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SYNTHESIS OF POLYAZAMACROCYCLES COMPRISING 6,6'-DIAMINO-2,2'-BIPYRIDINE MOIETIES *VIA* Pd-CATALYZED AMINATION

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Abstract – Pd-catalyzed amination of 6,6'-dibromo-2,2'-bipyridine with a variety of di-, tri-, tetraamines and oxadiamines was carried out for the synthesis of a new class of polyazamacrocycles comprising a 6,6'-diamino-2,2'-bipyridine unit. The obtained results of the catalytic amination reaction were shown to be dramatically dependent on the nature of the amines, mainly on the length of the amine chain. The shortest propane-1,3-diamine and butane-1,4-diamine derivatives provided only cyclic dimers whereas the longest di- and trioxadiamines gave desired macrocycles in very good yields. The formation of cyclic oligomers was observed in all cases. Different reaction conditions leading to cyclic dimers were explored.

INTRODUCTION

2,2'-Bipyridine (bipy) and its derivatives are well known as chelating ligands and serve as basic building blocks for various transition metal complexes. For example, bipy-ruthenium(II) complexes showed characteristic emission spectra and have been the subject of intense studies.[1-3] Different 2,2'-bipyridine derivatives were synthesized to evaluate the influence of the substituents upon the metal ion affinity of ligands and physical properties of the complexes.[4-17] Among these compounds, 6,6'-diamino-2,2'-bipyridine derivatives are of special interest due to their steric hindrance and original optical properties.

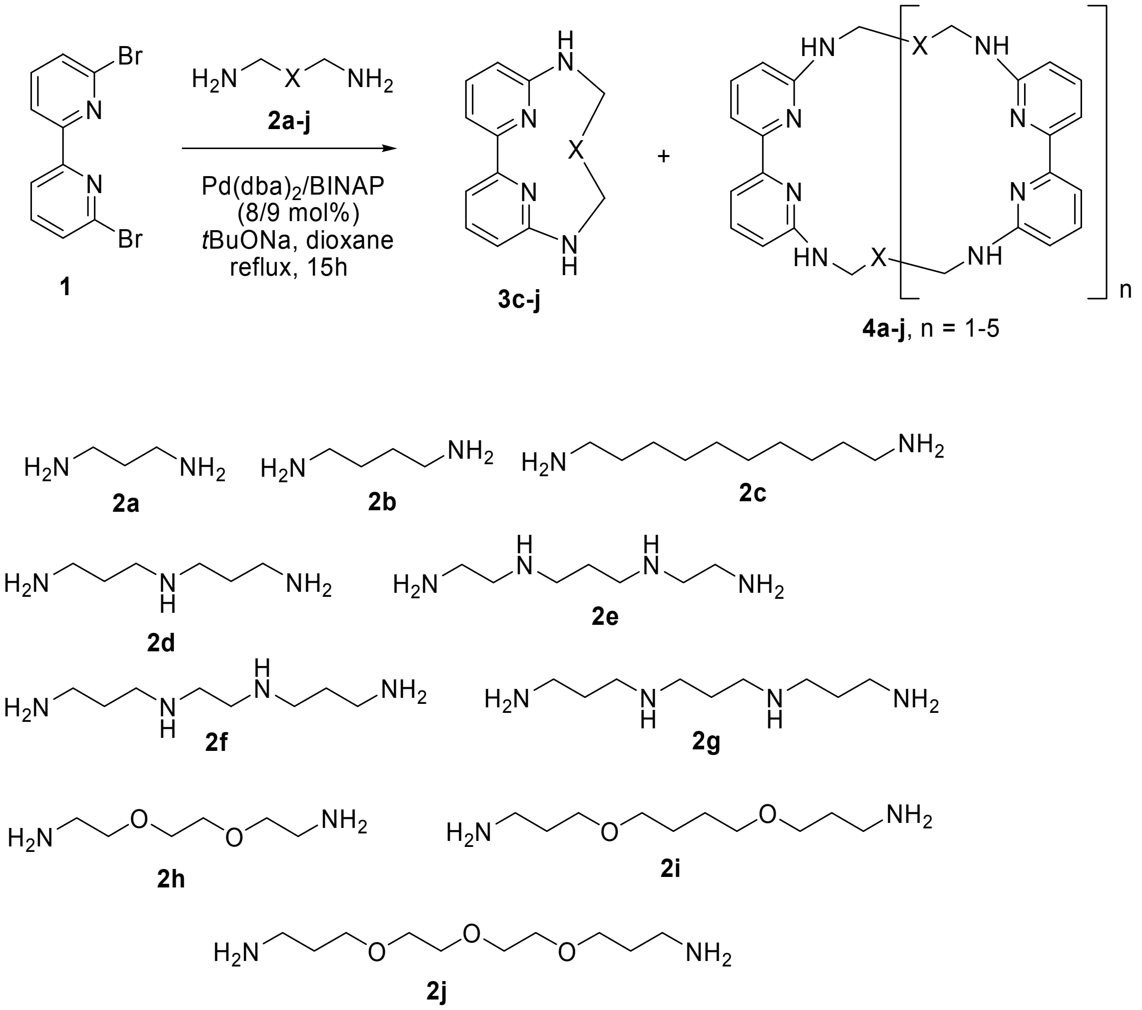
[‡] This paper is dedicated to Prof. Akira Suzuki on the occasion of his 80th birthday

Contrary to most of the non-fluorescent derivatives, bipyridines bearing an amino-group at C-6 position exhibit oxygen-independent fluorescence with high quantum yield.[18] On the other hand, 6,6’-disubstituted bipyridines give almost exclusively mono- and bis-bipy complexes with transition metals,[19-22] while many other derivatives usually form stable tris-bipy complexes. Therefore, 6,6’-diamino-2,2’-bipyridines and their complexes were extensively studied as models to mimic biological systems,[23-28] to extract or transport transition metal cations and anions,[29-32] in catalysis[33-36] or sensoring.[37, 38] However, chemical modification of parent 6,6’-diamino-2,2’-bipyridine is not a simple task. The acylation of the amino groups was often used to prepare tetradentate (N2O2) ligands.[19, 24-26, 32, 33, 35] The alkylation of the amino groups can be achieved after their deprotonation under harsh conditions.[18] The search of new synthetic routes to these derivatives may allow to develop a new strategy for designing pyridine-based fluorescent sensors or biomimetic models. The catalytic amination reaction of 6,6’-dibromo-2,2’-bipyridine can be an efficient method to prepare these derivatives. This reaction was used to obtain bismacrocyclic derivatives possessing 6,6’-diaminobipyridine moiety as a rigid spacer. Both azacrown ethers and tetraazamacrocycles can be linked by this fragment using Pd-catalyzed amination reactions.[39, 40] Moreover, Cu(I)-mediated amination was applied in the synthesis of camphor sultam based chiral bipyridines.[36] Here we report the synthesis of a new family of macrocyclic ligands incorporating one or two fluorescent 6,6’-diaminobipyridine moieties using Buchwald-Hartwig amination reaction.[41]

RESULTS AND DISCUSSION

We have decided to apply Pd-catalyzed amination of aryl halides for the synthesis of polyazamacrocycles which contain a 6,6’-diamino-2,2’-bipyridine moiety. Based on our knowledge in the synthesis of a great variety of macrocycles using this approach,[42-45] the conditions of the synthesis of the pyridine-based macrocycles starting from 2,6- and 3,5-dibromopyridines[46-49] was *a priori* the most relevant way to synthesize the aimed derivatives. The reaction of equimolar amounts of 6,6’-dibromo-2,2’-bipyridine **1** and polyamines **2a-j** (Scheme 1) was carried out in the presence of the catalytic system $Pd(dba)_2$/BINAP (8/9 mol%) which was found to be the most convenient and universal system for the arylation of mono- and polyamines.[50] Diluted solutions (c = 0.02 M) of starting compounds in dioxane and sodium *tert*-butoxide as a base were used and the completion of the reactions were obtained after 15 h of reflux. Reaction mixtures were analyzed using ^{1}H NMR spectroscopy and target macrocycles **3** were purified by chromatography on silica gel. The experimental data are given in Table 1.

