2 equivalents of compound 1 in boiling dioxane at $c = 0.1 \text{ M}$, and were catalyzed with 4 mol% Pd(dba)$_2$/BINAP (Scheme 1). BINAP was taken as a ligand because it was found to be the most versatile for the Pd-mediated amination of aryl halides in general, and the best ligand for the diarylation of linear polyamines in particular. In 10 h the diarylation was completed and the reaction mixtures were evaporated and subjected to column chromatography on silica gel. The yields of the target compounds 3a-d after purification were not high due to the formation of linear oligomers like 4, which were formed due to the diamination of one biphenyl fragment in compounds 3. However, it was impossible to increase the yields of the desired diarylated polyamines 3 either by decreasing the catalyst loading or by

![Scheme 1](image-url)
the application of a greater excess of 1: in the first case the diarylation process would not come to completion, in the second case the N,N-diarylation process would take place giving rise to triarylated species. Compound 3b was obtained in pure state by washing the reaction mixture with small amounts of dichloromethane because its solubility was found to be unusually low. In one case, with tetraamine 3d, the diarylation process was not completed, and monoarylated derivative 5d was obtained in 32% yield.

The formation of the macrocycles 6a-d was accomplished by the reactions of N,N'-bis(bromobiphenyl) polyamines 3a-d with one equivalent of corresponding di- and polyamines 2a-d, which were catalyzed by 8 mol% Pd(dba)$_2$/BINAP (Scheme 2). In these processes more dilute solutions were employed (c = 0.02 M) to suppress the formation of linear and cyclic oligomers. The reactions ran to completion after 30-40 h of reflux. Macrocycles with trioxadiamine and tetraamine chains 6c,d were isolated in 20 and 23% yields, respectively, while the yield of the macrocycle with dioxadiamine unit was small (9%), and the shortest 1,3-propanediamine 2a gave a mixture of the cyclic dimer 6a with cyclotetramer 7a (n=4) in total 6% yield. In the reaction of compound 4c with trioxadiamine 2c the formation of cyclic oligomers was also noted, and the mixture of 6c with 7c (n=4, 6) was isolated by column chromatography as a separate fraction. In this reaction the product of the bromine reduction 8c was obtained in 16% yield, though the reduction processes are not common in the Pd-catalyzed amination with di- and polyamines. We also tried to accomplish the synthesis of cyclodimers via a one-step procedure without isolation of the intermediate diaryl derivatives 3.

![Scheme 2](image-url)
For this purpose 2.5 equivalents of 4,4'-dibromobiphenyl were reacted with trioxadiamine 2c using 4 mol% catalyst at c = 0.1 M. After 10 h the reaction mixture was diluted to get 0.02 M solution, additional amount of the catalyst (8 mol%) and one equivalent of trioxadiamine 2c were added, and the reaction was refluxed for 35 h. The chromatography gave 28% of the reduction product 8c, only 5% of pure cyclic dimer 6c, and a separate fraction containing cyclodimer 6c with cyclic trimer 7c (n=3) (9% yield). This unsatisfactory result demonstrates the difficulties in the separation of cyclic oligomers and thus the pressure to diminish their amount and diversity, which can be done only using pure N,N'-bis(4-biphenyl) derivatives of polyamines for the synthesis of cyclic dimers.

While macrocycles based on 4,4'-biphenyls are well documented in the literature, macrocycles incorporating 3,3'-biphenyls are quite rare examples, and this fact makes the synthesis of cyclic dimers with two 3,3'-biphenyl moieties an important task. At first we tried a one-step approach described above without isolation of the intermediate N,N'-diarylated derivatives of polyamines (Scheme 3).

Scheme 3

N,N'-diarylation of polyamines 2a,b,d was achieved using 2.5 equivalents of 3,3'-dibromobiphenyl 9, 4 mol% catalyst, and 0.1 M solutions of polyamines in dioxane. After 10 h of reflux the reaction mixtures were analyzed by 1H NMR to verify the formation of diaryl derivatives 10, they were diluted to make 0.02 M solutions and new portions of the catalyst (8 mol%) were added. The additional reflux for 35-40 h was necessary to complete the intramolecular diamination, and after it the reaction mixtures were subjected to chromatography on silica gel. The result was moderate only for tetraamine derivative 11d (19%), while in other
cases pure cyclodimers 11a,b were obtained in low yields. Cyclic oligomers 13 were isolated in all reactions, and in the case of dioxadiamine 2b and tetraamine 2d also macrocycles 12b,d were obtained in comparable yields (10 and 18%, respectively). The reaction of equimolar amounts of 1,3-diaminopropane 2a with 3,3’-dibromobiphenyl 9 described by us previously afforded 24% yield of the cyclic dimer 11a. Thus it is clear that the approach via in situ obtained N,N’-bis(3-bromobiphenyl)diamine is not suitable for this compound.

Next we investigated the possibilities of this method with chromatographic isolation of compounds 10; this was thought also to reveal the formation of by-products (Scheme 4).

According to a given consideration, diamine 2a was excluded from this series of experiments. The reactions were run using 2.2 equivalents of 9, and at first they were catalyzed by 4 mol% Pd(dba)2/BINAP. The reactions of trioxadiamine 2c and tetraamine 2d gave target
products 10c,d in 21 and 26% yields, macrocycles 12c,d as well as linear oligomers 14c,d and 15d were also obtained. In the case of tetraamine 2d the application of 3 equivalents of 9 allowed to increase the yield of 10d to 34%. However, for dioxadiamine 2b it was found impossible to isolate the target compound 10b in pure state because it contained admixtures – products of N,N-diarylation and diamination reactions. The application of less amount of the catalyst (2 mol%) did not improve the situation. The change of BINAP ligand for a less active Xanthphos suppressed the undesirable reactions but the standard catalyst loading (4 mol%) together with the standard reaction time (10 h) led mainly to monoaryl derivative of dioxadiamine. The use of more catalyst (8 mol%) was unsuccessful because it promoted N,N-diarylation process, but the employment of 3 equivalents of 9 and prolonged reflux (45 h) with 4 mol% Pd(dba)2/Xanthphos resulted in 27% yield of pure product 10b. We tested the same conditions with trioxadiamine 2c and increased the yield of 10c to 35%.

The cyclization reactions of diaryl derivatives 10b-d were accomplished under standard conditions (Scheme 5) and their results were similar: the yields of target macrocycles 12b-d ranged from 25 to 30%, cyclic oligomers (cyclotetramers and cyclohexamers) were obtained as side products in comparable yields. In the case of the reaction of 10b with 2b cyclooligomers 13b (n=3, 5) were fully separated from the target cyclodimer 11b, while in other reactions the fractions containing cyclooligomers 13c,d contained also cyclodimers 11c,d what to some extent diminished the yields of the target macrocycles-cyclodimers. This macrocyclization was more successful than that with N,N'-bis(4-bromobiphenyl) derivatives 3 and here no influence of the nature of polyamine was noted.

Scheme 5

Having obtained data on the synthesis of the biphenyl-containing macrocycles via intermediate N,N'-bis(bromobiphenyl)polyamines, we tried an alternative approach, i.e. via intermediate bis(polyamine) substituted biphenyls. In this method intermediates were not isolated by column chromatography due to great difficulties caused by the presence of an excess of polyamines in the reaction mixture which possess very close Rf to that of bis(polyamine) derivatives of biphenyls.
The reactions of 4,4′-dibromobiphenyl 1 with 4 equivalents of di- and polyamines 2b-d were run in boiling dioxane (C = 0.1 M) and catalyzed by 8 mol% Pd(dba)2/BINAP, they were complete in 8-10 h (Scheme 6). Intermediate 4,4′-bis(polyamine) biphenyls 16a-d were analyzed by NMR and MALDI-TOF mass-spectra in the reaction mixtures. Then 3 equivalents of 4,4′-dibromobiphenyl, additional catalyst (8 mol%) and dioxane to make 0.02 M solution were added, and the reactions were refluxed for 35-40 h. Target cyclodimers 6b-d were isolated by column chromatography on silica gel. The best result was obtained for the macrocycle 6c (24%), the reactions with dioxadiamine 2b and tetraamine 2d gave poor yields of macrocycles (11 and 7% respectively). In these reactions substantial amounts of cyclic oligomers of higher masses were obtained (up to cyclononamer 7b (n=8)), obviously, they were formed via intermediate linear oligomers containing n biphenyl and n+1 polyamine units. It is notable that the reaction with trioxadiamine 2c gave rise to linear oligomers 17c with terminal biphenyl which were formed due to the reduction of the bromine atom.

A similar reaction with the isomeric 3,3′-dibromobiphenyl 9 conducted under the same conditions gave somewhat different results (Scheme 7).
Intermediate 3,3′-bis(polyamine)biphenyls 18b-d, obtained in situ using 4 equivalents of corresponding di- and polyamines 2b-d, were analyzed by NMR and MALDI-TOF spectroscopy, and they were further reacted with 3 equivalents of 3,3′-dibromobiphenyl. The best result was recorded for the macrocycle 11b with its highest 44% yield, whereas the yields of compounds 11c and 11d were much more modest (15 and 9% respectively). In all cases the formation of the macrocycles 12 containing one set of biphenyl and polyamine units was observed, and with longer trioxadiamine 2c and tetraamine 2d their yields were about 40% which is equal to the yields of these compounds when the reactions were run with equimolar amounts of starting compounds. Higher mass cyclooligomers were also formed in the case of dioxadiamine 2b and trioxadiamine 2c.

**Scheme 7**

As a result of the experiments described above, we can outline the following general findings. The synthesis of the macrocycles containing two biphenyl and two polyamine moieties can be carried out using two approaches: via $N,N'$-bis(bromobiphenyl) substituted polyamines or via bis(polyamine)biphenyls. The first route in a two-step version affords target macrocycles in
yields up to 30%, 3,3'-dibromobiphenyl providing better yields of the macrocycles than 4,4'-dibromobiphenyl. One-step version with in situ obtained N,N'-bis(bromobiphenyl) derivative can be recommended only for the synthesis of the cyclodimer with two 3,3'-biphenyls and two tetraamine chains (yield 19%). The second approach via bis(polyamine)biphenyls provides better yields of some cyclodimers, and in this case the dependence of the result on the nature of starting compounds is pronounced: 4,4'-dibromobiphenyl gave 24% yield of the macrocycle with two trioxadiamine chains, whereas 3,3'-dibromobiphenyl afforded the cyclodimer with dioxadiamine in the highest yield (44%). We suppose that two main factors govern the results of these two-step syntheses: the conformational factors of di- and polyamine chains at the macrocyclization step and the activity of the bromine atom in 4,4'- and 3,3'-dibromobiphenyls in competitive amination and reduction reactions at both steps of the processes. The application of more powerful separation techniques like HPLC may undoubtedly increase the yields of the target macrocycles.

