

Exploring the Potential of Doped Zero-Dimensional Cages for Proton Transfer in Fuel Cells: A Computational Study

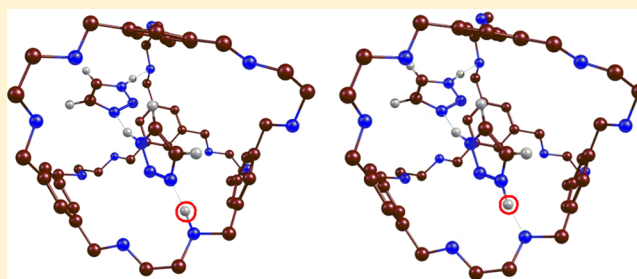
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S Supporting Information

ABSTRACT: Calculations with density functional theory (DFT) and MP2 have been done to investigate the potential of recently synthesized durable zero-dimensional (0D) nitrogen-based cage structures to perform as efficient proton-exchange membranes (PEMs) in fuel cells. Our calculations suggest that the hydrogenated 0-D cages, in combination with hydrogen-bonding 1,2,3- and 1,2,4-triazole molecules, would perform as highly efficient PEMs. The results are important in the context of the need for efficient PEMs for fuel cells, especially at higher temperatures (greater than 120 °C) where conventional water-based PEMs such as Nafion have been found to be ineffective.



INTRODUCTION

Fuel cells are considered a promising alternative energy conversion device. Their promise lies in their essential “green-ness”—they generate water, heat, and electricity without emitting pollutants, with hydrogen as the fuel and the oxygen in the air as the oxidant.^{1–3} The most important component of the fuel cell is the electrolyte that lies at the “heart” of the fuel cell.⁴ The electrolyte separates the anode and cathode and conducts a specific ion at very high rates during the operation of the fuel cell.

Among the various fuel cell types, proton-exchange membrane fuel cells (PEMFCs) are a type of fuel cell where proton-conducting membranes, or proton-exchange membranes (PEMs), are used as the electrolyte. The PEMFC that is most well-known is Nafion,⁵ a sulfonated tetrafluoroethylene-based fluoropolymer–copolymer, whose chemical structure is shown in Figure 1. This PEM operates best at temperatures below 80 °C, because Nafion functions in conjunction with water molecules, with the proton transport taking place through different processes—the vehicular mechanism⁶ or the Grotthuss mechanism^{4,7–13}—that require the use of the water as a medium for aiding the transport of the proton. Since, at

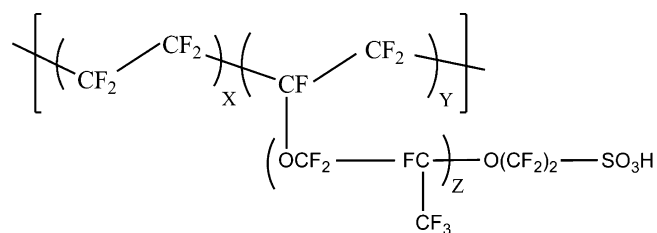


Figure 1. Chemical structure of Nafion.

temperatures above 80 °C, the chances of water evaporating increase, this reduces the efficiency of Nafion.

The inability of Nafion to function at temperatures above 80 °C has resulted in a search for new PEMs that can function at higher temperatures: specifically, those that can function at temperatures greater than 120 °C. This is because there are several applications where it might become necessary to operate the fuel cell at elevated temperatures. Moreover, under high-temperature conditions, catalyst poisoning from carbon monoxide (CO) impurities in fuels becomes less serious because the catalyst activity is improved at elevated temperatures. This enables the use of fuels with less stringent purity requirements. Therefore, several attempts have been made to operate fuel cells at higher temperatures using PEMs that are durable and efficient at higher temperatures. Different proton-conducting media and alternative polymer membranes have been proposed, developed, and tested. These include the use of alternative proton conduction media such as phosphoric acid and phosphonic acid¹⁴ and membranes such as polybenzimidazole.^{15,16} However, despite such progress, a PEM that can exhibit both high durability and high proton conductivity rates has not yet been found. Hence, there is still considerable interest in the development of novel, improved membranes for PEMFCs.