It was obvious that diamines **2a,b** would not give the corresponding monocycles, but rather the cyclic dimers **4**. Indeed, the shortest propane-1,3-diamine derivative (**2a**) afforded cyclodimer **4a** in 21% yield (Table 1, entry 1), and its analogue **2b** gave **4b** (n = 1) in a better yield (35% yield) (entry 2) while in parallel a mixture of cyclotrimer and cyclotetramer was isolated.



Scheme 1. Synthesis of macrocycles **3**

Much longer decane-1,10-diamine (**2c**) produced target macrocycle **3c** in a good yield of 30% (entry 3), because the chain length was quite sufficient to favor the ring closure. We have also studied the reactivity of triamine **2d** using the same experimental conditions. According the length of the molecule (9 atoms), the yield of the monocycle **3d** was very poor (entry 4) and a notable amount of cyclooligomers **4d** (n=1-3) was produced as well as linear oligomers. Surprisingly, the reaction of the tetraamine **2e** afforded the corresponding macrocycle **3e**, but in a low 10% yield (entry 5). To improve the process a double amount of the catalyst was used (entry 6) but no significant change was observed. Another electron donor 2-dicyclohexylphosphino-2'-dimethylamino-1,1'-biphenyl ligand which could stimulate diamination of dihaloarenes was also studied without success. It has to be noted that the yield of cyclodimer **4e** (n=1) was also low, while the formation of cyclic and acyclic oligomers of higher mass were observed. The presence of cyclooligomers **4e** (n = 2-4) was established by MALDI-TOF spectroscopy, and acyclic oligomers were observed as admixtures by NMR. We suggest that the low yield observed for compound **3e** is due to the presence of two ethylenediamine fragments in the tetraamine **2e**. These fragments may form 5-membered chelate complexes with Pd which cannot be intermediates in the amination catalytic cycle. The same low reactivity of polyamines comprising repeating ethylenediamine units in the reaction with dihalopyridines was already observed by our groups.[46, 48] This is in good agreement with the best yields observed with tetraamines **2f,g**: macrocycle **3f** was synthesized in 20% yield (entry 7), while compound **3g** was obtained in 29% yield (entry 8).

Table 1. Synthesis of the macrocycles **3**.

Entry	Amine	Yield of **3**, %[a)]	Yield of **4**, %[b)]
1	**2a**	0	**4a** (n = 1), 21
2	**2b**	0	**4b** (n = 1), 35 **4b**, (n = 2, 3), 50
3	**2c**	**3c**, 43 (30)	**4c** (n = 1), 32 **4c** (n = 2, 3) 15
4	**2d**	**3d**, (4)	**4d** (n = 1-3), 45
5	**2e**	**3e**, 20 (10)	**4e** (n = 1), 6 **4e** (n = 2, 3), 18[c)]
6[d)]	**2e**	**3e**, 20 (10)	**4e** (n = 1), 5 **4e** (n = 2-4), 15[c)]
7	**2f**	**3f**, 34 (20)	**3f** (n = 1), 15
8	**2g**	**3g**, 40 (29)	0
9	**2h**	**3h**, 15 (13)	**4h** (n = 1), 20 **4h** (n = 2-5), 26[c)]
10	**2i**	**3i**, 50 (47)	**4i** (n = 1), 17 **4i** (n = 2-5), 22[c)]
11	**2j**	**3j**, 52 (48)	**4j** (n = 1), 15

[a)] Yield in the reaction mixture, yield of isolated macrocycle is given in brackets

[b)] Yield after chromatography

[c)] Contains admixtures of linear oligomers

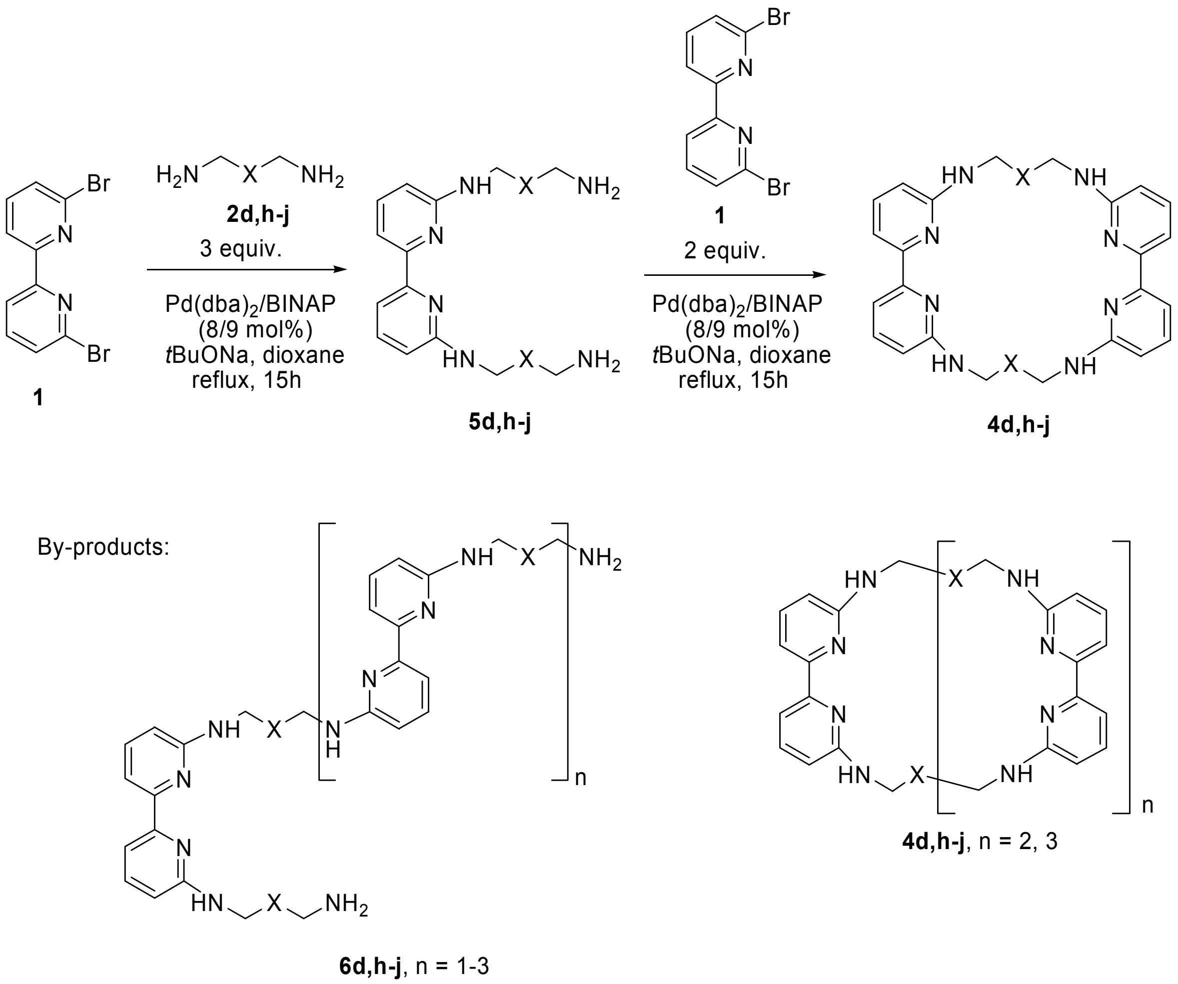
[d)] 16/18 mol% catalyst

Finally, we have also studied the reaction of various oxygen-containing diamines with dibromide derivative **1**. The length of dioxadiamine **2h** was not sufficient to obtain the corresponding macrocycle **3h** in a good yield (entry 9), and we have observed mainly the formation of cyclodimer and higher mass oligomers. The evolution of the reaction changed dramatically when the long dioxadiamine **2i** was used since the macrocycle **3i** was obtained in a very good yield (47%, entry 10). The same high yield was also observed with trioxadiamine **2j** (48%, entry 11), and it is remarkable to note that these yields of the cyclisation reaction obtained *via* catalytic amination of dihaloarenes are among the highest ever observed in such a cyclization reaction.[42-49] For example, they surpass substantially the yields obtained for the pyridine-based macrocycles described previously by our groups.[47, 49] One possible interpretation of such variations of the monocycle yields can be due to the template effect of sodium cations present in the reaction mixtures which form more stable complexes with oxadiamines compared to polyamines. Chromatographic purification of the macrocycles **3c,h-j** – derivatives of diamines was more easy than for the macrocycles **3d-g** – derivatives of tri- and tetraamines, this is evidenced by the comparison of the reaction before and after chromatography.

