

Macrocycles Incorporating an Endocyclic But Non-Sterically-Hindering Chelate: Synthesis and Structural Studies

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Two rings of different size have been prepared both incorporating a 3,3'-biisoquinoline (biiq) chelate. The biiq ligand bears phenyl groups at its 8- and 8'-positions, which provide it with an approximate crescent shape. The incorporation of the 8,8'-diaryl-3,3'-biisoquinoline motif in a ring leads to an unusual situation. The complexing site of the macroring is unambiguously pointing towards the inner part of the macrocycle, but, at the same time, it is not sterically hindered, due to the relatively large distance between the coordinating site and the various organic groups belonging to the macrocyclic structure. The synthesis of the two compounds is reported, as well as the X-ray structure of one of them, which confirms the expected geometrical properties of the molecules.

Introduction. – The field of catenanes and rotaxanes has experienced a remarkable development in the course of the last twenty years [1–3], in relation to the synthetic challenge that the preparation of such compounds represents, and to their novel properties, in particular, as controlled dynamic molecular systems, often referred to as 'molecular machines' [4]. The design and the preparation of the macrocyclic subunits, components of such species, is thus essential, both in terms of preparation of the target compounds, and as far as their properties are concerned. The use of transition metals as templates has been particularly useful in the field of interlocking topologies [5], and we would now like to report a new family of coordinating rings whose complexing properties are novel, and which will be incorporated in catenanes and rotaxanes in the future. These macrorings are also promising coordinating species in themselves and will also be studied as such.

As already briefly discussed in a preliminary report [6], the design and the preparation of coordinating rings incorporating an endocyclic but non-sterically-hindering bidentate chelate of the aromatic polyimine family (1,10-phenanthroline or 2,2'-bipyridine) is far from trivial. As far as we are aware, most of the systems reported so far contain a sterically congested coordination site, since the points of attachment of the chelate are the positions *ortho* to the N-atoms and thus close to the transition-metal centre to be complexed. The use of an 8,8'-diaryl-3,3'-biisoquinoline motif changes the situation in a dramatic manner: with such a building block, the coordination site will be located in the inner part of the ring. In addition, the distance between the two phenyl rings borne by the ligand will be such that no or only very limited steric hindrance will be experienced within the complex. We would now like to describe the synthesis of two such biiq-containing rings as well as the crystal structure of one of them, which provides

convincing evidence that the coordination site is indeed endotopic but not particularly congested from a steric viewpoint.

Results. – The target macrocyclic ligands are depicted in *Fig. 1*. Compound **1** is a 39-membered ring, whereas **2** is a 41-membered ring. From the chemical structure of the compounds, it is obvious that the biiq chelate will point towards the centre of the ring, and that steric hindrance will not be important provided the other ligands of the transition-metal complex are not too bulky.

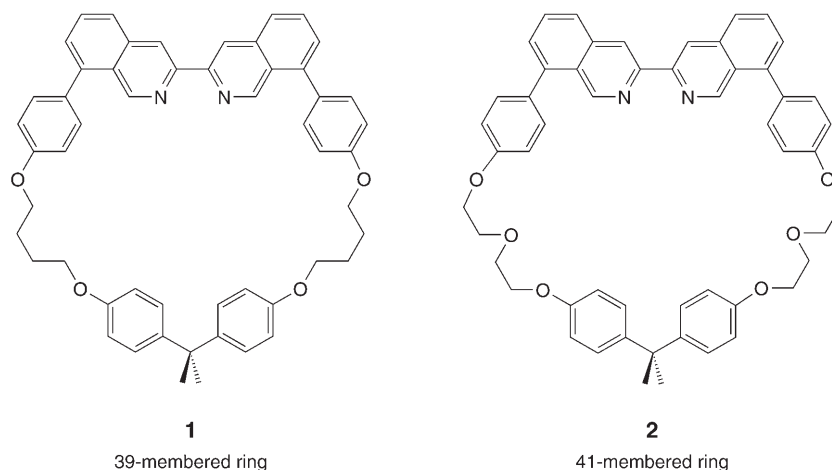
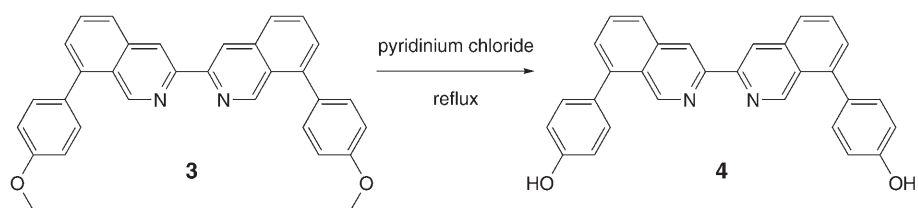