The objective of the current work is to propose a new material for use as a PEM and investigate its potential for efficient proton transfer, using computational methods. The material in question is a porous cage network that has been recently synthesized by Tozawa et al.¹⁷ This zero-dimensional

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(0-D) cage structure (shown in Figure 2) contains four phenyl rings separated by amine groups and will henceforth be referred

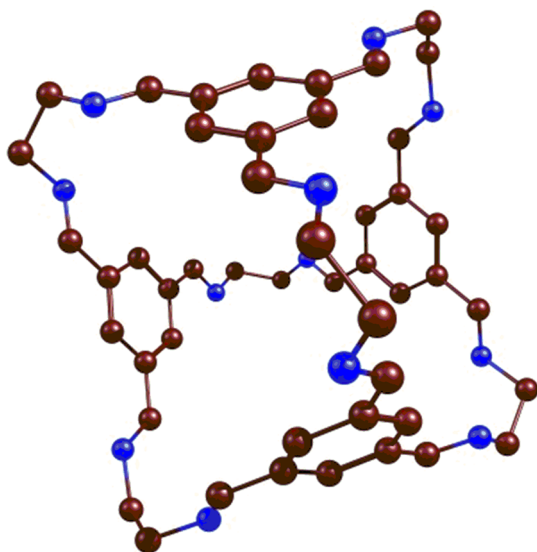


Figure 2. Recently synthesized zero-dimensional N-cage structure; the color scheme is as follows: carbon, brown; nitrogen, blue. The hydrogen atoms are not shown for the purpose of clarity.

to as “N-cage”. The N-cage structure has been found to exhibit good thermal stability, with the onset of decomposition having experimentally been observed only at temperatures above 300 °C.¹⁷ Each cage molecule contains 12 N=C imine double bonds. Calculations, which are discussed in the Results and Discussion section, indicate that these imine bonds can be easily hydrogenated to yield a saturated structure that will henceforth be referred to as “N-cage-H₂”. It is postulated that the saturated N-cage-H₂ structure, when combined with a dopant base that has the ability to exchange protons, can become an excellent candidate for PEMFCs. This is because of the possibility of forming hydrogen-bonded networks between the hydrogenated zero-dimensional cage structure and the dopant molecules that can reside inside the porous cages. Recent studies¹⁸ indicate that the formation of dynamic hydrogen bond networks within the membrane is an important prerequisite to high proton conductivity. Hence, it is likely that porous, doped N-cage-H₂-like zero-dimensional structures, which can accommodate many dopant molecules and which have 12 nitrogens in each cage that can be protonated, can become excellent candidates for the role of proton-exchange membranes in fuel cells.

The focus of the current work is to investigate this possibility through (DFT)/MP2 calculations. The favorability of making the N-cage-H₂ structure has first been investigated by studying the thermodynamic ease of the reaction between H₂ and the N-cage molecule. The potential of N-cage-H₂ to function as a PEM has then been studied by calculations on a system having N-cage-H₂ along with (i) phosphoric acid, (ii) imidazole, and (iii) triazole molecules in the porous cage structure. Investigations have been done to determine the feasibility of each of these dopants acting as an effective counterpart to N-cage-H₂ for proton transfer. Finally, the most promising of the three has then been considered for further calculations to determine the barrier to intermolecular proton transfer from the cage to the dopant and back to the cage.

■ COMPUTATIONAL DETAILS

All DFT calculations were performed using the Turbomole 6.0s programs.¹⁹ Geometry optimizations were performed using the Perdew, Burke, and Ernzerhof density functional (PBE).²⁰ The electronic configuration of the atoms was described by a triple- ζ basis set augmented by a polarization function (Turbomole basis set TZVP). The resolutions of identity (RI)²¹ along with the multipole accelerated resolution of identity (marij)²² approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. In order to improve the calculation of the energy values, a further correction was made through single-point MP2 calculations,²³ along with the RI approximation, for the DFT (PBE)-optimized structures. With regard to the transition states obtained during the investigations of the proton-transfer process, care was taken to ensure that the obtained transition-state structures possessed only one imaginary frequency corresponding to the correct normal mode.

That this approach, described above, provides reliable results has been further validated through benchmarking calculations done by comparison to previously published proton transfer barriers. As Figure S1 in the Supporting Information indicates, the potential energy (ΔE) surface published by Li et al.²⁴ reporting calculations done at the B3LYP/6-311+G(d)/MP2/ccpVTZ level of theory for the proton-transfer reaction in the 1,2,3-triazole–triazolium dimer matches almost exactly with the calculations that we have done at our aforementioned RIPBE/RIMP2 level of theory (see Figure S1 in the Supporting Information). Furthermore, using our RIPBE/RIMP2 computational approach, we have redone the calculations for determining the proton-transfer barriers (ΔE) for the imidazolium–imidazole (ImH⁺–Im), 1,2,3-triazolium–1,2,3-triazole (TrH⁺–Tr), and tetrazolium–tetrazole (TeH⁺–Te) complexes that have been published by Mangiatordi et al.²⁵ using a full MP2 approach. The results are shown in Table S1 in the Supporting Information and indicate practically no difference between the values obtained through the two different approaches. Thus, these validating benchmarking calculations indicate the reliability of the computational approach employed in our work.