**Experimental Section**

**General.** All chemicals were purchased from Aldrich and Acros companies and used without further purification. 3,3'-Dibromobiphenyl 9 was synthesized from 2-bromonitrobenzene according to a procedure described in ref. 34. Pd(dbam)2 was synthesized according to a described method. Commercial dioxane was distilled over NaOH and sodium under argon, dichloromethane and methanol were distilled prior to use. Column chromatography was carried out using silica gel (40-60 mkm) purchased from Fluka. 1H and 13C NMR spectra were registered in CDCl3 using Bruker Avance 400 spectrometer at 400 and 100.6 MHz respectively. Chemical shift values δ are given in ppm and coupling constants J in Hz. MALDI-TOF mass spectra of positive ions were recorded with Bruker Ultraflex spectrometer using 1,8,9-trihydroxyanthracene as matrix and PEGs as internal standards. Spectral data for compounds 6b,c, 7c (n=2) are given in ref. 30, and spectral data for compounds 11a-d, 12b-d and 13c (n=2) are given in ref. 31.

Standard method for the synthesis of N,N'-bis(bromobiphenyl)polyamines 3a-d and 10b-d. A two-neck flask equipped with a magnetic stirrer, flushed with dry argon was charged with 4,4'-dibromobiphenyl 1 or 3,3'-dibromobiphenyl 9 (2.2 mmol, 686 mg), Pd(dbam)2 (0.04 mmol, 23 mg), BINAP (0.045 mmol, 28 mg), absolute dioxane (10 ml), the mixture was stirred for 2 min, then appropriate polyamine 2a-d (1 mmol) was added, followed by tBuONa (3 mmol, 290 mg). The reaction mixture was refluxed for 10 h, cooled to ambient temperature, filtered and evaporated in vacuo. The residue was chromatographed on silica gel using a sequence of eluents: CH2Cl2, CH2Cl2/MeOH 500:1 – 3:1, CH2Cl2/MeOH/NH3aq 100:20:1 – 10:4:1.

N1,N3-Bis(4'-bromobiphenyl-4-yl)propane-1,3-diamine (3a) was synthesized from 1,3-propanediamine (2a) (74 mg). Eluent CH2Cl2, CH2Cl2/MeOH 500:1, yield 135 mg (25%), pale-yellow crystals, m.p. 209-210°C. 1H NMR δ 1.99 (quintet, 3J = 6.7 Hz, 2H), 3.32 (t, 3J = 6.7 Hz, 4H), 6.68 (d, 3J = 8.7 Hz, 4H), 7.38 (d, 3J = 8.4 Hz, 4H), 7.40 (d, 3J = 8.7 Hz, 4H), 7.49 (d, 3J =
8.4 Hz, 4H), NH protons were not assigned; $^{13}$C NMR $\delta$ 29.1 (1C), 42.0 (2C), 113.3 (4C), 120.0 (2C), 127.8 (8C), 129.0 (2C), 131.7 (4C), 140.0 (2C), 147.6 (2C); HRMS MALDI-TOF m/z: calcd. for $\text{C}_{27}\text{H}_{32}\text{Br}_2\text{N}_2$ 535.0384 [M+H]$^+$, found 535.0359.

$N^1,N^1'-(\text{Biphenyl-4,4'-diyl})bis(N^3-(4'-bromobiphenyl-4-yl)propane-1,3-diamine)$ (4a) was obtained as the second product in the synthesis of compound 3a. Eluent CH$_2$Cl$_2$-MeOH 200:1, yield 35 mg (9%), pale-yellow glassy solid. $^1$H NMR $\delta$ 1.98 (quintet, $^3J$ = 6.6 Hz, 4H), 3.31 (t, $^3J$ = 6.4 Hz, 4H), 3.32 (t, $^3J$ = 6.4 Hz, 4H), 3.80 (br s, 2H), 3.91 (br s, 2H), 6.66 (d, $^3J$ = 8.5 Hz, 4H), 6.67 (d, $^3J$ = 8.5 Hz, 4H), 7.35-7.42 (m, 12H), 7.49 (d, $^3J$ = 8.2 Hz, 4H); $^{13}$C NMR $\delta$ 29.2 (2C), 41.9 (2C), 42.1 (2C), 113.1 (4C), 113.2 (4C), 120.0 (2C), 127.2 (4C), 127.8 (8C), 129.0 (2C), 131.7 (4C), 132.0 (2C), 140.1 (2C), 146.7 (2C), 147.8 (2C); HRMS MALDI-TOF m/z: calcd. for $\text{C}_{27}\text{H}_{32}\text{Br}_2\text{N}_2$ 759.1698 [M+H]$^+$, found 759.1662.

$N,N'-(2,2'-(\text{Ethane-1,2-diyl}bis(oxy))bis(\text{ethane-2,1-diyl})bis(4'-bromobiphenyl-4-amine)}$ (3b) was synthesized from dioxa diamine 2b (148 mg). Isolated from the reaction mixture by treatment with CH$_2$Cl$_2$. Pale-yellow crystals, m.p. 184-185°C. $^1$H NMR $\delta$ 3.34 (t, $^3J$ = 5.2 Hz, 4H), 3.67 (s, 4H), 3.73 (t, $^3J$ = 5.2 Hz, 4H), 4.21 (br s, 2H), 6.65 (d, $^3J$ = 8.6 Hz, 4H), 7.35 (d, $^3J$ = 8.7 Hz, 8H), 7.47 (d, $^3J$ = 8.3 Hz, 4H); $^{13}$C NMR $\delta$ 43.4 (2C), 69.6 (2C), 70.3 (2C), 113.3 (4C), 120.0 (2C), 127.7 (4C), 127.8 (4C), 129.0 (2C), 131.7 (4C), 132.0 (2C), 140.1 (2C), 146.7 (2C), 147.8 (2C); HRMS MALDI-TOF m/z: calcd. for $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{N}_2$ 609.0752 [M+H]$^+$, found 609.0784.

$N,N'-(3,3'-(2,2'-Oxybis(\text{ethane-2,1-diyl})bis(oxy))bis(\text{propane-3,1-diyl})bis(4'-bromobiphenyl-4-amine)}$ (3c) was synthesized from trioxa diamine 2c (220 mg). Eluent CH$_2$Cl$_2$-MeOH 200:1-100:1, yield 235 mg (34%), pale-yellow crystals, m.p. 104-105°C. $^1$H NMR $\delta$ 1.91 (quintet, $^3J$ = 6.1 Hz, 4H), 3.27 (t, $^3J$ = 6.5 Hz, 4H), 3.63 (t, $^3J$ = 5.8 Hz, 4H), 3.62-3.66 (m, 4H), 3.69-3.73 (m, 4H), 4.23 (br s, 2H), 6.65 (d, $^3J$ = 8.5 Hz, 4H), 7.38 (d, $^3J$ = 8.7 Hz, 4H), 7.39 (d, $^3J$ = 8.5 Hz, 4H), 7.49 (d, $^3J$ = 8.7 Hz, 4H); $^{13}$C NMR $\delta$ 28.9 (2C), 41.7 (2C), 69.7 (2C), 70.2 (2C), 70.5 (2C), 112.9 (4C), 119.7 (2C), 127.5 (4C), 127.6 (4C), 128.3 (2C), 131.6 (4C), 140.1 (2C), 148.1 (2C); HRMS MALDI-TOF m/z: calcd. for $\text{C}_{25}\text{H}_{32}\text{Br}_2\text{N}_2\text{O}_3$ 681.1327 [M+H]$^+$, found 681.1345.

$N^4,N^4'-(\text{Bis-[3-[2-[3-(4'-bromobiphenyl-4-ylamino)propoxy]ethoxy]ethoxy]propyl})-biphenyl-4,4'-diamine$ (4c) was obtained as the second product in the synthesis of compound 3c. Eluent CH$_2$Cl$_2$-MeOH 50:1, yield 102 mg (19%), pale-yellow glassy solid. $^1$H NMR $\delta$ 1.90 (quintet, $^3J$ = 6.1 Hz, 8H), 3.25 (t, $^3J$ = 6.3 Hz, 4H), 3.26 (t, $^3J$ = 6.3 Hz, 4H), 3.61 (t, $^3J$ = 5.9 Hz, 8H), 3.61-3.65 (m, 8H), 3.67-3.71 (m, 8H), 4.07 (br s, 4H), 6.64 (d, $^3J$ = 8.4 Hz, 4H), 6.65 (d, $^3J$ = 8.6 Hz, 4H), 7.33-7.41 (m, 12H), 7.48 (d, $^3J$ = 8.5 Hz, 4H); $^{13}$C NMR $\delta$ 28.9 (2C), 29.0 (2C), 41.5 (2C), 41.8 (2C), 69.6 (4C), 70.1 (4C), 70.5 (4C), 112.8 (4C), 113.0 (4C), 119.6 (2C), 126.8 (4C), 127.4 (4C), 127.5 (4C), 128.5 (2C), 130.2 (2C), 131.5 (4C), 140.1 (2C), 146.8 (2C), 148.2 (2C); HRMS MALDI-TOF m/z: calcd. for $\text{C}_{56}\text{H}_{60}\text{Br}_2\text{N}_2\text{O}_6$ 1051.3584 [M+H]$^+$, found 1051.3532.