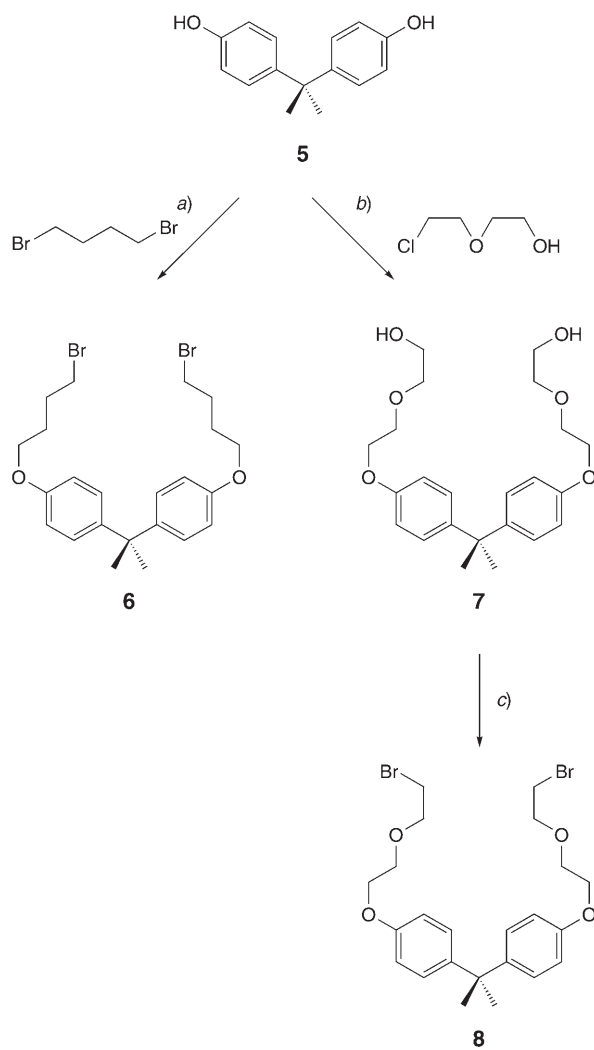
Fig. 1. The two macrocyclic ligands described in the present report

The key starting compound used for the synthesis of both macrocycles is the chelate 8,8'-bis(4-methoxyphenyl)-3,3'-biisoquinoline (**3**) whose synthesis has been described in a previous paper [7]. As shown in *Scheme 1*, the two 4-methoxyphenyl groups were first deprotected in melted pyridinium chloride, at high temperature, to give the diphenol compound **4** in a quantitative yield. To obtain a macrocycle by an intramolecular double *Williamson* reaction from **4**, it was necessary to have an end-functionalized linear fragment. Brominated chains have been chosen because of their better reactivity in nucleophilic substitutions than chlorinated ones, and due to their better resistance to eliminations than iodinated ones. The length of the chain is obviously a critical parameter. In fact, the dibrominated molecule obtained from the hexakis(ethylene glycol) appeared to be too short (since only a bigger macrocycle including two ligands and two chains has been analyzed), in spite of an apparently good design predicted by CPK models. In addition, we decided to build these chains around one central bisphenol A, or 2,2-bis(4-hydroxyphenyl)propane (**5**), in order to improve their shape and rigidity, in prevision of the cyclization. As represented in *Scheme 2*, two chains have been synthesized in such a way. The first one, 2,2-bis[4-(3-bromobutoxy)phenyl]propane (**6**), was obtained in one step by a double *Williamson* reaction between bisphenol A and a large excess of 1,4-dibromobutane. The second dibrominated chain was synthesized in two steps: first a double *Williamson* reaction between bisphenol **5** and 2-(2-chloroethoxy)ethanol led to the diol **7**, which was then

