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Synthesis, Structural Characterization and Metal Inclusion Properties of 18-, 20- and 22-Membered Oxaazacyclophanes and Oxaazacalix[4]arene Analogues: Macrocyclic Amine and Schiff Base Receptors with Variable N_xO_y Donor Sets

Ramón Moreno-Corral,[a] Herbert Höpfl,[b] Lorena Machi-Lara,[a] and Karen O. Lara*[a]

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A series of oxaazacyclophanes and oxaazacalix[4]arene analogues with 18-, 20- and 22-membered rings have been synthesized from diamine and dialdehyde building blocks and structurally characterized by spectroscopic methods. One diamine precursor and four macrocycles have additionally been analysed by single-crystal X-ray diffraction. Two of the oxaazacalix[4]arene analogues were employed for metal ion complexation studies based on UV/Vis absorption spectroscopy, showing both compounds to be able to form complexes with Cu^{2+} and Zn^{2+}.

1. Introduction

During the past few decades much effort has been dedicated to the design of macrocyclic receptors possessing specific structural features, as a result of their importance in the fields of supramolecular and coordination chemistry.[1–4] Accordingly, macrocycles have played a key role in the understanding of certain molecular processes, especially those relating to bioactive molecules such as porphyrins, corrins and antibiotics.[5–8] In addition, macrocyclic compounds have important applications in, among other fields, analytical chemistry, pharmaceutics, food chemistry, hydrometallurgy, agriculture and materials science.[9–12]

One representative group of macrocycles is the cyclophane family. Special attention has been drawn to oxaazacyclophanes, because they are versatile hosts for the recognition of organic and inorganic ions and molecules.[13–14] Depending on the number, position and orientation of the donor groups included in a macrocycle structure, as well as its ring size, highly selective ligands for certain metal ions can be obtained.[15–17] Although there are many reports on this topic in the literature, the coordination chemistry of ditopic macrocycles with mixed nitrogen–oxygen donors is an expanding domain of research with promising and diverse applications.[18–20]

From the synthetic point of view, these compounds can be obtained by a variety of methods, which typically involve either the high-dilution principle or the template effect, in order to increase the yield of the cyclization step.[21–22] In the metal template synthesis approach, however, stable metal-complexed macrocycles can be generated, and removal of the metal can be a problem in this case.[23]

A third synthetic method for macrocyclic enclosure is the high-pressure procedure. Although it is the least common method, there are several reports describing its efficacy in macrocycle synthesis, especially when suitable building blocks are employed for the cyclization.[24–26] We recently reported on the preparation of a series of Schiff base dioxadiazamacrocycles in moderate to high yields by this method, from combinations of dialdehyde precursors and diamines.[27,28] However, the structural characterization of these compounds showed that in some of the macrocycles the orientation of the lone pair electrons on the nitrogen atoms was not suitable for metal complexation.[28]

We now report on the synthesis and structural characterization of a series of oxaazacyclophanes and oxaazacalix[4]arene analogues, the preparation of which from diamine and dialdehyde building blocks has been optimized by exploration of the high-pressure, high-dilution and metal template methods. In view of the structural characteristics of the macrocycles, some of them might be employable as hosts for small organic compounds and metal ions. In order to verify this hypothesis, two of these and their oxaazacalix[4]arene analogues were employed for titration experiments with Cu^{2+}, Ni^{2+} and Zn^{2+}.

[a] Departamento de Investigación en Polímeros y Materiales, Universidad de Sonora,
Rosales y Encinas s/n, Col. Centro, 83000 Hermosillo, Sonora, México
Fax: +52-662-2592216
E-mail: karenol@polimeros.uson.mx
[b] Centro de Investigaciones Químicas,
Universidad Autónoma del Estado de Morelos,
Av. Universidad 1001, Cuernavaca 62209, México

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2. Results and Discussion

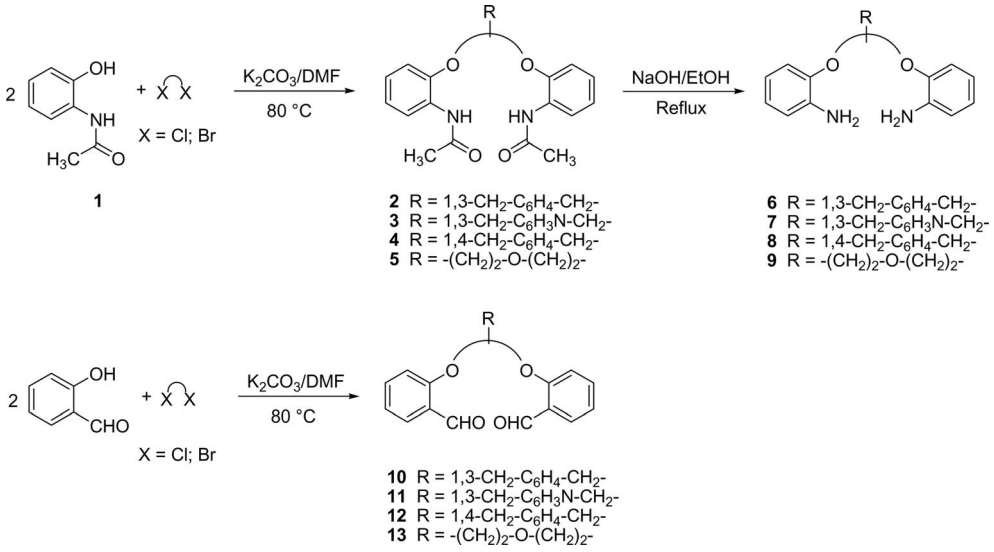
2.1. Synthetic Procedures

The diamines **6**–**9** were prepared by the synthetic procedure shown in Scheme 1. Treatment of 2-(acetylamino)-phenol (**1**) with suitable alkyl dihalides in a 2:1 molar ratio gave the corresponding ethers **2**–**5**, which were then deprotected to afford the corresponding diamine derivatives **6**–**9**. Compounds **1**–**2**, **5**–**7** and **9** had been reported in the literature previously,[29–35] but the diamines **3**, **4** and **8** had not.

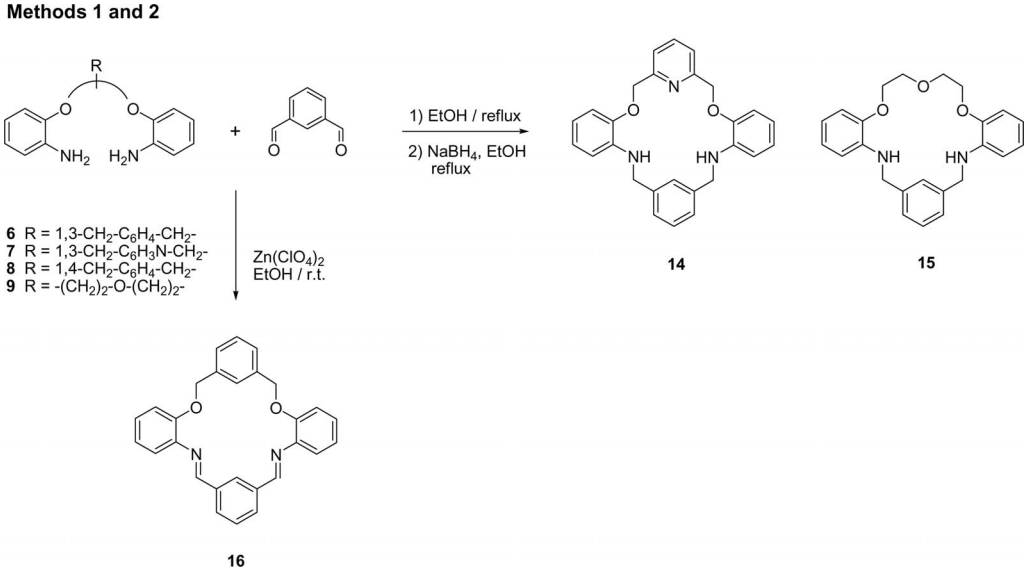
The dialdehyde building blocks **10**–**13** were prepared by an analogous Williamson ether synthesis with salicylaldehyde in place of the *N*-protected amine **1**. All of the dialdehyde compounds had been reported previously.[28,36,37]

Treatment of equimolar amounts of the diamines **6**–**9** with isophthalaldehyde in ethanol under high-dilution conditions to give the corresponding cyclic Schiff bases only succeeded in the cases of **7** and **9**. In situ reduction by addition of sodium borohydride to the reaction solutions afforded the corresponding 18-membered oxaazamacrocycles **14** and **15** (Scheme 2) in moderate yields.

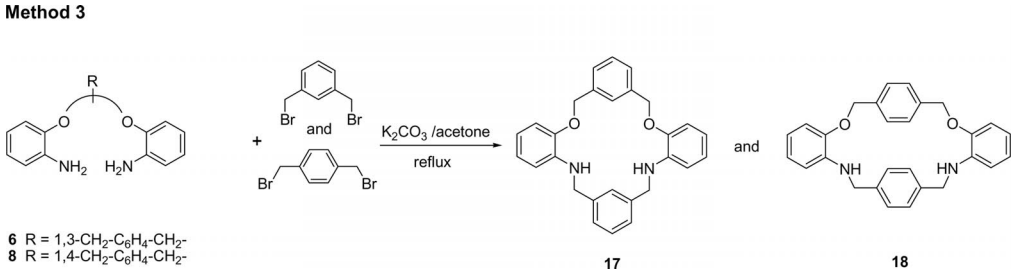
In an attempt to achieve reactivity of diamine **6** towards isophthalaldehyde, zinc perchlorate was employed as template to give the diimine **16** (Scheme 2). However, this reaction gave only low yields and in the case of the diamine **8** it did not take place. In order to test a third synthetic procedure, the diamines **6** and **8** were therefore combined with the appropriate alkyl dihalides in equimolar proportions



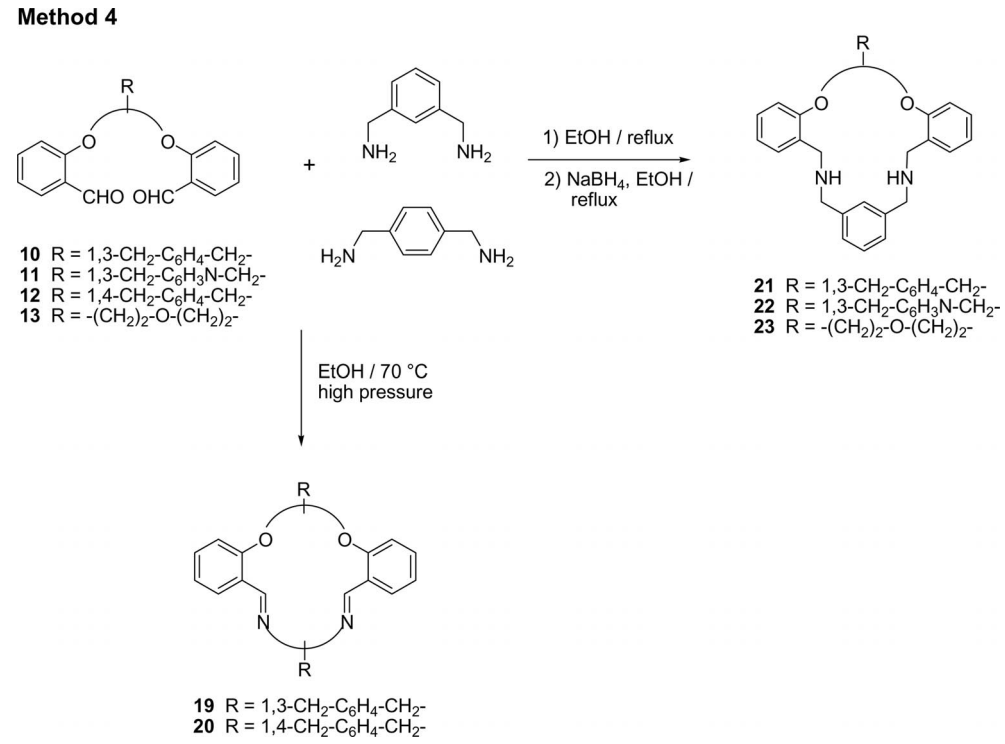
Scheme 1. Synthesis of the diamine (**6**–**9**) and dialdehyde (**10**–**13**) building blocks.



