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Synthesis of a new family of bi- and polycyclic compounds via Pd-catalyzed amination of 1,7-di(3-bromobenzyl)cyclen

Alexei D. Averin [a,*], Anton V. Shukhaev [a], Alexei K. Buryak [b], Franck Denat [c], Roger Guilard [c], Irina P. Beletskaya [a,*]

[a] *Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory, Moscow 119992, Russia*
[b] *A. N. Frumkin Institute of Physical and Electrochemistry, 31 Leninskii Prosp., Moscow 119991, Russia*
[c] *Institut de Chimie Moléculaire de l'Universite de Bourgogne (ICMUB-LIMRES) UMR CNRS 5260, 9 av. Alain Savary, 21078 Dijon, France*

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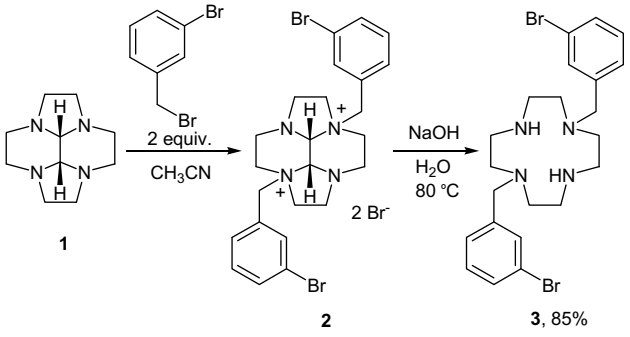
Abstract

New bicyclic cryptand type compounds are synthesized by reacting 1,7-di(3-bromobenzyl)cyclen with 1 equiv of linear polyamines under dilute conditions using Pd-catalyzed amination. Bis(cyclen) and tris(cyclen) compounds containing linear polyamine linkers between benzylated cyclens are obtained by a similar procedure using different reaction conditions. Cyclization of these species via intramolecular catalytic diamination led to tri- and tetracyclic polyaza compounds.

Tetraazamacrocyclic compounds, mainly cyclams and cyclens, are of major importance due to their unique properties for the selective binding of metal ions.[1] Numerous derivatives of these molecules find application as highly efficient sequestrating agents,[2] sensors,[3] catalysts,[4] and are used in biochemistry[5] or medicine.[6] Moreover, bis(polyazamacrocycles) attract significant interest due to their abilities to form binuclear complexes.[7] Such macrocycles can be synthesized either by attaching two tetraazamacrocycles to a rigid spacer via methylene groups, or by direct Pd-catalyzed diamination of dihaloarenes with azamacrocycles.[8] Here, we report the synthesis of a new family of polyazamacrocycles through catalytic amination of 1,7-di(3-bromobenzyl)cyclen with linear polyamines. This cyclen derivative was chosen as a starting material because the *meta*-position of the bromine atom pre-organizes the ring to favor the formation of a cryptand-like molecule through diamination.

1,7-Di(3-bromobenzyl)cyclen was obtained from *cis*-glyoxalcyclen **1** via intermediate salt **2** using a procedure already described for similar compounds (Scheme 1).[9] The reactions of **3** with a variety of linear polyamines **4a**–**i** in equimolar ratio were carried out in boiling dioxane using $Pd(dba)_2$/BINAP as a catalyst[10] (16/18 mol %). Dilute conditions were applied to favor intramolecular cyclization ($c = 0.02$ M). The reactions were complete in 24 h, and the target macrocycles **5a**–**i** were isolated in 13–65% yields (Scheme 2, Table 1).



Scheme 1. Synthesis of 1,7-di(3-bromobenzyl)cyclen **3**.

* Corresponding authors. Tel.: +7 495 939 11 39; fax: +7 495 939 36 18 (A.D.A.).
E-mail address: averin@org.chem.msu.ru (A. D. Averin).