Macrocycles **3** can be easily discriminated in the reaction mixtures from cyclic oligomers **4** by ^1H NMR spectra. $H^{3,3'}$ protons of the bipyridine moiety in the macrocycles were observed in the region 7.0-7.1 ppm, whereas the same protons of cyclic dimers are downfield shifted (7.4-7.5 ppm). The chemical shift of these protons depends on the size of the cycle: the larger is the cavity, the more downfield shifted the signal of these protons. These data might be due to the *s-cis* configuration (which is the only possible one) of the bipyridine moiety in monocycles and to *s-trans* configuration in the case of cyclic and linear oligomers. The ring current and the electrostatic effect of the nitrogen lone pair are responsible for the anomalous downfield shift of $H^{3,3'}$ protons of the bypiridine moiety of cyclic and linear oligomers, while for monocycles **3** the second parameter does not act.[37]

UV spectra of the macrocycles **3** are similar to the parent 6,6'-diaminopyridine and characterized by a broad absorption band in the region 340-350 nm which corresponds to a π-π^* transfer.[51] The starting dibromide **1** possesses two close absorption bands centered at 295 and 308 nm. Thus, as expected, the substitution of the halogen atoms by the amino groups induces a significant bathochrome shift of the absorption band.

Cyclodimers of type **4** are of great interest due to the presence of two 2,2'-bipyridine moieties and two polyamine chains which can be suitable for the coordination of metal cations or polar organic molecules. In our previous works we have elaborated two different approaches to cyclic dimers possessing two aromatic moieties in the macrocycle: *via* *N,N'*-di(haloaryl)susbtituted polyamines and *via* bis(polyamine)substituted arenes.[43, 47, 49] We have studied these two routes for the synthesis of cyclodimers **4** to determine the best way of synthesis. The first approach proved to be totally useless for the synthesis of desired *N,N'*-di(bromobipyridine)susbtituted diamines which were not obtained even in trace amounts. We tried other conditions for the synthesis of cyclodimers by reacting 1 equivalent of dibromide **1** with 3 equivalents of di- and triamines **2d,h-j**, and the resulting bis(amino)bipyridines **5d,h-j** were further reacted *in situ* with two equivalents of dibromide **1** (Scheme 2). The experimental data are detailed in Table 2. Intermediate compounds **5** were synthesized in enough high yields according to NMR and MALDI-TOF spectra of the reaction mixtures (*ca* 50%), but the yields of the target cyclodimers **4** were lower than those obtained in the above detailed data by reacting equimolar amounts of 6,6'-dibromo-2,2'-bipyridine with polyamines (Table 1). Cyclic oligomers of higher masses **4** (n = 2, 3) were also formed by cyclization of oligomeric by-products **6** obtained during the first step of the reaction as observed on MALDI-TOF spectra.



Scheme 2. Synthesis of cyclodimers **4**

It has to be noted that the main products in all syntheses were linear oligomers detected on NMR spectra as complex mixtures. This is the proof that the cyclization of compounds **5** and **6** with dibromide **1** proceeds reluctantly due to the unfavorable *s-trans* configuration of compound **5** and **6**. Surprisingly, mono-cycles **3** were also isolated in quite reasonable yields due to the reaction of an excess of polyamine formed in the reaction mixture with dibromide **1** added at the second step of the synthesis. In the case of

Table 2. Synthesis of the cyclodimers **4**.

Entry	Amine	Yield of **4** (n = 1), %	Yield of other products, %
1	**2d**	**4d**, 19	**3d**, 23 **4d** (n = 2, 3), 31 linear oligomers, 35
2	**2h**	**4h**, 8	**3h**, 44 **4h**, (n = 2), 4 linear oligomers, 86
3	**2i**	**4i**, 9	**3i**, 43 **4i** (n = 2, 3), 8 linear oligomers, 40
4	**2j**	**4j**, 12	**3j**, 39 **4j** (n = 2, 3), 11 linear oligomers, 57

short triamine **2d** and dioxadiamine **2h** we have obtained monocycles **3d,h** in substantially higher yields (19% and 44% respectively) than for the cyclization reactions carried out with equimolar amounts of starting compounds (Table 1, entries 4, 9). This result may be due to the higher concentration of dibromobipyridine at the second step of the synthesis of cyclodimers. Indeed, we carried out the reaction of equimolar amounts of dibromide **1** with triamine **2d** at higher concentration (c = 0.05 M instead of 0.02 M) and obtained corresponding macrocycle **3d** in 10% yield. The same reaction gave 11% yield of the cyclodimers **4d**.

In conclusion, we have elaborated an efficient one-step synthesis of the nitrogen- and oxygen-containing macrocycles comprising 6,6'-diamino-2,2'-bipyridine moiety. The yields of the target compounds depend on the nature of polyamines employed. We have studied the formation of cyclooligomeric by-products and proposed the synthesis of cyclic dimers using *N,N'*-di(bromobipyridyl)substituted polyamines.

EXPERIMENTAL

All chemicals were purchased from Aldrich and Acros companies and used without further purification. $Pd(dba)_2$ was synthesized according to a procedure already described.[52] 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 μm) purchased from Fluka. ^1H and ^{13}C NMR spectra were registered in $CDCl_3$ 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 spectra were recorded with Bruker Ultraflex spectrometer using 1,8,9-trihydroxyanthracene as matrix and PEGs as internal standards. UV spectra were registered on Perkin-Elmer Lambda-40 spectrometer in CH_2Cl_2.

Typical procedure for the synthesis of macrocycles **3c-k** and cyclodimers **4a,b** (n=1).

A two-neck flask (25 mL) flushed with dry argon, equipped with a magnetic stirrer and condenser was charged with 6,6'-dibromo-2,2'-bipyridine (**1**) (0.25 mmol, 79 mg), $Pd(dba)_2$ (11 mg, 8 mol%), BINAP (14 mg, 9 mol%) and absolute dioxane (12 mL). The mixture was stirred for 2 min, then appropriate amine **2a-k** (0.25 mmol) was added followed by sodium *tert*-butoxide (0.75 mmol, 72 mg). The reaction mixture was refluxed for 15 h, after cooling down to ambient temperature the residue was filtered off, dioxane evaporated *in vacuo*, and the residue was analyzed by NMR spectroscopy. Column chromatography was carried out using a sequence of eluents: CH_2Cl_2, CH_2Cl_2-MeOH 50:1 – 3:1, CH_2Cl_2-MeOH-NH_3aq 100:20:1 – 10:4:1.

7,11,22,26,31,32,33,34-Octaazapentacyclo[25.3.1.1^{2,6}.1^{12,16}.1^{17,21}]tetratriaconta-1(31),2(34),3,5,12(33),13,15,17(32),18,20,27,29-dodecaene (4a) (n = 1). Synthesized from 19 mg (0.25 mmol) of diamine **2a**. Eluent CH_2Cl_2-MeOH 3:1. Yield 12 mg (21%). Pale-yellow solid. Mp 214-215 °C. UV λ_{max} (CH_2Cl_2) 352 (ε 11000). ^{1}H NMR ($CDCl_3$): δ 1.80-1.85 (m, 4H), 3.29-3.34 (m, 8H), 6.35 (d, *J* = 8.1 Hz, 4H), 6.88 (d, *J* = 7.5 Hz, 4H), 7.35 (t, *J* = 7.8 Hz, 4H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 29.3 (2C), 38.2 (4C), 108. 5 (4C), 110.7 (4C), 138.0 (4C), quaternary carbons were not observed due to broad signals of aromatic carbons (25-100 Hz). HRMS (MALDI-TOF) *m/z* calcd for $C_{26}H_{28}N_8$ [M^+] 452.2437, found 452.2451.