Scheme 2. Synthesis of the oxaazacyclophanes **14**–**16**.



Scheme 3. Synthesis of the oxaazacyclophanes **17** and **18**.



Scheme 4. Synthesis of the oxaazacyclophanes **19**–**23**.

under high-dilution conditions to give the 18- and 20-membered dioxadiaza macrocycles **17** and **18** (Scheme 3) in moderate to good yields.

With the dialdehyde building blocks **10**, **11** and **13**, on the other hand, the high-dilution reaction sequence shown in Scheme 1 (Method 1) was explored. When **10**, **11** and **13** were each combined with *m*-xylylenediamine in ethanol under high-dilution conditions, followed by in situ treatment with sodium borohydride, the 20- and 22-membered *m*-xylylene derivatives **21**–**23** (Scheme 4) could be isolated in good yields. In order to explore an alternative method for the preparation of macrocycles, the high-pressure method was employed for the dialdehydes **10** and **12** in combination with *m*- and *p*-xylylenediamine, respectively. In this case the macrocyclic Schiff bases **19** and **20** (Scheme 4) were obtained in good to moderate yields.

2.2. Structural Characterization

All compounds described here were characterized by elemental analysis, IR and $^{1}H/^{13}C$ NMR spectroscopy (standard one- and two-dimensional techniques) and mass spectrometry. In all cases the spectroscopic data were consistent with the assigned structures (see the Experimental Section). In the cases of compounds **7**, **14**, **15**, **17** and **19**, the molecular structures were additionally established by single-crystal X-ray diffraction analysis. The most relevant crystallographic data are given in the Experimental Section (see Table 4, below).

The molecular structure of the diamine intermediate **7** is shown in Figure 1. As expected, the amino functions are not *syn*-oriented as in the macrocyclic ring structure. Interatomic distances and angles are in the expected ranges.

In the crystal structure the diamine molecules are linked through hydrogen bonding interactions with crystal lattice water molecules to give a 1D chain along the *c* axis, based on an interesting tetrameric assembly formed between two water and four diamine molecules (Figure 2). Within these chains each water molecule is connected to three diamines by O_w–H···N_{pyr}, O_w–H···N_{amine} and N_{amine}–H···O_w hydrogen bonding interactions (Table 1). The chains are linked through further N_{amine}–H···O_w interactions to give an overall 3D hydrogen-bonded network.

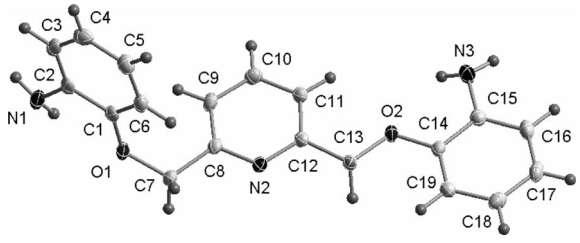


Figure 1. Perspective view of the molecular structure of the precursor **7**·H_2O. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius.

The molecular structures of compounds **14**, **15**, **17** and **19** are shown in Figure 3 and Figure 4, revealing that for the macrocyclic diamines **14**, **15** and **17** the NH hydrogen atoms and the lone pair electrons of the oxygen atoms are oriented towards the cavity of the macrocycle. In contrast, the diimine **19** has the *E* configuration (Figure 4, b), and the lone pair electrons on the nitrogen atoms are oriented towards the periphery of the macrocycle (*exo*), whereas the lone pair electrons of the oxygen atoms are oriented into the cavity (*endo*). This finding is in agreement with our recently published report on structurally related diimine macrocycles,[28] which have been analysed by molecular modelling and X-ray diffraction analysis.

Table 1. Hydrogen bonds in the crystal structure of **7**·H_2O (Å and °).[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
O31–H···N2	0.84	2.05	2.87	165
O31–H···N1^{i}	0.84	2.12	2.96	174
N1^{ii}–H···O31^{ii}	0.86	2.09	2.91	160
N3^{iii}–H···O31	0.86	2.50	3.23	144

[a] Symmetry operators: i) –*x*, 2 – *y*, –*z*; ii) –*x*, 2 – *y*, 1 – *z*; iii) –*x*, 1 – *y*, 1 – *z*.

"Calixarene" is the term coined for a series of macrocyclic phenol condensates connected through methylene bridges and capable of assuming basket-shaped (or calyx-shaped) conformations.[38] A variety of calixarenes and their analogues have been obtained: a) by derivatizations on the upper and/or lower rims of conventional calix[*n*]arenes, b) by the replacement of their phenylene units with heterocyclic moieties (such as furan, thiophene, pyridine, imid-

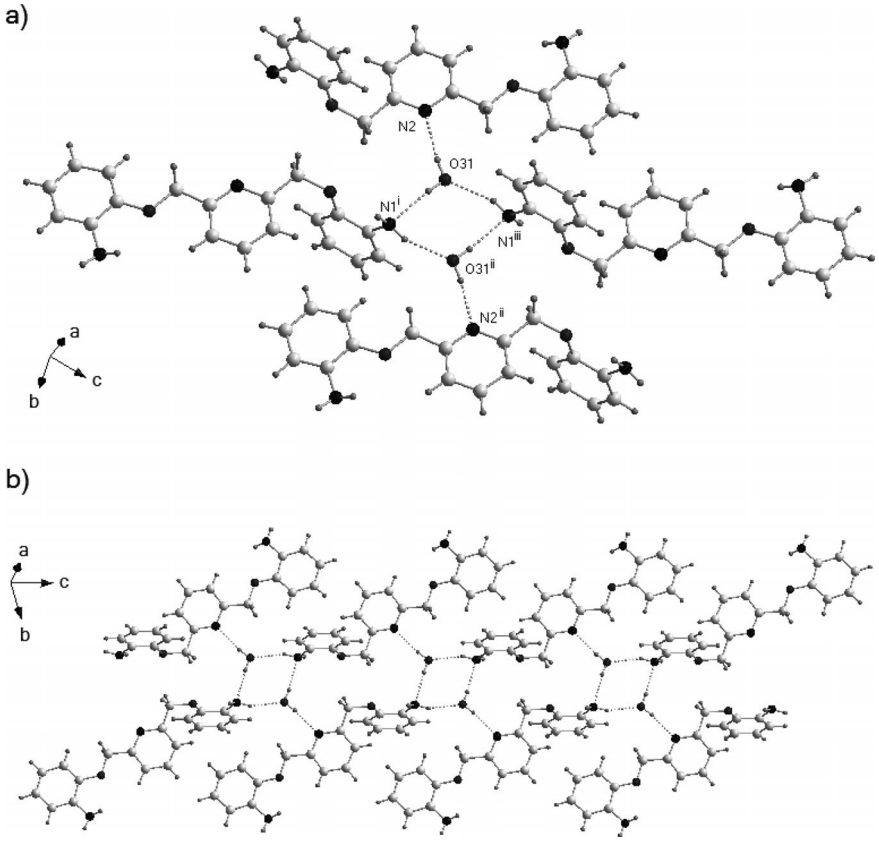


Figure 2. Fragment of the crystal structure of diamine **7**·H_2O showing a) the tetrameric assembly within b) the 1D hydrogen-bonded chain. Symmetry operators: i) –*x*, 2 – *y*, –*z*; ii) –*x*, 2 – *y*, 1 – *z*; iii) *x*, *y*, 1 + *z*.

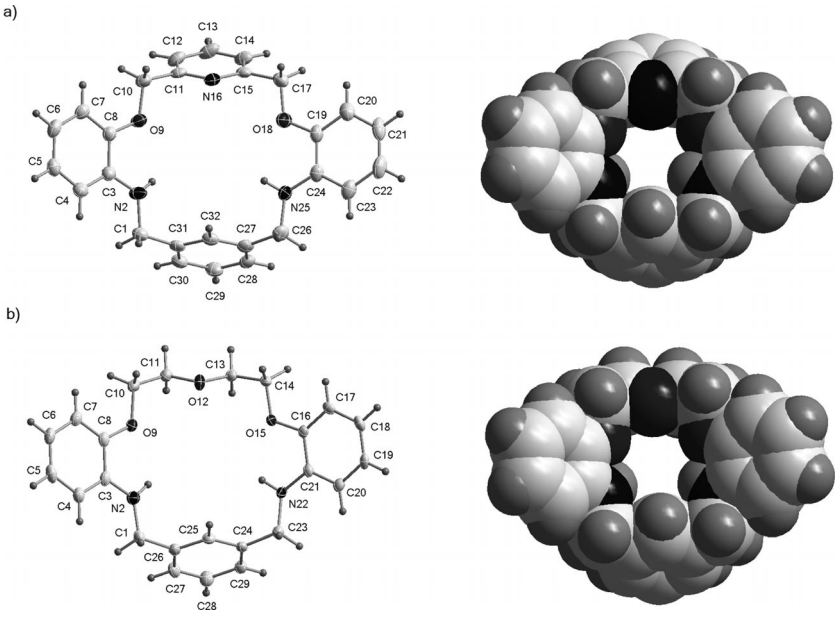


Figure 3. Perspective views and space-filling models of the molecular structures of compounds a) **14** and b) **15**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius.