$N^1,N^1'-(\text{Ethane-1,2-diyl})bis[N^3-(4'-bromobiphenyl-4-yl)propane-1,3-diamine}$ (3d) was synthesized from tetraamine 2d (174 mg). Eluent CH$_2$Cl$_2$-MeOH-NH$_3$aq 100:20:1, yield 142 mg (22%), pale-yellow crystals, m.p. 158-160°C. $^1$H NMR $\delta$ 1.81 (quintet, $^3J$ = 6.6 Hz, 4H), 2.75 (s, 4H), 2.77 (t, $^3J$ = 6.6 Hz, 4H), 3.22 (t, $^3J$ = 6.6 Hz, 4H), 6.63 (d, $^3J$ = 8.7 Hz, 4H), 7.36 (d, $^3J$ =
8.4 Hz, 8H), 7.47 (d, 3J = 8.6 Hz, 4H), NH protons were not assigned; 13C NMR δ 29.4 (2C), 42.7 (2C), 48.2 (2C), 49.4 (2C), 112.9 (4C), 119.9 (2C), 127.7 (8C), 128.5 (2C), 131.6 (4C), 140.1 (2C), 148.2 (2C); HRMS MALDI-TOF m/z: calcd. for C32H37Br2N4 635.1385 [M+H]+, found 635.1357.

N1,N1-(Biphenyl-4,4'-diyl)bis[N3-[2-[3-(4'-bromobiphenyl-4-ylamino)propylamino]ethyl]propane-1,3-diamine] (4d) was obtained as the second product in the synthesis of compound 3d. Eluent CH2Cl2-MeOH-NH3aq 100:20:2, yield 86 mg (18%), pale-yellow crystals, m.p. 164-165°C. 1H NMR δ 1.79 (quintet, 3J = 5.8 Hz, 8H), 2.73 (s, 8H), 2.75 (t, 3J = 6.4 Hz, 8H), 3.20 (t, 3J = 5.9 Hz, 8H), 6.61 (d, 3J = 8.2 Hz, 4H), 6.64 (d, 3J = 8.7 Hz, 4H), 7.32-7.39 (m, 12H), 7.46 (d, 3J = 8.3 Hz, 4H), NH protons were not assigned; 13C NMR δ 29.3 (2C), 29.5 (2C), 42.6 (2C), 42.8 (2C), 48.1 (4C), 49.4 (4C), 112.8 (4C), 113.0 (4C), 119.7 (2C), 126.9 (4C), 127.6 (8C), 128.2 (2C), 130.3 (2C), 131.5 (4C), 140.1 (2C), 146.9 (2C), 148.2 (2C); HRMS MALDI-TOF m/z: calcd. for C32H37Br2N4 635.1385 [M+H]+, found 635.1357.

N1-(2-(3-Aminopropylamino)ethyl)-N3-(4'-bromobiphenyl-4-yl)propane-1,3-diamine (5d) was obtained as the third product in the synthesis of compound 3d. Eluent CH2Cl2-MeOH-NH3aq 10:4:1, yield 131 mg (32%), pale-yellow oil. 1H NMR δ 1.62 (quintet, 3J = 6.7 Hz, 2H), 1.80 (quintet, 3J = 6.4 Hz, 2H), 2.67 (t, 3J = 6.6 Hz, 2H), 2.72 (s, 4H), 2.72-2.77 (m, 4H), 3.21 (t, 3J = 6.5 Hz, 2H), 6.63 (d, 3J = 8.2 Hz, 2H), 7.36 (d, 3J = 8.2 Hz, 2H), 7.37 (d, 3J = 8.1 Hz, 2H), 7.46 (d, 3J = 8.1 Hz, 2H), NH protons were not assigned; 13C NMR δ 29.1, 32.8, 40.2, 42.4, 47.6, 47.8, 49.1, 49.2, 112.7 (2C), 119.6, 127.4 (4C), 128.1, 131.4 (2C), 140.0, 148.1; HRMS MALDI-TOF m/z: calcd. for C20H36BrN8 959.3699 [M+H]+, found 959.3743.

N,N'-[2,2'-[Ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl)]bis(3'-bromobiphenyl-3-amine) (10b) was synthesized from 3,3-dibromobiphenyl 9 (0.75 mmol, 234 mg) and dioxadiamine 2b (0.25 mmol, 37 mg) in the presence of Pd(dbca2)2 (6 mg) and Xanthos (6.5 mg) in dioxane (2.5 ml), after 46 h reflux. Eluent CH2Cl2-MeOH 500:1-200:1, yield 41 mg (27%), pale-yellow glassy solid. 1H NMR δ 3.36 (t, 3J = 5.2 Hz, 4H), 3.68 (s, 4H), 3.74 (t, 5.2 Hz, 4H), 4.19 (br s, 2H), 6.62 (dd, 3J = 8.0 Hz, 4J = 2.2 Hz, 2H), 6.77 (t, 4J = 1.6 Hz, 2H), 6.88 (d, 3J = 7.6 Hz, 2H), 7.22 (t, 3J = 7.8 Hz, 2H), 7.25 (t, 3J = 7.7 Hz, 2H), 7.41-7.46 (m, 4H), 7.69 (t, 4J = 1.6 Hz, 2H); 13C NMR δ 43.5 (2C), 69.6 (2C), 70.2 (2C), 111.6 (2C), 112.6 (2C), 116.6 (2C), 122.7 (2C), 125.7 (2C), 129.7 (2C), 129.9 (2C), 130.0 (2C), 130.1 (2C), 140.8 (2C), 143.8 (2C), 148.6 (2C); HRMS MALDI-TOF m/z: calcd. for C30H13Br2N2O2 609.0752 [M+H]+, found 609.0739.

N3,N3'-Bis[2-[2-[3'-bromobiphenyl-3-ylamino)ethoxy]ethoxy]ethyl]biphenyl-3,3'-diamine (14b) was obtained as the second product in the synthesis of compound 10b. Eluent CH2Cl2-MeOH 100:1, yield 6 mg (5%), pale-yellow glassy solid. 1H NMR δ 3.34 (t, 3J = 5.0 Hz, 4H), 3.35 (t, 3J = 5.0 Hz, 4H), 3.66 (s, 8H), 3.72 (t, 3J = 5.0 Hz, 4H), 3.73 (t, 3J = 5.0 Hz, 4H), 6.58 (dd, 3J = 8.0 Hz, 4J = 1.8 Hz, 2H), 6.61 (dd, 3J = 8.2 Hz, 4J = 1.5 Hz, 2H), 6.76 (br s, 2H), 6.79 (br s, 2H), 6.87 (d, 3J = 7.2 Hz, 2H), 6.89 (d, 3J = 7.7 Hz, 2H), 7.13-7.29 (m, 6H), 7.40-7.46 (m, 4H), 7.68 (t, 4J = 1.8 Hz, 2H), NH protons were not assigned; 13C NMR δ 43.5 (4C), 69.6 (4C), 70.3 (4C), 111.7 (2C), 112.0 (4C), 112.7 (2C), 116.6 (2C), 116.8 (2C), 122.7 (2C), 125.8 (2C), 129.4 (2C), 129.7 (2C), 130.0 (2C), 130.1 (2C), 130.2 (2C), 140.8 (2C), 142.9 (2C), 143.9 (2C),
148.4 (2C), 148.6 (2C); HRMS MALDI-TOF m/z: calcd. for C_{48}H_{53}Br_2N_4O_4 907.2434 [M+H]^+, found 907.2479.

\[ N,N'-(3,3',2,2'-Oxybis(ethane-2,1-diyl))bis(oxy))bis(propane-3,1-diyl))bis(3'-bromo biphenyl-3-amine) \] (10c) was synthesized from 3,3-dibromobiphenyl 9 (0.75 mmol, 234 mg) and trioxadiamine 2c (0.25 mmol, 55 mg) in the presence of Pd(dba)_2 (6 mg) and Xanthphos (6.5 mg) in dioxane (2.5 ml). Eluent CH_2Cl_2-MeOH 200:1, yield 59 mg (35%), pale-yellow glassy solid. \(^1\)H NMR δ 1.90 (quintet, \(^3\)J = 6.1 Hz, 4H), 3.28 (t, \(^3\)J = 6.4 Hz, 4H), 3.61 (t, \(^3\)J = 5.8 Hz, 4H), 3.62–3.65 (m, 4H), 3.67–3.71 (m, 4H), 4.22 (br s, 2H), 6.62 (dd, \(^3\)J = 8.1 Hz, \(^4\)J = 2.3 Hz, 2H), 6.75 (br s, 2H), 6.86 (d, \(^3\)J = 7.4 Hz, 2H), 7.23 (t, \(^3\)J = 7.8 Hz, 2H), 7.27 (t, \(^3\)J = 7.8 Hz, 2H), 7.45 (d, \(^3\)J = 7.9 Hz, 2H) 7.49 (d, \(^3\)J = 7.8 Hz, 2H), 7.73 (br s, 2H); \(^13\)C NMR δ 29.0 (2C), 41.8 (2C), 69.7 (2C), 70.2 (2C), 70.6 (2C), 111.2 (2C), 111.6 (2C), 112.2 (2C), 115.9 (2C), 122.6 (2C), 125.7 (2C), 129.6 (2C), 129.9 (2C), 130.0 (2C), 130.1 (2C), 140.7 (2C), 144.0 (2C), 148.9 (2C); HRMS MALDI-TOF m/z: calcd. for C_{34}H_{38}Br_2N_2O_3 680.1249 [M]^+, found 680.1283.