7,12,23,28,33,34,35,36-Octaazapentacyclo[27.3.1.1^{2,6}.1^{13,17}.1^{18,22}]hexatriaconta-1(33),2(36),3,5,13(35),14,16,18(34),19,21,29,31-dodecaene (4b) (n = 1). Synthesized from 22 mg (0.25 mmol) of diamine **2b**. Eluent CH_2Cl_2-MeOH 3:1. Yield 21 mg (35%). Pale-yellow solid. Mp 208-210 °C. UV λ_{max} (CH_2Cl_2) 347 (ε 8900). ^{1}H NMR ($CDCl_3$): δ 1.86-1.91 (m, 8H), 3.32-3.37 (m, 8H), 6.58 (d, *J* = 8.1 Hz, 4H), 7.16 (d, *J* = 7.4 Hz, 4H), 7.56-5.61 (m, 4H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 25.5 (4C), 41.0 (4C), 108.5 (4C), 108.9 (4C), 138.4 (4C), quaternary carbons were not observed due to broad signals of aromatic carbons (30-40 Hz). HRMS (MALDI-TOF) *m/z* calcd for $C_{28}H_{32}N_8$ [M^+] 480.2750, found 480.2717.

Mixture of cyclotrimer **4b** (n = 2) and cyclotetramer **4b** (n = 3). Obtained as by-products in the synthesis of cyclodimer **4b** (n = 1). Eluent CH_2Cl_2-MeOH 20:1-10:1. Yield 30 mg (50%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 1.73-1.78 (m, 4(n+1)H), 3.33-3.38 (m, 4(n+1)H), 6.34-6.38 (m, 2(n+1)H), 7.38-7.42 (m, 2(n+1)H), 7.45-7.50 (m, 2(n+1)H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 26.3-26.7 (m, 2(n+1)C), 41.5 (2(n+1)C), 106.6 (2(n+1)C), 107.0 (2(n+1)C), 138.3 (2(n+1)C), quaternary carbons were not observed due to broad signals of aromatic carbons (20-35 Hz). MS (MALDI-TOF) *m/z* calcd for $C_{42}H_{48}N_{12}$ [M^+] 720.41, found 720.55 (**4b** (n = 2)); calcd for $C_{56}H_{64}N_{16}$ [M^+] 960.55, found 960.63 (**4b** (n = 3)). In this work the composition of the mixtures of cyclic oligomers was not determined precisely.

7,18,23,24-Tetraazatricyclo[17.3.1.1^{2,6}]tetracosa-1(23),2(24),3,5,19,21-hexaene (3c). Synthesized from 43 mg (0.25 mmol) of diamine **2c**. Eluent CH_2Cl_2-MeOH 20:1-10:1. Yield 24 mg (30%). Pale-yellow solid. Mp 123-124 °C. UV λ_{max} (CH_2Cl_2) 344 (ε 9700). ^{1}H NMR ($CDCl_3$): δ 1.30-1.34 (m, 4H), 1.38-1.42 (m, 8H), 1.70-1.75 (m, 4H), 3.52 (t, *J* = 7.6 Hz, 4H), 6.59 (bs, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.9 Hz, 2H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 26.1 (2C), 26.4 (2C), 27.3 (2C), 28.4 (2C), 41.6 (2C), 109.9 (4C), 138.1 (2C), 156.3 (2C), 158.2 (2C). HRMS (MALDI-TOF) *m/z* calcd for $C_{20}H_{28}N_4$ [M^+] 324.2314, found 324.2343.

7,18,29,40,45,46,47,48-Octaazapentacyclo[39.3.1.1^{2,6}.1^{19,23}.1^{24,28}]octatetraconta-1(45),2(48),3,5,19(47),20,22,24(46),25,27,41,43-dodecaene (4c) (n =1). Obtained as the second product in the synthesis of macrocycle **3c**. Eluent CH_2Cl_2-MeOH 3:1. Yield 26 mg (32%). Pale-yellow solid. Mp 109-111 °C. UV λ_{max} (CH_2Cl_2) 345 (ε 14000). ^{1}H NMR ($CDCl_3$): δ 1.26-1.31 (m, 16H), 1.34-1.39 (m, 8H), 1.59-1.63 (m, 8H), 3.31 (t, *J* = 6.6 Hz, 8H), 6.39 (d, *J* = 7.7 Hz, 4H), 7.43 (bs, 4H), 7.51 (t, *J* = 7.5 Hz, 4H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 27.0 (4C), 28.7 (4C), 29.3 (4C), 29.6 (4C), 42.3 (4C), 106.5 (4C), 112.9 (4C), 138.7 (4C), 152.4 (4C), 158.0 (4C). HRMS (MALDI-TOF) *m/z* calcd for $C_{40}H_{56}N_8$ [M^+] 648.4628, found 648.4620.

Mixture of cyclotrimer **4c** (n = 2) and cyclotetramer **4c** (n = 3). Obtained as by-products in the synthesis of macrocycle **3c**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:1. Yield 12 mg (15%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 1.26-1.40 (m, 12(n+1)H), 1.61 (t, *J* = 7.5 Hz, 4(n+1)H), 3.29 (t, *J* = 5.8 Hz, 4(n+1)H), 4.57 (bs, 2(n+1)H), 6.35 (d, *J* = 6.0 Hz, 2(n+1)H), 7.47-7.53 (m, 4(n+1)H). ^{13}C NMR ($CDCl_3$): δ 27.1 (2(n+1)C), 28.7-29.6 (m, 6(n+1)C), 42.4 (2(n+1)C), 106.1 (2(n+1)C), 110.0 (2(n+1)C), 138.0 (2(n+1)C), 155.1 (2(n+1)C), 158.4 (2(n+1)C). MS (MALDI-TOF) *m/z* calcd for $C_{60}H_{84}N_{12}$ [M^+] 972.69, found 972.34 (**4c** (n = 2)); calcd for $C_{80}H_{112}N_{16}$ [M^+] 1296.93, found 1296.78 (**4c** (n = 3)).

7,11,15,20,21-Pentaazatricyclo[14.3.1.1^{2,6}]henicosa-1(20),2(21),3,5,16,18-hexaene (3d). Synthesized from 33 mg (0.25 mmol) of triamine **2d** when running the reaction in 5 mL dioxane. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:3. Yield 7 mg (10%). Pale-yellow solid. Mp 135-137 °C. UV λ_{max} (CH_2Cl_2) 351 (ε 6600). ^{1}H NMR ($CDCl_3$): δ 1.95-2.00 (m, 4H), 3.03 (t, *J* = 5.6 Hz, 4H), 3.49 (t, *J* = 5.3 Hz, 4H), 6.38 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 29.2 (2C), 36.5 (2C), 46.2 (2C), 109.6 (2C), 110.8 (2C), 137.8 (2C), 153.8 (2C), 159.2 (2C). HRMS (MALDI-TOF) *m/z* calcd for $C_{16}H_{21}N_5$ [M$^+$] 283.1797, found 283.1819. Spectral data for cyclic oligomers **4d** (n = 1-3) are given below.

7,10,14,17,22,23-Hexaazatricyclo[16.3.1.1^{2,6}]tricosa-1(22),2(23),3,5,18,20-hexaene (3e). Synthesized from 40 mg (0.25 mmol) of tetraamine **2e**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:25:5. Yield 8 mg (10%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 1.57 (quintet, *J* = 6.0 Hz, 2H), 2.79 (t, *J* = 5.8 Hz, 4H), 2.90 (t, *J* = 5.9 Hz, 4H), 3.56 (q, *J* = 5.9 Hz, 4H), 5.13 (bs, 2H), 6.40 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), NH protons of dialkylamino groups were not observed. ^{13}C NMR ($CDCl_3$): δ 28.7 (1C), 41.9 (2C), 48.2 (2C), 49.2 (2C), 108.2 (2C), 111.1 (2C), 137.6 (2C), 155.3 (2C), 158.4 (2C). HRMS (MALDI-TOF) *m/z* calcd for $C_{17}H_{24}N_6$ [M$^+$] 312.2062, found 312.2093.