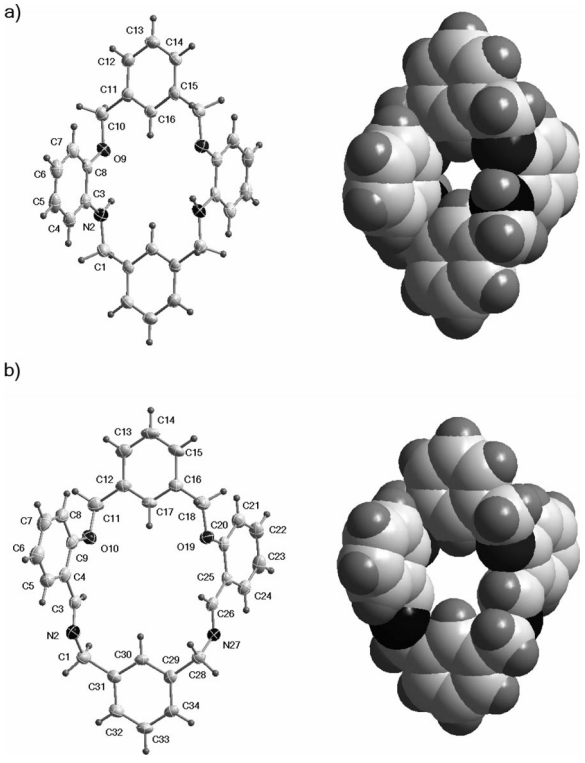


Figure 4. a) Perspective views and space-filling models of the molecular structures of compounds a) **17** and b) **19**. Displacement ellipsoids are drawn at the 50 and 30% probability level, respectively. Hydrogen atoms are shown as small spheres of arbitrary radius.

azole, indole, etc.),[39] or c) by linking the aromatic rings with atoms other than carbon (such as nitrogen, oxygen, silicon and sulfur, among others).[40]

From the structural characteristics of compounds **14**, **17** and **19**, they could be considered oxaazacalix[4]arene analogues. Calix[4]arenes exhibit four different conformations, termed *cone*, *partial cone*, *1,2-alternate* and *1,3-alternate*.[38] In the solid state, the two independent molecules in the crystal lattice of compound **14** have flattened *1,3-alternate* conformations, in which the cavities are partially occupied by water molecules. The oxygen atoms of the water molecules show a total of six short D···A contacts in the 2.88–3.35 Å range, of which five correspond to hydrogen bonds with the nitrogen and oxygen atoms of the macrocyclic ring and one to a C–H···O_w interaction (Figure 5). The large number of possible interactions is interesting, because a coordinated water molecule generally occupies a tetrahedral coordination environment with a maximum of four hydrogen bonding interactions. This structure indicates that the water molecules are scrambling around the cavity of the oxaazacalix[4]arene analogue, probably each having at least two different orientations.

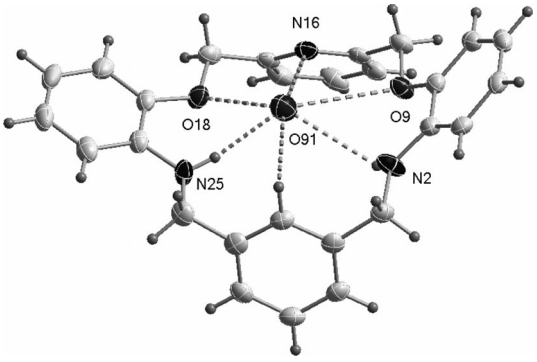


Figure 5. In the solid state, compound **14** forms inclusion complexes with crystal lattice water molecules. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius.

Table 2. Selected geometrical parameters for the description of size, cavity and conformation of the macrocycle components in compounds **14**, **15**, **17** and **19**.

	O···O [Å]	O···N [Å]	N···N [Å]	centr···centr[a] [Å]	C_{ar}–N–CH_2–C_{ar}[b] [°]	C_{Ar}–O–CH_2–C_{Ar}[c] [°]
14[d]	5.17	2.60/2.63	5.24	6.72/9.50	+174.6/+172.2	–176.0/–177.4
	5.19	2.62/2.63	5.39	6.72/9.65	–170.5/–167.6	+177.3/–178.7
15	5.05	2.63/2.61	5.36	–/9.26	–172.2/+166.1	+177.4/+174.6
17[e]	4.96	2.61/2.61	4.96	8.25/6.52	+69.8/+85.1	–85.1/–69.8
19	5.04	3.96/3.97	5.62	9.00/7.97	–115.5/+117.3	+78.0/+76.7

[a] The first value corresponds to the centroid···centroid distance between the phenylene groups and the second to the centroid···centroid distance between the 2-aminophenoxy groups. [b] C_H–N–CH_2–CH_{ar} in the case of compound **19**. [c] C_{ar}–O–CH_2–CH_2 in the case of compound **15**. [d] The crystal structure of this compound has two independent molecules in the asymmetric unit. [e] The molecules are disordered around crystallographic inversion centres within the crystal structure.

The molecular structure of **15** has a very similar conformation to the previous case (Figure 3, b). In compounds **17** and **19** the *meta*-phenylene rings are in or almost in the same plane (angle between the mean planes of the *meta*-phenylene rings: 0.0° for **17** and 12.2° for **19**), so that the conformations of these oxaazacalix[4]arene analogues are best described as chair conformations (Figure 4).

The geometric and topological properties of the macrocycles can be analysed in greater detail in terms of the series of intra-annular distances and torsion angles summarized in Table 2. The O···O, O···N, N···N and centroid···centroid distances between opposite aromatic rings allow the receptor shape to be outlined. For the diamine derivatives **14**, **15** and **17** the spatial orientations of the NH groups are best described by the C_{ar}/C_H–NH–CH_2–C_{ar} torsion angles, which together with the C_{ar}–CH_2–O–CH_2 torsion angles provide valuable information on the molecular conformations. The values of these torsion angles show that the conformational changes between the two types of macrocycles (**14** and **15** vs. **17** and **19**) arise from rotation of the 2-aminophenoxy groups around the O–CH_2 and N–CH_2 bonds groups together with rotation of the *meta*-phenylene rings around the C_{ar}–CH_2 bonds. As a consequence, the centroid···centroid distances between the *meta*-phenylene groups increase significantly, whereas the centroid···centroid distances between the 2-aminophenoxy groups decrease (Table 2).

Of the structures analysed by X-ray diffraction analysis, the crystal structures of compounds **15** and **19** show an interesting supramolecular organization. In compound **15** the macrocycles are arranged in pillars in 1D chains along the *b* axis. In these strands, the –$CH_2CH_2OCH_2CH_2$– groups are embedded within the cavities of neighbouring macrocycles (Figure 6). In the crystal structure of com-

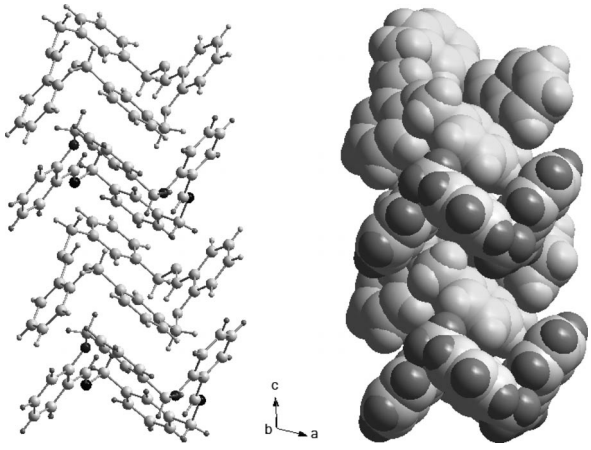


Figure 7. In the crystal structure of compound **19**, the macrocycles are arranged in pillars to give 1D chains along the *c* axis through inclusion of the -$OCH_2C_4H_4CH_2O$- and -$NCH_2C_4H_4CH_2N$- groups within the cavities of neighbouring macrocycles.

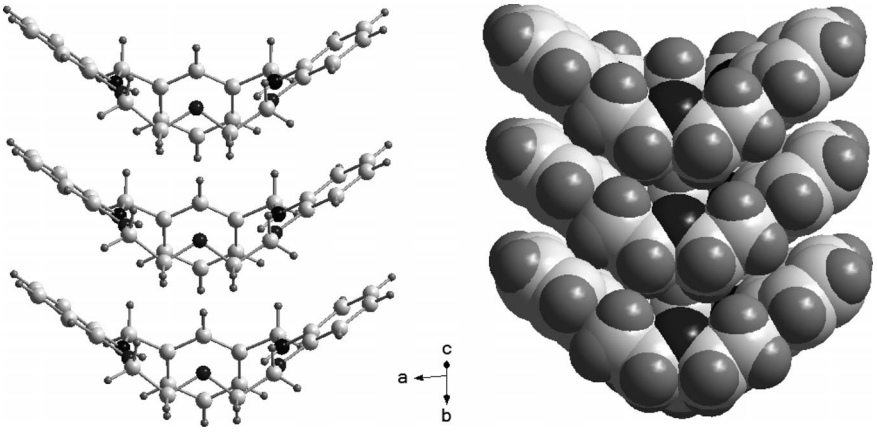


Figure 6. In the crystal structure of compound **15**, the macrocycles are arranged in pillars to give 1D chains along the *b* axis through inclusion of the -$CH_2CH_2OCH_2CH_2$- group within the cavity of a neighbouring macrocycle.

pound **19**, a similar 1D supramolecular arrangement arises from the inclusion of the $–OCH_2C_4H_4CH_2O–$ and $–NCH_2C_4H_4CH_2N–$ groups into neighbouring macrocycles (Figure 7).

2.3. Complexation Studies in Solution

From the chemical structures of the oxaazacalix[4]arene analogues **14** and **17** (see Figures 3 and 4), it can be expected that these multipoint coordination ligands might be capable of forming stable complexes with certain metals. For that reason, we carried out preliminary experiments to investigate the UV/Vis spectroscopic properties of these compounds. Characteristic absorption bands and molar absorptivity coefficients for compounds **14** and **17** are summarized in Table 3.

Table 3. Characteristic absorption bands and molar absorptivity coefficients for compounds **14** and **17** in different solvents.

