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Synthesis and X-ray Structures of Novel Macrocycles and Macrobicycles Containing *N,N*-Di(pyrrolylmethyl)-*N*-methylamine Moiety: Preliminary Anion Binding Study

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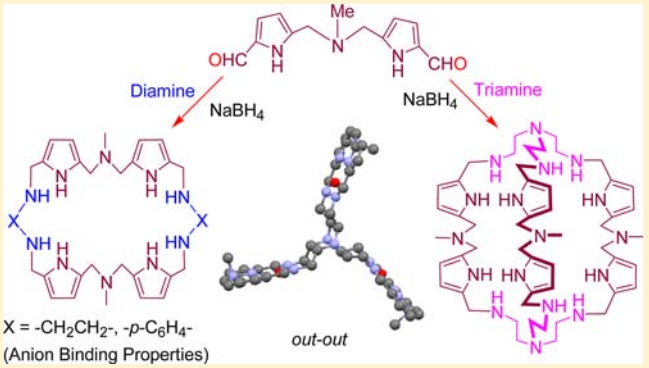
Supporting Information

ABSTRACT: The [2 + 2] Schiff base condensation reactions between the newly synthesized dialdehyde, *N,N*-di(*α*-formylpyrrolyl-*α*-methyl)-*N*-methylamine), and ethylenediamine or *p*-phenylenediamine dihydrochloride readily afforded the 30- and 34-membered large size macrocycles in very high yields. Subsequent reduction reactions of these macrocycles with $NaBH_4$ gave the corresponding saturated macrocyclic hexaamines in good yields. The analogous reaction of the new dialdehyde with a triamine molecule afforded the [3 + 2] Schiff base macrobicycle in high yield, which was then reduced by reaction with $NaBH_4$ to give the saturated macrobicycle. All these compounds were characterized by spectroscopic methods. The anion binding properties of the saturated macrocycles having the ethylene and the phenylene linkers in $CDCl_3$ were studied by NMR titration methods. Although they have similar pyrrolic and amine NH groups their binding properties are different and interesting, owing to the conformational flexibility or rigidness rendered by the ethylene or phenylene groups, respectively. The macrocycle having the ethylene linkers binds anions in a 1:1 fashion, while the other receptor having the phenylene linkers prefers to bind anions in a sequential 1:2 fashion and has a multiple equilibria between a 1:1 and a 1:2 complexes, as shown by their binding constants, curve fittings by EQNMR, and Job plots. The X-ray structures of the 1:2 methanol, the aqua and the benzoate anion complexes of the macrocycles show two cavities in which the guests are bound, correlating with the high affinity found for the formation of stable 1:2 complexes in solution. The X-ray structure showed that the macrobicycle Schiff base adopts an eclipsed paddle-wheel shaped conformation and exhibits an *out-out* configuration at the bridgehead nitrogen atoms.

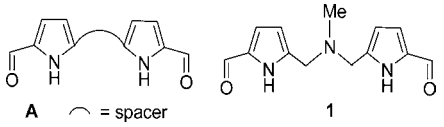


INTRODUCTION

The driving force for design and synthesis of artificial synthetic receptors for anions, inspired by selective anion recognition in nature, comes from biological, environmental, and industrial point of views.[1] Because of the inherent nature of the anions, developing synthetic receptors that recognize anions primarily by means of covalent or noncovalent interactions is a challenging task and remains an active area of research.[2,3] Among the various types of systems, pyrrole-based receptors in which Sessler and co-workers pioneered[4] have attracted attention as they form strong hydrogen bonding interactions with anions because of the acidic nature of the NH group.[5] Typically these pyrrole-based receptors have been synthesized by making use of the active *α*-positions of the pyrrole ring which has led to various sizes of macrocycles[6] and macrobicycles[7] incorporating both steric and electronic factors for recognizing and binding various types of anions.

Alternatively, anion receptors have also been synthesized by anion-templated[8] [2 + 2] Schiff base condensation reactions of pyrrole systems, which often give the desired large size Schiff bases in excellent yields which is essential for further applications.[9] In addition, these Schiff bases are reduced to give receptor molecules carrying additional hydrogen bonding NH groups for strongly interacting with an anion.[10] Usually large macrocyclic receptors are flexible and preorganized for ready binding with anions. One of the key strategies for synthesizing a large size pyrrole-based anion receptor which might have favorable conformation suitable for a specific anion is through varying the spacer unit between two pyrrolide units, **A** as shown in Chart 1. Macrocycles and macrobicycles[11] formed by these pyrrole systems have been used in studies such

Chart 1. Dialdehyde Derivatives for Schiff Base Condensation Reactions



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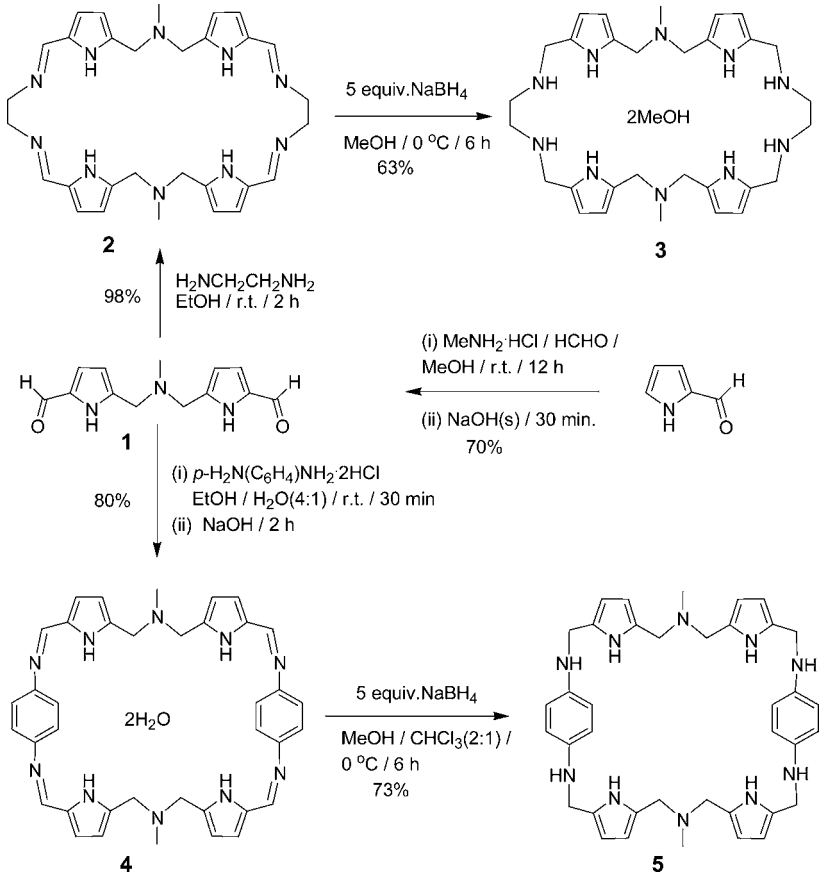
Scheme 1. Synthesis of the [2 + 2] Schiff Base Macrocycles Having the Ethylene and the Phenylene Linkers and Their Reduced Products



as selective anion[12] and carbohydrates recognition,[13] Pacman complexes,[14] hybrid macrocycles,[15] expanded porphyrins,[16] catalysis,[17] and metal complexes[18] among others.