7,10,14,17,28,31,35,38,43,44,45,46-Dodecaazapentacyclo[37.3.1.1^{2,6}.1^{18,22}.1^{23,27}]hexatetraconta-1(43),2(46),3,5,18(45),19,21,23(44),24,26,39,41-dodecaene (4e) (n = 1). Obtained as by-product in the synthesis of macrocycle **3e**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:25:5. Yield 4 mg (5%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 1.58 (quintet, *J* = 5.7 Hz, 4H), 2.64 (t, *J* = 7.0 Hz, 8H), 2.85 (t, *J* = 5.7 Hz, 8H), 3.49 (t, *J* = 5.0 Hz, 8H), 6.28 (d, *J* = 8.2 Hz, 4H), 7.14 (d, *J* = 7.6 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 29.3 (2C), 41.6 (4C), 47.9 (4C), 48.2 (4C), 107.2 (4C), 110.1 (4C), 137.8 (4C), 155.3 (4C), 159.0 (4C). HRMS (MALDI-TOF) *m/z* calcd for $C_{34}H_{48}N_{12}$ [M$^+$] 624.4125, found 624.4103.

Mixture of cyclotrimer **4e** (n = 2), cyclotetramer **4e** (n = 3) and cyclopentamer **4e** (n = 4). Obtained as by-products in the synthesis of macrocycle **3e**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:25:5. Yield 12 mg (15%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 1.61-1.66 (m, 2(n+1)H), 2.58-2.74 (m, 8(n+1)H), 3.38-3.47 (m, 4(n+1)H), 6.31-6.45 (m, 2(n+1)H), 7.44-7.65 (m, 4(n+1)H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 28.1 ((n+1)C), 41.6 (2(n+1)C), 48.1 (2(n+1)C), 48.9 (2(n+1)C), 109.9-110.2 (m, 4(n+1)C), 137.8-138.0 (m, 2(n+1)C), 155.3 (2(n+1)C), 158.3 + 158.4 (2(n+1)C). MS (MALDI-TOF) *m/z* calcd for $C_{51}H_{72}N_{18}$ [M$^+$] 936.62, found 936.31 (**4e** (n = 2)); calcd for $C_{68}H_{96}N_{24}$ [M$^+$] 1248.82, found 1248.64 (**4e** (n = 3)); calcd for $C_{85}H_{120}N_{30}$ [M^+] 1561.03, found 1561.27 (**4e** (n = 4)).

7,11,14,18,23,24-Hexaazatricyclo[17.3.1.1^{2,6}]tetracosa-1(23),2(24),3,5,19,21-hexaene (3f). Synthesized from 44 mg (0.25 mmol) of tetraamine **2f**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:3. Yield 16 mg (20%). Pale-yellow solid. Mp 108-110 °C. UV λ_{max} (CH_2Cl_2) 348 (ε 9200). ^{1}H NMR ($CDCl_3$): δ 1.83 (quintet, *J* = 5.5 Hz, 4H), 2.56 (s, 4H), 2.72 (t, *J* = 5.3 Hz, 4H), 3.61 (t, *J* = 6.4 Hz, 4H), 5.21 (bs, 2H), 6.36 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), NH protons of dialkylamino groups were not observed. ^{13}C NMR ($CDCl_3$): δ 29.3 (2C), 40.0 (2C), 47.5 (2C), 49.1 (2C), 107.3 (2C), 110.7 (2C), 137.6 (2C), 155.2 (2C), 159.1 (2C). HRMS (MALDI-TOF) *m/z* calcd for $C_{18}H_{26}N_6$ [M^+] 326.2219, found 326.2262.

7,11,14,18,29,33,36,40,45,46,47,48-Dodecaazapentacyclo[39.3.1.1^{2,6}.1^{19,23}.1^{24,28}]octatetraconta-1(45),2(48),3,5,19(47),20,22,24(46),25,27,41,43-dodecaene (4f) (n = 1). Obtained as by-product in the synthesis of macrocycle **3f**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:25:5. Yield 12 mg (15%). Pale-yellow glassy solid. UV λ_{max} (CH_2Cl_2) 348 (ε 21000). ^{1}H NMR ($CDCl_3$): δ 1.69 (quintet, *J* = 6.3 Hz, 8H), 2.58 (s, 8H), 2.61 (t, *J* = 6.3 Hz, 8H), 3.37 (t, *J* = 6.0 Hz, 8H), 5.06 (bs, 4H), 6.29 (*J* = 8.2 Hz, 4H), 7.44 (t, *J* = 7.8 Hz, 4H), 7.52 (d, *J* = 7.4 Hz, 4H), NH protons of dialkylamino groups were not observed. ^{13}C NMR ($CDCl_3$): δ 29.7 (4C), 40.1 (4C), 47.2 (4C), 49.0 (4C), 106.7 (4C), 110.0 (4C), 138.0 (4C), 154.9 (4C), 158.5 (4C). HRMS (MALDI-TOF) *m/z* calcd for $C_{36}H_{52}N_{12}$ [M^+] 652.4438, found 652.4417.

7,11,15,19,24,25-Hexaazatricyclo[18.3.1.1^{2,6}]pentacosa-1(24),2(25),3,5,20,22-hexaene (3g). Synthesized from 47 mg (0.25 mmol) of tetraamine **2g**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:3-100:25:5. Yield 25 mg (29%). Pale-yellow solid. Mp 112-113 °C. UV λ_{max} (CH_2Cl_2) 347 (ε 8600). ^{1}H NMR ($CDCl_3$): δ 1.39 (quintet, *J* = 5.7 Hz, 2H), 1.85 (bs, 4H), 2.52 (t, *J* = 5.9 Hz, 4H), 2.68 (t, *J* = 4.8 Hz, 4H), 3.58 (bs, 4H), 5.20 (bs, 2H), 6.36 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), NH protons of dialkylamino groups were not observed. ^{13}C NMR ($CDCl_3$): δ 28.7 (1C), 29.4 (2C), 39.7 (2C), 46.6 (2C), 47.3 (2C), 107.9 (2C), 110.7 (2C), 137.9 (2C), 155.5 (2C), 159.0 (2C). HRMS (MALDI-TOF) *m/z* calcd for $C_{19}H_{28}N_6$ [M^+] 340.2375, found 340.2395.

10,13-Dioxa-7,16,21,22-tetraazatricyclo[15.3.1.1^{2,6}]docosa-1(21),2(22),3,5,17,19-hexaene (3h). Synthesized from 37 mg (0.25 mmol) of dioxadiamine **2h**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:1. Yield 10 mg (13%). Pale-yellow solid. Mp 114-115 °C. ^{1}H NMR ($CDCl_3$): δ 3.46-3.51 (m, 4H), 3.74 (s, 4H), 3.85 (t, *J* = 7.2 Hz, 4H), 5.00 (bs, 2H), 6.37 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.8

Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 41.5 (2C), 69.2 (2C), 69.7 (2C), 108.7 (2C), 111.2 (2C), 137.2 (2C), 154.7 (2C), 158.3 (2C). HRMS (MALDI-TOF) *m/z* calcd for $C_{16}H_{20}N_4O_2$ [M^+] 300.1586, found 300.1528.

10,13,30,33-Tetraoxa-7,16,27,36,41,42,43,44-octaazapentacyclo[35.3.1.1^{2,6}.1^{17,21}.1^{22,26}]tetratetraconta-1(41),2(44),3,5,17(43),18,20,22(42),23,25,37,39-dodecaene (4h) (n = 1). Obtained as by-product in the synthesis of macrocycle **3h**. Eluent CH_2Cl_2-MeOH 10:1. Yield 15 mg (20%). Pale-yellow solid. Mp 91-93°C. UV λ_{max} (CH_2Cl_2) 342 (ε 20000). ^{1}H NMR ($CDCl_3$): δ 3.53 (t, *J* = 5.2 Hz, 8H), 3.64 (s, 8H), 3.69 (t, *J* = 5.5 Hz, 8H), 5.00 (bs, 4H), 6.26 (d, *J* = 8.1 Hz, 4H), 7.29 (t, *J* = 7.8 Hz, 4H), 7.44 (t, *J* = 7.9 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 41.8 (4C), 69.9 (4C), 70.3 (4C), 107.5 (4C), 110.3 (4C), 137.8 (4C), 154.6 (4C), 157.9 (4C). HRMS (MALDI-TOF) *m/z* calcd for $C_{32}H_{40}N_8O_4$ [M^+] 600.3173, found 600.3153.