	Solvent	λ_{max} [nm]	ε_{max} [$dm^3 mol^{-1} cm^{-1}$]
14	acetonitrile	246	14500
		289	5830
	methylene chloride	275	5830
		293	7014
17	acetonitrile	249	20540
		292	10207
	methylene chloride	287	23229

The coordination capabilities of the oxaazamacrocyclic ligand **14** towards Cu^{2+}, Ni^{2+} and Zn^{2+} ions were first investigated by UV/Vis spectroscopy in acetonitrile. The UV/Vis spectra of the macrocycle and of its corresponding metal complexes were recorded in 10^{-3} to 10^{-5} M solutions. As summarized in Table 3, in acetonitrile the free macrocycle exhibits two strong broad absorption bands at 246 and 289 nm, which correspond to π–π* and n–π* transitions of benzene rings and amine groups, respectively. The presence of copper and zinc ions caused small changes in the absorption spectra, but no spectral change was detected in the presence of nickel. Because the spectral changes were not very significant, it was not possible to determine the binding constants. The low-affinity binding for the metal ions can be attributed to the coordinative nature of the solvent (acetonitrile), which thus competes for the binding sites at the metal centre. The UV/Vis spectra of the free macrocycles **14** and **17** and their corresponding metal complexes with Cu^{2+}, Ni^{2+} and Zn^{2+} in dichloromethane (10^{-4} to 10^{-6} M solutions) were recorded and significant spectral changes for the ligands were observed in the presence of Cu^{2+} and Zn^{2+}. In particular, a new strong absorption band appeared for each receptor, at approximately 380 nm for the copper complexes and at approximately 390 nm for the zinc complexes (see Figures 8 and 9). If it is taken into account that Zn^{2+} is a closed-shell metal ion, the new absorption band around 390 nm in the spectra of copper and zinc complexes of the macrocycles can only be attributed either to intraligand charge transfer transition of mixed ππ*/nπ* character[41] or to charge transfer between a cyclophane molecule and metal acetonitrile complexes $[M(CH_3CN)_n]$. This latter due to acetonitrile was employed as co-solvent, typically at 3% v/v (see Experimental Section: Solution Studies by UV/Vis Electronic Absorption). As was also observed for the titrations in acetonitrile, the presence of nickel ions did not cause changes in the absorption spectra of compounds **14** and **17**. This may be attributed to the rigidity of the structures of the cyclophane ligands, which reduces their ability to adapt themselves to the stereochemical requirements of Ni^{2+}, which are much stricter than those of Cu^{2+} and Zn^{2+}, producing a decrease in the thermodynamic stability of the nickel complexes.

Titration plots of the absorbance at 380 or 390 nm showed different behaviour for the two metal ions: for the copper complexes a hyperbolic shape characteristic of 1:1 stoichiometry was observed, whereas the zinc complexes

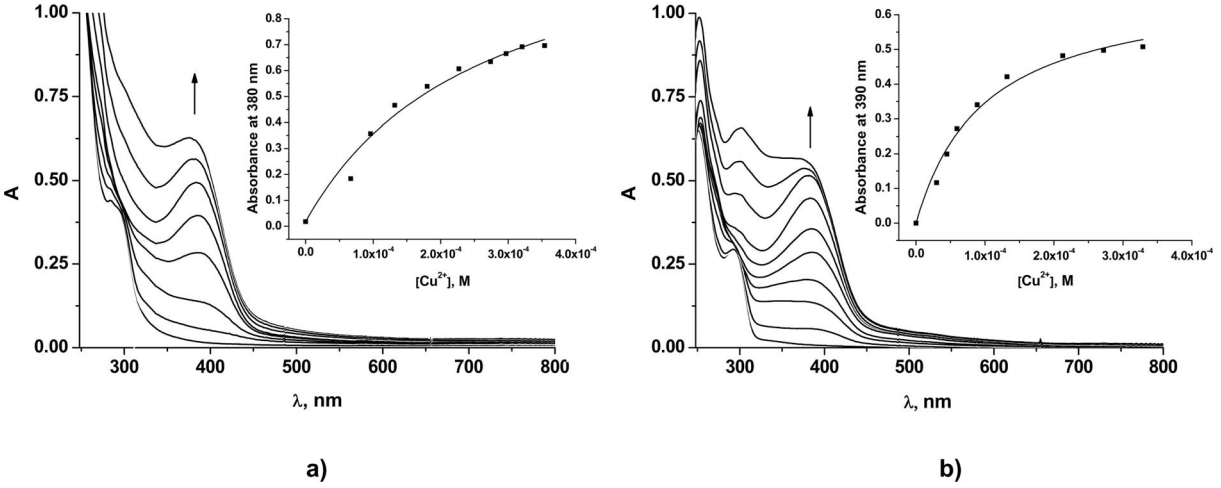


Figure 8. Variation of the absorption spectra (in CH_2Cl_2) in the presence of Cu^{2+} (10^{-6} to 10^{-4} M) for: a) macrocycle **14**, and b) macrocycle **17**. Insets: plots of the absorbance at 380 and 390 nm, respectively, with respect to the concentration of Cu^{2+}. For both solutions the concentration of the macrocycle was 3×10^{-5} M. Solid lines are the fitting curves in accordance with Equation (1).

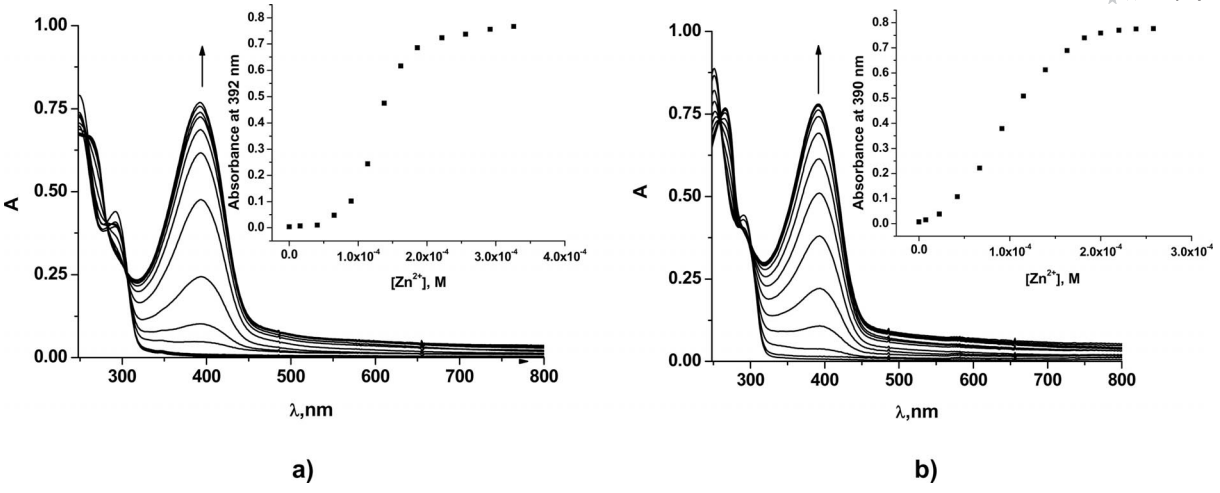


Figure 9. Variation of the absorption spectra (in CH_2Cl_2) in the presence of Zn^{2+} (10^{-6} to 10^{-4} M) for: a) macrocycle **14**, and b) macrocycle **17**. Insets: plots of the absorbance at 392 and 390 nm, respectively, with respect to the concentration of Zn^{2+}. For both solutions the concentration of the macrocycle was 3×10^{-5} M.

generated a sigmoid shape, suggesting that the ligands were not forming complexes with definite compositions. The spectral changes accompanying complex formation and the titration plots are shown in Figures 8 and 9.

The hyperbolic behaviour observed in the titration plots of the copper complexes indicates a 1:1 ligand/metal stoichiometry, so the data were fitted in accordance with Equation (1).[42,43]

$$A_{obs} = (A_0 + A_{\infty}K[G]_T)/(1 + K[G]_T) \quad (1)$$

where A_{obs} is the observed absorbance, A_0 is the absorbance of free ligand, $A_{\∞}$ is the maximum absorbance induced by the presence of a given metal ion, $[G]_T$ is the total concentration of the metal ion and K is the binding constant. This gave $K = 4600\ M^{-1}$ for **14**-Cu^{2+} and $K = 10\,200\ M^{-1}$ for **17**-Cu^{2+}.

On the other hand, in order to observe the d–d transitions of the copper complexes, additional UV/Vis measurements were carried out in dichloromethane at a higher ligand concentration ([**17**] = 5.0×10^{-4} M). A solution of a **17**/Cu^{2+} mixture at a molar ratio [Cu]/[L] = 1 showed a new broad band in the absorption spectrum, its centre at about 770 nm, characteristic of copper complexes with octahedral geometry (see the Supporting Information).[44] The two oxygen and two nitrogen atoms on the macrocycle ring are coordinated to the metal cation, and the six-coordination sphere is believed to be completed by two acetonitrile molecules (for the titration experiments, stock solutions of Cu^{2+}, Ni^{2+} and Zn^{2+} were prepared from the corresponding nitrates in acetonitrile; see the Experimental Section: Solution Studies by UV/Vis Electronic Absorption.).

Finally, in order to confirm the possibility of multiple equilibria for zinc complexes, a Job experiment was performed for the **14**/Zn^{2+} system, which confirmed a ligand-to-metal stoichiometry of 1:2 (see the Supporting Information).

3. Conclusions

The above discussion shows that the diamine and dialdehyde building blocks used here allow macrocyclic structures to be prepared easily and in good yields by the high-pressure, high-dilution or metal template methods. The solid-state characterization of one diimine and three diamine macrocycles by X-ray diffraction analysis indicates that these compounds are good candidates for receptors for metal ions or small molecules. Titration studies with copper(II), nickel(II) and zinc(II) nitrate have shown that some of the macrocyclic hosts described are indeed capable of metal complexation. On the other hand, it is important to emphasize that some of the cyclic diamines described in this report could also serve as receptors for anions, in particular if the nitrogen atoms were protonated. In this respect, we are currently working on anion complexation studies of some of these macrocyclic hosts. We are also working on the preparation of further oxaazyclophanes with additional binding sites, in order to generate hosts with a more specific capability for guest complexation in organic and aqueous media.

Experimental Section

General: All solvents were of analytical reagent grade and reagents from Sigma–Aldrich were used without further purification. For spectrophotometric measurements HPLC-grade solvents were used. The 1D and 2D NMR spectra were recorded with a Bruker Advance 400 instrument. Chemical shifts (δ) are reported as values in ppm in relation to TMS (δ^1H = 0 ppm and $\delta^{13}C$ = 0 ppm). IR spectra were recorded with Bruker Vector 22 and Perkin–Elmer Spectrum GX FTIR spectrophotometers. Mass spectrometry was conducted with a high-resolution Jeol MStation 700 mass spectrometer and use of the FAB^+ technique. Elemental analyses were carried out with an Elementar Vario ELIII instrument. Melting points are uncorrected. The UV/Vis absorption spectra were measured with an Agilent 8435 UV/Vis spectrophotometer (Agilent Technologies).

Table 4. Crystallographic data[a] for compounds **7**, **14**, **15**, **17** and **19**.