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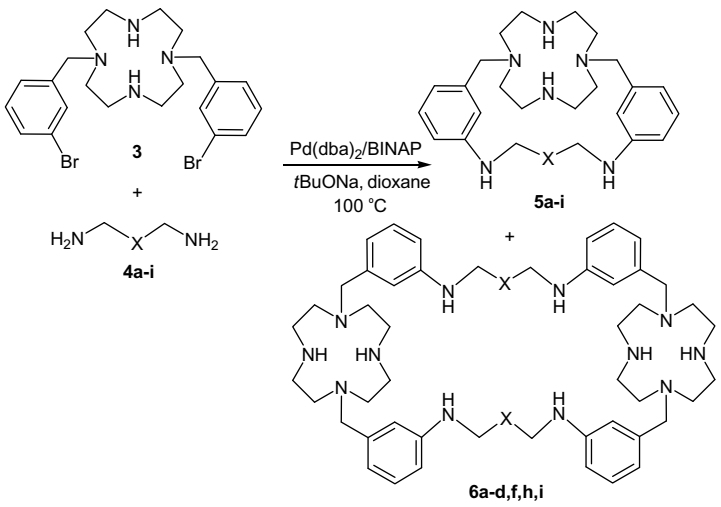


Scheme 2. Synthesis of bicyclic compounds **5**.

Table 1
Synthesis of bicyclic compounds **5**

Entry	Polyamine	Yield of **5** (%)	Yield of cyclodimers **6**[a] (%)
1	$H_2N(CH_2)_3NH_2$ **4a**	13	**6a**, 5
2	$H_2N(CH_2)_3NH(CH_2)_3NH_2$ **4b**	26	**6b**, 53
3	$H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ **4c**	38	**6c**, 44
4	$H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ **4d**	45	**6d**, 34
5	$H_2N(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$ **4e**	65	
6	$H_2N(CH_2)_2[NH(CH_2)_2]_3NH_2$ **4f**	43	**6f**, 36
7	$H_2N(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ **4g**	35	
8	$H_2N(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$ **4h**	29	**6h**, 36
9	$H_2N(CH_2)_3O[(CH_2)_2O]_2(CH_2)_3NH_2$ **4i**	42	**6i**, 46

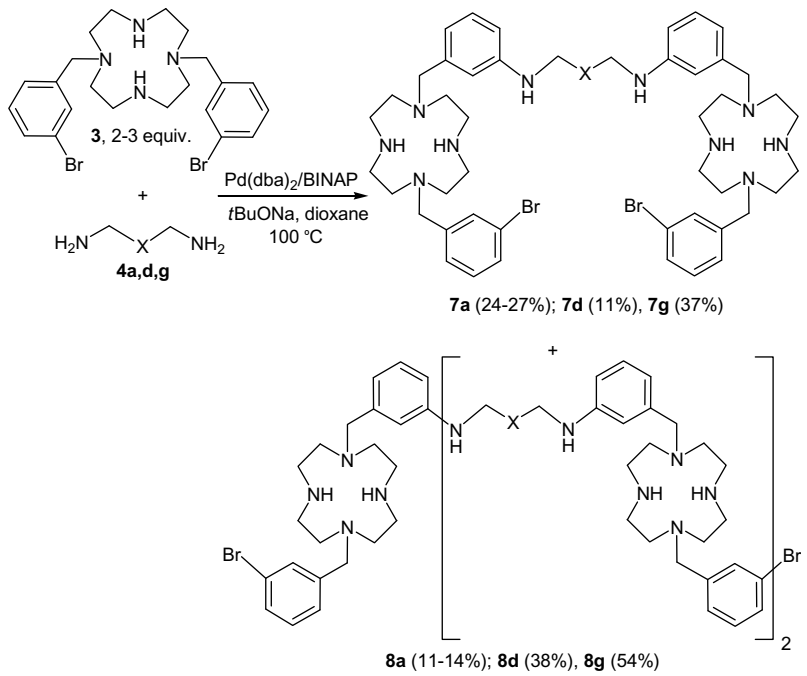
[a] Cyclodimers **6** often contain some compounds **5**.

Diaminopropane **4a** was too short a linker to form the expected cryptand in a reasonable yield, and **5a** was obtained in 13% yield; the tricyclic compound **6a** resulting from [2+2] condensation was isolated in 5% yield (Table 1, entry 1). Almost all the other polyamines also provided tricyclic compounds **6** though mixed with bicyclic species **5** (Table 1). The highest yield (65%) of the desired product, **5e**, was observed in the case of tetraamine **4e** (Table 1, entry 5), whereas no dimer of type **6** was isolated. Similar results were observed for the reaction with dioxadiamine **4g** (Table 1, entry 7). Cryptand-like molecules **5** possess a polyamine (oxadiamine) chain more or less remote from the cyclen tetraazacycle, and differ in the number of nitrogen and/or oxygen atoms, which can serve as additional donor sites for metal ion coordination. This makes such structures very valuable ligands for coordination chemistry.