In contrast to the well explored dipyrromethane dialdehyde system which has one sp^3-C atom between two pyrrole rings, we set out to synthesize new receptor systems using a dipyrroyl moiety in which the two pyrole rings are separated by the three-atom spacer unit $-CH_2N(Me)CH_2-$, **1**, which might give conformational flexibility to macrocyclic receptors having multisite bindings for large free energy of complexation.[19] Herein we report a new class of large size macrocycles and macrobicycles containing *N,N*-di(pyrrolylmethyl)-*N*-methylamine moieties connected through alkyl or aryl groups, which are synthesized in excellent yields by the Schiff base condensation reactions between the corresponding amines and the new dialdehyde molecule **1**. We also report the preliminary anion binding study of the macrocycles by ^{1}H NMR titration methods and the X-ray structures of the macrocycles, macrobicycle, and the benzoate anion complex of the macrocycle.

RESULT AND DISCUSSION

The Mannich reaction of pyrrole-2-carbaldehyde with a mixture of HCHO and methylamine hydrochloride in 1:1:0.5 molar ratio, respectively, yielded the new dialdehyde, *N,N*-di(*α*-formylpyrrolyl-*α*-methyl)-*N*-methylamine), **1**, in 70% crystalline yield after silica gel column chromatographic separation (Scheme 1). The dialdehyde was fully characterized including single crystal X-ray diffraction study (See Supporting Information, Figure S33). The X-ray revealed the formyl groups are oriented in an opposite direction to each other and have intermolecular hydrogen bonds, resulting in a one-dimensional chain. Interestingly, these formyl groups have to turn to one side to condense with primary amines for forming macrocycles and macrobicycle. Thus, the [2 + 2] Schiff base condensation reactions between the dialdehyde and an equimolar quantity of ethylenediamine or *p*-phenylenediamine dihydrochloride readily afforded the 30- and 34-membered large size macrocycles **2** and **4** in near-quantitative or excellent (98% or 80%) yields, respectively. Subsequent reduction reactions of **2** and **4** with $NaBH_4$ gave the corresponding macrocyclic hexaamines **3** and **5**, respectively, in good yields. The [2 + 2] macrocyclic nature of these compounds **2**−**5** are characterized by spectroscopic methods including HRMS spectra, some of which were confirmed by X-ray.

The ^{1}H NMR spectra of **2** and **4** in $CDCl_3$ feature resonances due to all protons except the pyrrolic NH protons, probably because of the signal broadening and deuterium exchange. But in a strongly hydrogen bonding solvent, DMSO-d_6 the pyrrolic NH resonance appears as a broad singlet at δ = 11.76 ppm for **4**. **2** is not soluble in DMSO-d_6. Conversely, the ^{1}H NMR spectra of the corresponding reduced products **3** and **5** in $CDCl_3$ showed broad singlets for their pyrrolic NH protons, but their more basic secondary amine NH protons do not appear. All resonances appear when the spectra were recorded in DMSO-d_6, whose integrated intensities are matching with the structures.

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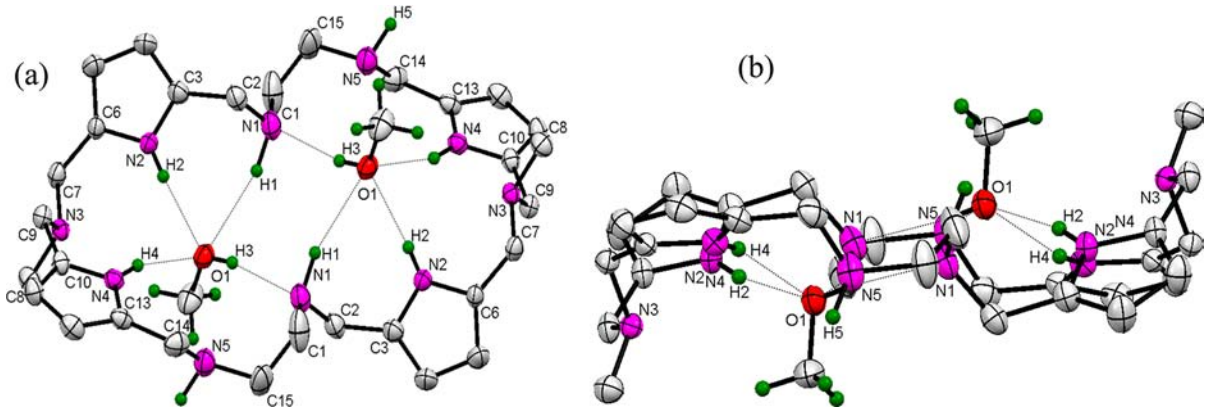

Figure 1. X-ray crystal structure of the [2 + 2] Schiff base macrocycle molecule, **3**·2MeOH: (a) top view and (b) side view, showing the cavities for guest binding. Dotted lines indicate hydrogen bonds. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: N2···O1 2.885(5), H2···O1 2.09(4), N2−H2···O1 168(5), N4···O1 3.073(6), H4···O1 2.29(4), N4−H4···O1 161(5), N1···O1 3.452(6), H1···O1 2.49(5), N1−H1···O1 150(4), O1···N1 2.787(6), H3···N1 2.03(6), O1−H3···N1 168(6).

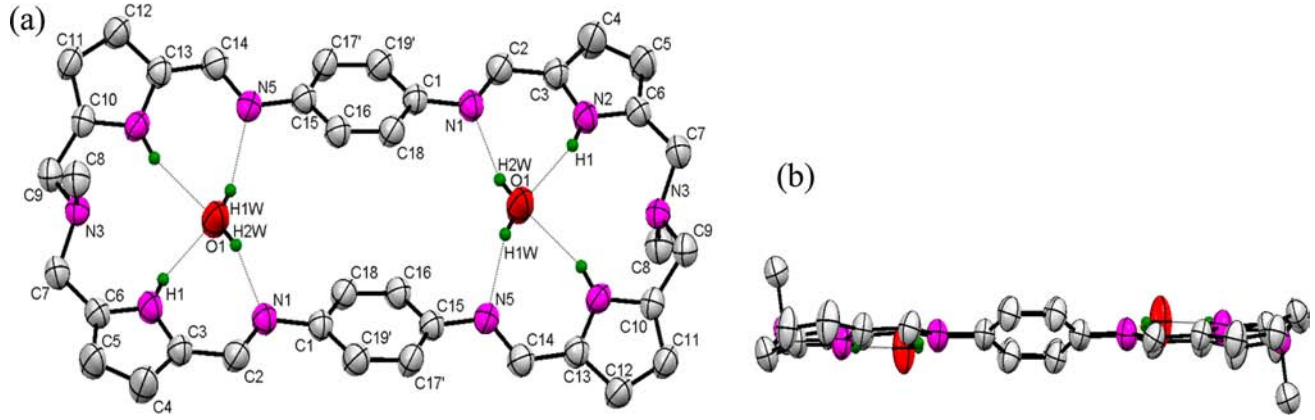

Figure 2. X-ray crystal structure of the [2 + 2] Schiff base macrocycle molecule, **4**·2H_2O: (a) top view and (b) side view, showing a flat conformation. Dotted lines indicate hydrogen bonds. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: N2···O1 2.905(3), H1···O1 2.08(2), N2−H1···O1 163(3), N4···O1 2.895(3), H3···O1 2.08(2), N4−H3···O1 163(3), O1···N1 2.817(3), H2W···N1 2.01(3), O1−H2W···N1 163(4), O1···N5 2.823(3), H1W···N5 2.03(3), O1−H1W···N5 164(4).