	7	**14**	**15**	**17**	**19**
Formula	$C_{19}H_{19}N_3O_2{\cdot}H_2O$	$C_{27}H_{25}N_3O_2{\cdot}0.175\ H_2O$	$C_{24}H_{26}N_2O_3$	$C_{28}H_{26}N_2O_2$	$C_{30}H_{26}N_2O_2$
MW [g mol^{-1}]	339.39	426.65	390.47	422.51	446.53
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1$
Temperature [K]	100(2)	100(2)	100(2)	173(2)	293(2)
a [Å]	7.5478(11)	9.0783(14)	14.729(2)	8.0946(14)	9.746(3)
b [Å]	10.5612(15)	12.1441(19)	4.9912(7)	7.8455(13)	13.056(4)
c [Å]	10.9098(16)	21.050(3)	27.837(4)	17.134(3)	9.796(3)
α [°]	76.035(3)	103.970(2)	90	90	90
β [°]	80.438(3)	96.166(3)	98.351(2)	101.389(3)	106.831(5)
γ [°]	89.909(3)	90.441(3)	90	90	90
V [Å^3]	831.6(2)	2237.7(6)	2024.7(5)	1066.7(3)	1193.0(6)
Z	2	4	4	2	2
M [mm^{-1}]	0.093	0.081	0.085	0.083	0.078
$\rho_{calcd.}$ [g cm^{-3}]	1.355	1.266	1.281	1.315	1.243
Collected reflections	4362	16742	18053	5244	11431
Independent reflections (R_{int})	2817 (0.02)	7823 (0.03)	3539 (0.05)	1874 (0.03)	2206 (0.05)
Observed reflections[b]	2372	6549	3098	1498	1878
Variables	244	607	270	151	307
R[b,c]	0.049	0.062	0.059	0.055	0.065
R_w[d,e]	0.133	0.134	0.148	0.116	0.151

[a] $\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å. [b] $F_o > 4\sigma(F_o)$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] All data. [e] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

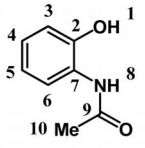
X-ray Crystallographic Studies: X-ray diffraction analyses were performed with a Bruker-APEX diffractometer and CCD area detector ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å, graphite monochromator). Frames were collected through ω- and ϕ-rotation at 10 s per frame (SMART).[45a] The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT).[45b] Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.[45c–45d] Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in geometrically calculated positions by use of a riding model. O–H and N–H hydrogen atoms were localized by use of difference Fourier maps and refined by fixing the bond lengths to 0.84 and 0.86 Å, respectively; the isotropic temperature factors were restrained to values 1.5 times those of the corresponding oxygen/nitrogen atoms. Compounds **7** and **14** crystallized as solvates (**7**·H_2O and **14**·0.175 H_2O). In **14**·0.175 H_2O, the asymmetric unit contains two independent macrocyclic molecules, in which the cavities are occupied partially by water molecules (occ = 0.10 and 0.25). Because of the low occupancy, the O_w–H hydrogen atoms could not be localized by difference Fourier maps in the latter case. In the crystal structure of compound **17**, the macrocycles are disordered over two positions around crystallographic inversion centres (occ = 0.50), which introduces apparent inversion symmetry. EXYZ and EADP instructions were used for the refinement of this structure. Crystals of compound **19** diffracted only weakly, so the data/parameter ratio was low (7.2). Despite this, the data were of sufficient quality to allow determination of the molecular structure and discussion of the molecular geometry. Figures were created with SHELXTL-NT and DIAMOND.[46] Hydrogen bonding interactions in the crystal lattice were calculated with the WINGX program package.[47] The most relevant crystallographic data are given in Table 4.

CCDC-787531 (for **7**), -787532 (for **14**), -787533 (for **15**), -787534 (for **17**), and -787535 (for **19**) contain 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.

Solution Studies by UV/Vis Electronic Absorption: For the titration experiments receptor concentrations of 3×10^{-5} M were employed. Stock solutions of Cu^{2+}, Ni^{2+} and Zn^{2+} were prepared from the corresponding nitrates in acetonitrile. For the determination of the ligand/metal stoichiometry by a continuous variation experiment (Job's method), the total concentrations employed for all solutions were 6×10^{-5} M. Spectrometric titration curves were fitted with the aid of the Microcal Origin 8.1 program.[48]

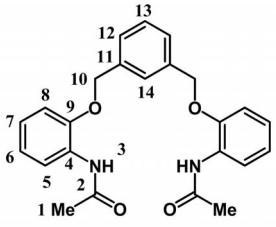
Syntheses

Compound 1: This compound was prepared by a modification of the procedure reported previously.[29] A solution of acetic anhydride (0.11 g, 14.7 mmol) in methanol (3 mL) was added slowly to a suspension of 2-aminophenol (0.70 g, 6.42 mmol) in water (20 mL). The reaction mixture was then stirred for 5 h at room temperature. The reaction was monitored by TLC (hexane/acetone 60:40) until a single product was observed and the starting material had disappeared. The reaction mixture was filtered in order to remove the solvent. A pale yellow solid was obtained after filtration, recrystallization from EtOH and drying in vacuo; yield 0.95 g, 98%; m.p. 218–220 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 9.73 (s, 1 H, 8-H), 9.30 (s, 1 H, 1-H), 7.68 (dd, J = 1.4, J = 8 Hz, 1 H, 6-H), 6.93 (dt, J = 1.4, J = 8 Hz, 1 H, 4-H), 6.86 (dd, J = 1.4, J = 8 Hz, 3-H), 6.75 (dt, J = 1.4, J = 8 Hz, 1 H, 5-H), 2.09 (s, 3 H, 10-H) ppm. ^{13}C NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 169.5 (C-9), 148.3 (C-6), 126.9 (C-3), 125.1, 122.9 (C-2, C-7), 119.4 (C-4), 116.4 (C-5), 24.1 (C-10) ppm. IR (KBr): $\tilde{\nu}$ = 3403 (s), 3084 (s), 2882 (m), 2747 (m), 2619 (m), 1659 (s), 1284 (s), 755 (s). FAB$^+$-MS: m/z (%) = 152 (45) [M + H]$^+$, 136 (75), 108 (26). $C_8H_9NO_2$·EtOH (197.23): calcd. C 60.90, H 7.67, N 7.10, O 24.33; found C 60.86, H 7.66, N 7.08.



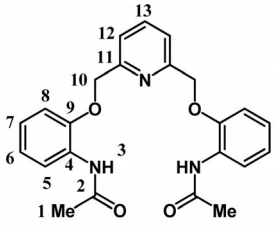
1

Compound 2: This compound was prepared by a modification of the procedure reported previously.[30] A solution of **1** (3.36 g, 17.04 mmol) in anhydrous DMF (5 mL) was added to a suspension of K_2CO_3 (in excess) in the same solvent (25 mL). The suspension was kept under nitrogen and stirred at 80 °C for 30 min. A solution of 1,3-bis(bromomethyl)benzene (2.25 g, 8.52 mmol) in anhydrous DMF (5 mL) was then added slowly to the mixture and the resulting suspension was stirred at 80 °C. The reaction was monitored by TLC (hexane/acetone 60:40) until a single product was observed and the starting material had disappeared. The suspension was filtered in order to remove the potassium salt. The filtrate was evaporated in vacuo to dryness and acetone was added until a precipitate appeared. A light brown solid was obtained after filtration, acetone washing and drying in vacuo; yield 3.05 g, 93%; m.p. 183–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.34 (dd, J = 2.1, J = 7.3 Hz, 2 H, 5-H), 7.74 (s, 2 H, 3-H), 7.52 (d, J = 7.5 Hz, 2 H, 12-H), 7.45 (m, 2 H, 13-H, 14-H), 6.90 (m, 4 H, 6-H, 7-H), 6.92 (dd, J = 2.2, J = 7.2 Hz, 2 H, 8-H), 5.29 (s, 4 H, 10-H), 2.17 (s, 6 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 165.59 (C-2), 144.4 (C-4), 134.7 (C-9), 126.8 (C-11), 125.5 and 123.9 (C-13 and C-14), 124.9 (C-12), 121.2 (C-7), 119.2 (C-6), 117.8 (C-5), 109.3 (C-8), 68.2 (C-10), 22.4 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3301 (s), 1662 (s), 1600 (s), 1545 (s), 1494 (s), 1446 (s), 1252 (m), 1117 (w), 746 (w), 693 (w) cm^{-1}. FAB-MS: m/z (%) = 405 (32) [M + H]$^+$, 270 (15), 254 (35), 212 (27). $C_{24}H_{24}N_2O_4$ (404.46): calcd. C 71.27, H 5.98, N 6.93, O 15.82; found C 71.26, H 5.98, N 6.95.



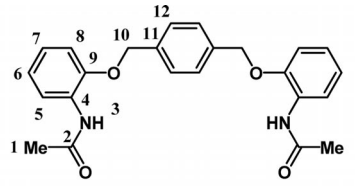
2

Compound 3: This compound was prepared in a manner similar to that described for compound **2**, from **1** (3.36 g, 17.04 mmol) and 2,6-bis(chloromethyl)pyridine (1.47 g, 8.33 mmol). The product was obtained as a white solid; yield 2.97 g, 86%; m.p. 226–228 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.37 (dd, J = 3.6, J = 6.9 Hz, 2 H, 5-H), 7.95 (s, 2 H, 3-H), 7.77 (t, J = 7.8 Hz, 1 H, 13-H), 7.36 (d, J = 7.8 Hz, 2 H, 12-H), 7.00 (m, 4 H, 6-H, 7-H), 6.90 (dd, J = 3.5, J = 6.9 Hz, 2 H, 8-H), 5.29 (s, 4 H, 10-H), 2.17 (s, 6 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 155.5 (C-2), 145.6 (C-4), 136.9 (C-13), 127.5 (C-9), 122.7 (C-11), 121.0 (C-12), 119.6 and 119.4 (C-6 and C-7), 117.76 (C-5), 111.1 (C-8), 70.5 (C-10), 23.9 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3303 (m), 1663 (s), 1248 (m), 1123 (w), 774 (w), 774 (w), 750 (w) cm^{-1}. FAB-MS: m/z (%) = 406 (97) [M + H]$^+$, 388 (5), 364 (10), 362 (5), 346 (4), 256 (53), 254 (51), 212 (26). $C_{23}H_{23}N_3O_4$ (405.45): calcd. C 68.13, H 5.72, N 10.36, O 15.78; found C 68.14, H 5.75, N 10.40.



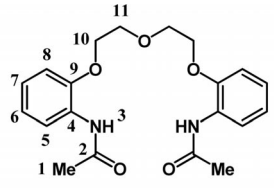
3

Compound 4: This compound was prepared in a manner similar to that described above, from **1** (5.20 g, 26.4 mmol) and 1,4-bis(bromomethyl)benzene (3.60 g, 13.2 mmol). The product was obtained as a light brown solid; yield 5.2 g, 98%; m.p. 197–200 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.38 (d, J = 7.48 Hz, 2 H, 5-H), 7.78 (s, 2 H, 3-H), 7.47 (s, 4 H, 12-H), 7.02 (m, 4 H, 6-H, 7-H), 6.96 (d, J = 7.65 Hz, 2 H, 8-H), 5.29 (s, 4 H, 10-H), 2.17 (s, 6 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 167.0 (C-2), 137.1 (C-4), 136.7 (C-9), 127.9 (C-11), 128.0 (C-12), 123.7 (C-7), 121.7 (C-6), 120.2 (C-5), 111.8 (C-8), 70.6 (C-10), 24.9 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3293 (s), 1657 (m), 1260 (s), 1119 (w), 802 (w) cm^{-1}. FAB-MS: m/z (%) = 405 (95) [M + H]$^+$, 363 (10), 307 (17), 289 (15), 254 (83), 212 (35). $C_{24}H_{24}N_2O_4$ (404.46): calcd. C 71.27, H 5.98, N 6.93, O 15.82; found C 71.26, H 5.95, N 6.93.



