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## COMMUNICATION

## 1D Water chain stabilized by meso-expanded calix[4]pyrrole

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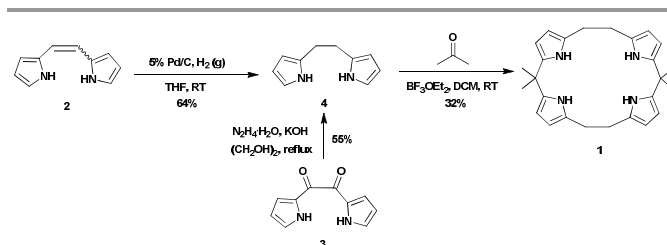
**A new core expanded calix[4]pyrrole is reported, where the opposite bridging  $sp^3$ -carbons are replaced by ethylene moieties. This macrocycle forms a unique helical pattern and binds to two water molecules that form an infinite 1D chain stabilized synergistically through hydrogen bonding with the two outwardly projected pyrrolic NHs of the calixpyrrole.**

The pre-eminence of water is mostly derived from the unique properties it possesses in pure form as well as a solvent, which are quite unusual when compared to similar molecules. Therefore, its solid state structure is of immense curiosity to researchers.<sup>1</sup> In this regard, water is found to exist in several interesting forms in the solid states and is of great interest to supramolecular chemists. Again, water in confined domains possesses dramatic structural variation and dynamics as many body effects are involved in determining the size, shape and arrangement of the water molecules. This led to a great deal of experimental and computation studies to understand its behavior.<sup>2</sup> However, one dimensional (1D) water chains are little understood and recently of great interest in order to understand key biological phenomenon like selective water transport and proton translocation through membranes by acting as a conducting wire.<sup>3</sup>

As water molecule attains optimal stability through intermolecular hydrogen bonding by acting as two hydrogen bond donors and two hydrogen bond acceptors, one dimensional water chains possess water molecules relatively at a higher energy. Although, detail structural features needed to stabilize a 1D water chain is not known, however the common attributes are strong hydrogen bonding between the neighbouring water molecules along the chain, besides additional interactions (including H-bonding) with the structural motifs associated with the water chain. This is probably due to lack of synthetic model systems containing one dimensional water chains. In 2001, Rasaiah and coworkers through molecular dynamics (MD) simulations showed spontaneous and continuous filling of a nonpolar carbon nanotube with a one-dimensionally ordered chain of water molecules.<sup>4</sup> Similarly, Won and Aluru later demonstrated again through MD simulations boron nitride nanotubes conduct water, whereas carbon nanotubes do not.<sup>5</sup> There are only few reports containing 1D water chains, for example Buchanan and coworkers reported hydrates of 1-methylimidazole-4-carboxaldehyde and 4,4'-methylene-bis(2,5-dimethylimidazole)

possess one dimensional water chains, where the water molecules are stabilized by hydrogen bonding interaction with neighbouring two water molecules in the chain and further becomes coordinatively saturated by additional H-bonding with the imidazoles.<sup>6</sup> In 2009, Ono and coworkers demonstrated a 1D columnar structure for the macrocyclic tetramer of 2-phenyl-1,3,4-oxadiazole, which was filled by 1D water chain and display very high thermal stability (upto 470 °C) due to dense molecular packing in the crystal structure.<sup>7</sup> Most of the examples containing 1D water chains are made of small molecules or metal complexes bearing strong basic or acidic functional groups.<sup>8</sup> To our knowledge apart from Ono's work, there is only one report by Kim et al. where a macrocycle possess this type of 1D water chains in their solid state.<sup>9</sup> In the latter's report, a supramolecular self-assembly of Sn(IV)porphyrin contains an 1D water chain. Again here the porphyrin moiety is endowed with relatively basic functionalities in the form of axial coordination via carboxylate bridges to two pyridine moieties. Herein, we would like to present a new macrocyclic host, namely calix[2]bispyrrolylethane, a new expanded calix[4]pyrrole moiety which could stabilize an infinite 1D water chain in its crystal lattice. In general, calix[4]pyrroles, (contains four very weakly acidic pyrrole units in its core), are well known neutral host for anions, further they also bind small polar organic molecules.<sup>10</sup> To our knowledge, this is the first example of a calix[4]pyrrole derivative stabilizing a 1D water chain.