Attempts to get suitable single crystals of all the Schiff bases and their reduced products for X-ray diffraction study were not successful except for **3** and **4**. **3** crystallizes in a centrosymmetric space group *Pbca* with one-half of the molecule together with one MeOH molecule in the asymmetric unit. The molecular structure along with selected bond lengths and angles is given in Figure 1. The molecule adopts an "S-shape" conformation with two cavities containing two methanol molecules which are bound by H-bond interactions involving both H-bond donors (pyrrolic NH and the secondary amine NH) and H-bond acceptors (N-Me and the secondary amine N atoms) present in the scaffold of the macrocycle. Similar 2:1 methanol complexes formed by pyrrole based macrocyclic Schiff bases have been reported by Sessler and co-workers.[16]

As a solid state structural evidence for the unsaturated [2 + 2] macrocycles, the structure of **4** was determined by X-ray. The compound crystallizes in a centrosymmetric $P\bar{1}$ space group with one-half of the molecule together with one H_2O molecule in the asymmetric unit. The molecular structure along with selected bond lengths and angles is given in Figure 2. The X-ray structure revealed that the molecule is a long stretched 34-membered macrocycle exhibiting a nearly planar conformation containing two water molecules. As such the molecule looks like a wreath. It consists of two compartments of π-conjugations occurring between the pyrrole, imine, and phenylene groups which are separated by $-CH_2N(Me)CH_2-$ units. The N-Me groups are oriented above and below the plane of the macrocycle. This π-conjugation can be inferred from the bond distances; C13−C14 and C3−C2 bond distances [1.426(4) Å and 1.427(4) Å] are lower than the single bond distances [1.486(4) Å and 1.492(4) Å] found for C10−C9 and C6−C7 bonds, respectively. In addition, the imine bond distances N5−C14 and N1−C2 are 1.274(3) Å and 1.272(3) Å, respectively, indicating a double bond character of the bond. As a result, the compound is yellow in color giving an absorption maximum at 379 nm with molar absorption coefficient ε value of 66711 M^{-1} cm^{-1} (See Supporting Informatio, Figure S32). Additionally, all the *ortho* and the *meta* carbon atoms of each phenylene ring are disordered over two positions probably because of the free rotation along their C−N single bonds.

Preliminary anion binding studies of the reduced macrocycles **3** and **5** were carried out using ^1H NMR titration methods. In this method, an incremental amount of anions (F^-, Cl^-, Br^-, HSO_4^-, and $PhCOO^-$) as their *n*-tetrabutylammonium salts were added to a receptor solution in $CDCl_3$ and the gradual downfield shifts of the NH resonances were followed; the corresponding binding constants were determined by use of the

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EQNMR program[20] with a model of 1:1 and/or 1:2 (Host:Guest) complexes. The titration curve fittings are given in Figure 3, and the binding constants are summarized in Table 1.

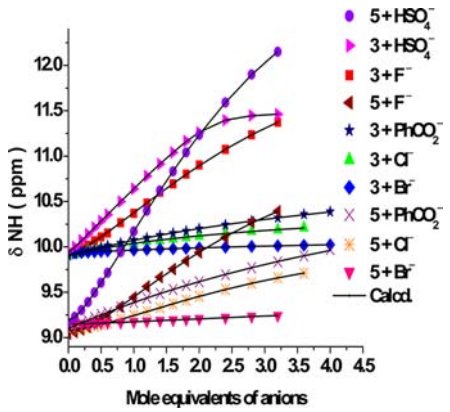


Figure 3. ^{1}H NMR titration curve fittings for **3** and **5**, showing the shift of the pyrrolic NH resonance upon addition of increasing concentrations of anions.

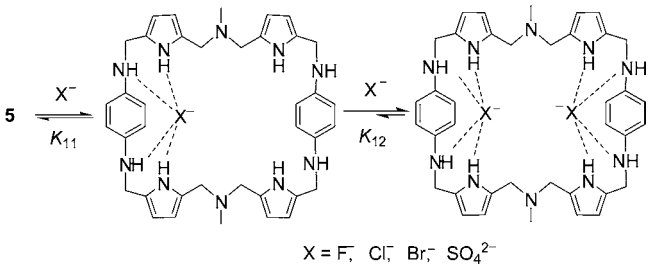
Table 1. Binding Constants[a] (K_a, M^{-1}) for 3 and 5 with Anions as Their *n*-Tetrabutylammonium Salts in $CDCl_3$ at Room Temperature

receptor	anion	K_a	H:G[c]
3	F^-	K_{11} = 20	1:1/1:2
		K_{12} = 6719	
3	Cl^-	26[b]	1:1
3	Br^-	14[b]	1:1
3	HSO_4^-	>(10^4)[b]	1:2
3	$PhCO_2^-$	<10[b]	1:1
5	F^-	$K_{11} \leq 10$	1:1/1:2
		K_{12} = 7490	
5	Cl^-	K_{11} = 33	1:1/1:2
		K_{12} = 4969	
5	Br^-	K_{11} = 28	1:1/1:2
		K_{12} = 838	
5	HSO_4^-	K_{11} = 26	1:1/1:2
		$K_{12} \geq 10^4$	
5	$PhCO_2^-$	<10[b]	1:1

[a]The pyrrolic NH resonances were used for calculating K_a; each experiment was carried out two times (see Supporting Information) and an average binding constant value is given here. [b]Error is <15%; for all other cases the error is less than 1%. [c]H:G = Receptor:Anion.

Although both receptors have similar H-bonding groups they have different binding phenomena with anions. For example, when aliquots of F^- were added to a solution of **3** in $CDCl_3$ the intensity of the pyrrolic NH resonance decreased gradually and disappeared after addition of 2 equiv of F^-, indicating deprotonation and fluoride ion mediated hydrogen-deuterium exchanges. However, the ^{1}H NMR spectra of **3** in the presence of varying concentrations of F^- in either $CDCl_3$ or DMSO-d_6 showed no triplet around the 16 ppm region for the HF_2^- ion, probably because of a fast deuterium exchange on the NMR time scale. In contrast to this, in the case of titration of **5** with F^-, the rate of deprotonation seems to be much lower as shown by the appearance of NH resonance even after addition of 3 equiv of F^- (See Supporting Information, Figure S45). The titration curves of both the receptors with F^- appear to be a sort of sigmoidal shape. A good curve fitting was obtained for a sequential 1:2 binding isotherm model with K_{11} and K_{12} binding constants as shown in Scheme 2. In addition, their

Scheme 2. Schematic Representation of the Multiple Equilibria Existing between a 1:1 and a 1:2 Complexes, and the Receptor 5 in $CDCl_3$



Job plots[21] (Figure 4a) showed a maximum at 0.4 mol fraction value of the receptor which lies between the maxima expected for a 1:1 and a 1:2 complexes. These results suggests that the receptors **3** and **5** binds with F^- to form exclusively neither a 1:1 nor a 1:2 (receptor:anion) complex in solution, instead the formation of both complexes and the existence of a multiple equilibria between them as shown in Scheme 2. Their binding constants for F^- are comparable. As given in Table 1, in both cases, although the binding constants for 1:1 complexes are lower showing weak binding, K_{12} values are much higher than K_{11} values indicating cooperative bindings and the relative high stability of a 1:2 complex. On the contrary, **3** forms only 1:1 complexes with the large size spherical anions such as Cl^- and Br^- and the bidirectional anion $PhCOO^-$, but their binding constants are lower suggesting very weak bindings. Their binding stoichiometries were confirmed by the corresponding Job plot showing a maximum at 0.5 mol fraction value. In contradiction to this, the receptor **5** having the phenylene linkers, which gives rigidity, forms both 1:1, and 1:2 complexes with the same large size halide ions and has a multiple equilibria (Scheme 2), as it can be inferred from the sigmoidal shape of their titration curves and from their Job plots (Figure 4b) showing a maximum at 0.4 mol fraction value of the receptor (see Supporting Information for other Job plots). Here also K_{12} is much higher than K_{11} suggesting that in a 1:2 complex the anion is strongly bound. Interestingly, although SO_4^{2-} is a large size tetrahedral anion, **3** forms a 1:2 complex whereas **5** forms both 1:1 and 1:2 complexes. Their binding constants are >10^4 M^{-1} for a 1:2 complex formation.[22] This can be due to the in situ formation of the tetrapositively charged macrocycle by the protonation of all the four secondary amine nitrogen atoms by the acidic HSO_4^- ion. Resultant charged receptor containing additional hydrogen bonding ammonium N^+H groups can have a favorable conformation, as was observed in the benzoate anion structure (vide infra), for strongly binding with sulfate ions. Similar receptors systems showing multiple equilibria involving 1:1 and 1:2 complexes and a maximum around 0.4 or 0.6 in their Job plots have been reported.[7d,23]