4

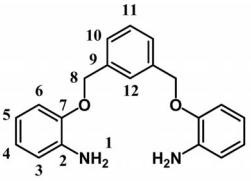
Compound 5: This compound was prepared in a manner similar to that described for compound **2** (by a modification of the procedure reported previously),[31] from compound **1** (3.89 g, 19.70 mmol) and bis(2-chloroethyl) ether (1.41 g, 9.85 mmol). The product was obtained as a dark green solid; yield 3.34 g, 91%; m.p. 130–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.34 (d, J = 7.48 Hz, 2 H, 5-H), 7.94 (s, 2 H, 3-H), 7.01 (m, 4 H, 6-H, 7-H), 6.93 (dd, J = 3.0, J = 7.11 Hz, 2 H, 8-H), 4.24 (m, 4 H, 10-H), 3.92 (m, 4 H, 11-H), 2.08 (s, 6 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 168.0 (C-2), 146.9 (C-4), 127.0 (C-9), 123.9 and 122.5 (C-6 and C-7), 120.6 (C-5), 112.0 (C-8), 70.0 (C-11) 69.0 (C-10), 24.6 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3290 (s), 1640 (m), 1200 (s), 1109 (w), 802 (w) cm^{-1}. FAB-MS: m/z (%) = 373 (100) [M + H]$^+$, 331 (44), 313 (12), 222 (11), 136 (85), 109 (38). $C_{20}H_{24}N_2O_5$ (372.41): calcd. C 64.50, H 6.50, N 7.52, O 21.48; found C 64.51, H 6.42, N 7.55.



5

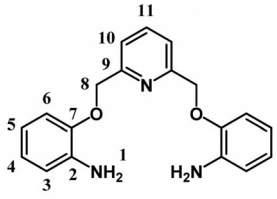
Compound 6: This compound was prepared by a modification of the procedure reported previously.[30] A solution of compound **2** (3.00 g, 7.42 mmol) in ethanol (30 mL) and a solution of NaOH (6.86 g, 49.63 mmol) in water (10 mL) were mixed, stirred and heated at reflux (80 °C) for several days. The reaction was monitored by TLC (hexane/acetone 60:40) until a single product was observed and the starting material had disappeared. The reaction mixture was evaporated in vacuo to dryness in order to remove the solvent. A chloroform/water extraction (70:30) was performed, the phases were separated, and the solvent was removed from the organic phase. The product was obtained as an orange solid; yield 1.82 g, 77%; m.p. 62–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.55 (s, 1 H, 12-H), 7.45 (m, 3 H, 10-H, 11-H), 6.86 (m, 4 H, 4-H, 6-H), 6.7 (m, 4 H, 3-H, 5-H), 5.13 (s, 4 H, 8-H), 3.78 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 146.41 (C-7),

137.66 (C-2), 136.57 (C-9), 128.86 (C-11), 127.16 (C-10), 126.61 (C-12), 121.61 (C-4), 118.43 (C-3), 115.30 (C-5), 112.18 (C-6), 70.25 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3476 (m), 3438 (m), 3037 (w), 2931 (w), 1283 (m), 1140 (m), 783 (m), 747 (m) cm^{-1}. FAB-MS: *m/z* (%) = 321 (42) $[M + H]^+$, 212 (98), 211 (45), 195 (14), 167 (15), 149 (28), 136 (10). $C_{20}H_{20}N_2O_2$ (320.39): calcd. C 74.98, H 6.29, N 8.74, O 9.99; found C 75.47, H 6.35, N 8.98.



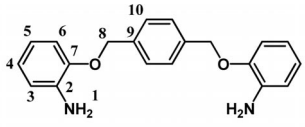
6

Compound 7: This compound was reported previously.[32] It was prepared in a manner similar to that described for compound **6**, from **3** (3.80 g, 9.38 mmol) and NaOH (6.86 g, 49.23 mmol). The product was obtained as an orange solid; yield 2.06 g, 68%; m.p. 63–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.33 (t, *J* = 7.76 Hz, 1 H, 11-H), 7.43 (d, *J* = 7.76 Hz, 2 H, 10-H), 6.83 (m, 4 H, 4-H, 5-H), 6.76 (dd, *J* = 1.59, *J* = 8.04 Hz, 2 H, 3-H), 6.70 (m, 2 H, 6-H), 5.25 (s, 4 H, 8-H), 3.92 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 155.0 (C-7), 146.1 (C-2), 137.7 (C-11), 136.5 (C-9), 121.8 (C-5), 120.2 (C-10), 118.5 (C-6), 115.4 (C-4), 112.4 (C-3), 71.1 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3438 (m), 3365 (m), 3060 (w), 1280 (m), 1114 (w), 741 (s), 633 (w) cm^{-1}. FAB-MS: *m/z* (%) = 322 (100) $[M + H]^+$, 214 (85), 196 (8), 120 (18). $C_{19}H_{19}N_3O_2 \cdot 1/4\,EtOH$ (350.91): calcd. C 71.88, H 5.89, N 11.97, O 10.26; found C 71.86, H 5.83, N 11.92.



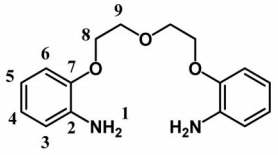
7

Compound 8: This compound was prepared in a manner similar to that described for compound **6**, from **4** (2.80 g, 6.91 mmol) and NaOH (6.86 g, 49.23 mmol). The product was obtained as a pale orange solid; yield 1.79 g, 81%; m.p. 110–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.42 (s, 4 H, 10-H), 6.79 (m, 4 H, 4-H, 5-H), 6.70 (m, 4 H, 3-H, 6-H), 5.09 (s, 4 H, 8-H), 3.99 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 146.5 (C-7), 137.1 (C-2), 136.6 (C-9), 127.9 (C-10), 121.7 and 118.4 (C-4 and C-5), 115.3 and 112.2 (C-3 and C-6), 70.2 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3463 (w), 3436 (m), 3370 (m), 1276 (m), 1212 (m), 793 (m) cm^{-1}. FAB-MS: *m/z* (%) = 321 (31) $[M + H]^+$, 288 (6), 239 (6), 210 (28), 211 (100), 212 (92). $C_{20}H_{20}N_2O_2$ (320.39): calcd. C 74.98, H 6.29, N 8.74, O 9.99; found C 74.89, H 6.29, N 8.76.



8

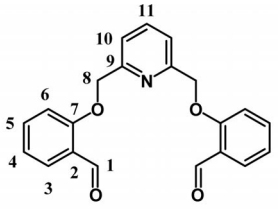
Compound 9: This compound was reported previously.[33–35] It was prepared in a manner similar to that described for compound **6**, from **5** (2.80 g, 6.91 mmol) and NaOH (6.86 g, 49.23 mmol). The product was obtained as a pale orange solid; yield 1.79 g, 81%; m.p. 64.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.79 (m, 4 H, 4-H, 5-H), 6.67 (m, 4 H, 3-H, 6-H), 4.15 (m, 4 H, 8-H), 3.88 (m, 4 H, 9-H), 3.72 (s, 2 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 146.5 (C-7), 137.1 (C-2), 121.9 (C-5), 118.3 (C-4), 115.9 (C-3), 114.0 (C-6), 70.5 (C-8), 68.6 (C-9) ppm. IR (KBr): $\tilde{\nu}$ = 3462 (w), 3420 (m), 3270 (s), 1276 (m), 1212 (m), 790 (m) cm^{-1}. FAB-MS: *m/z* (%) = 289 (68) $[M + H]^+$, 250 (28), 210 (15), 180 (17). $C_{16}H_{20}N_2O_3$ (288.34): calcd. C 66.65, H 6.99, N 9.72, O 16.65; found C 66.67, H 7.01, N 9.78.



9

Compound 10: This compound was previously reported by our research group.[28]

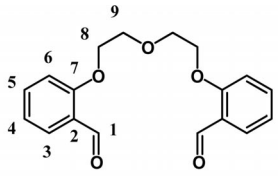
Compound 11: This compound was prepared by a modification of the procedure reported previously.[36] A solution of salicylaldehyde (0.56 g, 4.59 mmol) in anhydrous DMF (6 mL) was added to a suspension of K_2CO_3 (in excess) in the same solvent. The suspension was kept under a flow of nitrogen and stirred at 80 °C for 30 min. A solution of 2,6-bis(chloromethyl)pyridine (0.28 g, 2.29 mmol) in anhydrous DMF (20 mL) was then added slowly to the mixture and the resulting suspension was stirred at 80 °C. The reaction was monitored by TLC (hexane/acetone 60:40) until a single product was observed and the starting material had disappeared. The suspension was filtered in order to remove the potassium salt. The filtrate was evaporated in vacuo to dryness and acetone was added until a precipitate appeared. A light pink solid was obtained after filtration, acetone washing and drying in vacuo; yield 0.63 g, 79%; m.p. 183–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.55 (s, 2 H, 1-H), 7.81 (dd, *J* = 1.71, 7.65 Hz, 2 H, 3-H), 7.75 (t, *J* = 7.77 Hz, 1 H, 11-H), 7.47 (m, 4 H, 5-H, 10-H), 7.09 (m, 4 H, 4-H, 6-H), 5.35 (s, 4 H, 8-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 189.5 (C-1), 160.5 (C-11), 156.0 (C-9), 138.0 (C-7), 136.0 (C-3), 129.0 (C-10), 125.2 (C-2), 121.4 and 120.5 (C-4 and C-5), 113.0 (C-6), 70.9 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 2854 (w), 1687 (s), 1241 (s), 1108 (w), 849 (w), 779 (m) cm^{-1}. FAB-MS: *m/z* (%) = 348 (98) $[M + H]^+$, 325 (36), 245 (15), 226 (35), 220 (16). $C_{21}H_{17}NO_4 \cdot 1/2\,H_2O$ (358.39): calcd. C 70.94, H 5.06, N 3.91, O 20.09; found C 70.62, H 5.13, N 3.95.