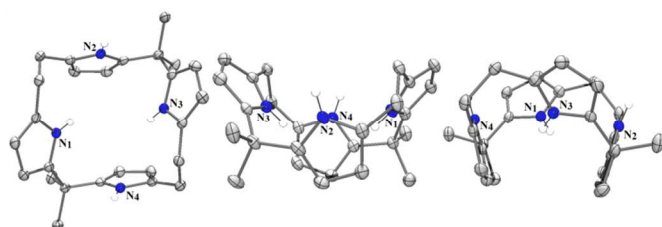
The new expanded calix[4]pyrrole was synthesized as part of our efforts towards understanding their anion binding properties with respect to core size of calix[4]pyrrole moiety, which will be reported separately. Bispyrrolylethane **4** was employed as the building block, which was synthesized following two routes (Scheme 1). Firstly, the *cis/trans* mixture of bispyrrolylethane **2**<sup>11</sup>



Scheme 1. Synthesis of meso-expanded calix[4]pyrrole 1

were hydrogenated to form compound **4** in 64% yield (characterized by all spectroscopic methods and X-ray diffraction analysis), whereas in the other route the diketobipyrrole **3**<sup>12</sup> was reduced by Wolf Kishner method to form **4** in 55% yield (ESI). Subsequently, the precursor **4** was condensed with acetone in presence of  $\text{BF}_3 \cdot \text{OEt}_2$  as the acid catalyst, to form macrocycle **1** in 32% yield. We found the former method more efficient, although it uses a slightly expensive Pd/C as catalyst, on the other hand the latter method was found convenient for scale up reaction. Overall yield from pyrrole to **1** is 10% in former route, whereas in case of latter it is 5% only.

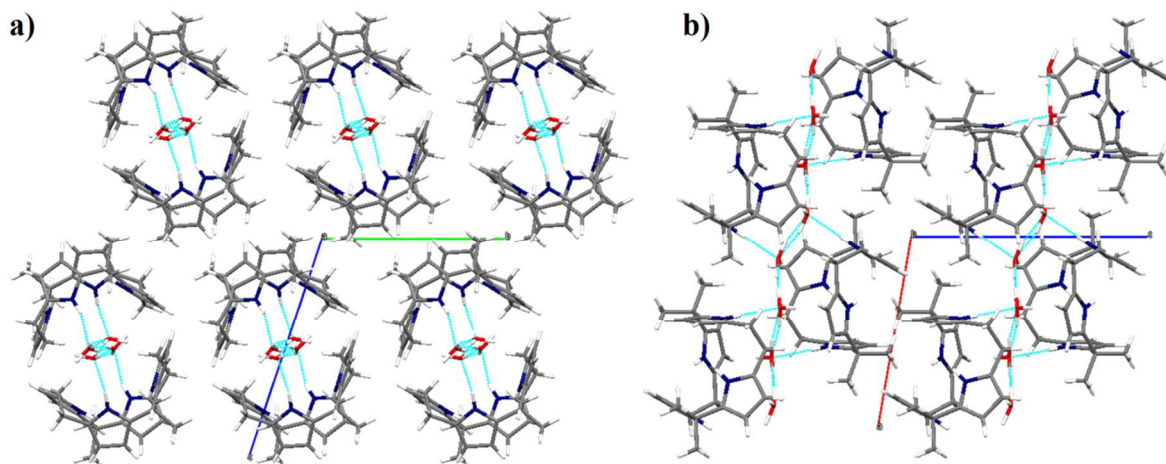
The new meso-expanded calix[4]pyrrole **1** was found to be air stable (melting point 170 °C) in spite of possessing oxidisable meso-positions and is characterized by standard spectroscopic techniques (ESI), further its solid state structure was also ascertained by X-ray diffraction analysis (Figure 1). Diffraction grade crystals for **1** were



**Figure 1.** ORTEP-POV ray diagram of **1** for representation of 1,3-alternate conformation, top view (left) and two different side views (right). Water molecules ( $2\text{H}_2\text{O}$ ), all hydrogens bound to carbon atoms are excluded for clarity and thermal ellipsoids are scaled upto 50% probability level. Color code: blue: Nitrogen, grey: Carbon, and white: Hydrogen.

grown by slow evaporation of its hexane solutions containing 10 % of ethylacetate. This macrocycle adopts 1,3-alternate conformation, with two of the opposite pyrrole units (N2 and N4) display almost orthogonal geometry w.r.t. the calixpyrrole core and the alternate NHs are directed in opposite direction w.r.t. each other [dihedral angles  $35.8^\circ$  and  $35.5^\circ$ ]. On the other hand, the remaining two pyrroles (N1 and N3) are more tilted with their NHs disposed towards the core (because of the flexible ethylene bridges). Interestingly, compound **1** was crystallized as a dihydrate (**1**· $2\text{H}_2\text{O}$ ), which exhibits a unique helical arrangement of calix[4]pyrrole water moieties stabilized around an one dimensional (1D) network of