Mixture of cyclotrimer **4h** (n = 2), cyclotetramer **4h** (n = 3), cyclopentamer **4h** (n = 4) and cyclohexamer **4h** (n = 5). Obtained as by-products in the synthesis of macrocycle **3h**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:1. Yield 20 mg (26%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 3.57-3.62 (m, 4(n+1)H), 3.64 (s, 4(n+1)H), 3.68-3.73 (m, 4(n+1)H), 6.35 (d, *J* = 8.2 Hz, 2(n+1)H), 7.42 (t, *J* = 7.6 Hz, 2(n+1)H), 7.59 (d, *J* = 7.2 Hz, 2(n+1)H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 41.6 (2(n+1)C), 70.0 (2(n+1)C), 70.2 (2(n+1)C), 107.5 (2(n+1)C), 110.1 (2(n+1)C), 137.8 (2(n+1)C), 154.7 (2(n+1)C), 158.0 (2(n+1)C). MS (MALDI-TOF) *m/z* calcd for $C_{64}H_{80}N_{16}O_8$ [M^+] 1200.63, found 1200.55 (**4h** (n = 3)); calcd for $C_{80}H_{100}N_{20}O_{10}$ [M^+] 1500.76, found 1500.72 (**4h** (n = 4)); calcd for $C_{96}H_{120}N_{24}O_{12}$ [M^+] 1800.96, found 1800.78 (**4h** (n = 5)), data for cyclotrimer **4h** (n = 2) *vide infra*.

11,16-Dioxa-7,20,25,26-tetraazatricyclo[19.3.1.1^{2,6}]hexacosa-1(25),2(26),3,5,21,23-hexaene (3i). Synthesized from 51 mg (0.25 mmol) of dioxadiamine **2i**. Eluent CH_2Cl_2-MeOH 10:1. Yield 42 mg (47%). Pale-yellow solid. Mp 93-95 °C. UV λ_{max} (CH_2Cl_2) 345 (ε 7100). ^{1}H NMR ($CDCl_3$): δ 1.71-1.73 (m, 4H), 1.97 (quintet, *J* = 5.4 Hz, 4H), 3.40-3.45 (m, 8H), 3.59 (t, *J* = 5.2 Hz, 4H), 6.61 (bs, 2H), 7.06 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 2H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 27.0 (2C), 28.7 (2C), 42.0 (2C), 70.5 (2C), 71.4 (2C), 107.2 (2C, line width 70 Hz), 109.8 (2C), 138.7 (2C), 157.9 (2C), one quaternary carbon was not observed due to broad signal. HRMS (MALDI-TOF) *m/z* calcd for $C_{20}H_{28}N_4O_2$ [M^+] 356.2212, found 356.2222.

11,16,35,40-Tetraoxa-7,20,31,44,49,50,51,52-octaazapentacyclo[43.3.1.1^{2,6}.1^{21,25}.1^{26,30}]dopentaconta-1(49),2(52),3,5,21(51),22,24,26(50),27,29,45,47-dodecaene (4i) (n = 1). Obtained as by-product in the synthesis of macrocycle **3i**. Eluent CH_2Cl_2-MeOH 20:1. Yield 15 mg (17%). Pale-yellow solid. Mp 78-80

^{o}C. UV λ_{max} (CH_2Cl_2) 345 (ε 22000). ^{1}H NMR ($CDCl_3$): δ 1.65-1.68 (m, 8H), 1.87 (quintet, *J* = 6.0 Hz, 8H), 3.41 (t, *J* = 6.5 Hz, 8H), 3.42-3.45 (m, 8H), 3.52 (t, *J* = 5.2 Hz, 8H), 6.34 (d, *J* = 7.6 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.47 (d, *J* = 7.8 Hz, 4H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 26.5 (4C), 29.5 (4C), 40.0 (4C), 68.9 (4C), 70.7 (4C), 106.7 (4C), 109.6 (4C), 138.2 (4C), 153.0 (4C), 158.0 (4C). HRMS (MALDI-TOF) *m/z* calcd for $C_{40}H_{56}N_8O_4$ [M$^+$] 712.4425, found 714.4471.

Mixture of cyclotrimer **4i** (n = 2), cyclotetramer **4i** (n = 3), cyclopentamer **4i** (n = 4) and cyclohexamer **4i** (n = 5). Obtained as by-products in the synthesis of macrocycle **3i**. Eluent CH_2Cl_2-MeOH-NH_3aq 100:20:1. Yield 20 mg (22%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 1.65-1.68 (m, 4(n+1)H), 1.87-1.92 (m, 4(n+1)H), 3.41-3.45 (m, 8(n+1)H), 3.51-3.55 (m, 4(n+1)H), 4.85 (bs, 2(n+1)H), 6.35 (d, *J* = 8.1 Hz, 2(n+1)H), 7.47 (t, *J* = 7.7 Hz, 2(n+1)H), 7.57 (d, *J* = 7.3 Hz, 2(n+1)H). ^{13}C NMR ($CDCl_3$): δ 26.5 (2(n+1)C), 29.5 (2(n+1)C), 40.0 (2(n+1)C), 69.1 (2(n+1)C), 70.8 (2(n+1)C), 106.4 (2(n+1)C), 109.9 (2(n+1)C), 137.9 (2(n+1)C), 154.9 (2(n+1)C), 158.3 (2(n+1)C). MS (MALDI-TOF) *m/z* calcd for $C_{60}H_{84}N_{12}O_6$ [M$^+$] 1068.66, found 1068.57 (**4i** (n = 2)); calcd for $C_{80}H_{112}N_{16}O_8$ [M$^+$] 1424.89, found 1424.80 (**4i** (n = 3)); calcd for $C_{100}H_{140}N_{20}O_{10}$ [M$^+$] 1781.11, found 1781.27 (**4i** (n = 4)); calcd for $C_{120}H_{168}N_{24}O_{12}$ [M$^+$] 2137.33, found 2137.43 (**4i** (n = 5)).

11,14,17-Trioxa-7,21,26,27-tetraazatricyclo[20.3.1.1^{2,6}]heptacosa-1(26),2(27),3,5,22,24-hexaene (3j). Synthesized from 55 mg (0.25 mmol) of dioxadiamine **2j**. Eluent CH_2Cl_2-MeOH 10:1-3:1. Yield 45 mg (48%). Pale-yellow viscous oil. UV λ_{max} (CH_2Cl_2) 345 (ε 9900). ^{1}H NMR ($CDCl_3$): δ 1.99 (quintet, *J* = 5.8 Hz, 4H), 3.53 (t, *J* = 6.2 Hz, 4H), 3.56-3.60 (m, 4H), 3.63-3.68 (m, 8H), 6.80 (bs, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 2H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 28.6 (2C), 39.3 (2C), 68.9 (2C), 70.5 (4C), 108.6 (2C), 110.7 (2C, line width 50 Hz), 139.7 (2C), 156.1 (2C), one quaternary carbon was not observed due to broad signal. HRMS (MALDI-TOF) *m/z* calcd for $C_{20}H_{28}N_4O_3$ [M$^+$] 372.2161, found 372.2185.