The contributions of internal energy and entropy were further obtained from frequency calculations done on the optimized structures at 298.15 K in order to obtain the ΔG values that are discussed in the paper (see Figures 9 and 11 below). It is to be noted that important energy contributions such as the contribution of the zero point energy correction (ZPE) to the internal energy, which takes into account nuclear quantum effects are also included through the frequency calculations. It is further noted that there is the possibility of tunneling that might occur in such systems, since the proton transfer involves the movement of the light proton moiety from one atom to another. Such possible tunneling effects have not been considered in the current study.

■ RESULTS AND DISCUSSION

Proton Transfer through N-Cage in Tandem with H₃PO₄. The N-cage structure was optimized using the input obtained from a crystal structure.¹⁷ The addition of 12 molecules of H₂ to this structure would lead to the hydrogenated “N-cage-H₂” structure through the hydrogenation of the 12 imine moieties in the cage. The optimized

structure of the N-cage- H_2 is shown in Figure 3. The ΔG for the formation of the N-cage- H_2 is -72.8 kcal/mol, which

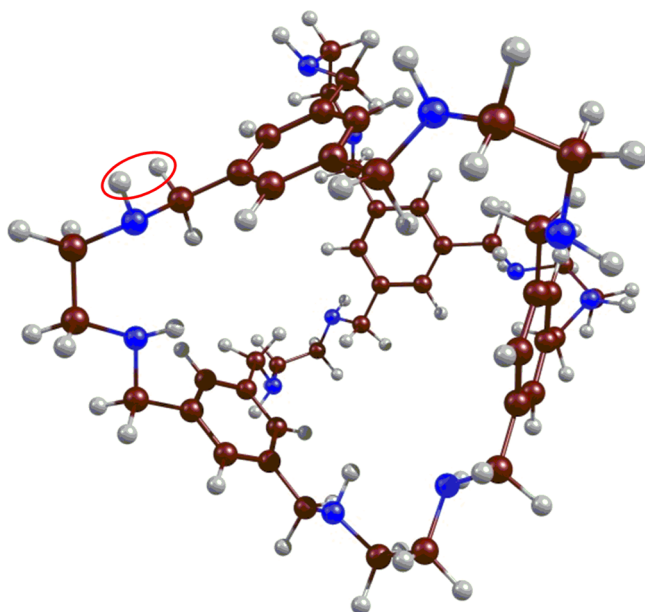


Figure 3. Zero-dimensional cage structure where all the imine groups in the cage have been hydrogenated: N-cage- H_2 ; an N–C bond is circled in red to indicate one of the 12 imine groups that have been hydrogenated; the color scheme is as follows: carbon, brown; nitrogen, blue; hydrogen, gray.

indicates the favorability of the reaction. Further calculations were done to explore the addition of molecules of the dopant X (where X = phosphoric acid, imidazole, and triazole) to N-cage- H_2 . The addition of two molecules of X was found to lead to the formation of a hydrogen-bonded network between the two dopant molecules and N-cage- H_2 (see Figures 4, 5, and 6). This system “[N-cage- H_2][2X]” will be considered as the model for studying the possibility of proton transfer through the cage. It is noted here that larger models can also be considered by the addition of more dopant molecules into the porous cage, and, therefore alternative proton-conducting routes can also be investigated connecting other amine nitrogens in the cage. However, the purpose of the current investigation is to illustrate the efficiency of the proton-transfer process for a given, representative hydrogen-bonded network formed between the cage and the dopant molecules, and the [N-cage- H_2][2X] model adopted here is adequate for this purpose.

In order to investigate the energetics of proton transfer through this [N-cage- H_2] network, the first study conducted is as follows: the structures of [N-cage- H_2][2X] were optimized with the addition of a proton: that is, the structures optimized were [N-cage- H_2][2X][H] $^+$. During the optimization procedure, two structures were considered—one where the proton was placed on the amine nitrogen on the cage and the other where the proton was placed on the adjacent, hydrogen-bonding dopant molecule, X. This procedure yielded the following interesting results for the three cases considered:

- (i) For the case where the dopant employed was phosphoric acid, only one final optimized structure was obtained, even though two different structures had been considered, as mentioned above. In this final, optimized structure, the proton was found to be on the amine

nitrogen of N-cage- H_2 . This optimized structure is shown in Figure 4—the proton is circled in red in the