To summarize, as shown by their K_a's both the receptors prefer to form a 1:2 complex. In addition, both receptor systems have two compartments each forming one cavity to accommodate one guest, correlating with the high affinity found for the formation of stable 1:2 complexes in solution as supported by the X-ray structure of the 1:2 methanol complex

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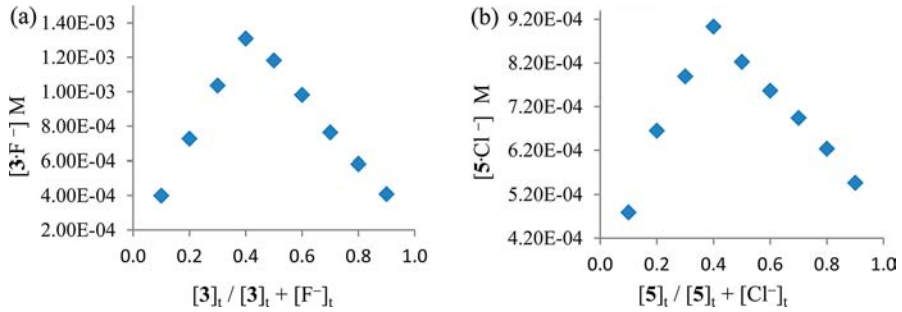
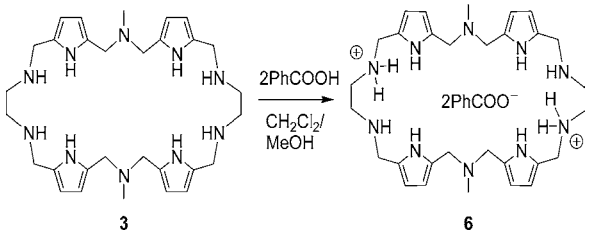


Figure 4. Job plots for **3** with F^- (a) and for **5** with Cl^- (b), showing maxima at 0.4 mol fraction value of the receptor for the multiple equilibria existing between the receptors, a 1:1 and 1:2 complexes in $CDCl_3$. These two Job plot experiments were carried out two times to confirm their 0.4 mol fraction maxima.

of **3** or the aqua complex of **4** or the structure of the benzoate anion complex **6** (vide infra).

To understand the nature of the conformation that the macrocycles would have after forming anion complexes, attempts were made to isolate them as single crystals. Fortunately, the reaction between the receptor **3** and 2 equiv of PhCOOH in CH_2Cl_2/MeOH resulted in the isolation of colorless crystals of the benzoate anion complex **6** in nearly quantitative yield (Scheme 3). This crystalline material is not

Scheme 3. Synthesis of the Benzoate Anion Complex 6 from the Reduced Schiff Base 3



soluble in common organic solvents and hence **6** could not be characterized by NMR method. The molecular structure of **6** along with selected bond lengths and angles is given in Figure 5. The X-ray structure revealed the formation of the 1:2 (receptor:benzoate ion) complex. Benzoic acid protonates only two of the secondary amine nitrogen atoms leading to the formation of a dipositively charged and preorganized macrocycle having a pronounced S-shape conformation as compared to that in the methanol complex of **3** (Figure 1). The benzoate anion one in each cavity of the S-shape conformation is bound by four N−H···O type hydrogen bonds: two from the pyrrolic NH and two from the ammonium N^+H protons, in addition to C−H···O type interactions. Interestingly, the potentially hydrogen bonding secondary amine NH groups are not bonded to the anion as they are pointing in opposite directions. Further, the torsion angle of N3−C9−C10-N4 is 55.9°, which is lower compared to that in the free receptor structure (60.8°) and indicates the conformational flexibility of the macrocycle **3**.

Having successfully synthesized and studied anion binding properties of the macrocycles derived from diamines, we set to synthesize three dimentional macrobicyclic azacryptand molecules from a triamine. The reaction between the dialdehyde and tris(2-aminoethyl)amine in a 1.5:1 molar ratio in CH_3CN afforded the expected [3 + 2] Schiff base macrobicycle molecule **7** as colorless solid in 85% yield. The corresponding saturated azacryptand molecule **8** was synthesized in 88% yield by reacting **7** with $NaBH_4$ in $CHCl_3$/MeOH solvent (Scheme 4). **7** and **8** are soluble in solvents such as CH_2Cl_2 and $CHCl_3$ and are characterized by spectroscopic methods. **7** and **8** give molecular ion peaks m/z at 920.5985 and 932.5885 (calcd mass 920.6000 and 932.6939, respectively) corresponding to the mass of their $[M+H^+]$ ions in the HRMS spectra.

The bicyclic nature of the azacryptand **7** was further confirmed by the X-ray diffraction study. The molecular structure along with selected bond lengths and angles is given in Figure 6. The X-ray structure revealed that the molecule adopts an eclipsed paddle-wheel shaped conformation containing three water molecules inside its cavity. The planar part of

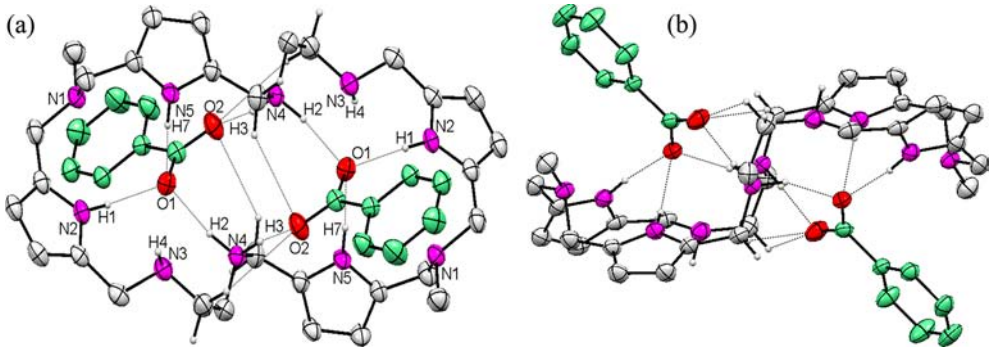


Figure 5. X-ray crystal structure of the benzoate anion complex, **6**: (a) top view and (b) side view, showing the cavities in which the benzoate anions are bound. Most hydrogen atoms are omitted for clarity. Dotted lines indicate hydrogen bonds. Selected bond lengths [Å] and angles [deg]: N2···O1 2.887(4), H1···O1 1.97(3), N2−H1···O1 171(3), N5···O1 3.032(4), H7···O1 2.17(3), N5−H7···O1 160(3), N4···O1 2.799(4), H2···O1 1.88(2), N4−H2···O1 156(3), N4···O2 2.692(4), H3···O2 1.74(2), N4−H3···O2 168(3).