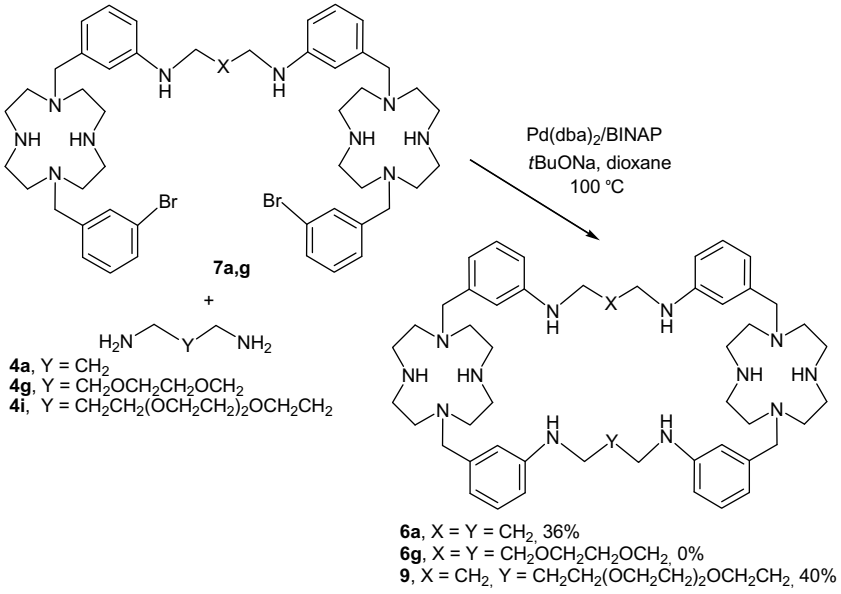
Tricyclic compounds **6** are also of interest as polydentate ligands where two cyclen moieties are linked by polyamine chains of various lengths. We have synthesized such compounds by a two-step procedure. In the first stage, 1,7-di(3-bromobenzyl)cyclen **3** (2–3 equiv) was reacted with polyamines **4a**,**d**,**g** ($Pd(dba)_2$/BINAP 4/4.5 mol %, $c = 0.1$ M) (Scheme 3). Target bis(cyclen) derivatives **7** were obtained in rather moderate yields (11–37%) due to the competitive formation of tris(cyclen) derivatives **8** (yields 11–54%). Increasing the amount of starting compound **3** from 2 to 3 equiv did not change the ratio of the isolated products. Products **7** and **8** possessing two or three macrocyclic units linked by polyamine chains are polytopic ligands.

Bis(cyclen) derivatives **7a**,**g** and tris(cyclen) derivatives **8a**,**g** were used as precursors for the formation of cyclic dimers and trimers (Schemes 4 and 5).

Reactions were run in dilute dioxane solution using 8–16 mol% of the catalyst. Compound **7a** gave tricyclic dimer **6a** in 36% yield upon reacting with an equivalent amount of **4a**. The reaction of the same derivative **7a** with trioxadiamine **4i** afforded tricycle **9** in 40% yield. In contrast, bis(cyclen) derivative **7g** did not lead to the expected tricyclic dimer of type **6**, which was also not observed by reacting **3** with diamine **4g** (Table 1, entry 7). Nevertheless, the reaction of tris(cyclen) derivative **8g** with 1 equiv of dioxadiamine **4g** afforded target tetracyclic compound **10**, though the yield was poor (13%). At the same time, tris(cyclen) compound **8a** did not provide the corresponding



Scheme 3. Synthesis of bis(cyclen) and tris(cyclen) compounds **7** and **8**.



Scheme 4. Synthesis of tricyclic compounds **6** and **9**.

cyclic trimer. Unexpectedly, the formation of less sterically demanding cyclic dimers and trimers (**6**, **9**, and **10**) is subject to greater limitations than the synthesis of bicyclic polyaza compounds **5**. Studies to determine the range of conditions for the formation of cyclic dimers and trimers are now underway.