\[ N_3,N_3'-Bis[3-2-[3-(3'-bromobiphenyl-3-ylamino)propoxy]ethoxy]ethoxy]propyl] biphenyl-3,3'-diamine \] (14c) was obtained as the second product in the synthesis of compound 10c. Eluent CH_2Cl_2-MeOH 75:1-50:1, yield 25 mg (19%), pale-yellow glassy solid. \(^1\)H NMR δ 1.89 (quintet, \(^3\)J = 5.9 Hz, 8H), 3.26 (t, \(^3\)J = 6.3 Hz, 4H), 3.27 (t, \(^3\)J = 6.1 Hz, 4H), 3.56–3.62 (m, 16H), 3.65–3.69 (m, 8H), 4.16 (br s, 4H), 6.56 (d, \(^3\)J = 8.2 Hz, 2H), 6.58 (d, \(^3\)J = 8.3 Hz, 2H), 6.74 (br s, 2H), 6.78 (br s, 2H), 6.84 (d, \(^3\)J = 7.5 Hz, 2H), 6.88 (d, \(^3\)J = 7.2 Hz, 2H), 7.19 (t, \(^3\)J = 7.8 Hz, 2H), 7.21 (t, \(^3\)J = 8.2 Hz, 2H), 7.25 (t, \(^3\)J = 8.1 Hz, 2H), 7.44 (d, \(^3\)J = 7.1 Hz, 2H), 7.48 (d, \(^3\)J = 6.8 Hz, 2H), 7.71 (br s, 2H); \(^13\)C NMR δ 29.0 (2C), 29.1 (2C), 41.8 (4C), 69.7 (4C), 70.2 (4C), 70.6 (4C), 111.2 (2C), 111.5 (2C), 111.6 (2C), 112.2 (2C), 115.9 (2C), 116.2 (2C), 122.6 (2C), 125.7 (2C), 129.3 (2C), 129.9 (2C), 130.0 (2C), 130.1 (2C), 140.7 (2C), 143.0 (2C), 144.0 (2C), 148.7 (2C), 149.0 (2C); HRMS MALDI-TOF m/z: calcd. for C_{56}H_{58}Br_2N_4O_6 1050.3506 [M]^+, found 1050.3516.

\[ N_1,N_1'-(Ethane-1,2-diyl))bis[N_3-(3'-bromobiphenyl-3-yl)propane-1,3-diamine] \] (10d) was synthesized from 3,3-dibromobiphenyl 9 (1.1 mmol, 343 mg) and tetraamine 2d (0.5 mmol, 87 mg) in the presence of Pd(dba)_2 (12 mg) and BINAP (14 mg) in dioxane (5 ml). Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:1, yield 82 mg (26%), pale-yellow glassy solid. \(^1\)H NMR δ 1.81 (quintet, \(^3\)J = 6.5 Hz, 4H), 2.76 (s, 4H), 2.78 (t, \(^3\)J = 6.6 Hz, 4H), 3.23 (t, \(^3\)J = 6.5 Hz, 4H), 6.61 (dd, \(^3\)J = 8.1 Hz, \(^4\)J = 1.5 Hz, 2H), 6.75 (br s, 2H), 6.87 (d, \(^3\)J = 7.6 Hz, 2H), 7.23 (t, \(^3\)J = 7.8 Hz, 2H), 7.27 (t, \(^3\)J = 7.8 Hz, 2H), 7.45 (d, \(^3\)J = 8.1 Hz, 2H), 7.49 (d, \(^3\)J = 7.7 Hz, 2H), 7.72 (br s, 2H), NH protons were not assigned; \(^13\)C NMR δ 29.4 (2C), 42.7 (2C), 48.1 (2C), 49.3 (2C), 111.2 (2C), 112.2 (2C), 116.0 (2C), 122.6 (2C), 125.7 (2C), 129.6 (2C), 129.9 (2C), 130.0 (4C), 140.7 (2C), 143.9 (2C), 148.9 (2C); HRMS MALDI-TOF m/z: calcd. for C_{32}H_{37}Br_2N_4 635.1385 [M+H]^+, found 635.1370.

\[ N_1,N_1'-(Biphenyl-3,3'-diyl))bis[N_3-[2-[3-(3'-bromobiphenyl-3-ylamino)propylamino]ethyl] propane-1,3-diamine] \] (14d) was obtained as the second product in the synthesis of compound 10d. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:2, yield 68 mg (28%), pale-yellow glassy solid. \(^1\)H NMR δ 1.79 (quintet, \(^3\)J = 5.8 Hz, 8H), 2.74 (s, 8H), 2.75 (t, \(^3\)J = 6.4 Hz, 8H), 3.21 (t, \(^3\)J = 5.7 Hz, 4H).
atographed on silica gel using a sequence of eluents: CH$_2$N$_6$, 10, 19, 23, 32, 36, 45, 49.

MALDI modes (2C), 143.9 (2C), 148.7 (2C), 148.9 (2C); HRMS MALDI-TOF m/z: calcd. for C$_{52}$H$_{65}$Br$_2$N$_8$ 959.369 [M+H]$^+$, found 959.3662.

N$_3$,N$_3'$-[3,3'-[Ethane-1,2-diylbis(azanediyl)]bis(propane-3,1-diy)]bis[N$_3$-[3-[2-[3-(3'-bromobiphenyl-3-ylamino)propylamino]ethylamino]propyl]biphenyl-3,3'-diamine] (15d) obtained as the third product in the synthesis of compound 10d. Eluent CH$_2$Cl$_2$- MeOH-NH$_3$aq 100:20:3, yield 12 mg (12%), pale-yellow glassy solid. $^1$H NMR δ 1.77 (br s, 12H), 2.72 (br s, 24H), 3.20 (br s, 12H), 6.55 (d, $^3$J = 7.6 Hz, 4H), 6.57 (d, $^3$J = 8.0 Hz, 2H), 6.72 (br s, 2H), 6.77 (br s, 4H), 6.84 (d, $^3$J = 8.5 Hz, 2H), 6.87 (d, $^3$J = 7.0 Hz, 4H), 7.14-7.28 (m, 8H), 7.42 (d, $^3$J = 8.0 Hz, 2H), 7.46 (d, $^3$J = 7.7 Hz, 2H), 7.69 (br s, 2H), NH protons were not assigned; $^{13}$C NMR δ 29.4 (2C), 29.5 (4C), 42.8 (6C), 48.2 (6C), 49.4 (6C), 111.2 (2C), 111.6 (4C), 111.7 (4C), 112.3 (2C), 116.0 (2C), 116.3 (4C), 125.8 (2C), 129.4 (4C), 129.7 (2C), 129.9 (2C), 130.1 (2C), 130.1 (4C), 140.8 (2C), 143.0 (4C), 144.0 (2C), 148.7 (4C), 149.0 (2C) HRMS MALDI-TOF m/z: calcd. for C$_{72}$H$_{93}$Br$_2$N$_{12}$ 1283.6013 [M+H]$^+$, found 1283.5970.

Standard method for the synthesis of cyclic dimers 6a-d and 11b-d via isolated N,N'-bis(bromobiphenyl)polyamines (3a-d) and (10b-d)

A two-neck flask equipped with a magnetic stirrer, flushed with dry argon was charged with N,N'-bis(bromobiphenyl)polyamines 3a-d and 10b-d (1 equiv.), Pd(dbac)$_2$ (8 mol%), BINAP (9 mol%), absolute dioxane (to make 0.02 M conc.), the mixture was stirred for 2 min, then appropriate polyamine 2a-d (1 equiv.) was added, followed by tBuONa (3 equiv.). The reaction mixture was refluxed for 30-40 h, cooled to ambient temperature, filtered and evaporated in vacuo. The residue was chromatographed on silica gel using a sequence of eluents: CH$_2$Cl$_2$, CH$_2$Cl$_2$/MeOH 200:1 - 3:1, CH$_2$Cl$_2$/MeOH/NH$_3$aq 100:20:1 - 10:4:1.

6,10,19,23-Tetraazapentacyclo[22.2.2.2.5.2.11.14.21.15.18]tetratriaconta-1(26),4,11,13,15,17,24,27,29,31,33-dodecaene (6a) was synthesized from compound 3a (0.3 mmol, 175 mg), 1,3-diaminopropane 2a (0.3 mmol, 23 mg) in the presence of Pd(dba)$_2$ (14 mg), BINAP (17 mg), tBuONa (90 mg), in 15 ml dioxane. Isolated as a mixture with cyclic tetramer 7a (n=3) Eluent CH$_2$Cl$_2$/MeOH 75:1, yield (for the mixture) 8 mg (6%) $^1$H NMR δ 1.97 (br s, 4H), 3.30 (br s, 8H), 6.42 (d, $^3$J = 8.5 Hz, 8H), 7.07 (d, $^3$J = 8.5 Hz, 8H), NH protons were not assigned; $^{13}$C NMR δ 29.2 (2C), 42.2 (4C), 113.2 (8C), 127.2 (8C), quaternary carbons were not detected; MS MALDI-TOF m/z: calcd. for C$_{30}$H$_{35}$N$_4$ 449.27 [M+H]$^+$, found 449.25.

6,10,19,23,32,36,45,49-Octaazanonacyclo[48.2.2.2.25.2.11.14.21.15.18.24.27.28.31.237.40.241.44]-octahexaconta-1(52),2,4,11,13,15,17,24,26,28,30,37,39,41,43,50,53,55,57,59,61,63,65,67-tetracosaene (7a, n=3) was isolated together with cyclic dimer 6a. $^1$H NMR δ 1.97 (br s, 8H), 3.30 (br s, 16H), 6.61 (d, $^3$J = 8.4 Hz, 16H), 7.37 (d, $^3$J = 8.4 Hz, 16H), NH protons were not
assigned; $^{13}$C NMR $\delta$ 29.2 (4C), 42.2 (8C), 113.1 (16C), 127.2 (16C), quaternary carbons were not detected; MS MALDI-TOF $m/z$: calcd. for C$_{50}$H$_{63}$N$_8$ 897.53 [M+H]$^+$, found 897.57.

9,12,27,30-Tetraoxa-6,15,24,33-tetraazapentacyclo[32.2.2.2$^5$.2$^{16,19}$.2$^{20,23}$]tetraetraconta-1(36),2,4,16,18,20,22,24,37,39,41,43-dodecaene (6b) was synthesized from compound 3b (0.18 mmol, 110 mg), dioxadiamine 2b (0.18 mmol, 27 mg) in the presence of Pd(dba)$_2$ (8 mg), BINAP (10 mg), tBuONa (52 mg), in 9 ml dioxiane. Eluent CH$_2$Cl$_2$/MeOH 50:1, yield 10 mg (9%).

10,13,16,33,36,39-Hexaoxa-6,20,29,43-tetraazapentacyclo[42.2.2.2$^5$.2$^{21,24}$.2$^{25,28}$]tetrapentaconta-1(46),2,4,21,23,25,27,44,47,49,51,53-dodecaene (6c) was synthesized from compound 3c (0.3 mmol, 205 mg), trioxadiamine 2c (0.3 mmol, 65 mg) in the presence of Pd(dba)$_2$ (14 mg), BINAP (17 mg), tBuONa (90 mg), in 15 ml dioxiane. Eluent CH$_2$Cl$_2$/MeOH 50:1, yield 44 mg (20%).