11,14,17,36,39,42-Hexaoxa-7,21,32,46,51,52,53,54-octaazapentacyclo[45.3.1.1^{2,6}.1^{22,26}.1^{27,31}]-tetrapentaconta-1(51),2(54),3,5,22(53),23,25,27(52),28,30,47,49-dodecaene (4j) (n = 1). Obtained as by-product in the synthesis of macrocycle **3j**. Eluent CH_2Cl_2-MeOH 25:1-10:1. Yield 14 mg (15%). Pale-yellow solid. Mp 78-80 ^{o}C. UV λ_{max} (CH_2Cl_2) 345 (ε 19000). ^{1}H NMR ($CDCl_3$): δ 1.87 (quintet, *J* = 6.1 Hz, 8H), 3.41 (t, *J* = 6.2 Hz, 8H), 3.53-3.58 (16H), 3.61-3.66 (m, 8H), 6.36 (d, *J* = 8.0 Hz, 4H), 7.39-7.45 (m, 8H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 29.3 (4C), 39.7 (4C), 69.2 (4C), 70.2 (4C), 70.6 (4C), 107.0 (4C), 109.5 (4C), 138.2 (4C), 151.6 (4C), 158.0 (4C). HRMS (MALDI-TOF) *m/z* calcd for $C_{40}H_{56}N_8O_6$ [M^+] 744.4323, found 744.4302.

Typical procedure for the synthesis of cyclodimers **4d, h-j** (n = 1).

A two-neck flask (25 mL) flushed with dry argon, equipped with a magnetic stirrer and condenser was charged with 6,6'-dibromo-2,2'-bipyridine (**1**) (0.2 mmol, 63 mg), Pd(dba)$_2$ (4.5 mg, 4 mol%), BINAP (5.5 mg, 4.5 mol%) and absolute dioxane (2 mL). The mixture was stirred for 2 min, then appropriate amine **2d, h-j** (0.6 mmol) was added followed by sodium *tert*-butoxide (0.6 mmol, 58 mg). The reaction mixture was refluxed for 8 h, after cooling down to ambient temperature 0.5 mL (25%) of the solution was taken, evaporated *in vacuo*, and analyzed with NMR and MALDI-TOF spectroscopy. Then 6,6'-dibromo-2,2'-bipyridine (**1**) (0.3 mmol, 94 mg), Pd(dba)$_2$ (14 mg, 8 mol%), BINAP (17 mg, 9 mol%), absolute dioxane (8 mL) and sodium *tert*-butoxide (0.9 mmol, 87 mg) were added, the reaction was then refluxed for 15 h. After cooling down to ambient temperature, the residue was filtered off, dioxane evaporated *in vacuo*, and the residue was analyzed by NMR spectroscopy. Column chromatography was carried out using a sequence of eluents: CH_2Cl_2, CH_2Cl_2-MeOH 50:1 – 3:1, CH_2Cl_2-MeOH-NH_3aq 100:20:1 – 10:4:1.

N^1,$N^{1'}$-(2,2'-Bipyridine-6,6'-diyl)bis(N^3-(3-aminopropyl)propane-1,3-diamine) (5d). Obtained *in situ* from triamine **2d** (0.6 mmol, 79 mg). ^{1}H NMR (CDCl$_3$): δ 1.57 (quintet, J = 6.9 Hz, 4H), 1.75 (quintet, J = 6.7 Hz, 4H), 2.60 (t, J = 7.0 Hz, 4H), 2.69 (t, J = 6.6 Hz, 8H), 3.38 (t, J = 6.3 Hz, 4H), 6.32 (d, J = 8.1 Hz, 2H), 7.45 (t, J = 7.9 Hz, 2H), 7.54 (d, J = 7.1 Hz, 2H), NH protons were not observed. ^{13}C NMR (CDCl$_3$): δ 29.6 (2C), 33.7 (2C), 40.2 (2C), 40.3 (2C), 47.7 (2C), 47.8 (2C), 106.5 (2C), 109.8 (2C), 137.8 (2C), 154.8 (2C), 158.2 (2C). MS (MALDI-TOF) *m/z* calcd for $C_{22}H_{38}N_8$ [M^+] 414.32, found 414.38. Following by-products were registered in the reaction mixture: *m/z* calcd for $C_{38}H_{59}N_{13}$ [M^+] 697.50, found 697.48 (**6d** (n = 1)); calcd for $C_{54}H_{80}N_{18}$ [M^+] 980.68, found 980.52 (**6d** (n = 2)). Compound **5d** was introduced in the reaction with 6,6'-dibromo-2,2'-bipyridine (**1**) *in situ* to produce cyclodimer **4d** (n = 1) (eluent CH_2Cl_2-MeOH-NH_3aq 100:25:5-10:4:1, yield 16 mg (19%)), macrocycle **3d** (eluent CH_2Cl_2-MeOH-NH_3aq 100:20:3-100:25:5, yield 10 mg (23%)), a mixture of cyclotrimer **4d** (n = 2) and cyclotetramer **4d** (n = 3) (eluent CH_2Cl_2-MeOH-NH_3aq 100:20:3, yield 26 mg (31%)), a mixture of linear oligomers (CH_2Cl_2-MeOH-NH_3aq 10:4:1, yield 30 mg (35%)).

7,11,15,26,30,34,39,40,41,42-Decaazapentacyclo[33.3.1.1^{2,6}.1^{16,20}.1^{21,25}]dotetraconta-1(39),2(42),3,5,16(41),17,19,21(40),22,24,35,37-dodecaene (4d) (n = 1). Eluent CH_2Cl_2-MeOH-NH_3aq 100:25:5-10:4:1. Yield 16 mg (19%). Pale-yellow solid. Mp 118-120 °C. UV λ_{max} (CH_2Cl_2) 347 (ε

20000). ^{1}H NMR ($CDCl_3$): δ 1.45 (quintet, *J* = 6.4 Hz, 8H), 2.36 (t, *J* = 6.4 Hz, 8H), 3.15-3.20 (m, 8H), 6.23 (d, *J* = 8.2 Hz, 4H), 7.27 (d, *J* = 7.4 Hz, 4H), 7.37 (t, *J* = 7.8 Hz, 4H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 29.3 (4C), 38.7 (4C), 46.4 (4C), 107.0 (4C), 110.0 (4C), 137.9 (4C), 154.9 (4C), 158.4 (4C). HRMS (MALDI-TOF) *m/z* calcd for $C_{32}H_{42}N_{10}$ [M^+] 566.3594, found 566.3651.

Mixture of cyclotrimer **4d** (n = 2) and cyclotetramer **4d** (n = 3). Eluent CH_2Cl_2-MeOH-NH_3aq 100:25:5. Yield 26 mg (31%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 1.50-1.60 (m, 4(n+1)H), 2.40-2.52 (m, 4(n+1)H), 3.24 (bs, 4(n+1)H), 6.28 (d, *J* = 8.2 Hz, 6H, cyclotrimer), 6.34 (d, *J* = 5.2 Hz, 8H, cyclotetramer), 7.32 (d, 6H, *J* = 7.9 Hz, 6H, cyclotrimer), 7.34-7.43 (m, 16H, cyclotetramer), 7.39 (d, 6H, *J* = 7.6 Hz, 6H, cyclotrimer), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 28.1-29.0 (m, 2(n+1)C), 39.1-39.7 (m, 2(n+1)C), 46.3-47.3 (m, 2(n+1)C), 107.0 (2(n+1)C), 109.9 (2(n+1)C), 138.0 (2(n+1)C), 154.5 (2(n+1)C), 158.4 + 158.5 (2(n+1)C). MS (MALDI-TOF) *m/z* calcd for $C_{48}H_{63}N_{15}$ [M^+] 849.54, found 849.38 (**4d** (n = 2)); calcd for $C_{64}H_{84}N_{20}$ [M^+] 1132.72, found 1132.41 (**4d** (n = 3)).