To sum up, we have elaborated an efficient one-pot method for the synthesis of bicyclic polyaza compounds using disubstituted cyclen as a precursor and demonstrated that it is possible to isolate polycyclic compounds containing two, three, and four cyclen moieties. Experimental details and spectral data for some representative compounds are given below.[11]

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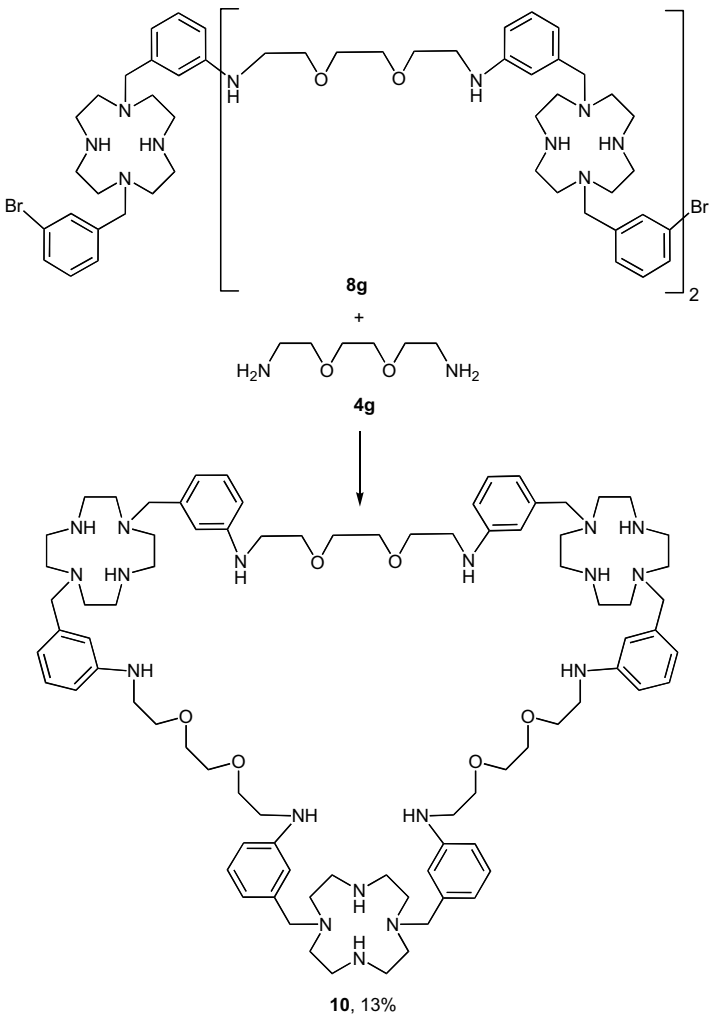

Scheme 5. Synthesis of a cyclic trimer **10** from tris(cyclen) derivative **8g**.

ous provision of glyoxalcyclen and personally to Dr. F. Boschetti.