11

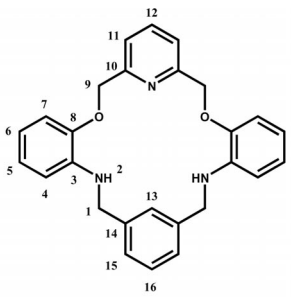
Compound 12: This compound was previously reported by our research group.[28]

Compound 13: This compound was prepared by a modification of the procedure reported previously,[37] in a manner similar to that described for compound **11**, from salicylaldehyde (3 g, 4.49 mmol) and bis(2-chloroethyl) ether (1.7 g, 12 mmol). The product was obtained as a pale pink solid; yield 2.27 g, 59%; m.p. 59–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.50 (s, 2 H, 1-H), 7.76 (dd, J = 2.1, J = 8.0 Hz, 2 H, 3-H), 7.45 (t, J = 8.0 Hz, 2 H, 5-H), 6.95 (m, 4 H, 4-H, 6-H), 4.20 (m, 4 H, 8-H), 3.93 (m, 4 H, 9-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 189.8 (C-1), 161.2, 135.7, 125.2, 121.9, 113.6, 112.9 (C-2 to C-7), 70.6 (C-9), 24.9 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3293 (s), 1657 (m), 1260 (s), 1119 (w), 802 (w) cm^{-1}. FAB-MS: *m*/*z* (%) = (%), 315 (32) $[M + H]^+$, 267 (8), 231 (10), 148 (80), 121 (58). $C_{18}H_{18}O_5$ (314.33): calcd. C 68.78, H 5.77, O 25.45; found C 68.80, H 5.78.



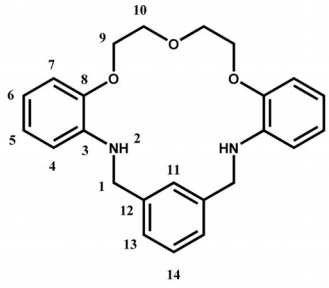
13

Macrocycle 14: A solution of isophthalaldehyde (0.13 g, 0.95 mmol) in anhydrous ethanol (60 mL) was added dropwise to a solution of compound **7** (0.31 g, 0.95 mmol) in the same solvent (100 mL). The solution was kept under nitrogen and stirred at 79 °C. The reaction was monitored by TLC (hexane/acetone 60:40) until a single product was observed and the starting material had disappeared. Sodium borohydride (0.14 g, 3.8 mmol) was then added. The reaction progress was monitored by TLC (hexane/acetone 60:40) until completion. The reaction mixture was evaporated to dryness, a chloroform/water extraction (70:30) was then performed, the phases were separated, and the solvent was removed from the organic phase to give the compound as an orange solid; yield 0.13 g, 33%; m.p. 242–244 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.73 (t, J = 7.0 Hz, 1 H, 12-H), 7.62 (s, 1 H, 13-H), 7.35 (d, J = 7.0 Hz, 2 H, 11-H), 7.23 (m, 3 H, 15-H, 16-H), 6.92 (m, 4 H, 5-H, 6-H), 6.70 (m, 4 H, 4-H, 7-H), 5.05 (s, 4 H, 9-H), 4.34 (s, 2 H, 2-H), 4.22 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 155.9, 146.3, 139.9, 138.4, 137.6, 128.4, 127.1, 123.9, 121.8 (C-3, C-5, C-8, C-10 to C-16), 116.6, 110.3, 110.0 (C-4, C-6, C-7), 71.4 (C-9), 48.2 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3421 (s), 2860 (m), 2300 (m), 1600 (s), 1512 (s), 1247 (m), 742 (m) cm^{-1}. FAB-MS: *m*/*z* (%) = 424 (73) $[M + H]^+$, 318 (18), 226 (55), 212 (5), 197 (8), 191 (63), 105 (10). $C_{27}H_{25}N_3O_2 \cdot 0.175\,H_2O$ (426.66): calcd. C 76.01, H 5.99, N 9.85, O 8.16; found C 76.26, H 6.51.



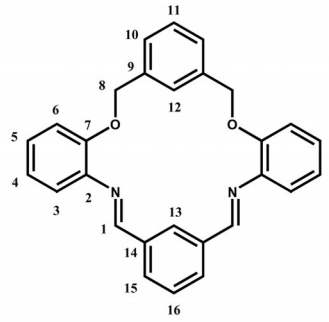
14

Macrocycle 15: This compound was prepared in a manner similar to that described for macrocycle **14**, from compound **9** (0.40 g, 1.38 mmol) and isophthalaldehyde (0.13 g, 0.95 mmol). The product was obtained as a yellow pale solid; yield 0.24 g, 44%; m.p. 210–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.72 (s, 2 H, 11-H), 7.30 (m, 3 H, 13-H, 14-H), 6.89 (dd, J = 1.4, J = 7.62 Hz, 2 H, 4-H), 6.70 (m, 6 H, 5-H, 6-H, 7-H), 4.49 (s, 2 H, 2-H), 4.28 (d, 4 H, 1-H), 4.16 (m, 4 H, 9-H), 3.84 (m, 4 H, 10-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 146.0 (C-12), 140.2 (C-8), 138.2 (C-3), 128.5 (C-14), 127.8 (C-13), 126.7 (C-11), 121.4, 116.6, 109.8, 109.7 (C-4 to C-6, C-7), 70.0 (C-10), 67.1 (C-9), 48.0 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3433 (s), 3033 (w), 2917 (m), 1612 (s), 1590 (s), 1519 (w), 1492 (s), 1486 (s), 1458 (s), 1363 (m), 1306 (s), 1219 (s), 1152 (m), 1061 (m), 1032 (s), 809 (s), 755 (s) cm^{-1}. FAB-MS: *m*/*z* (%) = 391 (80) $[M + H]^+$, 314 (42), 286 (35), 209 (60), 181 (82). $C_{24}H_{26}N_2O_3$ (390.45): calcd. C 73.82, H 6.71, N 7.17, O 12.29; found C 73.75, H 6.68, N 7.19.



15

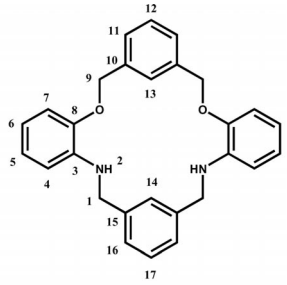
Macrocycle 16: A solution of **6** (0.31 g, 0.98 mmol) in anhydrous acetonitrile (10 mL) was added to a solution of isophthalaldehyde (0.13 g, 0.98 mmol), and a catalytic amount of zinc perchlorate was then added. The reaction was monitored by TLC (hexane/acetone 60:40) until a single product was observed and the starting material had disappeared. The suspension was filtered in order to remove the solvent, and a yellow solid was obtained after acetone washing and drying in vacuo; yield 0.14 g, 35%; m.p. 140–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.46 (s, 2 H, 1-H), 8.61 (s, 2 H, 13-H), 8.33 (s, 1 H, 12-H), 7.66 (d, J = 7.2 Hz, 2 H, 3-H), 7.53 (t, J = 6.8 Hz, 1 H, 11-H), 7.38 (d, J = 7.2 Hz, 2 H, 10-H), 7.23 (m, 7 H, 4-H, 6-H, 15-H, 16-H), 7.09 (t, J = 7.2 Hz, 2 H, 5-H), 5.20 (s, 4 H, 8-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 157.9 (C-1), 153.3 (C-7), 142.3 (C-10), 137.9 (C-15), 137.5 (C-16), 133.1 (C-9), 128.5 (C-11), 128.2, 127.9, 127.5, 125.5 (C-2 to C-4), 122.7 (C-12), 118.5 (C-14), 117.1 (C-13), 116.8 (C-6), 73.1 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3063 (w), 3006 (w), 2928 (w), 2870 (m), 1615 (m), 1478 (m), 1368, 763 (m) cm^{-1}. FAB-MS: *m*/*z* (%) = 419 (25) $[M + H]^+$, 392 (5), 209 (15), 210 (12), 120 (18). $C_{28}H_{22}N_2O_2$ (418.49): calcd. C 80.36, H 5.30, N 6.69, O 7.65; found C 80.34, H 5.31, N 6.70.



16

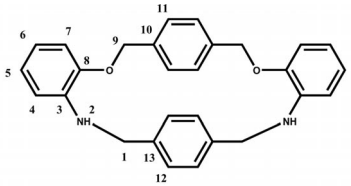
Macrocycle 17: A solution of 1,3-bis(bromomethyl)benzene (0.43 g, 1.56 mmol) in anhydrous acetone (60 mL) was added dropwise to

a suspension of compound **7** (0.50 g, 1.56 mmol) and Na_2CO_3 (in excess) in the same solvent (100 mL). The suspension was kept under nitrogen and stirred at 80 °C for 24 h. The reaction was monitored by TLC (hexane/acetone 60:40) until a single product was observed and the starting material had disappeared. The suspension was filtered in order to remove the sodium salt. The filtrate was evaporated in vacuo to dryness and acetone was added until a precipitate appeared. An orange solid was obtained after filtration, acetone washing and drying in vacuo; yield 0.3 g, 45%; m.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.71 (s, 1 H, 14-H), 7.64 (s, 1 H, 13-H), 7.22 (m, 6 H, 11-H, 12-H, 16-H, 17-H), 6.88 (m, 4 H, 4-H, 5-H), 6.62 (m, 4 H, 6-H, 7-H), 4.95 (s, 4 H, 9-H), 4.32 (s, 2 H, 2-H), 4.20 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 145.03 (C-8), 138.90 (C-10), 137.08 (C-3), 136.41 (C-15), 127.44, 127.40 (C-14, C-17), 127.31 (C-12), 127.16 (C-16), 126.80 (C-11), 125.4 (C-13), 120.56 (C-5), 115.57 (C-6), 109.01 (C-7), 108.84 (C-4), 68.96 (C-9), 47.09 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (m), 2865 (m), 2316 (m), 1600 (s), 1512 (s), 1245 (m), 1210 (m), 741 (s) cm^{-1}. FAB-MS: *m*/*z* (%) = 423 (9) $[M]^+$, 345 (32), 313 (38), 319 (30), 286 (58), 219 (15). $C_{28}H_{26}N_2O_2$ (422.52): calcd. C 79.59, H 6.20, N 6.63, O 7.57; found C 79.26, H 6.09.



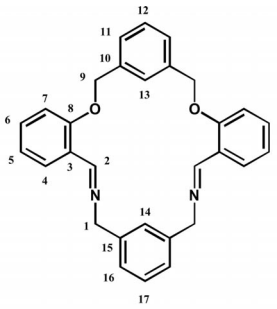
17

Macrocycle 18: This compound was prepared in a manner similar to that described for macrocycle **17**, from compound **8** (0.51 g, 1.56 mmol) and 1,4-bis(bromomethyl)benzene (0.43 g, 1.56 mmol). The product was obtained as a pale brown solid; yield 0.13 g, 19%; m.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.21 (s, 4 H, 11-H), 7.17 (s, 4 H, 12-H), 6.84 (m, 4 H, 4-H, 5-H), 6.65 (m, 4 H, 6-H, 7-H), 4.97 (s, 4 H, 9-H), 4.12 (s, 4 H, 1-H), 4.0 (s, 2 H, 2-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 140.8 (C-8), 137.2 (C-10), 135.9 (C-3), 133.1 (C-13), 128.3 (C-11), 122.4 (C-12), 120.2 (C-6), 117.2 (C-5), 115.8 (C-4), 111.1 (C-7), 68.9 (C-9), 47.2 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3421 (s), 3061 (w), 2868 (m), 2360 (m), 1600 (s), 1246 (s), 1005 (s), 844 (m), 726 (s) cm^{-1}. FAB-MS: *m*/*z* (%) = 423 (80) $[M + H]^+$, 422 (42), 331 (12), 287 (15), 225 (64), 197 (84), 135 (38), 91 (23). $C_{28}H_{26}N_2O_2 \cdot 2H_2O$ (458.55): calcd. C 73.34, H 6.59, N 6.11, O 13.96; found C 73.38, H 6.50, N 6.12.