N^6,$N^{6'}$-Bis(2-(2-(2-aminoethoxy)ethoxy)ethyl)-2,2'-bipyridine-6,6'-diamine (5h). Obtained *in situ* from diamine **2h** (0.6 mmol, 89 mg). ^{1}H NMR ($CDCl_3$): δ 2.80 (t, *J* = 4.2 Hz, 4H), 3.46 (t, *J* = 4.5 Hz, 4H), 3.58 (s, 8H), 3.59-3.62 (m, 4H), 3.66-3.69 (m, 4H), 6.36 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 2H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 41.4 (4C), 69.9 (2C), 70.2 (4C), 73.3 (2C), 107.4 (2C), 110.0 (2C), 137.7 (2C), 154.7 (2C), 157.9 (2C). MS (MALDI-TOF) *m/z* calcd for $C_{22}H_{36}N_6O_4$ [M^+] 448.28, found 448.24. Following by-products were registered in the reaction mixture: *m/z* calcd for $C_{38}H_{56}N_{10}O_6$ [M^+] 748.44, found 748.56 (**6h** (n = 1)); calcd for $C_{54}H_{76}N_{14}O_8$ [M^+] 1048.60, found 1048.57 (**6h** (n = 2)); calcd for $C_{70}H_{96}N_{18}O_{10}$ [M^+] 1348.76, found 1348.55 (**6h** (n = 3)). Compound **5h** was introduced in the reaction with 6,6’-dibromo-2,2’-bipyridine (**1**) *in situ* to produce cyclodimer **4h** (n = 1) (eluent CH_2Cl_2-MeOH 20:1, yield 7 mg (8%)), cyclotrimer **4h** (n = 2) (eluent CH_2Cl_2-MeOH 20:1, yield 4 mg (4%)), macrocycle **3h** (eluent CH_2Cl_2-MeOH 10:1-3:1, yield 20 mg (44%)), a mixture of linear oligomers (CH_2Cl_2-MeOH 3:1, CH_2Cl_2-MeOH-NH_3aq 100:20:1, yield 78 mg (86%)). The spectral data for the cyclodimer **4h** (n = 1) are given above.

10,13,30,33,50,53-Hexaoxa-7,16,27,36,47,56,61,62,63,64,65,66-dodecaazaheptacyclo-[55.3.1.$1^{2,6}$.$1^{17,21}$.$1^{22,26}$.$1^{37,41}$.$1^{42,46}$]hexahexaconta-1(61),2(66),3,5,17(65),18,20,22(64),23,25,37(63),38,40,42(62),43,45,57,59-octadecaene (4h) (n = 2). Obtained as by-product in the synthesis of cyclodimer **4h** (n = 1). Eluent CH_2Cl_2-MeOH 20:1. Yield 4 mg (4%). Pale-yellow glassy solid. ^{1}H NMR ($CDCl_3$): δ 3.57 (t, *J* = 5.0 Hz, 12H), 3.65 (s, 12H), 3.72 (t, *J* =

5.1 Hz, 12H), 4.57 (bs, 6H), 6.31 (d, *J* = 8.2 Hz, 6H), 7.37 (t, *J* = 7.8 Hz, 6H), 7.56 (d, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 41.8 (6C), 69.9 (6C), 70.3 (6C), 107.4 (6C), 110.1 (6C), 137.9 (6C), 154.7 (6C), 158.0 (6C). HRMS (MALDI-TOF) *m/z* calcd for $C_{48}H_{60}N_{12}O_6$ [M^+] 900.4759, found 900.4819.

***N^6,$N^{6'}$*-Bis(3-(4-(3-aminopropoxy)butoxy)propyl)-2,2'-bipyridine-6,6'-diamine (5i)**. Obtained *in situ* from diamine **2i** (0.6 mmol, 121 mg). ^{1}H NMR ($CDCl_3$): δ 1.58-1.60 (m, 4H), 1.61-1.63 (m, 4H), 1.67 (quintet, *J* = 6.5 Hz, 4H), 1.88 (quintet, *J* = 6.2 Hz, 4H), 2.73 (t, *J* = 6.5 Hz, 4H), 3.36-3.42 (m, 12H), 3.45 (t, *J* = 6.3 Hz, 4H), 3.52 (t, *J* = 5.9 Hz, 4H), 6.33 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 26.4 (4C), 29.5 (2C), 33.4 (2C), 39.4 (2C), 39.9 (2C), 68.9 (2C), 69.0 (2C), 70.6 (2C), 70.7 (2C), 106.4 (2C), 109.8 (2C), 137.8 (2C), 154.9 (2C), 158.2 (2C). MS (MALDI-TOF) *m/z* calcd for $C_{30}H_{52}N_6O_4$ [M^+] 560.41, found 560.39. Following by-products were registered in the reaction mixture: *m/z* calcd for $C_{50}H_{80}N_{10}O_6$ [M^+] 916.63, found 916.86 (**6i** (n = 1)); calcd for $C_{70}H_{108}N_{14}O_8$ [M^+] 1272.85, found 1272.59 (**6i** (n = 2)). Compound **5i** was introduced in the reaction with 6,6'-dibromo-2,2'-bipyridine (**1**) *in situ* to produce cyclodimer **4i** (n = 1) (eluent CH_2Cl_2-MeOH 20:1, yield 10 mg (9%)), a mixture of cyclotimer **4i** (n = 2) and cyclotetramer **4i** (n = 3) (eluent CH_2Cl_2-MeOH 20:1, yield 9 mg (8%)), macrocycle **3i** (eluent CH_2Cl_2-MeOH 20:1-10:1, yield 23 mg (43%)), a mixture of linear oligomers (CH_2Cl_2-MeOH 10:1-3:1, yield 43 mg (40%)). The spectral data for the cyclodimer **4i** (n = 1) are given above.

***N^6,$N^{6'}$*-Bis(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)-2,2'-bipyridine-6,6'-diamine (5j)**. Obtained *in situ* from diamine **2j** (0.6 mmol, 132 mg). ^{1}H NMR ($CDCl_3$): δ 1.64 (quintet, *J* = 6.5 Hz, 4H), 1.83 (quintet, *J* = 6.1 Hz, 4H), 2.70 (t, *J* = 6.7 Hz, 4H), 3.47 (t, *J* = 6.2 Hz, 4H), 3.49-3.59 (m, 24H), 6.30 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 29.2 (2C), 33.2 (2C), 39.4 (2C), 39.6 (2C), 69.2 (2C), 69.3 (2C), 70.0 (2C), 70.1 (2C), 70.4 (4C), 106.5 (2C), 109.6 (2C), 137.6 (2C), 154.8 (2C), 158.0 (2C). MS (MALDI-TOF) *m/z* calcd for $C_{30}H_{52}N_6O_6$ [M^+] 592.39, found 592.45. Compound **5j** was introduced in the reaction with 6,6'-dibromo-2,2'-bipyridine (**1**) *in situ* to produce cyclodimer **4j** (n = 1) (eluent CH_2Cl_2-MeOH 20:1, yield 13 mg (12%)), a mixture of cyclotimer **4j** (n = 2) and cyclotetramer **4j** (n = 3) (eluent CH_2Cl_2-MeOH 20:1, yield 12 mg (11%)), macrocycle **3j** (eluent CH_2Cl_2-MeOH 20:1-10:1, yield 22 mg (39%)), a mixture of linear oligomers (CH_2Cl_2-MeOH 10:1-3:1, yield 64 mg (57%)). The spectral data for the cyclodimer **4j** (n = 1) are given above.

Mixture of cyclotrimer **4j** (n = 2) and cyclotetramer **4j** (n = 3). Obtained as by-products in the synthesis of cyclodimer **4j** (n = 1). Eluent CH_2Cl_2-MeOH 20:1. Yield 12 mg (11%). Pale-yellow glassy solid. ^1H NMR ($CDCl_3$): δ 1.87 (quintet, *J* = 6.1 Hz, 4(n+1)H), 3.41 (t, *J* = 6.2 Hz, 4(n+1)H), 3.53-3.58 (8(n+1)H), 3.61-3.66 (m, 4(n+1)H), 6.36 (d, *J* = 8.0 Hz, 2(n+1)H), 7.39-7.45 (m, 4(n+1)H), NH protons were not observed. ^{13}C NMR ($CDCl_3$): δ 29.4 (2(n+1)C), 39.7 (2(n+1)C), 69.2 (2(n+1)C), 70.3 (2(n+1)C), 70.7 (2(n+1)C), 107.0 (2(n+1)C), 109.5 (2(n+1)C), 138.2 (2(n+1)C), 151.5 (2(n+1)C), 157.8 (2(n+1)C). MS (MALDI-TOF) *m/z* calcd for $C_{60}H_{84}N_{12}O_9$ [M^+] 1116.65, found 1116.63 (**4j** (n = 2)); calcd for $C_{80}H_{112}N_{16}O_{12}$ [M^+] 1488.86, found 1488.89 (**4j** (n = 3)).

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