References and notes

1. (a) Meyer, M.; Dahaoui-Gindrey, V.; Lecomte, C.; Guilard, R. *Coord. Chem. Rev.* **1998**, *180*, 1313; (b) Lukes, I.; Kotek, J.; Vojtisek, P.; Hermann, P. *Coord. Chem. Rev.* **2001**, *216*, 287.
2. (a) Barbette, F.; Rascalou, F.; Chollet, H.; Babouhot, J. L.; Denat, F.; Guilard, R. *Anal. Chim. Acta* **2004**, *502*, 179; (b) Cuenot, F.; Meyer, M.; Bucaille, A.; Guilard, R. *J. Mol. Liq.* **2005**, *118*, 89.
3. (a) Gunnlaugsson, T.; Leonard, J. P. *Chem. Commun.* **2005**, 3114; (b) Gunnlaugsson, T.; Stomeo, F. *Org. Biomol. Chem.* **2007**, *5*, 1999.
4. Reichenbach-Klinke, R.; König, B. *J. Chem. Soc., Dalton Trans.* **2002**, 121.
5. (a) Aoki, S.; Kimura, E. *Chem. Rev.* **2004**, *104*, 769; (b) Ritter, S. C.; Eiblmaier, M.; Michlova, V.; König, B. *Tetrahedron* **2005**, *61*, 5241.
6. (a) Liu, S.; Edwards, D. S. *Bioconjugate Chem.* **2001**, 7; (b) Delgado, R.; Felix, V.; Lima, L. M. P.; Price, D. W. *Dalton Trans.* **2007**, 2734.
7. (a) Brandès, S.; Gros, C.; Denat, F.; Pullumbi, P.; Guilard, R. *Bull. Soc. Chim. Fr.* **1996**, *133*, 65; (b) Valks, G. C.; McRobbie, G.; Lewis, E. A.; Hubin, T. J.; Hunter, T. M.; Sadler, P. J.; Pannecouque, C.; De Clercq, E.; Archibald, S. J. *J. Med. Chem.* **2006**, *49*, 6162.
8. Beletskaya, I. P.; Bessmertnykh, A. G.; Averin, A. D.; Denat, F.; Guilard, R. *Eur. J. Inorg. Chem.* **2005**, 281.
9. (a) Rohovec, J.; Gyepes, R.; Cisarova, I.; Rudovsky, J.; Lukes, I. *Tetrahedron Lett.* **2000**, *41*, 1249; (b) Boschetti, F.; Chaux, F.; Denat, F.; Guilard, R.; Ledon, H. WO 2005/000823 A1; *Chem. Abstr.* **2004**, *142*, 56374.
10. Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1144.
11. *Synthesis of 1,7-di(3-bromobenzyl)cyclen* **3**: *cis*-glyoxalcyclen **1** (0.02 mol, 3.90 g) was dissolved in acetonitrile (52 mL) and 3-bromobenzyl bromide (0.04 mol, 10 g) was added dropwise, and the reaction mixture was stirred at room temperature for 72 h. The precipitate was filtered off, washed with cold acetonitrile (3 × 100 mL), and then with hot acetonitrile (70 °C, 2 × 100 mL). The residue was dried under vacuum and salt **2** was obtained as a white powder. Yield 12.32 g (87%). The salt was treated with NaOH (0.4 mol, 16 g) solution in water (130 mL) for 46 h at 80 °C, then the reaction mixture was cooled to ambient temperature and extracted with dichloromethane (2 × 40 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under vacuum. Compound **3** was obtained as a pale brown powder. Yield 8.65 g (98%). Mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (br s, 2H), 2.55 (br s, 8H), 2.63 (br s, 8H), 3.56 (s, 4H), 7.20–7.29 (m, 4H), 7.34–7.39 (m, 2H), 7.41–7.44 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 45.0 (4C), 51.6 (4C), 59.2 (2C), 122.4 (2C), 127.6 (2C), 131.1 (2C), 130.3 (2C), 132.0 (2C), 141.3 (2C); MALDI-TOF *m*/*z* 508.9 $[M+H]^+$.
Method for the synthesis of macrocycles **5a**–**i**: A flask equipped with a magnetic stirrer and condenser, flushed with dry argon, was charged with 1,7-di(3-bromobenzyl)cyclen **3** (0.5 mmol, 255 mg), $Pd(dba)_2$

(16 mol %, 46 mg), BINAP (18 mol %, 55 mg), abs. dioxane (25 mL), and the appropriate amine (0.5 mmol) was added followed by sodium *tert*-butoxide (1.5 mmol, 144 mg), and the reaction mixture was refluxed for 24–30 h. The mixture was allowed to cool down and a drop of water was added. Dioxane was evaporated under vacuum, and the residue was chromatographed on silica gel using the following sequence of eluents: CH_2Cl_2, CH_2Cl_2,/MeOH 20:1–3:1, CH_2Cl_2/MeOH/NH_3 aq 100:20:1–10:4:1.

Selected experimental and spectral data: 1,8,12,19,22,27-hexaazatetracyclo[17.5.5.13,7.113,17]-hentriaconta-3(31),4,6,13(30),14,16-hexaene **5a**. Eluent: CH_2Cl_2/MeOH/NH_3aq 100:20:1. Yellow oil, yield 28 mg (13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (quintet, $J = 5.6$ Hz, 2H), 2.53–2.66 (m, 16H), 3.28 (br s, 4H), 3.41 (s, 4H), 4.30 (br s, 2H), 6.49 (d, $J = 7.3$ Hz, 2H), 6.51 (dd, $J = 8.3$, 2.0 Hz, 2H), 6.69 (s, 2H), 7.06 (t, $J = 7.7$ Hz, 2H) (two NH protons of cyclen were not unambiguously assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 26.6 (1C), 43.3 (2C), 45.4 (4C), 51.8(4C), 61.3 (2C), 111.0 (2C), 114.6 (2C), 118.7 (2C), 128.8 (2C), 140.4 (2C), 148.6 (2C); MALDI-TOF *m*/*z* 423.3 $[M+H]^+$.