molecules (Figure 2). While linear 1D water channels are of great interest to understand the biological water channels and proton transfer processes, to our knowledge so far there is no precedence of their formation in calixpyrrole chemistry. The strong affinity of **1** to stabilize 1D water channel could be gauged from the fact that it's crystallization from any solvent systems containing a polar solvent (viz. ethyl acetate, acetone, acetonitrile, methanol and ethanol) and hence water as an impurity, led to crystallization of the above mentioned dihydrate. The two pyrrole units of **1** hydrogen bonded with two water molecules (O1 and O2), display  $\text{N}\cdots\text{O}$  distances of 3.066 and 3.062 Å, with associated  $\text{N}-\text{H}\cdots\text{O}$  angles of  $163^\circ$  and  $171^\circ$  respectively (Figure 3). In the water chain, each water molecule acts as a donor and acceptor for hydrogen bonds with the adjacent water molecules having  $\text{O}\cdots\text{O}$  bond distances of 2.859, 2.824, 2.806 and 2.824 Å (avg. 2.828 Å), which is longer than the hexagonal ice (2.75 Å), and the average O-O-O bond angle of  $127.16^\circ$ , which is again higher than ideal tetrahedral geometry of water molecules in ice ( $109.47^\circ$ ).<sup>13</sup> Further, the first and fourth O atoms (of water molecules) of the water chain are hydrogen bonded with the two orthogonally oriented pyrrolic-NHs (N2 and N4) of each calix[4]pyrrole like a strap, whose other two inwardly disposed pyrrolic-NHs (N1 and N3) remain free of any H-bonding (Figure 3). In addition, each water strapped calixpyrrole moiety is connected via another hydrogen bond of the water chain ( $\text{O}\cdots\text{O}$  bond distance 2.824 Å) to extend the network, and those two oxygen atoms, on the other hand are hydrogen bonded to one of the pyrrolic-NH of two calixpyrrole units separately (Figure 3), to form the helical network of expanded calix[4]pyrrole **1** synergistically stabilized by the zig-zag 1D water channel. This clearly reflects the three coordinated nature of the oxygens in the 1D water chain and hence stabilization of the energetic water molecules by **1**. In the 1D water chain, each oxygen atom coordinated with three hydrogen atoms and these are positionally disordered (pseudo C2) in which one of the hydrogen (H33 for O1, H35 for O2) not involved in hydrogen bonding treated as full occupancy, and the other two (H34A, H34B for O1, H36A, H36B for O2) are involved in strong hydrogen bonding with the oxygen atom (acting as donor and acceptor simultaneously), treated as half occupancy during refinement. Overall, the 1D water chains resemble an infinite wave in the channel created by the helical arrangement of macrocycle **1**.



**Figure 2.** Crystal packing diagram of **1**·( $2\text{H}_2\text{O}$ ): capped sticks view along a-axis (left) and along b-axis (right)

