Fast Water Nanochannels with a Densely Fluorous Interior Surface

Background and Significance

In 2003, the Nobel Prize in Chemistry was awarded to several biologists for their work on aquaporins(AQPs Family, Fig.1) and ion channel proteins.[1] The fact that natural channel proteins have won awards has inspired the development of synthetic chemistry, specifically macrocycle, synthesis, and nanochannels. Using macrocyclic molecules as selective water/ion channels and surpassing natural channel proteins in performance has become the goal of scientific research and industry. Fig.2 shows a fluorous oligoamide nanoring from the Aida group. It is a nanochannel with an incredible rate of water passing and selectivity.[2] In this proposal, we plan to develop a new nanochannel that is both highly fluorinated and suitable diameter to break water clusters, leading to a densely interior surface and allowing for water permeation while the anion is impenetrable.

The fluorous polymer polytetrafluoroethylene (PFTE) provides a distinct superhydrophobic surface on which densely packed carbon-fluorine (C–F) bonds repel water.[2] Nevertheless, individual C–F bonds are highly polar and can interact electrostatically with polar functional groups to form hydrogen bonds.[3] This notable bilateral characteristic—known as polar hydrophobicity—can be attributed to the properties of fluorine, which include the largest electronegativity and the second smallest atomic size among all elements.[4]

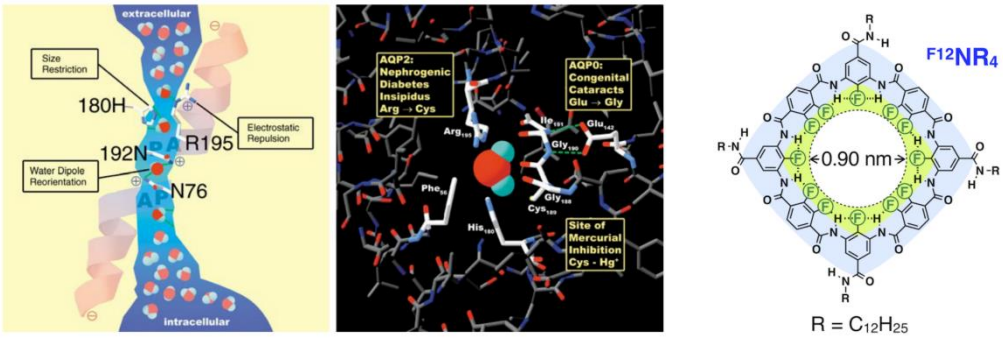
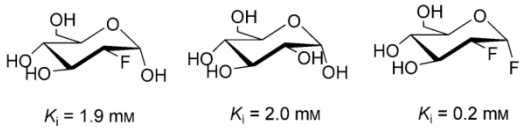


Fig.1, Examples of AQPs Family; Fig.2, Aida's

The core of the Proposal: Polar Hydrophobicity

If an enzyme has an H-B receptor site, in general, A hydrogen-bond acceptor results in decreased free energies of binding (higher inhibition constant (K_i) values) for the fluorinated carbohydrate. However, in yeast hexokinase, which has an H-B receptor site and a hydrophobic cavity, the corresponding monofluorinated derivatives had a greater affinity for the respective enzymes than D-glucose difluorinated derivatives had even more. [5] (Fig.3) Recent reports based on Raman spectroscopy showed that water clusters in the vicinity of fluorous compounds break to yield many hydroxy dangling bonds. In contrast, considerably fewer dangling bonds are generated with hydrocarbon analogs.[6] (Fig.4) This observation suggests that nanochannels with a densely fluorous interior surface can inhibit the formation of water clusters that diffuse more slowly than non-clustered water molecules.[7]

We hypothesize that by utilizing a highly fluorinated nanochannel, we could achieve water permeation while the anion is impenetrable.



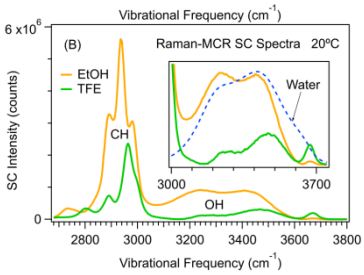


Fig.3, D-glucose derivatives to yeast hexokinase inhibition constant; Fig.4, Raman spectroscopy for TFE and EtOH

Design of Highly Fluorinated Nanochannel

From Amar H. Flood's work, we learned a very effective reaction and impressive structure (CyanoStar) with a high yield.[8] (Fig.5) Similarly, we use substrate derivatives to perform this reaction. (Fig.6, besides, the R group should be a long hydrocarbon chain to achieve dissolution within the phospholipid membrane) In Aida's work, all the fluorine atoms in the optimized structures were suggested to point inward to form intramolecular "C–F···H–N" H-bonds,[2] While in our proposal, the conformation is Spontaneous fixation due to the π properties of the double bond making it difficult to rotate. Fig. 7 shows the proposed molecule's most stable conformation via MM Optimization, showing that the fluorous atoms are all pointing inward.

Apart from this, a dominant factor for AQPs and CNTs to permeate water faster is that their interior diameters [~0.3 nm[9] and ~0.4 nm[10], respectively] are smaller than those of the water clusters (~0.8 nm) [11]. The cluster-breaking function of AQPs and CNTs can also be accomplished in this nanochannel to permeate water. The CS macrocycle has a pseudospherical shape and a diameter of 4.5[8]. The interior diameter is also smaller than those of the water clusters (~0.8 nm) [11].
Since the interior surface is highly fluorinated, thus **we hypothesize the electronic density of the internal cavity is also high enough to inhibit anions such as chloride ions.** We can demonstrate this hypothesis employed carboxyfluorescein (CF).[13]

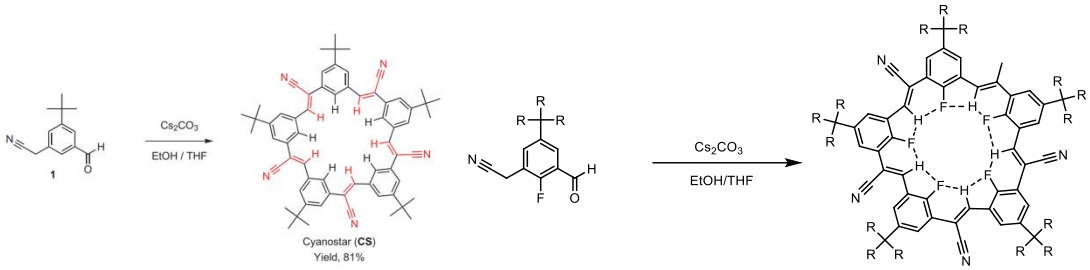


Fig.5, Amar's work; Fig.6, Our Design Reaction

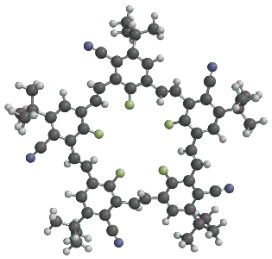


Fig.7, Proposed molecule's most stable conformation via MM Optimization

Summary

By polar hydrophobicity and size cluster-breaking function, the proposed nanochannel would have fast water permeation and good ion inhibition since it is generally believed that when anions cannot pass through, cations cannot pass through either. **Our proposed approach aims to design faster water nanochannels with a much higher yield, which is extremely useful in industry.**

References:

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