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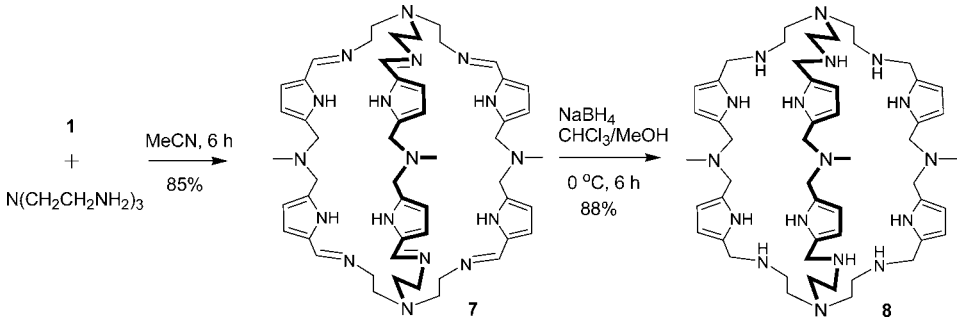
Scheme 4. Synthesis of the [3 + 2] Schiff Base Macrobicyclic Molecule 7 and the Reduced Product 8



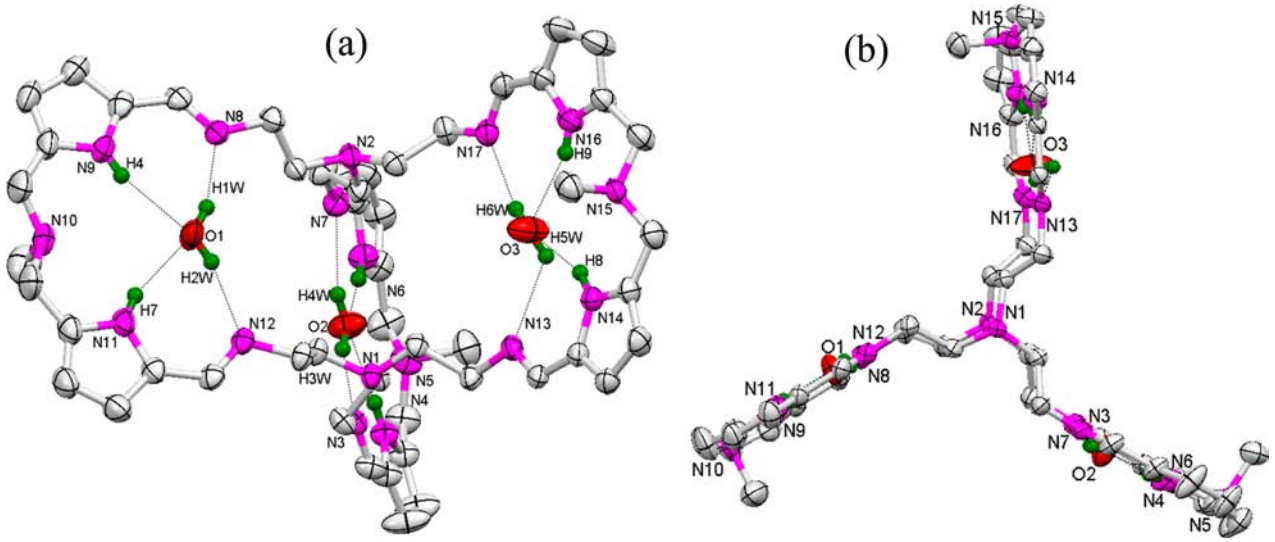


Figure 6. X-ray crystal structure of the [3 + 2] Schiff base macrobicycle molecule, $7 \cdot 5.16H_2O$ (50% thermal ellipsoids): (a) top view and (b) side view, showing an eclipsed conformation about each bond in the wing and the *out/out* configuration at the bridgehead nitrogen atoms. Most hydrogen atoms are omitted for clarity. Dotted lines indicate hydrogen bonds. Selected bond lengths [Å] and angles [deg]: N4···O2 2.961(4), H1···O2 2.19(2), N4–H1···O2 163(3), N(6)···O(2) 2.967(4), H2···O2 2.17(2), N6–H2···O2 171(4), N9···O1 2.979(4), H4···O1 2.21(2), N9–H4···O1 158(4), N11···O1 2.893(4), H7···O1 2.13(2), N11–H7···O1 160(4), N14···O3 2.949(4), H8···O3 2.17(2), N14–H8···O3 157(3), N16···O3 2.922(4), H9···O3 2.17(2), N16–H9···O3 159(4), O1···N8 2.812(4), H1W···N8 2.04(3), O1–H1W···N8 161(4), O1···N12 2.865(3), H2W···N12 2.13(3), O1–H2W···N12 153(4).

each wing consists of the imine and the dipyrrolyl moieties in which the oxygen atom of the water molecule is present and complementarily hydrogen bonded to the pyrrolic NH and imine groups. The molecule has a C_3 axis passing the bridgehead nitrogen atoms whose N---N distance is surprisingly lower (5.524 Å), given the large size of the molecule. The lone pairs of electrons in the bridgehead nitrogen atoms are oriented outside with respect to the cavity of the azacryptand exhibiting an *out/out* configuration, which is probably due to the planarity that each wing maintains. Consequently, there is no water molecule bound in the center of the azacryptand. This is in contrast to the *in/in* configuration adopted by an azacryptand recently reported by us[7a] and others.[10] This solid state *out/out* configuration is supported by its ^{1}H NMR spectrum recorded in $CDCl_3$. Two separate resolved multiplets are observed for the methylene groups connecting the bridgehead nitrogen to the imine nitrogen atom. This indicates the presence of only one isomer, *out/out*, which is probably not in equilibrium with either an *in/in* or *out/in* isomer in solution. This rigidness in solution can also be due to the planarity that the dipyrrolylimine moiety maintains. Conversely, two slightly broadened singlets are observed for the methylene groups in the reduced Schiff base **8**.

CONCLUSION

A new class of large size macrocycles and macrobicycles containing *N,N*-di(pyrrolylmethyl)-*N*-methylamine moieties were easily synthesized in very high yields by Schiff base condensation reactions in the absence of a metal or an anion template. Although both receptors have similar pyrrolic and amine NH environments the observed anion binding differences can be attributed to the inherent conformational flexibility or rigidness rendered by the linker (ethylene or phenylene, respectively) present in the receptor system. The crystal structures of the methanol, the aqua, and the benzoate anion complexes show the cavities for guest binding and supporting the predominant 1:2 complex formation with high binding constants. Both the receptors (**3** and **5**) follow the order of binding $SO_4^{2-} > F^- > Cl^- > Br^- > PhCOO^-$, which is primarily determined by the electrostatic interactions, the basicity of the anion, and the conformation of the receptor. To the best of our knowledge, the crystal structure of the bicycle **7** represents a rare example; to date only a few azacryptands showing an *out/out* configuration are structurally characterized.[24] In addition, the hydrogen bond donors and acceptors present on the periphery of the macrocycle are suitable for

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binding anions and cations together, and which is work in progress in our group.

EXPERIMENTAL SECTION

General Procedures. Solvents and chemicals were purchased from commercial sources. Pyrrole-2-carbaldehyde was prepared according to the literature procedure.[25] Chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents. Pyrrole, methylamine hydrochloride, tetrabutylammonium fluoride solution (1.0 M in THF), *n*-tetrabutylammonium salts (Cl^-, Br^-, HSO_4^-, and $PhCO_2^-$), *p*-phenylenediamine dihydrochloride, tris(2-aminoethyl)amine, and $CDCl_3$ were purchased from Aldrich and were used without further purification except pyrrole, which was distilled, and methylamine hydrochloride, which was dried under vacuum with warm water. Melting points were determined in open capillaries and are corrected using benzophenone as a reference.