$N,N'$-[Oxybis(ethane-2,1-diyoxypropane-3,1-diyl)]dibiphenyl-4-amine (8c) was obtained as the second product in the synthesis of compound 6c. Eluent CH$_2$Cl$_2$/MeOH 100:1, yield 25 mg (16%), slightly beige glassy solid. $^1$H NMR $\delta$ 1.91 (quintet, $^3J = 5.9$ Hz, 4H), 3.28 (t, $^3J = 6.5$ Hz, 4H), 3.59-3.65 (m, 8H), 3.67-3.72 (m, 4H), 4.05 (br s, 2H), 6.67 (d, $^3J = 8.6$ Hz, 4H), 7.24 (t, $^3J = 7.9$ Hz, 2H), 7.38 (t, $^3J = 7.7$ Hz, 4H), 7.43 (d, $^3J = 8.5$ Hz, 4H), 7.54 (d, $^3J = 7.8$ Hz, 4H); $^{13}$C NMR $\delta$ 29.1 (2C), 41.7 (2C), 69.7 (2C), 70.2 (2C), 70.6 (2C), 112.9 (4C), 125.9 (2C), 126.2 (4C), 127.8 (4C), 128.6 (4C), 129.8 (2C), 141.3 (2C), 148.0 (2C); HRMS MALDI-TOF $m/z$: calcd. for C$_{34}$H$_{41}$N$_2$O$_5$ 525.3117 [M+H]$^+$, found 525.3092.

Cyclic oligomers 7c, (n=3, 5) were isolated as a mixture in the synthesis of compound 6c. Eluent CH$_2$Cl$_2$/MeOH 20:1-10:1, yield 50 mg (23%). $^1$H NMR $\delta$ 1.88 (quintet, $^3J = 5.8$ Hz, 4(n+1)H), 3.28 (br s, 4(n+1)H), 3.56-3.64 (m, 8(n+1)H), 3.68 (br s, 4(n+1)H), 6.62 (d, $^3J = 8.1$ Hz, 4(n+1)H), 7.34 (d, $^3J = 8.1$ Hz, 4(n+1)H), NH protons were not assigned; $^{13}$C NMR $\delta$ 29.1 (2(n+1)C), 41.9 (2(n+1)C), 69.7 (2(n+1)C), 70.2 (2(n+1)C), 70.6 (2(n+1)C), 113.0 (4(n+1)C), 127.0 (4(n+1)C), 128.6 (2(n+1)C), 147.0 (2(n+1)C); MS MALDI-TOF $m/z$: calcd. for C$_{88}$H$_{121}$N$_6$O$_{12}$ 1481.91 [M+H]$^+$, found 1481.85 (7c, n=3); $m/z$: calcd. for C$_{132}$H$_{181}$N$_{12}$O$_{18}$ 2222.36 [M+H]$^+$, found 2222.27 (7c, n=5).

6,10,13,17,26,30,33,37-Octaazapentacyclo[36.2.2.2$^5$.2$^{18,21}$.2$^{22,25}$]octatetraconta-1(40),2,4,18,20,22,24,38,41,43,45,47-dodecaene (6d) was synthesized from compound 3d (0.26 mmol, 175 mg), tetraamine 2d (0.26 mmol, 45 mg) in the presence of Pd(dba)$_2$ (12 mg), BINAP (14 mg), tBuONa (75 mg), in 13 ml dioxiane. Eluent CH$_2$Cl$_2$/MeOH/NH$_3$aq 100:20-100:20:3, yield 39 mg (23%), pale-yellow crystals, m.p. 99-100°C. $^1$H NMR $\delta$ 1.78 (quintet, $^3J = 6.4$ Hz, 8H), 2.75 (s, 8H), 2.76 (t, $^3J = 6.2$ Hz, 8H), 3.18 (t, $^3J = 6.4$ Hz, 8H), 6.55 (d, $^3J = 8.6$ Hz, 8H), 7.24 (d, $^3J = 8.6$ Hz, 8H), NH protons were not assigned; $^{13}$C NMR $\delta$ 29.4 (4C), 43.1 (4C), 48.1 (4C), 49.0 (4C), 113.1 (8C), 127.0 (8C), 130.4 (4C), 147.0 (4C); HRMS MALDI-TOF $m/z$: calcd. for C$_{40}$H$_{57}$N$_8$ 649.4706 [M+H]$^+$, found 649.4725.

Synthesis of cyclic dimer (6c) via in situ obtained compound (3c). A two-neck flask equipped with a magnetic stirrer, flushed with dry argon was charged with 4,4’-dibromobiphenyl 1 (1.25 mmol, 390 mg), Pd(dba)$_2$ (12 mg), BINAP (14 mg), absolute dioxiane (5 ml), the mixture was
stirred for 2 min, then trioxadiamine 2c (0.5 mmol, 110 mg) was added, followed by tBuONa (144 mg). The reaction mixture was refluxed for 10 h, cooled to ambient temperature, then Pd(dba)$_2$ (35 mg), BINAP (42 mg), absolute dioxane (20 ml) were added, the reaction mixture was stirred for 2 min, trioxadiamine 2c (0.75 mmol, 155 mg) was added, followed by tBuONa (200 mg). The reaction mixture was refluxed for 35 h, cooled to ambient temperature, filtered and evaporated in vacuo. The residue was chromatographed on silica gel using a sequence of eluents: CH$_2$Cl$_2$, CH$_2$Cl$_2$/MeOH 200:1 – 3:1. Compound 8c was isolated with eluent CH$_2$Cl$_2$/MeOH 75:1 (74 mg, 28%), cyclic dimer 6c was isolated with eluent CH$_2$Cl$_2$/MeOH 50:1 (17 mg, 5%), a mixture of cyclic dimer 6c and cyclic trimer 7c (n = 2) was isolated with eluent CH$_2$Cl$_2$/MeOH 20:1 (34 mg, 9%).

10,13,16,33,36,39,56,59,62-Nonaoxa-6,20,29,43,52,66-hexaazaheptacyclo [65.2.2.2$^5$.2$^{21}$.2$^{24}$.2$^{25}$.2$^{28}$.2$^{44}$.2$^{47}$.2$^{48}$.51]henoctaconta-1(69),2,4,21,23,25,27,44,46,48,50,67,70,72,74,76,78,80-octadecaene (7c, n=2): $^1$H NMR $\delta$ 1.88 (br s, 12H), 2.35 (br s, 12H), 3.58-3.65 (m, 24H), 3.68 (br s, 12H), 6.62 (d, $^3$J = 8.3 Hz, 12H), 7.34 (d, $^3$J = 8.3 Hz, 12H), NH protons were not assigned; $^{13}$C NMR $\delta$ 29.1 (6C), 41.8 (6C), 69.7 (6C), 70.2 (6C), 70.6 (6C), 113.0 (12C), 126.9 (12C), 129.0 (6C), 147.0 (6C); MS MALDI-TOF $m/z$: calcd. for C$_{66}$H$_{91}$N$_6$O$_9$ 1111.68 [M+H]$^+$, found 1111.73.

10,13,30,33-Tetraoxa-7,16,27,36-tetraazapentacyclo[35.3.1.1$^{26}$.1$^{17}$.2$^{21}$.1$^{23}$].2$^{26}$]-tetratetraconta-1(41),2(44),3,5,17(43),18,20,22(42),23,25,37,39-dodecaene (11b) was synthesized from compound 10b (0.1 mmol, 60 mg), dioxadiamine 2b (0.1 mmol, 15 mg) in the presence of Pd(dba)$_2$ (4.5 mg), BINAP (5 mg), tBuONa (29 mg), in 5 ml dioxane. Eluent CH$_2$Cl$_2$/MeOH 100:1-75:1, yield 16 mg (27%).

10,13,30,33,50,53,70,73-Octaoxa-7,16,27,36,47,56,67,76-octaazanonacyclo [75.3.1.1$^{26}$.1$^{17}$.2$^{21}$.1$^{22}$.2$^{6}$.1$^{37}$.41].1$^{42}$.46].1$^{57}$.61].1$^{62}$.66]octaoctaconta-1(81),2(88),3,5,17(87),18,20,22(86),23,25,37(85),38,40,42(84),43,45,57(83),58,60,62(82),63,65,77,79-tetracosaene (13b, n=3) was obtained as the second product in the synthesis of compound 10b. Eluent CH$_2$Cl$_2$/MeOH 50:1, yield 8 mg (13%), pale-yellow glassy solid. $^1$H NMR $\delta$ 3.31 (t, $^3$J = 5.2 Hz, 16H), 3.62 (s, 16H), 3.68 (t, $^3$J = 5.2 Hz, 16H), 6.56 (d, $^3$J = 7.5 Hz, 8H), 6.79 (s, 8H), 6.88 (d, $^3$J = 7.3 Hz, 8H), 7.15 (t, $^3$J = 7.8 Hz, 8H), NH protons were not assigned; $^{13}$C NMR $\delta$ 43.5 (8C), 69.6 (8C), 70.2 (8C), 111.9 (8C), 121.1 (8C), 116.7 (8C), 129.4 (8C), 142.8 (8C), 148.4 (8C), HRMS MALDI-TOF $m/z$: calcd. for C$_{72}$H$_{89}$N$_8$O$_8$ 1193.6803 [M+H]$^+$, found 1193.6758.

Cyclic oligomers (13b, n=3, 5) were isolated as a mixture in a separate fraction in the synthesis of cyclic dimer 11b. Eluent CH$_2$Cl$_2$/MeOH 20:1, yield 11 mg (18%). Cyclic hexamer 13b (n=5): $^1$H NMR $\delta$ 3.31 (br s, 24H), 3.63 (s, 24H), 3.68 (br s, 24H), 3.98 (br s, 12H), 6.57 (d, $^3$J = 8.1 Hz, 12H), 6.78 (s, 12H), 6.88 (d, $^3$J = 7.3 Hz, 12H), 7.16 (t, $^3$J = 7.6 Hz, 12H); $^{13}$C NMR $\delta$ 43.5 (12C), 69.7 (12C), 70.2 (12C), 111.9 (12C), 112.0 (12C), 116.8 (12C), 129.4 (12C), 142.8 (12C), 148.4 (12C); MS MALDI-TOF $m/z$: calcd. for C$_{105}$H$_{133}$N$_{12}$O$_{12}$ 1790.02 [M+H]$^+$, found 1790.14.