Scheme 1. Demethylation Reaction Leading to Diphenol **4**



Scheme 2. Formation of Brominated Chains

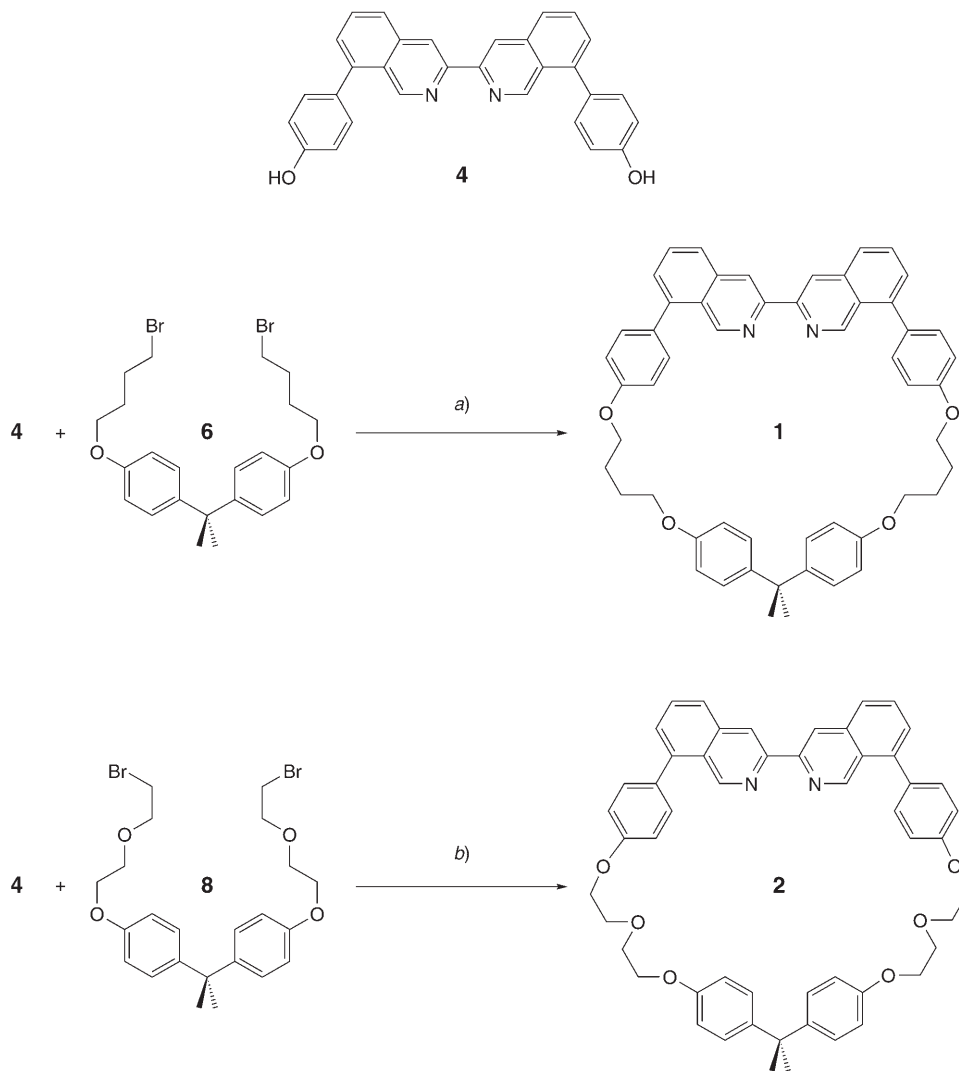


a) Cs_2CO_3 , DMF, 60° , 16 h, 48%. b) Cs_2CO_3 , DMF, 90° , 16 h; 40%. c) MsCl, Et_3N , CH_2Cl_2 , 0° , 3 h, followed by LiBr, acetone, reflux, 16 h; 82%.

converted, according to a classical strategy [5], to the dibrominated chain **8**, via a dimesylated species.