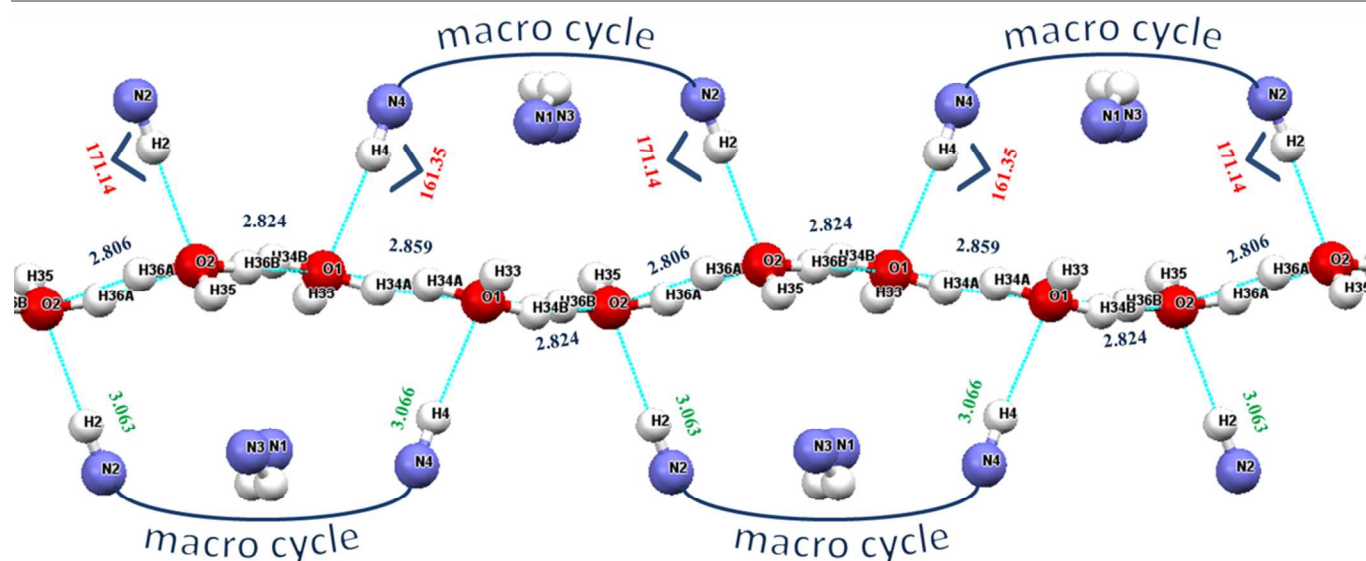


Figure 3. Ball and stick view of **1**•(2H<sub>2</sub>O) showing hydrogen bond angles and distances associated with 1D-water channel.

Elemental analysis also confirms the presence of two water molecules in the crystals of the expanded calix[4]pyrrole macrocycle **1** (ESI). To check the stability of the water chain, we have performed thermo gravimetric analysis (TGA) experiments on the crystals. DTA-TG was measured at the scanning rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. A change of 7.24 % in mass was observed at 80-140 °C, which is close to the calculated value 8.25 % for the formula (**1**•2H<sub>2</sub>O) and the presence of one endotherm, indicates the water loss is gradual. Under the similar condition about 1-3 % weight loss was observed for powder sample, which may be attributed to presence of some associated water in normal powder form for self-assembly and/or the probable presence of crystals in micro/nano size. Further, variable temperature powder X-ray analysis performed on the crystals of compound **1**•2H<sub>2</sub>O shows the probable loss of water beginning by 80 °C and the process is not reversible in the solid/molten state (ESI). The relatively greater affinity for water by the expanded calix[4]pyrrole and hence greater stability in the crystal owing to this unique molecular arrangement is reflected in the relatively higher melting point of the crystal (178-180 °C) than the bulk sample (170-172 °C). This again reflects on the uniqueness of the structure of the expanded calix[4]pyrrole and the synergy involved in the stabilization of the crystal structure of **1**•2H<sub>2</sub>O.

## Conclusions

A new expanded calix[4]pyrrole is synthesized, which forms a helical pattern in the crystal lattice stabilizing an infinite one dimensional water chain through hydrogen bonding via two of its alternate outwardly projected pyrrolic NHs and without any precedence in calixpyrrole chemistry. While self-assembled dimers in the solid state, by functionalized calixpyrroles are reported earlier by Sessler and recently by our group,<sup>14</sup> this type of unique structural attribute of the expanded calixpyrrole **1** provides a new vista for the host guest chemistry of this class of macrocycles in solid state. Further, this system in particular can

be a potential synthetic model for water/proton transport for the helical membrane proteins possessing 1D water chains.

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## Notes and references

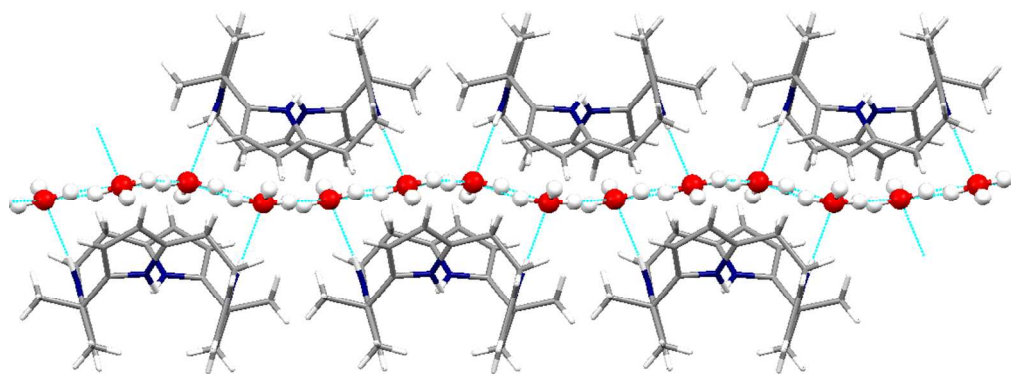
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<sup>†</sup> Electronic Supplementary Information (ESI) available: [Experimental details with characterization data; CCDC 1007110 (**1**), 1007111 (**4**) contain the supplementary crystallographic data, packing diagrams showing 1D-water chain, DTA-TG analysis etc.] See DOI: 10.1039/c000000x/

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