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# Triangle amine artificial channels for selective water purification

Elettra XRD1

Water scarcity is a growing threat worldwide, affecting billions of people due to factors like climate change and rising populations. Traditional methods of obtaining fresh water can be taxing on resources. However, advancements in purification and membrane technologies offer a glimmer of hope. These new methods can treat unconventional sources like seawater and wastewater, while also using less energy or relying on renewable sources like solar power. This technological leap could be a game-changer in providing clean water for people and agriculture in water-stressed regions.

A promising approach involves biomimetic technologies, specifically artificial water channels (AWCs), which emulate nature's energy-efficient desalination processes. Nature's ingenuity provides inspiration for designing innovative, efficient, and cost-effective desalination technologies. Aquaporins (AQPs) are protein-based membrane channels that regulate cellular osmotic pressure by efficiently transporting water across membrane bilayers while excluding hydrated ions (salts) and protons. With exceptional selectivity and high water transport rates (approximately  $10^9$  H<sub>2</sub>O molecules/second/channel), AQPs have garnered significant interest in both academia and industry. Efforts have been made to incorporate them into artificial membranes for various water purification applications, including medical and desalination uses.

However, creating AQP-based membranes presents challenges due to their low stability under the high pressure and salinity conditions typical of desalination processes. As an alternative, bioinspired AWCs have been developed to overcome these limitations. AWCs offer several advantages, including lower production costs, high tunability, stability, and compatibility with membranes, as well as high pore packing density, which enhances membrane permeability.

Since 2011, our team in Montpellier, France, has proposed various efficient artificial water channels, including the I-quartet and systems based on pillar[5]arenes. However, only a few channels can translocate water with complete salt rejection, and achieving high water versus ion/proton selectivity remains a significant challenge in designing novel AWCs. In this study, we have investigated the use of trianglamine macrocycles for AWCs. These molecules offer several advantages, including easy fabrication, purification, and scalability at relatively low cost, making them excellent candidates for constructing artificial aquaporins.

We have succeeded in manufacturing AWCs from self-assembled alkyl-ureido-trianglamines that achieve a single-channel permeability of  $\sim 10^8$  water molecules/second/channel, which is within 1 order of magnitude lower than AQPs with good ability to sterically reject ions and preventing the proton transport. In order to understand the mechanism of water transport we have investigated the self-assembly in the solid state by single-crystal x-ray diffraction experiments of alkyl-ureido-trianglamine macrocycles  $\Delta$  and  $\Delta C4$  (Figure 1a). The quality of the crystals being inherently poor, we had to rely for a part of the structure determinations on synchrotron radiation at the XRD1 beamline of the Elettra synchrotron. The flexibility of the alkyl chains causes conformational disorder leading to poor and often non-atomic resolution in addition to the presence of solvent disorder. Most carbon atoms could be located in difference Fourier maps, but could not freely be refined. The distances and angles between the carbon atoms were therefore restrained to their ideal  $sp^3$  values and similarity and vibrations restraints were also applied during the refinements. A central water oxygen within the triangular core of the structures could easily be located from the difference Fourier maps, but the hydrogens were added in calculated positions as to make one possible hydrogen bond motif with the

triangles nitrogens and oxygens. In reality the water molecule displays rotational disorder around an axis perpendicular to the triangular plane. The structure of the reference triangleamine  $\Delta$  could easily be determined from data obtained with a laboratory x-ray source, but for butyl-ureido-triangleamine  $\Delta C4$  synchrotron data were required followed by elaborate modeling of the six alkyl-ureido side chains.

The six butyl-ureido groups are attached to the triangleamine backbone, resulting in a “bouquet”-like conformation. Each side chain contains three amide groups, with two N–H donor groups and one C=O acceptor group. Three of them form optimal hydrogen bonds with a water molecule situated in the pocket created by the lateral arms (Figure 1b). This interaction causes the central phenyl segment's triangular backbone to constrict towards the narrowest twisted water-binding pores, which have a diameter of 3 Å and are surrounded by larger hydrophobic pockets of 5 Å diameter between the macrocycles. The other three lateral arms adjust to connect with neighboring arms, linking different triangleamines and forming a network of four water channels in the solid state. This network is assembled through hydrophobic packing of cyclohexane rings of monomers at the center of the tetramer, resembling the human AQP1 tetrameric structure (Figure 1c). This biomimetic directional pore features a combined size restriction hydrogen-bonding pore and a larger hydrophobic pocket, similar to natural AQPs. It selectively allows water molecules to pass rapidly through the structure while rejecting hydrated cations. Notably, this structure prevents the formation of water wires in the solid state, which is an important feature for proton rejection as seen in AQPs.

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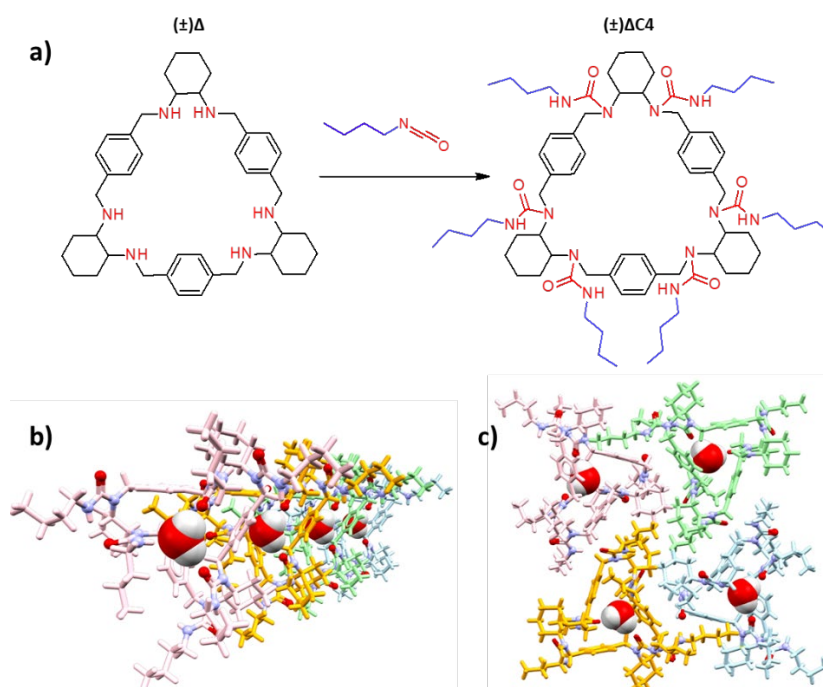


Figure 1: (a) Chemical structures of  $(\pm)\Delta$ , and  $(\pm)\Delta C4$ . Similar structures with longer alkyl chains have been synthesized and characterized and are discussed in the original paper; (b) Channel type packing of  $(\pm)\Delta C4$  composed of external hydrophobic moieties and twisted 3 Å triamide H-bonding pores encapsulating water; (c) Tetrameric crystal packing of alkyl-ureido-triangleamine channels, resembling the tetrameric protein structure of human AQP.

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