As shown in *Scheme 3*, macrocycles **1** and **2** were obtained by an intramolecular double *Williamson* reaction from the dibrominated chains **6** and **8**, respectively, and diphenol **4**. To favor intramolecular reactions instead of intermolecular ones, these two reactions were carried out in high-dilution conditions. Macrocycle **2** was obtained in a much better yield than **1**, certainly because of the longer and more flexible dibromo

Scheme 3. High-Dilution Reactions Leading to Macrocycles 1 and 2



a) Cs_2CO_3 , DMF, 65° , 75 h; 34%. b) Cs_2CO_3 , DMF, 65° , 60 h; 62%.

chain **8**. As a matter of fact, the dibrominated chain **6**, obtained from dibromobutane, was the shortest that could undergo cyclization with diphenol **4**, since a little shorter dibromo chain, obtained from dibromopropane and bisphenol **5**, has been tried before without any result. However macrocycle **1**, thanks to its rigidity, can be crystallized from CH_2Cl_2 and $(i\text{-Pr})_2\text{O}$, which allowed structure determination by X-ray diffraction, as shown in *Fig. 2*. From the molecular structure represented in *Fig. 1*, it is obvious that the chelate is not sterically hindering but is endocyclic. In other words, the coordination site always points towards the inner part of ring.

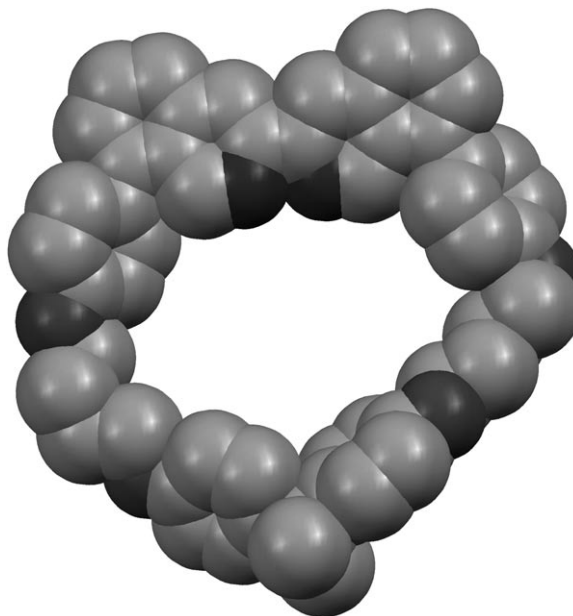


Fig. 2. Crystal structure of macrocycle 1

Conclusions. – In conclusion, two new macrocyclic compounds have been prepared which incorporate a non-sterically-hindering but obviously endocyclic chelate. The synthesis procedure relies on a double ether-forming reaction performed under approximate high-dilution conditions. The largest cycle is a 41-membered ring obtained in good yield (62%) from its two linear di-end-functionalized components. The incorporation of the presently reported cyclic systems into catenanes and rotaxanes is under way.

Experimental Part

General. The following chemicals were obtained commercially and were used without further purification: 2,2-bis(4-hydroxyphenyl)propane (*Lancaster*), 1,4-dibromobutane (*Aldrich*), Cs_2CO_3 (*Aldrich*), 2-(2-chloroethoxy)ethanol (*Aldrich*), MsCl (*Fluka*), LiBr (*Lancaster*). Dry solvents were obtained with suitable dessicants: CH_2Cl_2 from NaH , Et_3N from KOH . All column chromatographies (CC) were performed with *Merck* silica gel 60 (0.063–0.200 mm). ^1H - and ^{13}C -NMR spectra were