Synthesis of *N,N*-di(*α*-formylpyrrolyl-*α*-methyl)-*N*-methylamine), 1. A methanol solution of pyrrole-2-carbaldehyde (10 g, 105.16 mmol) was added dropwise to a mixture of formaldehyde (38%, 8.3 mL, 105.16 mmol) and methylamine hydrochloride (3.55 g, 52.6 mmol) at 0 °C and then the solution was stirred overnight (15 h). To this solution solid NaOH (2.10 g, 52.6 mmol) was added and stirred for additional half an hour. The solvent was removed under vacuum, and the residue was extracted with dichloromethane which was loaded onto a column chromatography filled with silica gel. Elution using ethyl acetate/petroleum ether (v/v 1/2) afforded the dialdehyde compound **1** as a colorless crystalline solid (9.02 g, 36.8 mmol, 70%) after removing the solvent under vacuum. mp 130 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): δ = 2.21 (s, 3H, N*Me*), 3.62 (s, 4H, CH_2N(Me)CH_2), 6.17 (t, 2H, pyrrole *β*-*CH*), 6.93 (t, 2H, pyrrole *β*-*CH*), 9.46 (s, 2H, C*H*O), 10.78 (br s, 2H, N*H*). ^{13}C{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.5 (NCH_3), 54.5 (CH_2N(Me)CH_2), 110.7 (pyrrole *β*-*C*), 123.1 (pyrrole *β*-*C*), 133.0 (pyrrole *α*-*C*), 140.1 (pyrrole *α*-*C*), 179.4 (CHO). FT-IR (KBr, cm^{-1}): ν = 3263 (vs), 3114 (m), 2973 (m), 2942 (m), 2828 (s), 1644 (vs), 1554 (m), 1489 (s), 1420 (s), 1350 (s), 1263 (m), 1185 (s), 1114 (w), 1055 (m), 1036 (m), 964 (w), 816 (s), 776 (s), 625 (w), 521(w), 473 (w). Anal. Calcd for $C_{13}H_{15}N_3O_2$: C, 63.66; H, 6.16; N, 17.13. Found: C, 63.40; H, 6.26; N, 16.89. LRMS (+ESI): calcd *m*/*z* for [M+H$^+$] $C_{13}H_{16}N_3O_2$: 246.1, found: 246.1.

Synthesis of the [2 + 2] Macrocycle Schiff Base Containing the Ethylene Linkers, 2. Ethylenediamine (1.2 mL, 17.94 mmol) was added to a warmed ethanol solution (80 mL) of **1** (4.4 g, 17.94 mmol). The solution was stirred for 2 h to give a colorless precipitate. The solution was filtered, and the precipitate was washed twice with diethyl ether and then dried under vacuum to give **2** (4.74 g, 8.88 mmol, 98%). mp 171 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): δ = 2.25 (s, 6H, N*Me*), 3.63 (s, 8H, CH_2N(Me)CH_2), 3.79 (s, 8H, NCH_2CH_2N), 6.01 (d, 4H, ^3J(H,H) = 3.6 Hz, pyrrole *β*-*CH*), 6.43 (d, 4H, ^3J(H,H) = 3.6 Hz, pyrrole *β*-*CH*), 7.98 (s, 4H, imine *HC*═N). ^{13}C{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.6 (NCH_3), 55.0 (CH_2N(Me)CH_2), 60.6 (NCH_2CH_2N), 107.7 (pyrrole *β*-*C*), 116.4 (pyrrole *β*-*C*), 129.2 (pyrrole *α*-*C*), 136.7 (pyrrole *α*-*C*), 153.0 (HC═N, imine). DEPT-135{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.4(NCH_3), 54.8 (CH_2N(Me)CH_2), 60.4 (NCH_2CH_2N), 107.5(pyrrole *β*-*C*), 116.2 (pyrrole *β*-*C*), 152.8 (HC═N, imine) . FT-IR (KBr, cm^{-1}): ν = 3298 (s), 2872 (m), 2833 (m), 1636 (vs), 1569 (w), 1493 (w), 1457 (w), 1363 (w), 1260 (m), 1186 (w), 1120 (w), 1031 (m), 781 (s). HRMS (+ESI): calcd *m*/*z* for [M+H$^+$] $C_{30}H_{39}N_{10}$: 539.3359, found: 539.3353.

Synthesis of the Reduced [2 + 2] Macrocycle Schiff Base Containing the Ethylene Linkers, 3. A suspension of **2** (2.5 g, 4.64 mmol) in MeOH was degassed for 15 min. To this suspension was added solid $NaBH_4$ (0.88 g, 23.2 mmol) and stirred, resulting in a clear solution within 10 min. The solution was stirred for 3 h in total to give a colorless precipitate. The solution was filtered, and the precipitate was washed twice with diethyl ether and then dried under vacuum to give **3** (1.80 g, 2.95 mmol, 63%) as a colorless solid. mp >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): δ = 2.14 (s, 6H, N*Me*), 2.72(s, 8H, pyrrole *α*-CCH_2N), 3.40 (s, 8H, CH_2N(Me)CH_2), 3.49(s, CH_3OH), 3.73 (s, 8H, NCH_2CH_2N), 5.85 (s, 8H, pyrrole *β*-*CH*), 9.90 (br s, 4H, pyrrolic N*H*).^{13}C{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.8 (NCH_3), 46.6 (pyrrole *α*-CCH_2NH), 48.1-(NCH_2CH_2N), 50.6(CH_3OH), 54.3 (CH_2N(Me)CH_2), 106.4 (pyrrole *β*-*C*), 106.6 (pyrrole *β*-*C*), 129.8 (pyrrole *α*-*C*), 130.5 (pyrrole *α*-*C*). DEPT-135{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.0 (NCH_3), 46.5 (pyrrole *α*-CCH_2NH), 48.6(NCH_2CH_2N), 49.1-(CH_3OH), 54.1 (CH_2N(Me)CH_2), 105.9 (pyrrole *β*-*C*), 106.7 (pyrrole *β*-*C*). ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C, ppm): δ = 1.81(br s, 4H, secondary amine N*H*), 2.01 (s, 6H, N*Me*), 2.50(s, 8H, pyrrole *α*-CCH_2N, merged with the solvent peak), 3.16(d, ^3J(H,H) = 4.2 Hz, CH_3OH), 3.32(s, 8H, CH_2N(Me)CH_2, merged with the water peak), 3.53 (s, 8H, NCH_2CH_2N), 4.10 (br m, OH of MeOH), 5.71 (s, 8H, pyrrole *β*-*CH*), 10.26 (br s, 4H, pyrrolic N*H*). FT-IR (KBr, cm^{-1}): ν = 3340 (vs), 3261 (vs), 2929 (s), 2826 (s), 2360 (m), 1647 (m), 1542 (m), 1438 (s), 1362 (m), 1267 (m), 1190 (m), 1115 (m), 1020 (m), 785 (vs). HRMS (−ESI): calcd *m*/*z* for [M−H$^-$] $C_{30}H_{45}N_{10}$: 545.3829, found: 545.3828.