11,14,17,36,39,42-Hexaaza-7,21,32,46-tetraazapentacyclo[45.3.1.1$^{26}$.1$^{22}$.2$^{6}$.1$^{37}$.31]tetrapentaconta-1(51),2(54),3,5,22(53),23,25,27(52),28,30,47,49-dodecaene (11c) was synthesized from...
compound 10c (0.085 mmol, 58 mg), trioxadiamine 2c (0.085 mmol, 19 mg) in the presence of Pd(dba)$_2$ (4 mg), BINAP (5 mg), tBuONa (26 mg), in 4 ml dioxane. Eluent CH$_2$Cl$_2$/MeOH 75:1-50:1, yield 19 mg (30%).

**Cyclic oligomers 13c (n=3, 5)** were isolated as a mixture in a separate fraction in the synthesis of cyclic dimer 11c, contains also cyclic dimer 11c. Eluent CH$_2$Cl$_2$/MeOH 75:1-50:1, yield 19 mg (30%).

$^1$H NMR $\delta$ 1.87 (quintet, $^3$$J$ = 5.5 Hz, 4(n+1)H), 3.23 (t, $^3$$J$ = 6.0 Hz, 4(n+1)H), 3.52-3.60 (m, 8(n+1)H), 3.61-3.66 (m, 4(n+1)H), 6.55 (d, $^3$$J$ = 6.6 Hz, 2(n+1)H), 6.76 (br s, 2(n+1)H), 6.86 (d, $^3$$J$ = 7.5 Hz, 2(n+1)H), 7.17 (t, $^3$$J$ = 7.3 Hz, 2(n+1)H), NH protons were not assigned; $^{13}$C NMR $\delta$ 29.1 (2(n+1)C), 41.8 (2(n+1)C), 69.7 (2(n+1)C), 70.2 (2(n+1)C), 70.6 (2(n+1)C), 111.6 (4(n+1)C), 116.2 (2(n+1)C), 129.3 (2(n+1)C), 142.9 (2(n+1)C), 148.7 (2(n+1)C); MS MALDI-TOF $m/z$: calcd. for C$_{88}$H$_{121}$N$_8$O$_{12}$ 1481.91 [M+H]$^+$, found 1481.85 (13, n=3); $m/z$: calcld. for C$_{132}$H$_{181}$N$_{12}$O$_{18}$ 2222.36 [M+H]$^+$, found 2222.24 (13, n=5).

7,11,14,18,29,33,36,40-Octaazapentacyclo[39.3.1.1$_2$.6.1$^{19,23}$.1$^{12,28}$]octatetraconta-1(45),2(48),3,5,19(47),20,22,24(46),25,27,41,43-dodecaene (11d) was synthesized from compound 10d (0.19 mmol, 120 mg), tetraamine 2d (0.19 mmol, 33 mg) in the presence of Pd(dba)$_2$ (9 mg), BINAP (11 mg), tBuONa (55 mg), in 10 ml dioxane. Eluent CH$_2$Cl$_2$/MeOH/NH$_3$aq 100:20:3, yield 31 mg (25%).

7,11,14,18,29,33,36,40,51,55,58,62,73,77,80,84-Hexadecaazanonacyclo[83.3.1.1$_2$.6.1$^{19,23}$.1$^{14,28}$]hexadecacosanoconta-1(89),2(96),3,5,19(95),20,22,24(94),25,27,41(93),42,44,46(92),47,49,63(91),64,66,68(90),69,71,85,87-tetracosaene (13d, n=3) was obtained as a mixture with cyclic compound 11d in a separate fraction. Eluent CH$_2$Cl$_2$/MeOH/NH$_3$aq 100:25:5, yield (for a mixture) 34 mg (28%). $^1$H NMR $\delta$ 1.75 (br s, 16H), 2.70 (br s, 32H), 3.16 (br s, 16H), 6.53 (br s, 8H), 6.76 (br s, 8H), 6.86 (br s, 8H), 7.15 (br s, 8H), NH protons were not assigned; $^{13}$C NMR $\delta$ 29.4 (8C), 42.7 (8C), 48.1 (8C), 49.2 (8C), 111.5 (8C), 111.6 (8C), 116.2 (8C), 129.4 (8C), 142.9 (8C), 148.8 (8C); MS MALDI-TOF $m/z$: calcld. for C$_{80}$H$_{113}$N$_8$O$_{12}$ 1297.93 [M+H]$^+$, found 1297.84.

**Standard method for the synthesis of cyclic dimers 11a,c,d via in situ obtained N,N'-bis(bromobiphenyl)polyamines (10a,c,d)**

A two-neck flask equipped with a magnetic stirrer, flushed with dry argon was charged with 3,3'-dibromobiphenyl 9 (1.25 mmol, 390 mg), Pd(dba)$_2$ (12 mg), BINAP (14 mg), absolute dioxane (5 ml), the mixture was stirred for 2 min, then appropriate polyamine 2a,c,d (0.5 mmol) was added, followed by tBuONa (144 mg). The reaction mixture was refluxed for 10 h, cooled to ambient temperature, then Pd(dba)$_2$ (34 mg), BINAP (41 mg), absolute dioxane (20 ml) were added, the reaction mixture was stirred for 2 min, appropriate polyamine 2a,c,d (0.6 mmol) was added, followed by tBuONa (170 mg). The reaction mixture was refluxed for 30-40 h, cooled to ambient temperature, filtered and evaporated in vacuo. The residue was chromatographed on silica gel using a sequence of eluents: CH$_2$Cl$_2$, CH$_2$Cl$_2$/MeOH 200:1 – 3:1, CH$_2$Cl$_2$/MeOH/NH$_3$aq 100:20:1 – 10:4:1.
7,11,22,26-Tetraazapentacyclo[25.3.1.12,6.112,16,117,21]tetratriaconta-1(31),2(34),3,5,12(33),13,15,17(32),18,20,27,29-dodecaene (11a) was synthesized from 1,3-diaminopropane 2a. Eluent CH₂Cl₂/MeOH 200:1, yield 12 mg (5%). 7,11,22,26,37,41-Hexazaheptacyclo[40.3.1.12,6.112,16,117,21,1127,31.123,36]henpentaconta-1(46),2(51),3,5,12(50),13,15,17(49),18,20,27(48),28,30,32(47),33,35,42,44-octadecaene (13a, n=2) was obtained as the second product in the synthesis of cyclic dimer 11a and isolated as a mixture with it in a separate fraction. Eluent CH₂Cl₂/MeOH 100:1, yield (for a mixture) 35 mg (15%). ¹H NMR δ 1.93 (quintet, 3 J = 6.3 Hz, 6H), 3.29 (t, 3 J = 6.3 Hz, 12H), 3.63 (br s, 6H), 6.58 (d, 3 J = 7.6 Hz, 6H), 6.76 (br s, 6H), 6.90 (d, 3 J = 7.7 Hz, 6H), 7.20 (t, 3 J = 7.8 Hz, 6H); ¹³C NMR δ 29.1 (3C), 41.9 (6C), 111.7 (6C), 111.8 (6C), 116.6 (6C), 129.5 (6C), 142.8 (6C), 148.4 (6C); MS MALDI-TOF m/z: calcd. for C₄₅H₉₀N₆ 673.42, found 673.42.

Cyclic dimer (11b) was synthesized from dioxadiamine 2b. Eluent CH₂Cl₂/MeOH 75:1, yield 24 mg (8%).

10,13-Dioxa-7,16-diazatricyclo[15.3.1.12,6]docosa-1(21),2(22),3,5,17,19-hexaene (12b) was obtained as the second product in the synthesis of cyclic dimer 11b Eluent CH₂Cl₂/MeOH 100:1, yield 15 mg (10%).

Cyclic oligomers (13b, n=2, 3) was obtained as a separate mixture in the synthesis of cyclic dimer 11b. Eluent CH₂Cl₂/MeOH 50:1-20:1, yield 20 mg (7%).

Cyclic dimer (11d) was synthesized from tetraamine 2d. Eluent CH₂Cl₂/MeOH/NH₃aq 100:25:5, yield 63 mg (19%).

7,11,14,18-Tetraazatriacyclo[17.3.1.12,6]tetracosa-1(23),2(24),3,5,19,21-hexaene (12d) was obtained as the second product in the synthesis of cyclic dimer 11d Eluent CH₂Cl₂/MeOH/NH₃aq 100:20:1-100:20:2, yield 30 mg (18%).

7,11,14,18,29,33,36,40,51,55,58,62-Dodecaazaheptacyclo-[61.3.1.12,6.119,23,124,28,141,45,146,50]henpentaconta-1(67),2(72),3,5,19(71),20,22,24(70),25,27,41(69),42,44,46(68),47,49,63,65-octadecaene (13d, n=2) was obtained as a mixture with cyclic dimer 11d in a separate fraction. Eluent CH₂Cl₂/MeOH/NH₃aq 100:35:8, yield (for a mixture) 38 mg (12%). ¹H NMR δ 1.78 (br s, 12H), 2.70 (br s, 24H), 3.18 (t, 3 J = 7.0 Hz, 12H), 6.55 (br s, 6H), 6.77 (br s, 6H), 6.87 (d, 3 J = 6.2 Hz, 6H), 7.16 (t, 3 J = 6.9 Hz, 6H), NH protons were not assigned; ¹³C NMR δ 29.4 (6C), 42.6 (6C), 48.0 (6C), 49.2 (6C), 111.5 (12C), 112.6 (6C), 129.3 (6C), 142.8 (6C), 148.7 (6C); MS MALDI-TOF m/z: calcd. for C₆₀H₆₅N₁₂ 973.70 [M+H]+, found 973.74.