1,8,12,16,23,26,31-heptaazatetracyclo[21.5.5.1^{3,7}.1^{17,21}]-pentatriaconta-3(35),4,6,17(34),18,20-hexaene **5b**. Eluent: CH_2Cl_2/MeOH/NH_3aq 100:20:2. Yellow oil, yield 64 mg (26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 (quintet, $J = 5.5$ Hz, 4H), 2.55 (br s, 8H), 2.58–2.63 (m, 8H), 2.67 (t, $J = 5.7$ Hz, 4H), 3.20 (t, $J = 5.6$ Hz, 4H), 3.48 (s, 4H), 6.48 (dd, $J = 7.9$, 1.5 Hz, 2H), 6.54 (d, $J = 7.5$ Hz, 2H), 6.66 (s, 2H), 7.08 (t, $J = 7.7$ Hz, 2H) (five NH protons were not unambiguously assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 28.5 (2C), 42.9 (2C), 45.0 (4C), 48.5 (2C), 51.7 (4C), 60.6 (2C), 110.7 (2C), 113.9 (2C), 118.4 (2C), 130.0 (2C), 140.0 (2C), 149.0 (2C); MALDI-TOF *m*/*z* 480.5 $[M+H]^+$.

Bis(cyclen) and tris(cyclen) derivatives **7a**,**d**,**g** and **8a**,**d**,**g** were obtained according to the above-mentioned procedure, starting from 1,7-di(3-bromobenzyl)cyclen **3** (1.5–2 mmol), $Pd(dba)_2$ (2–4 mol %), BINAP (2.3–4.5 mol %), abs. dioxane (5–8 mL), the appropriate amine (0.5–0.8 mmol), and sodium *tert*-butoxide (1.5–2.4 mmol). The reaction mixture was refluxed for 5 h.

Selected experimental and spectral data: N,N′-(2,2′-(Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))di(3-((7-(3-bromobenzyl)-1,4,7,10-tetraaza-cyclododecan-1-yl)methyl)benzenamine) **7g**. Eluent: CH_2Cl_2/MeOH/NH_3aq 100:20:2. Yellow oil, yield 297 mg (37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (br s, 32H), 3.20 (br s, 4H), 3.48 (s, 4H), 3.50 (s, 4H), 3.51 (s, 4H), 3.57 (t, $J = 4.8$ Hz, 4H), 4.11 (br s, 2H), 6.44 (d, $J = 8.2$ Hz, 2H), 6.47 (s, 2H), 6.65 (d, $J = 7.2$ Hz, 2H), 7.10 (t, $J = 7.6$ Hz, 2H), 7.15 (t, $J = 7.7$ Hz, 2H), 7.21 (d, $J = 7.4$ Hz, 2H), 7.30 (d, $J = 7.7$ Hz, 2H), 7.38 (s, 2H) (four NH protons of cyclens were not unambiguously assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 43.1 (2C), 44.9 (4C), 44.9 (4C), 51.3 (4C), 51.4 (4C), 59.0 (2C), 59.8 (2C), 69.3 (2C), 69.8 (2C), 111.2 (2C), 113.9 (2C), 118.0 (2C), 122.1 (2C), 127.3 (2C), 129.0 (2C), 129.7 (2C), 129.9 (2C), 131.6 (2C), 139.5 (2C), 141.2 (2C), 147.9 (2C); MALDI-TOF *m*/*z* 1005.5 $[M+H]^+$.

N^1-[3-[[7-[(3-Bromophenyl)methyl]-1,4,7,10-tetraazadodec-1-yl]methyl]phenyl]-N^3-[3-[[7-[[4-[[3-[[3-[[7-(3- bromophenyl)-1,4,7,10-tetraazadodec-1-yl]methyl]phenyl]amino]propyl]amino]phenyl]methyl]-1,4,7,10-tetraazadodec-1-yl]methyl]phenyl]-propanediamine-1,3 **8a**. Eluent: CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yellowish crystals, mp 118–120 °C, yield 101 mg (11%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (quintet, $J = 6.1$ Hz, 4H), 2.58 (br s, 48H), 3.10 (br s, 8H), 3.49 (s, 4H), 3.50 (s, 4H), 3.52 (s, 4H), 6.42 (d, $J = 7.9$ Hz, 4H), 6.49 (s, 2H), 6.56 (s, 2H), 6.62 (d, $J = 7.3$ Hz, 2H), 6.64 (d, $J = 7.5$ Hz, 2H), 7.05–7.36 (m, 10H), 7.42 (s, 2H) (10 NH protons were not unambiguously assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 28.7 (2C), 41.5 (4C), 45.0 (4C), 45.1 (8C), 51.4 (12C), 59.1 (2C), 60.0 (4C), 111.0 (2C), 111.1 (2C), 113.6 (2C), 113.8 (2C), 117.7 (2C), 117.9 (2C), 122.3 (2C), 127.4 (2C), 129.1 (2C), 129.1 (2C), 129.9 (2C), 130.1 (2C), 131.7 (2C), 139.7 (2C), 139.8 (2C), 141.3 (2C), 148.3 (2C), 148.4 (2C); MALDI-TOF *m*/*z* 1353.6 $[M+H]^+$, 1273.6 $[M-Br]^+$.