Synthesis of the [2 + 2] Macrocycle Schiff Base Containing the Phenylene Linkers, 4. The dialdehyde **1** (2.0 g, 8.15 mmol) was dissolved in 100 mL of EtOH/H_2O (v/v 4/1) mixture. To this solution was added *p*-phenylenediamine dihydrochloride (1.48 g, 8.15 mmol) and stirred for 30 min to give a yellow orange precipitate. To this solution solid NaOH (0.65 g, 16.30 mmol) was added and stirred for additional 2 h. The solution was filtered, and the yellow precipitate was washed with diethyl ether twice and then dried under vacuum to give **4** (2.2 g, 3.28 mmol, 80%). mp >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): δ = 2.27 (s, 6H, N*Me*), 3.74 (s, 8H, CH_2N(Me)CH_2), 6.11 (d, 4H, ^3J(H,H) = 3.6 Hz, pyrrole *β*-*CH*), 6.64 (d, 4H, ^3J(H,H) = 3.4 Hz, pyrrole *β*-*CH*), 7.17 (s, 8H, benzene C*H*), 8.27 (s, 4H, imine *HC*═N). ^{13}C{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.4 (NCH_3), 55.3 (CH_2N(Me)CH_2), 108.6 (pyrrole *β*-*C*), 118.6 (pyrrole *β*-*C*), 122.3 (benzene *C*H), 130.2 (pyrrole *α*-*C*), 138.1 (pyrrole *α*-*C*), 147.3 (imine HC═N), 148.0 (ipso C of phenylene ring). DEPT-135{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.2 (NCH_3), 55.1 (CH_2N(Me)CH_2), 108.4 (pyrrole *β*-*C*), 118.4 (pyrrole *β*-*C*), 122.1 (benzene *C*H), 147.8 (imine HC═N). ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C, ppm): δ = 1.95 (s, 6H, N*Me*), 3.33 (H_2O), 3.63 (s, 8H, CH_2N(Me)CH_2), 6.09 (s, 4H, pyrrole *β*-*CH*), 6.56 (s, 4H, pyrrole *β*-*CH*), 7.32 (s, 8H, benzene C*H*), 8.46 (s, 4H, imine *HC*═N), 11.76 (br s, 4H, pyrrolic N*H*). FT-IR (KBr, cm^{-1}): ν = 3295 (s), 2820 (w), 2780 (w), 2361 (w), 1606 (vs), 1562 (s), 1478 (s), 1360 (m), 1334 (m), 1257 (s), 1174 (s), 1034 (s), 842 (m), 783 (s), 710 (w), 539 (w). HRMS (+ESI): calcd *m*/*z* for [M +H$^+$] $C_{38}H_{39}N_{10}$: 635.3359, found: 635.3339.

Synthesis of the Reduced [2 + 2] Macrocycle Schiff Base Containing the Phenylene Linkers, 5·2H$_2$O. Solid $NaBH_4$ (0.60 g, 15.9 mmol) was added to a clear, degassed solution of **4** (0.5 g, 0.74 mmol) in MeOH/$CHCl_3$ (v/v 2/1) at 0 °C. The color of the solution turned to a light color. The solution was stirred for 6 h to give a colorless precipitate. The solution was filtered, and the precipitate was washed with diethyl ether twice and then dried under vacuum to give **5**. Its molecular weight is based on the formulation, **5**·2H_2O (0.37 g, 0.54 mmol, 73%). mp >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): δ = 2.21 (s, 6H, N*Me*), 3.44 (s, 8H, CH_2N(Me)CH_2), 4.15 (s, 8H, pyrrole *α*-CCH_2N), 5.94 (d, 8H, pyrrole *β*-*CH*), 6.60 (s, 8H, benzene C*H*), 9.12 (br s, 4H, pyrrolic N*H*).^{13}C{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.9 (NCH_3), 43.5 (pyrrole *α*-CCH_2NH), 55.4 (CH_2N(Me)CH_2), 106.5 (pyrrole *β*-*C*), 107.2 (pyrrole *β*-*C*), 115.9 (benzene *C*H), 129.4 (pyrrole *α*-*C*), 130.2 (pyrrole *α*-*C*), 141.3 (ipso C of pheny ring). DEPT-135{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.6 (NCH_3), 43.3 (pyrrole *α*-CCH_2NH), 54.2 (CH_2N(Me)CH_2), 106.4 (pyrrole *β*-*C*), 106.7 (pyrrole *β*-*C*), 115.8 (benzene *C*H). ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C, ppm): δ = 2.06 (s, 6H, N*Me*), ∼3.34 (s, 8H, CH_2N(Me)CH_2, merged with the solvent peak), 4.00 (d, 8H, ^3J(H,H) = 4.8 Hz, pyrrole *α*-CCH_2N), 4.82 (t, 4H, secondary amine N*H*, ^3J(H,H) = 4.8 Hz), 5.74 (s, 4H, pyrrole *β*-*CH*), 5.81 (s, 4H, pyrrole *β*-*CH*), 6.51 (s, 8H, benzene C*H*), 10.52 (br s, 4H, pyrrolic N*H*). FT-IR(KBr, cm^{-1}): ν = 3637 (m), 3400 (s),

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Table 2. Crystallographic Data for Compounds 3·2MeOH, 4·2H_2O, 6, and 7·5.16H_2O

	3·2MeOH	4·2H_2O	6	7·5.16H_2O
empirical formula	$C_{32}H_{54}N_{10}O_2$	$C_{38}H_{42}N_{10}O_2$	$C_{44}H_{58}N_{10}O_4$	$C_{51}H_{80.32}N_{17}O_{5.16}$
formula weight	610.85	670.82	791.00	1014.20
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
temperature (K)	293(2)	295(2)	293(2)	293(2)
crystal system	orthorhombic	triclinic	triclinic	monoclinic
color and shape	colorless, prism	yellow, needle	colorless, prism	colorless, prism
space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	*C2/c*
a/Å	17.504(2)	5.243(12)	9.482(6)	34.044(3)
b/Å	7.869(10)	11.614(3)	10.882(7)	11.7179(12)
c/Å	25.007(3)	15.391(4)	11.463(7)	34.807(5)
α/deg	90.0	105.366(8)	90.55(2)	90.0
β/deg	90.0	97.274(8)	92.84(2)	117.956(3)
γ/deg	90.0	101.051(8)	113.245(19)	90.0
volume (Å^3)	3444.2(8)	871.1(3)	1085.0(12)	12265(2)
Z	4	1	1	8
D_{calcd}, g cm^{-3}	1.178	1.279	1.211	1.098
μ/mm^{-1}	0.077	0.083	0.080	0.074
F(000)	1328	356	424	4373
crystal size/mm	0.72 × 0.61 × 0.26	0.29 × 0.16 × 0.08	0.43 × 0.31 × 0.24	0.23 × 0.15 × 0.15
θ range (degree)	1.63 to 25.00	1.87 to 25.00	1.78 to 25.00	1.87 to 25.00
limiting indices	$-20 \le h \le 20$	$-6 \le h \le 6$	$-11 \le h \le 11$	$-39 \le h \le 40$
	$-9 \le k \le 9$	$-13 \le k \le 13$	$-12 \le k \le 11$	$-13 \le k \le 13$
	$-29 \le l \le 29$	$-18 \le l \le 18$	$-13 \le l \le 13$	$-41 \le l \le 41$
total/unique no. of reflns.	37610/3029	10515/3053	12889/3812	70341/10736
R_{int}	0.180	0.0679	0.0855	0.0392
data/restr./ params.	3029/2/215	3053/16/251	3812/4/277	10736/30/676
GOF (F^2)	1.073	0.975	1.015	1.082
R1, *wR2*	0.0782, 0.1943	0.0562, 0.1098	0.0685, 0.1371	0.0769, 0.2508
R indices (all data) *R1*, *wR2*	0.1760, 0.2726	0.1336, 0.1397	0.1575, 0.1776	0.1068, 0.2746
largest different peak and hole (e Å^{-3})	0.531 and −0.323	0.151 and −0.217	0.213 and −0.231	0.927 and −0.312

3297 (s), 2828 (m), 1617 (w), 1588 (w), 1515(vs),1436 (s), 1399 (m), 1339 (m), 1290 (m), 1228 (s), 1121 (m), 1022 (m), 966 (w), 783 (s), 664 (w), 517 (w). HRMS (+ESI): calcd *m*/*z* for [M+Na$^+$] $C_{38}H_{46}N_{10}Na$: 665.3805, found: 665.3785.