Standard method for the synthesis of cyclic dimers 6b-d and 11b-d via in situ obtained bis(polyamine) substituted biphenyls (16b-d) and (18b-d)

A two-neck flask equipped with a magnetic stirrer, flushed with dry argon was charged with 4,4′-dibromobiphenyl 1 or 3,3′-dibromobiphenyl 9 (0.25 mmol, 78 mg), Pd(dba)₂ (6 mg), BINAP (7 mg), absolute dioxane (2.5 ml), the mixture was stirred for 2 min, then appropriate polyamine 2b-d (1 mmol) was added, followed by tBuONa (72 mg). The reaction mixture was refluxed for 10 h, cooled to ambient temperature, 0.25 ml of the reaction mixture was taken for NMR and mass-spectroscopic investigations of compounds 16 and 18, then Pd(dba)₂ (28 mg), BINAP (34
mg), absolute dioxane (10 ml) were added, the reaction mixture was stirred for 2 min, 4,4′-dibromobiphenyl 1 or 3,3′-dibromobiphenyl 9 (0.6 mmol, 187 mg) was added, followed by tBuONa (170 mg). The reaction mixture was refluxed for 30-40 h, cooled to ambient temperature, filtered and evaporated in vacuo. The residue was chromatographed on silica gel using a sequence of eluents: CH₂Cl₂, CH₂Cl₂/MeOH 200:1 – 3:1, CH₂Cl₂/MeOH/NH₃aq 100:20:1 – 10:4:1.

**N,N'-Bis[2-[2-(aminoethoxy)ethoxy]ethyl]biphenyl-4,4′-diamine (16b)** was obtained in situ from dioxadiamine 2b (1mmol, 148 mg). ¹H NMR δ 2.82 (t, 3J = 5.1 Hz, 4H), 3.29 (t, 3J = 5.2 Hz, 4H), 3.48 (t, 3J = 5.2 Hz, 4H), 3.50-3.63 (m, 8H), 3.69 (t, 3J = 5.2 Hz, 4H), 6.64 (d, 3J = 8.6 Hz, 4H), 7.34 (d, 3J = 8.6 Hz, 4H), NH protons were not assigned; ¹³C NMR δ 41.5 (2C), 43.5 (2C), 69.5 (2C), 70.2 (2C), 73.4 (2C), 113.4 (4C), 127.0 (4C), 130.8 (2C), 146.7 (2C); MS MALDI-TOF m/z: calcd. for C₄₁H₃₀N₃O₄ 447.30, found 447.32.

**Cyclic dimer 6b** was synthesized from compound 16b. Eluent CH₂Cl₂/MeOH 75:1, yield 16 mg (11%).

9,12,27,30,45,48-Hexaaza-6,15,24,33,42,51-hexaazaheptacyclo-[50.2.2.2.2.2.2.2.2.2.2.16.19.20.23.24.37.2.38.41]-hexaconta-1(54),2,4,16,18,20,22,34,36,38,40,52,55,57,59,61,63,65-octadecaene (7b, n=2) was obtained as the second product in the synthesis of cyclic dimer 6b. CH₂Cl₂/MeOH 75:1, yield 14 mg (9%).

A mixture of cyclic oligomers (7b, n=2-4) was obtained as a separate fraction in the synthesis of cyclic dimer 6b. Eluent CH₂Cl₂/MeOH 50:1, yield 17 mg (11%).

9,12,27,30,45,48,63,66,Octaaza-6,15,24,33,42,51,60,69-octaazanonacyclo-[68.2.2.2.2.2.2.2.2.2.2.2.16.19.20.23.24.37.2.38.41]-octaoctaconta-1(72),2,4,16,18,20,22,34,36,38,40,52,55,57,59,61,63,65,hexaazaheptacyclo-[68.2.2.2.2.2.2.2.2.2.2.2.16.19.20.23.24.37.2.38.41]-hexaconta-1(54),2,4,16,18,20,22,34,36,38,40,52,55,57,59,61,63,65,67-tetracosaene (7b, n=3) was obtained as a separate fraction in the synthesis of cyclic dimer 6b. Eluent CH₂Cl₂/MeOH 50:1, yield 17 mg (11%).

9,12,27,30,45,48,63,66,81,84-Decaaza-6,15,24,33,42,51,60,69,78,87-decaazaundecacyclo-[86.2.2.2.2.2.2.2.2.2.2.2.16.19.20.23.24.37.2.38.41]-decaoctacontacyclo-[86.2.2.2.2.2.2.2.2.2.2.2.16.19.20.23.24.37.2.38.41]-decaconta-1(90),2,4,16,18,20,22,34,36,38,40,52,54,56,58,70,73,75,77,79,81,83,85,87-tetracosaene (7b, n=4) was obtained as a separate fraction in the synthesis of cyclic dimer 6b. Eluent CH₂Cl₂/MeOH 20:1, yield 43 mg (29%).
N\textsuperscript{4},N\textsuperscript{4}′-Bis(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)biphenyl-4,4′-diamine (16c) was obtained \textit{in situ} from trioxadiamine 2c (1mmol, 220 mg). \textsuperscript{1}H NMR \(\delta 1.67\) (quintet, \(3J = 6.5\) Hz, 4H), 1.85 (quintet, \(3J = 5.2\) Hz, 4H), 2.71 (t, \(3J = 6.7\) Hz, 4H), 3.20 (t, \(3J = 6.4\) Hz, 4H), 3.50 (t, \(3J = 6.2\) Hz, 4H), 3.52-3.64 (m, 20H), 6.59 (d, \(3J = 8.6\) Hz, 4H), 7.30 (d, \(3J = 8.6\) Hz, 4H), NH protons were not assigned; \textsuperscript{13}C NMR \(\delta 29.0\) (2C), 33.2 (2C), 39.3 (2C), 41.7 (2C), 69.3 (2C), 69.6 (2C), 70.0 (2C), 70.1 (2C), 70.5 (4C), 112.9 (4C), 126.9 (4C), 130.3 (2C), 146.9 (2C); MS MALDI-TOF \(m/z\): calcd. for C\textsubscript{32}H\textsubscript{55}N\textsubscript{4}O\textsubscript{6} 591.41 [M+H\textsuperscript{+}], found 591.38.

Cyclic dimer (6c) was synthesized from compound 16c. Eluent CH\textsubscript{2}Cl\textsubscript{2}/MeOH 50:1-20:1, yield 46 mg (24%).

Cyclic trimer (7c, \(n=2\)) was obtained as the second product in the synthesis of cyclic dimer 6c. Eluent CH\textsubscript{2}Cl\textsubscript{2}/MeOH 20:1, yield 8 mg (4%).

Oligomers (17c, \(n=1-4\)) were isolated as separate mixture in the synthesis of cyclic dimer 6c. Eluent CH\textsubscript{2}Cl\textsubscript{2}/MeOH 10:1-5:1, yield 94 mg (50%). 1.81 (br s, 2H), 1.88 (quintet, \(3J = 5.0\) Hz, (4n+2)H), 2.99 (br s, 2H), 3.23 (t, \(3J = 5.2\) Hz, (4n+2)H), 4.59 (br s, (2n+1)H), 6.62 (d, \(3J = 8.1\) Hz, 4nH), 6.70 (d, \(3J = 8.6\) Hz, 2H), 7.24 (t, \(3J = 8.0\) Hz, 1H), 7.34 (d, \(3J = 8.1\) Hz, 4nH), 7.38 (t, \(3J = 7.7\) Hz, 2H), 7.42 (d, \(3J = 8.5\) Hz, 2H), 7.52 (d, \(3J = 7.5\) Hz, 2H), protons of NH\textsubscript{2} group were not assigned; \textsuperscript{13}C NMR \(\delta 26.6\) (1C), 28.8 (1C), 29.0 (2nC), 39.7 (1C), 41.6 (1C), 41.7 (2nC), 69.6 (2(n+1)C), 70.1 (2(n+1)C), 70.5 (2(n+1)C), 112.9 (4nC), 113.5 (2C), 126.0 (2C), 126.9 (4nC), 127.7 (2C), 128.5 (2C), 129.0 (1C), 130.2 (2nC), 146.9 (2(n+1)C), two aromatic quaternary carbons were not detected; MS MALDI-TOF \(m/z\): calcd. for C\textsubscript{44}H\textsubscript{63}N\textsubscript{4}O\textsubscript{6} 743.47 [M+H\textsuperscript{+}], found 743.44 (17c, \(n=1\)); \(m/z\): calcd. for C\textsubscript{68}H\textsubscript{93}N\textsubscript{5}O\textsubscript{9} 1113.70 [M+H\textsuperscript{+}], found 1113.65 17c (n=2); \(m/z\): calcd. for C\textsubscript{88}H\textsubscript{123}N\textsubscript{6}O\textsubscript{12} 1483.93 [M+H\textsuperscript{+}], found 1483.85 17c (n=3); \(m/z\): calcd. for C\textsubscript{110}H\textsubscript{155}N\textsubscript{10}O\textsubscript{15} 1854.15 [M+H\textsuperscript{+}], found 1854.01 17c (n=4).

N\textsuperscript{4},N\textsuperscript{4}′-Bis(phenyl-4,4′-diyl)bis[N\textsuperscript{3}-[2-(3-aminopropylamino)ethyl]propane-1,3-diamine] (16d) was obtained \textit{in situ} from tetraamine 2d (1mmol, 174 mg). \textsuperscript{1}H NMR \(\delta 1.58\) (quintet, \(3J = 6.9\) Hz, 4H), 1.76 (quintet, \(3J = 6.4\) Hz, 4H), 2.61 (t, \(3J = 7.0\) Hz, 4H), 2.67 (s, 8H), 2.68-2.72 (m, 8H), 3.16 (t, \(3J = 6.4\) Hz, 4H), 6.59 (d, \(3J = 8.5\) Hz, 4H), 7.31 (d, \(3J = 8.5\) Hz, 4H), NH protons were not assigned; \textsuperscript{13}C NMR \(\delta 29.5\) (2C), 33.8 (2C), 40.2 (2C), 42.8 (2C), 47.6 (2C), 48.0 (2C), 49.4 (4C), 112.9 (4C), 129.9 (4C), 130.4 (2C), 146.9 (2C); MS MALDI-TOF \(m/z\): calcd. for C\textsubscript{28}H\textsubscript{51}N\textsubscript{8} 499.42 [M+H\textsuperscript{+}], found 499.43.