Cyclic oligomers **6a**, **9**, and **10** were obtained according to the same method, starting from bis(cyclen) derivative **7a** (1 equiv) or tris(cyclen) derivative **8g**, $Pd(dba)_2$ (16 mol %), BINAP (18 mol %), the appropriate volume of abs. dioxane to reach 0.02 M concd amine (1 equiv) and sodium *tert*-butoxide (3 equiv). The reaction mixture was refluxed for 30 h.

1,8,12,19,22,25,32,36,43,46,51,58-Dodecaazaheptacyclo-[41.5.5.5^{19,25}.1^{3,7}.1^{13,17}.1^{27,31}.1^{37,41}]dohexaconta-3(62),4,6,13(61),14,16,27(55),28,30,37(54),38,40-dodecaene **6a**. Eluent: CH_2Cl_2/MeOH/NH_3aq 100:20:2. Yellowish crystals, mp 103–105 °C, yield 53 mg (36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (quintet, $J = 6.3$ Hz, 4H), 2.57 (br s, 16H), 2.61 (br s, 16H), 3.08 (br s, 8H), 3.50 (s, 8H), 4.30 (br s, 4H), 6.37 (d, $J = 8.0$ Hz, 4H), 6.56 (s, 4H), 6.60 (d, $J = 7.5$ Hz, 4H), 7.06 (t, $J = 7.9$ Hz, 4H) (four NH protons of cyclens were not unambiguously assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 28.9 (2C), 41.5 (4C), 45.1 (8C), 51.7 (8C), 60.0 (4C), 111.2 (4C), 113.2 (4C), 117.6 (4C), 129.0 (4C), 140.1 (4C), 148.5 (4C); MALDI-TOF *m*/*z* 845.6 $[M+H]^+$.

36,39,42-Trioxa-1,8,12,19,22,25,32,46,53,56,61,68-dodecaazaheptacyclo[51.5.5.5^{19,25}.1^{3,7}.1^{13,17}.1^{27,31}.1^{47,51}]doheptaconta-3(72),4,6,13(71),14,16,27(65),28,30,47(64),-48,50-dodecaene **9**. Eluent CH_2Cl_2/MeOH/NH_3aq 100:20:2. Yellow oil, yield 70 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72–1.82 (m, 6H), 2.62 (br s, 32H), 3.06–3.25 (m, 8H), 3.45–3.60 (m, 12H), 3.57 (s, 8H), 4.31 (br s, 2H), 4.76 (br s, 2H), 6.38–6.68 (m,10H), 6.89–7.18 (m, 6H) (four NH protons of cyclens were not unambiguously assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 28.5 (1C), 29.0 (2C), 41.4 (4C), 47.0 (8C), 51.5 (8C), 61.2 (4C), 69.4 (2C), 70.0 (2C), 70.4 (2C), 111.0 (4C), 113.6 (4C), 117.3 (4C), 129.1 (4C), 139.6 (4C), 148.8 (4C); MALDI-TOF *m*/*z* 991.7 $[M+H]^+$.

Cyclic trimer **10**. Eluent CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yellow oil, yield 29 mg (13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61 (s, 48H), 3.25 (br s, 12H), 3.52–3.70 (m, 36H), 6.48 (d, $J = 6.2$ Hz, 6H), 6.53 (s, 6H), 6.69 (d, $J = 7.5$ Hz, 6H), 7.13 (t, $J = 7.6$ Hz, 6H) (12 NH protons were not unambiguously assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 43.4 (6C), 45.6 (12C), 51.7 (12C), 60.3 (6C), 69.6 (6C), 70.2 (6C), 111.6 (6C), 114.0 (6C), 118.2 (6C), 129.2 (6C), 139.8 (6C), 148.3 (6C); MALDI-TOF *m*/*z* 1490.2 $[M+H]^+$.