Synthesis of the Benzoate Anion Complex, 6. To a solution of **3a**·2MeOH (0.05 g, 0.09 mmol) in dichloromethane/methanol (50 mL, v/v 1/1) mixture was added solid benzoic acid (0.15 g, 0.18 mmol) with stirring. The reaction mixture was allowed to evaporate slowly over a period of 10 h to give single crystals of the benzoate anion complex **6** in near quantitative yield. When the reaction was carried out in 15 mL of the same solvent the precipitate of **6** was formed immediately in quantitative yield. This crystalline material is not soluble in solvents such as CH_2Cl_2, $CHCl_3$, acetone, THF, MeCN, and MeOH and hence it could not be characterized by the NMR method. mp >200 °C. FT-IR (KBr, cm^{-1}): ν = 3279 (m), 3154 (m), 3006 (w), 2830 (m), 2777 (m), 2363 (m), 1596 (m), 1548 (s), 1441 (m), 1388 (s), 1256 (w), 1121 (w), 1024 (w), 837 (w), 785 (w), 719 (m), 670 (w).

Synthesis of the [3 + 2] Macrobicycle Schiff Base, 7·5.16H_2O. A solution of tris(2-aminoethyl)amine (0.6 mL, 4.0 mmol) in MeCN (50 mL) was added dropwise over a period of 10 min to a solution of the dialdehyde **1** (1.50 g, 6.1 mmol) in MeCN (300 mL) at room temperature. Precipitate begins to form, and the solution was stirred for 6 h. The solution was filtered, and the precipitate was washed with diethyl ether twice and then dried under vacuum to give **7** (1.75 g, 1.73 mmol, 85%). mp >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): δ = 2.20 (s, 9H, N*Me*), 3.05 (m, 12H, NCH_2CH_2N), 3.56 (s, 12H, *C*H_2N(Me)CH_2), 3.69 (m, 12H, NCH$_2$CH_2N), 5.99 (d, 4H, ^3J(H,H) = 3.6 Hz, pyrrole β-*CH*), 6.41 (d, 4H, ^3J(H,H) = 3.6 Hz, pyrrole β-*CH*), 7.98 (s, 4H, imine *HC*═N). ^{13}C{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.7 (NCH_3), 54.7 ($CH_2N(Me)CH_2$), 58.0 (NCH_2CH_2N), 60.4 (NCH$_2$CH_2N), 107.8 (pyrrole β-*C*), 116.8 (pyrrole β-*C*), 129.1 (pyrrole α-*C*), 136.4 (pyrrole α-*C*), 153.6 (imine HC═N). DEPT-135{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.5(NCH_3), 54.6 ($CH_2N(Me)CH_2$), 57.9 (NCH$_2$CH_2N), 60.3 (NCH$_2$CH_2N), 107.6 (pyrrole β-*C*), 116.6 (pyrrole β-*C*), 153.4 (imine HC═N). FT-IR (KBr, cm^{-1}): ν = 3298 (s), 2839 (m), 1638 (vs), 1566 (w), 1493 (w), 1454 (w), 1356 (w), 1259 (m), 1184 (w), 1035 (m), 792 (s). HRMS (+ESI): calcd *m*/*z* for [M+H$^+$] $C_{51}H_{70}N_{17}$: 920.6000, found: 920.5985.

Synthesis of the Reduced [3 + 2] Macrobicycle Schiff Base, 8. Solid $NaBH_4$ (0.65 g, 17.182 mmol) was added to a degassed clear solution of **7** (0.160 g, 0.158 mmol) in MeOH/$CHCl_3$ (25 mL, v/v 2/1) mixture at 0 °C, resulting in an immediate evolution of H_2 gas. The reaction mixture was stirred for 6 h and then quenched by adding water (10 mL). The solution was concentrated and then extracted with dichloromethane. The dichloromethane solution was then dried over sodium sulfate and then filtered. The solvent was removed to give a fluffy solid. This solid was dissolved in dichloromethane/hexane (v/v 1/2) mixture which upon slow evaporation yielded a pure form of **8** as colorless solid. Its molecular weight is based on the formulation, **8**·3H_2O (0.137 g, 0.139 mmol, 88%). mp >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): δ = 2.18 (s, 9H, N*Me*), 2.45 (s, 12H, NCH_2CH_2NH), 2.61 (s, 12H, NCH$_2$CH_2NH), 3.46 (s, 12H, *C*H_2N(Me)CH_2), 3.76 (s, 12H, pyrrole α-CCH_2NH), 5.86 (s, 12H, pyrrole β-*CH*), 10.55 (br s, 6H, pyrrolic N*H*). ^{13}C{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.5 (NCH_3), 44.9 (NCH$_2$CH_2NH), 46.3 (pyrrole α-CCH_2NH), 52.9 (NCH$_2$CH_2N), 54.5($CH_2N(Me)CH_2$), 106.2 (pyrrole β-*C*), 106.9 (pyrrole β-*C*), 129.6 (pyrrole α-*C*), 130.6 (pyrrole α-*C*). DEPT-135{^{1}H} NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): δ = 42.3 (NCH_3), 44.8 (NCH$_2$CH_2NH), 46.1 (pyrrole α-CCH_2NH), 52.7 (NCH$_2$CH_2N), 54.3($CH_2N(Me)CH_2$), 106.0 (pyrrole β-*C*), 106.8 (pyrrole β-*C*). FT-IR (KBr, cm^{-1}): ν = 3746 (w), 3277 (s), 2926 (m), 2829 (m), 1648 (w), 1636 (w), 1538 (w), 1457 (s), 1359 (m), 1267 (w), 1186 (w), 1116 (w), 1021 (m), 782

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(s). HRMS (+ESI): calcd m/z for $[M+H^+]$ $C_{51}H_{82}N_{17}$: 932.6939, found: 932.5885.

NMR Titrations. Using 20 μL micropipet, we carried out all titrations by adding an incremental amount of anions (F^-, Cl^-, Br^-, HSO_4^-, and $PhCOO^-$) as their *n*-tetrabutylammonium salts from a stock solution in $CDCl_3$ to a NMR tube containing the receptor in $CDCl_3$. After each addition, spectra were recorded and the NH resonance was monitored for calculating the association constants K_a by the EQNMR[20] program and by the Hirose two-parameter methods (see Supporting Information).[21]

X-ray Crystallography. Suitable single crystals of **1**, **3**·2MeOH, **4**·2H_2O, and **7**·5.16H_2O were obtained by slow evaporation of a solution of **1** in methanol, **3** in ethylacetate/methanol/dichloromethane (v/v 1/1/2), **4** in dichloromethane, and **7** in chloroform/petroleum ether (v/v 2/1), respectively, for X-ray diffraction studies.

Single crystal X-ray diffraction data collections for these crystals were performed using a Bruker-APEX-II CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequently, least-squares refinements were carried out on F^2 using SHELXL-97 (WinGX version)[26] to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on calculated positions using riding models except the pyrrolic NH, water OH, methanol OH, ammonium N^+H, and the secondary amine NH hydrogen atoms. These hydrogen atoms were located from the difference Fourier map and then refined isotropically with the thermal parameters equivalent to 1.2 times the thermal parameter value of the atom to which hydrogen atoms are bonded and with restraints, SADI. In the structure of **4**·2H_2O, the *ortho* and the *meta* carbon atoms C16, C17, C18, and C19 of the phenylene rings are disordered over two positions with the site occupancy factors of 51% and 49%. These were handled with EADP and SADI options available in the SHELXL-97 program. The unit cell of the structure **7**·5.16H_2O contains 2.16 lattice water molecules, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[27] This necessarily contributes to the discrepancy between calculated and reported formula in the cif-file. Other perspective views of the structures and packing diagrams are given in the Supporting Information. Crystallographic refinement data are given in Table 2.

■ ASSOCIATED CONTENT

Supporting Information

NMR, IR, crystallographic data (CIF), crystal structure of **1**, UV−visible spectrum of **4**·2H_2O, NMR titration spectra, EQNMR calculations, Job plots, and packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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