recorded with a Bruker AVANCE-300 (300 MHz (^1H)) spectrometer using deuterated solvent as the lock. The spectra were collected at 25°, and the chemical shifts were referenced to residual solvent H-atoms as internal standards. ^1H : CD_2Cl_2 5.32 ppm, (D_6)DMSO 2.50 ppm. Mass spectra were obtained with a VG ZAB-HF spectrometer (FAB) and a VG-BIOQ triple quadrupole in positive- or negative-ion mode (ES-MS). Single-crystal X-ray diffraction experiments were carried out with a Kappa CCD diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The SHELX-97 program was used for structure solution and refinement.

4,4'-(3,3'-Biisoquinoline-8,8'-diyl)diphenol (**4**). 8,8'-(4-Methoxyphenyl)-3,3'-biisoquinoline (**3**; 1.00 g, 2.13 mmol) and pyridinium chloride (ca. 10 equiv., 2.5 g) were mixed into a little flask and heated to reflux in an adapted microwave oven for 10 min. Twice, the same quantity of pyridinium chloride was added, and the mixture was heated to reflux again for 10 min. The mixture was dissolved in dist. H_2O (1 l) and then neutralized with NaOH to give a suspension of a pale yellow precipitate. After filtration, compound **4** was quantitatively obtained without any purification (pale yellow solid; 940 mg, 100%). $^1\text{H-NMR}$ ((D_6) DMSO, 300 MHz): 9.35 (s, 2 H); 9.09 (s, 2 H); 8.15 (d, $J = 8.2$, 2 H); 7.94 (t, $J = 7.7$, 2 H); 7.65 (d, $J = 7.0$, 2 H); 7.45 (d, $J = 8.4$, 4 H); 7.00 (d, $J = 8.4$, 4 H). ES-MS: 441.1559 ($[M + 1]^+$, $\text{C}_{30}\text{H}_{21}\text{N}_2\text{O}_2^+$; calc. 441.1598).

1,1'-Propane-2,2-diylbis[4-(4-bromobutoxy)benzene] (**6**). 4,4'-(Propane-2,2-diyl)diphenol (**5**; 2.28 g, 10 mmol), 1,4-dibromobutane (21.6 g, 12.1 ml, 100 mmol), and Cs_2CO_3 (3.9 g, 12 mmol) were mixed in DMF (30 ml) and heated, with stirring, at 60° overnight. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (100 ml) and dist. H_2O (100 ml). The org. phase was separated, and the aq. phase was extracted twice with CH_2Cl_2 . The combined org. phases were washed first with brine, then with dist. H_2O . The solvent was evaporated, and the residue was purified by CC (silica gel; $\text{CH}_2\text{Cl}_2/\text{pentane}$ 1:4) to give **6** (2.38 g, 48%). Colorless solid. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 7.11 (d, $J = 8.6$, 4 H); 6.76 (d, $J = 8.8$, 4 H); 3.95 (t, $J = 6.1$, 4 H); 3.49 (t, $J = 6.6$, 4 H); 2.09–1.99 (m, 4 H); 1.94–1.85 (m, 4 H); 1.61 (s, 6 H). ES-MS: 514.102 ($[M + 18]^+$, $\text{C}_{23}\text{H}_{34}\text{NO}_2\text{Br}_2^+$; calc. 514.096).