Cyclic dimer (6d) was synthesized from compound 16d. Eluent CH\textsubscript{2}Cl\textsubscript{2}/MeOH/ NH\textsubscript{3}aq 100:20:3, yield 12 mg (7%).

6,10,13,17,26,30,33,37,46,50,53,57-Dodecaazaheptacyclo-[56.2.2.2.2.5.2]18,21,22,25,28,41,42,45]dodeheptacona-1(60),2,4,18,20,22,24,38,40,42,44,58,61,63,65,67,69,71-octadecaene (7d, \(n=2\)) was obtained as the second product in the synthesis of cyclic dimer 6d. Eluent CH\textsubscript{2}Cl\textsubscript{2}/MeOH/NH\textsubscript{3}aq 100:20:3, yield 6 mg (4%), pale-yellow glassy solid. \textsuperscript{1}H NMR \(\delta 1.77\) (quintet, \(3J = 6.5\) Hz, 12H), 2.73 (s, 12H), 2.76 (t, \(3J = 6.2\) Hz, 12H), 3.13 (t, \(3J = 6.4\) Hz, 12H),
6.60 (d, $^3J = 8.5$ Hz, 12H), 7.33 (d, $^3J = 8.5$ Hz, 12H), NH protons were not assigned; $^{13}$C NMR δ 29.2 (6C), 42.9 (6C), 48.1 (6C), 49.0 (6C), 113.1 (12C), 127.0 (12C), 130.4 (6C), 147.0 (6C); HRMS MALDI-TOF m/z: calcd. for C$_{69}$H$_{85}$N$_{12}$ 973.7020 [M+H]$^+$, found 973.7039.

$N^3,N^3'$-Bis[2-[2-(aminopropoxy)ethoxy]ethyl]biphenyl-3,3'$'$-diamine (18b) was obtained in situ from dioxadiamine 2b (1mmol, 148 mg). $^1$H NMR δ 2.83 (t, $^3J = 5.2$ Hz, 4H), 3.32 (t, $^3J = 5.2$ Hz, 4H), 3.49 (t, $^3J = 5.2$ Hz, 4H), 3.61-3.65 (m, 8H), 3.71 (t, $^3J = 5.2$ Hz, 4H), 6.58 (dd, $^3J = 8.0$ Hz, $^4J = 2.3$ Hz, 2H), 6.80 (t, $^4J = 1.9$ Hz, 2H), 6.89 (d, $^4J = 7.6$ Hz, 2H), 7.19 (t, $^3J = 7.8$ Hz, 2H), NH protons were not assigned; $^{13}$C NMR δ 41.5 (2C), 43.4 (2C), 69.6 (2C), 70.2 (4C), 73.4 (2C), 112.0 (4C), 116.7 (2C), 129.3 (2C), 142.8 (2C), 148.4 (2C); MS MALDI-TOF m/z: calcd. for C$_{24}$H$_{39}$N$_{4}$O$_{6}$ 447.30 [M+H]$^+$, found 447.27.

Cyclic dimer (11b) was synthesized from compound 18b. Eluent CH$_2$Cl$_2$/MeOH 100:1, yield 66 mg (44%).

Cyclic oligomers (13b, n=2, 3) were obtained as a separate fraction in the synthesis of cyclic dimer 11b. Eluent CH$_2$Cl$_2$/MeOH 50:1, yield 56 mg (32%).

Cyclic trimer (13b, n=2) was isolated as a mixture with cyclic dimer 11b in a separate fraction. Eluent CH$_2$Cl$_2$/MeOH 20:1, yield 46 mg (24%).

Macrocycle (12b) was obtained as the second product in the synthesis of cyclic dimer 11b. Eluent CH$_2$Cl$_2$/MeOH 20:1, yield 24 mg (15%).

$N^3,N^3'$-Bis[3-[2-[2-(aminopropoxy)ethoxy]ethoxy]propyl]biphenyl-3,3'$'$-diamine (18c) was obtained in situ from trioxadiamine 2c (1mmol, 220 mg). $^1$H NMR δ 1.64 (quintet, $^3J = 6.5$ Hz, 4H), 1.85 (quintet, $^3J = 5.6$ Hz, 4H), 2.70 (t, $^3J = 6.8$ Hz, 4H), 3.21 (t, $^3J = 5.5$ Hz, 4H), 3.45-3.60 (m, 24H), 6.51 (d, $^3J = 8.0$ Hz, 2H), 6.72 (s, 2H), 6.81 (d, $^3J = 7.4$ Hz, 2H), 7.12 (t, $^3J = 7.7$ Hz, 2H), NH protons were not assigned; $^{13}$C NMR δ 29.0 (2C), 33.2 (2C), 39.4 (2C), 41.6 (2C), 69.3 (2C), 69.6 (2C), 70.0 (2C), 70.1 (2C), 70.5 (4C), 111.4 (4C), 116.0 (2C), 129.2 (2C), 142.8 (2C), 148.6 (2C); MS MALDI-TOF m/z: calcd. for C$_{32}$H$_{55}$N$_{4}$O$_{6}$ 591.41 [M+H]$^+$, found 591.39.

Cyclic dimer (11c) was synthesized from compound 18c. Eluent CH$_2$Cl$_2$/MeOH 75:1-50:1, yield 28 mg (15%).

11,14,17-Trioxa-7,21-diazatricyclo[20.3.1.1$^{6}$]heptacosa-1(26),2(27),3,5,22,24-hexaene (12c) was obtained as the second product in the synthesis of cyclic dimer 11c. Eluent CH$_2$Cl$_2$/MeOH 100:1, yield 72 mg (39%).

Cyclic oligomers (13c, n=2, 3) were obtained as a separate fraction in the synthesis of cyclic dimer 11c. Eluent CH$_2$Cl$_2$/MeOH 20:1, yield 56 mg (30%).

11,14,17,36,39,42,61,64,67-Nonaoxa-7,21,32,46,57,71-hexaazaheptacyclo-[70.3.1.1$^{26}$,1$^{22,26}$,1$^{27,31}$,1$^{45,51}$,1$^{52,56}$]henoctaconta-1(76),2(81),3,5,22(80),23,25,27(79),28,30,47(78),48,50,52(77),53,55,72,74-octadecaene (13c, n=2). $^1$H NMR δ 1.87 (quintet, $^3J = 6.0$ Hz, 12H), 3.24 (t, $^3J = 6.2$ Hz, 12H), 3.53-3.62 (m, 24H), 3.63-3.68 (m, 12H), 4.00 (br s, 6H), 6.55 (br s, 6H), 6.78 (s, 6H), 6.88 (br s, 6H), 7.18 (t, $^3J = 7.7$ Hz, 6H); $^{13}$C NMR δ 29.0 (6C), 41.7 (6C), 69.6 (6C), 70.2 (6C), 70.5 (6C), 111.4 (6C), 111.6 (6C), 116.1 (6C), 129.2 (6C), 142.9 (6C), 148.7 (6C); MS MALDI-TOF m/z: calcd. for C$_{66}$H$_{91}$N$_{6}$O$_{9}$ 1111.68 [M+H]$^+$, found 1111.63.
11,14,17,36,39,42,61,64,67,86,89,92-Dodecaoxa-7,21,32,46,57,71,82,96-octaazanonacyclo
[95.3.1.1.2.6.1.22.26,1.27.31.1.47.51.1.52.56.1.72.76.1.77.81]octahecta-1(101),2(108),3,5,22(107),23,25,
27(106),28,30,47(105),48,50,52(104),53,55,72(103),73,75,77(102),78,80,97,99-tetracosaene (13c, n=3). 1H NMR δ 1.88 (quintet, 3J = 6.2 Hz, 16H), 3.25 (t, 3J = 6.2 Hz, 16H), 3.53-3.62 (m, 32H), 3.63-3.68 (m, 16H), 4.05 (br s, 8H), 6.57 (br s, 8H), 6.78 (s, 8H), 6.88 (br s, 8H), 7.19 (t, 3J = 7.8 Hz, 8H); 13C NMR δ 29.0 (8C), 41.7 (8C), 69.6 (8C), 70.2 (8C), 70.5 (8C), 111.5 (16C), 116.1 (8C), 129.2 (8C), 142.9 (8C), 148.7 (8C); MS MALDI-TOF m/z: calcd. for C88H121N8O12 1481.91 [M+H]+, found 1481.83.

N1,N1′-(Biphenyl-3,3′-diyl)bis[N3-2-(3-aminopropylamino)ethyl]propane-1,3-diamine (18d) was obtained in situ from tetraamine 2d (1mmol, 174 mg). 1H NMR δ 1.58 (quintet, 3J = 7.0 Hz, 4H), 1.77 (quintet, 3J = 5.9 Hz, 4H), 2.62 (t, 3J = 7.0 Hz, 4H), 2.67 (s, 8H), 2.68-2.73 (m, 8H), 3.18 (t, 3J = 5.7 Hz, 4H), 6.53 (d, 3J =7.3 Hz, 2H), 6.74 (s, 2H), 6.83 (d, 3J = 7.3 Hz, 2H), 7.15 (t, 3J = 7.6 Hz, 2H), NH protons were not assigned; 13C NMR δ 29.5 (2C), 33.8 (2C), 40.3 (2C), 42.7 (2C), 47.7 (2C), 48.1 (2C), 49.5 (4C), 111.4 (2C), 111.5 (2C), 116.2 (2C), 129.3 (2C), 142.9 (2C), 148.7 (2C); MS MALDI-TOF m/z: calcd. for C28H51N8 499.42 [M+H]+, found 499.40

Cyclic dimer (11d) was synthesized from compound 18d. Eluent CH2Cl2/MeOH/MH3aq 100:20:3, yield 14 mg (9%).

Macrocycle (12d) was obtained as the second product in the synthesis of cyclic dimer 11d. Eluent CH2Cl2/MeOH/NH3aq 100:20:1-100:20:2, yield 65 mg (40%).

Acknowledgements

This work was supported by RFBR grants N 09-03-00735, 08-03-00628, by the Russian Academy of Sciences program "Elaboration of the methods for the synthesis of chemical compounds and construction of new materials” and by the ARCUS project Bourgogne-Russie.

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