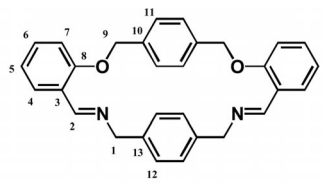
18

Macrocycle 19: This compound was prepared from **10** (0.12 g, 0.33 mmol) and [3-(aminomethyl)phenyl]methanamine (0.05 g, 0.33 mmol). The reaction mixture was stirred in ethanol (25 mL) under high pressure for 24 h at 70 °C with employment of a heavy-walled borosilicate glass tube. A considerable amount of yellow crystals appeared during the reaction and were removed by filtration, washed with ethanol and dried under vacuum; yield 0.10 g, 67%; m.p. 80–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.88 (s, 2 H, 2-H), 7.97 (dd, *J* = 1.74, 7.7 Hz, 2 H, 4-H), 7.49 (s, 1 H, 13-H), 7.44 (m, 1 H, 12-H), 7.34 (d, *J* = 7.1 Hz, 2 H, 11-H), 7.30 (m, 4 H, 14-H, 16-H, 17-H), 6.95 (m, 4 H, 5-H, 6-H), 6.82 (dd, *J* = 1.8, 7.61 Hz, 2 H, 7-H), 5.21 (s, 4 H, 9-H), 4.79 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 158.4 (C-2), 157.5 (C-8), 139.0 (C-10), 137.8 (C-15), 131.8 (C-6), 128.7 and 127.7 (C-16 and C-17), 127.6 and 126.3 (C-3, C-12, C-11), 125.0 (C-13, C-14), 124.7 (C-4), 121.0 (C-5), 112.0 (C-7), 69.7 (C-9), 65.7 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3069 (m), 2928 (m), 3034 (w), 2809 (m), 1635 (s), 1598 (s), 1483 (s), 1298 (m), 1027 (s), 753 (s) cm^{-1}. FAB-MS: *m*/*z* (%) = 447 (52) $[M + H]^+$, 391 (100), 371 (9), 279 (13), 220 (32). $C_{30}H_{26}N_2O_2$ (446.54): calcd. C 80.69, H 5.87, N 6.27, O 7.17; found C 80.69, H 6.27, N 6.31.



19

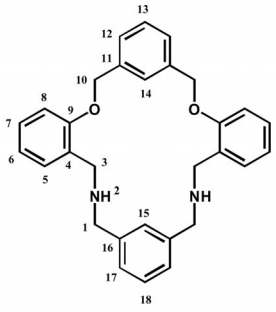
Macrocycle 20: This compound was prepared in a manner similar to that described for macrocycle **19**, from [4-(aminomethyl)phenyl]-methanamine (0.04 g, 0.28 mmol) and compound **12** (0.10 g, 0.28 mmol). The product was obtained as a yellow solid; yield 0.04 g, 35%; m.p. 140–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.70 (s, 2 H, 2-H), 7.79 (dd, *J* = 2.5, 8.1 Hz, 2 H, 4-H), 7.39 (dt, *J* = 3.0, 8.1 Hz, 2 H, 5-H), 7.32 (s, 4 H, 11-H) 7.29 (s, 4 H, 12-H), 7.03 (m, 4 H, 6-H, 7-H), 5.11 (s, 4 H, 9-H), 4.90 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 157.9 (C-2), 157.8 (C-8), 137.2 and 136.3 (C-10 and C-13), 131.6 (C-6), 129.1 (C-12), 128.9 (C-4), 127.7 (C-3), 126.8 (C-11), 121.3 (C-5), 113.1 (C-7), 70.0 (C-9), 63.7 (C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3398 (w), 3071 (w), 3034 (w), 2896 (m), 2880 (m), 2824 (m), 1905 (w), 1573 (s), 1473 (s), 1455 (s), 1367 (s), 1161 (s), 1142 (m), 1003 (s), 963 (m), 862 (m), 799 (m) cm^{-1}. FAB-MS: *m*/*z* (%) = 447 (25) $[M + H]^+$, 446 (9), 289 (12), 223 (18), 92 (44), 78 (38). $C_{30}H_{26}N_2O_2$ (446.54): calcd. C 80.69, H 5.87, N 6.27, O 7.17; found C 80.69, H 5.50, N 6.30.



20

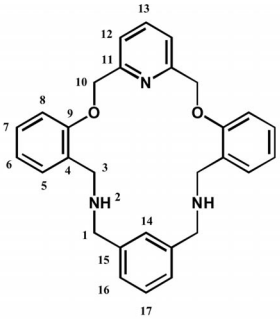
Macrocycle 21: This compound was prepared in a manner similar to that described for macrocycle **14**, from [3-(aminomethyl)phenyl]-methanamine (0.19 g, 1.39 mmol), compound **10** (0.48 g, 1.39 mmol) and sodium borohydride (0.14 g, 3.8 mmol). The prod-

uct was obtained as a white solid; yield 0.44 g, 70%; m.p. 147–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.51 (s, 1 H, 14-H), 7.35 (m, 3 H, 12-H, 13-H), 7.30 (d, J = 8.5 Hz, 2 H, 17-H), 7.22 (m, 2 H, 15-H, 18-H), 7.15 (dd, J = 2.8, 8.0 Hz, 2 H, 5-H), 7.09 (dt, J = 1.58, 8.0 Hz, 2 H, 7-H), 6.94 (m, 4 H, 6-H, 8-H), 5.02 (s, 4 H, 10-H), 3.84 (s, 4 H, 3-H), 3.67 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 157.0 (C-9), 140.5 (C-11), 137.4 (C-16), 130.3 (C-7), 128.8 (C-14), 128.7 (C-15), 128.3 (C-4, C-6), 127.8 (C-12), 127.0 (C-13), 126.9 (C-17), 126.8 (C-18), 120.9 (C-5), 111.7 (C-8), 70.2 (C10), 53.3 (C-1), 50.2 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3314 (w), 3059 (w), 2878 (w), 1586 (w), 1490 (m), 1448 (m), 1238 (m), 754 (m) cm^{-1}. FAB-MS: m/z (%) = 451 (90) [M + H]$^+$, 346 (32), 254 (60), 241 (45), 225. $C_{30}H_{30}N_2O_2$ (450.57): calcd. C 79.97, H 6.71, N 6.22, O 7.10; found C 79.71, H 6.58, N 6.23.



21

Macrocycle 22: This compound was prepared in a manner similar to that described for macrocycle **14**, from [3-(aminomethyl)phenyl]-methanamine (0.19 g, 1.4 mmol), compound **11** (0.49 g, 1.4 mmol) and sodium borohydride (0.14 g, 3.8 mmol). A white solid was obtained; yield 0.22 g, 35%; m.p. 169–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.63 (t, J = 7.8 Hz, 1 H, 13-H), 7.29 (d, J = 7.8 Hz, 2 H, 12-H), 7.18 (d, J = 8.1 Hz, 2 H, 16-H), 7.16 (m, 2 H, 5-H), 6.95 (m, 7 H, 6-H, 7-H, 8-H, 17-H), 6.75 (s, 1 H, 14-H), 5.03 (s, 4 H, 10-H), 3.75 (s, 4 H, 3-H), 3.50 (s, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 157.2, 156.3, 140.5, 137.5, 130.7, 129.4, 128.5, 128.0, 127.0, 126.7, 122.0, 121.5 (C-4 to C-7, C-9, C-11 to C-17), 112.8 (C-8), 71.9 (C-10), 53.5 (C-1), 50.2 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3419 (m), 3059 (s), 2874 (m), 2342 (s), 1597 (s), 1230 (s), 786 (m), 757 (s) cm^{-1}. FAB-MS: m/z (%) = 452 (95) [M + H]$^+$, 393 (18), 378 (7), 327 (8), 322 (38), 250 (12), 136 (84). $C_{29}H_{29}N_3O_2 \cdot 1/2\,H_2O$ (460.58): calcd. C 75.63, H 6.57, N 9.12, O 8.68; found C 75.63, H 6.59, N 9.01.



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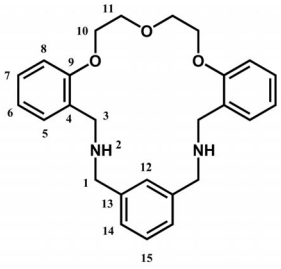
Macrocycle 23: This compound was prepared in a manner similar to that described for macrocycle **14**, from compound **13** (1.62 g, 5.16 mmol), [3-(aminomethyl)phenyl]methanamine (0.70 g, 5.16 mmol) and sodium borohydride (0.73 g, 19 mmol). A white solid was obtained; yield 1.19 g, 56%; m.p. 143–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.27 (m, 4 H, 5-H, 6-H), 7.19 (m, 3 H, 8-H, 12-H), 7.08 (d, J = 6.54 Hz, 2 H, 7-H), 6.92 (t, J = 8.15 Hz, 1 H, 15-H), 6.80 (d, J = 8.15 Hz, 2 H, 14-H), 4.06 (m, 4 H, 10-H), 3.82 (m, 4 H, 3-H), 3.79 (m, 4 H, 11-H), 3.75 (m, 4 H, 1-H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 157.8 (C-9), 136.6 (C-13), 128.9 (C-15), 128.7 (C-12), 128.3 (C-5), 127.6 (C-7), 126.2 (C-14), 122.42 (C-4), 120.1 (C-6), 112.2 (C-8), 69.42 (C-11), 68.22 (C-10), 56.34 (C-1), 52.6 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 3310 (m), 3058 (s), 2874 (m), 2342 (s), 1598 (s), 1210 (m), 782 (m), 752 (m) cm^{-1}. FAB-MS: m/z (%) = 419 (95) [M + H]$^+$, 298 (12), 225 (12), 120 (30), 105 (60). $C_{26}H_{30}N_2O_3$ (418.53): calcd. C 74.61, H 7.22, N 6.69, O 11.47; found C 74.65, H 7.21, N 6.69.



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Supporting Information (see footnote on the first page of this article): UV/Vis spectra of **17** and **17** in the presence of Cu^{2+} (1:1 molar ratio) and the Job plot for the **14**-Zn^{2+} system.

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