33,34-Dimethyl-24,29,39,44-tetraoxa-9,12-diazanonacyclo[43.2.2.2^{20,23}; 2^{30,33}.2^{35,38}.1^{6,10}.1^{11,15}.0^{2,7}.0^{14,19}]-heptapentaconta-1(47),2,4,6(57),7,9,11(56),12,14,16,18,20,22,30,32,35,37,45,48,50,52,54-docosaene (**1**). A mixture of **4** (500 mg, 1.14 mmol) and **6** (576 mg, 1.16 mmol) in 300 ml of degassed DMF was introduced in a high-dilution funnel fitted on a 2-l round-bottom flask containing Cs_2CO_3 (20 g, 0.06 mol) in suspension in 1 l of degassed DMF. The vessel was heated at 65°, and the mixture in the funnel was added dropwise during 75 h. After further stirring for 30 h, the solvent was removed, and the residue was taken up in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$. The org. phase was separated, and the aq. phase was extracted twice with CH_2Cl_2 . The combined org. phases were washed first with brine, then with dist. H_2O . The solvent was removed, and the residue was mixed with 100 ml of CH_2Cl_2 . The white product in suspension was removed by filtration through a fritted-glass filter funnel with porosity 4, the solvent of the filtrate was evaporated, and the residue was purified by CC (silica gel; $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 99:1) to give **1** (297 mg, 34%). Yellow solid. In a crystallization tube, with CH_2Cl_2 as a good solvent and heptane as a bad solvent, this compound gave one single big yellow crystal. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 9.38 (s, 2 H); 8.37 (s, 2 H); 7.94 (d, $J = 8.2$, 2 H); 7.77 (t, $J = 8.2$, 2 H); 7.58 (d, $J = 8.2$, 2 H); 7.46 (d, $J = 8.7$, 4 H); 7.15 (d, $J = 8.9$, 4 H); 7.09 (d, $J = 8.7$, 4 H); 6.81 (d, $J = 8.9$, 4 H); 4.26 (t, $J = 6.2$, 4 H); 3.99 (t, $J = 6.1$, 4 H); 2.02–1.95 (m, 8 H); 1.59 (s, 6 H). ES-MS: 777.3757 ($[M + 1]^+$, $\text{C}_{53}\text{H}_{49}\text{N}_2\text{O}_4^+$; calc. 777.3692). Crystal-structure analysis of **1**: $\text{C}_{65}\text{H}_{20}\text{Cl}_4\text{N}_2\text{O}_4$, $M_r = 1034.63$, triclinic, $a = 13.6610(3)$, $b = 14.4330(3)$, $c = 14.8440(3) \text{ \AA}$, $\alpha = 103.7910(7)^\circ$, $\beta = 105.6240(9)^\circ$, $\gamma = 92.9520(7)^\circ$, $V = 2716.35(10) \text{ \AA}^3$, $T = 173(2) \text{ K}$, space group $P1$, $Z = 2$, $\mu(\text{MoK}_\alpha) = 0.268 \text{ mm}^{-1}$, 24318 collected reflections, 15825 independent reflections ($R(\text{int}) = 0.029$), final R indices $R_1 = 0.089$, $wR_2 = 0.3872$ (there are two disordered CH_2Cl_2 molecules). CCDC-621657 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2,2'-[Propane-2,2-diylbis(benzene-4,1-diyloxyethane-2,1-diyloxy)]diethanol (**7**). Compound **5** (2 g, 8.8 mmol), 2-(2-chloroethoxy)ethanol (3.3 g, 26.5 mmol), and Cs_2CO_3 (6 g, 18 mmol) were mixed in DMF (30 ml) and heated, with stirring, at 90° overnight. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (100 ml) and dist. H_2O (100 ml). The org. phase was separated, and the aq. phase was extracted twice with CH_2Cl_2 . The combined org. phases were washed first with brine, then with dist. H_2O . The solvent was evaporated, and the residue was purified by CC (silica gel; $\text{Et}_2\text{O}/\text{EtOH}$ 95:5, 90:10 and

80:20) to give **7** (1.4 g, 40%). Colorless oil. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 7.12 (*d*, $J = 8.8$, 4 H); 6.79 (*d*, $J = 9.0$, 4 H); 4.08 (*t*, $J = 4.7$, 4 H); 3.81 (*t*, $J = 4.7$, 4 H); 3.72–3.66 (*m*, 4 H); 3.63–3.59 (*m*, 4 H); 1.61 (*s*, 6 H). ES-MS: 427.212 ($[M + 23]^+$, $\text{C}_{23}\text{H}_{32}\text{NaO}_6^+$; calc. 427.210).

1,1'-Propane-2,2-diylbis[4-[2-(2-bromoethoxy)ethoxy]benzene] (**8**). Compound **7** (1.4 g, 3.5 mmol) was dissolved in dry CH_2Cl_2 (150 ml). The soln. was cooled to *ca.* -2° in an ice/salt mixture, then Et_3N (8 ml) was added. The subsequent addition of MsCl (1.3 g, 0.9 ml, 11 mmol) in CH_2Cl_2 (50 ml) was conducted dropwise over a period of 1 h, under Ar. The soln. was then allowed to stir at 0° for 3 h. Dist. H_2O (50 ml) was then added dropwise over a period of 15 min, and the mixture was allowed to warm to r.t. The org. phase was separated, and the aq. phase was extracted twice with CH_2Cl_2 . The combined org. phases were washed with dist H_2O . The solvent was evaporated, and the residue was directly used without further purification: it was dissolved in 50 ml of acetone with LiBr (3.3 g, 38 mmol), and the soln. was heated to reflux overnight, under Ar. A white precipitate of lithium methanesulfonate appeared. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (100 ml) and dist. H_2O (100 ml). The org. phase was separated, and the aq. phase was extracted twice with CH_2Cl_2 . The combined org. phases were washed with dist. H_2O . The solvent was evaporated, and the residue was purified by CC (silica gel; $\text{Et}_2\text{O}/\text{EtOH}$ 98:2) to give **8** (1.5 g, 82%). Yellow oil. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 7.12 (*d*, $J = 9.0$, 4 H); 6.79 (*d*, $J = 9.0$, 4 H); 4.08 (*t*, $J = 4.7$, 4 H); 3.81–3.87 (*m*, 8 H); 3.49 (*t*, $J = 6.1$, 4 H); 1.62 (*s*, 6 H). ES-MS: 546.090 ($[M + 18]^+$, $\text{C}_{23}\text{H}_{34}\text{Br}_2\text{NO}_4^+$; calc. 546.086).

35,35-Dimethyl-24,27,30,40,43,46-hexaoxa-9,12-diazaonacyclo[45.2.2.2^{20,23}.2^{31,34}.2^{36,69}.1^{6,10}.1^{11,15}.0^{2,7}.0^{4,19}]nonapentaconta-1(49),2,4,6(59),7,9,11(58),12,14,16,18,20,22,31,33,36,38,47,50,52,54,56-docosaene **2**. A mixture of **4** (200 mg, 0.45 mmol) and **8** (258 mg, 0.49 mmol) in 120 ml of degassed DMF was introduced in a high-dilution funnel fitted on a 1-l round-bottom flask containing Cs_2CO_3 (2.5 g, 7.7 mmol) in suspension in 250 ml of degassed DMF. The vessel was heated at 65° , and the mixture in the funnel was added dropwise during 60 h. After further stirring for 20 h, the solvent was removed, and the residue was taken up with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$. The org. phase was separated, and the aqueous phase was extracted twice with CH_2Cl_2 . The combined org. phases were washed first with brine, and then with dist. H_2O . The solvent was removed, and the residue was purified by CC (silica gel; $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 99:1) to give **2** (229 mg, 62%). Yellow solid. $^1\text{H-NMR}$ (CD_2Cl_2 , 300 MHz): 9.35 (*s*, 2 H); 8.39 (*s*, 2 H); 7.95 (*d*, $J = 8.2$, 2 H); 7.77 (*t*, $J = 8.2$, 2 H); 7.57 (*d*, $J = 8.2$, 2 H); 7.46 (*d*, $J = 8.9$, 4 H); 7.14–7.09 (*m*, 8 H); 6.78 (*d*, $J = 8.9$, 4 H); 4.31 (*t*, $J = 4.4$, 4 H); 4.07 (*t*, $J = 4.6$, 4 H); 3.94–3.86 (*m*, 8 H); 1.62 (*s*, 6 H). ES-MS: 809.3686 ($[M + 1]^+$, $\text{C}_{53}\text{H}_{49}\text{N}_2\text{O}_6^+$; calc. 809.3585).

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