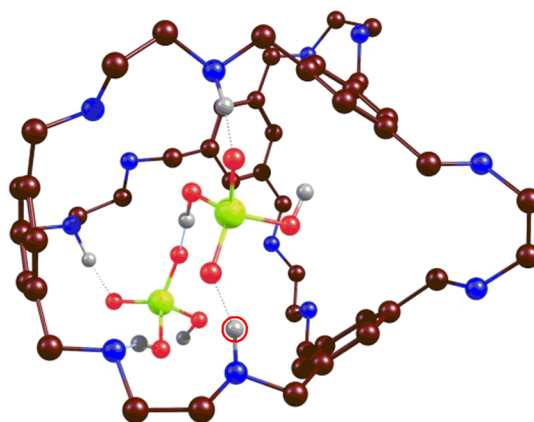


Figure 4. Optimized structure where the proton, circled in red, is always found to be situated on the amine nitrogen of the cage; the color scheme is as follows: carbon, brown; nitrogen, blue; hydrogen, gray; phosphorous, green-yellow; oxygen, red; only a few hydrogen atoms that take part in the hydrogen-bonding network have been shown, for the purpose of clarity.

structure. All attempts to start with different input conformations in order to obtain a geometry where the proton was stable on the phosphoric acid proved unsuccessful. This result indicates that, if phosphoric acid is employed as the dopant in the N-cage- H_2 structure, it will fail to remove the proton from the cage. It is pertinent to note in this regard that if the hydrogenation of the cage was done in an alternate fashion: if one of the carbons of the phenyl ring and a nitrogen of an adjoining imine group,²⁶ which can act as “a frustrated Lewis pair”, were to be hydrogenated in preference to the N=C bond, then calculations indicate that such a hydrogenated cage would be able to transfer a proton to the hydrogen-bonded network formed by the two phosphoric acid molecules. However, such an alternative hydrogenation pathway may only exist for certain hydrogenating agents such as ammonia borane. For the remaining cases, it is likely that the 12 N=C bonds in N-cage would be preferentially hydrogenated. Hence, the calculations indicate that for such structures the phosphoric acid would not be a good dopant: even though it would be able to form a hydrogen-bonded network, it would fail to be an effective counterpart to the cage in doing a proton transfer.

- (ii) For the case where the dopant employed was imidazole, the situation was found to be exactly reversed. For this case, it was seen that the proton remained only on the imidazole molecule in all the optimized structures. This is shown in Figure 5: the proton is circled in red and is seen to remain only on the nitrogen of the imidazole moiety. All attempts made to obtain optimized structures where the proton was transferred on to the nitrogen of the cage proved unsuccessful: the proton was found to be only stable on the imidazole in all the cases. Hence, this result indicates that imidazole would also fail to be an effective counterpart to N-cage- H_2 for proton transfer.
- (iii) For [N-cage- H_2][2X][H] $^+$, the final case discussed is X = triazole. For triazole, two possible isomers exist, 1,2,3-

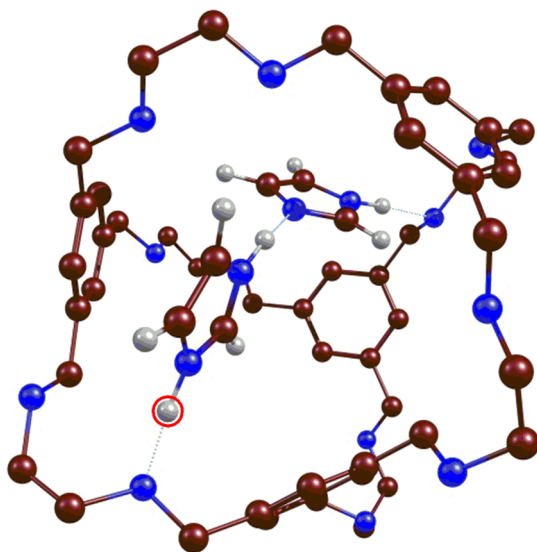


Figure 5. Optimized structure where the proton, circled in red, is always found to be situated on the nitrogen of the dopant imidazole; the color scheme is as follows: carbon, brown; nitrogen, blue; hydrogen, gray; only a few hydrogen atoms that take part in the hydrogen-bonding network have been shown, for the purpose of clarity.

triazole and 1,2,4-triazole, and the formation of a protonated hydrogen-bonded network, $[\text{N-cage-H}_2]\text{-}[2\text{X}][\text{H}]^+$, is possible for both isomers. Both 1,2,3-triazole²⁷ and 1,2,4-triazole²⁸ have been experimentally employed as dopants in proton-conducting studies with proton-exchange membranes. What is discussed in this section are the results for $\text{X} = 1,2,3\text{-triazole}$, with the results with 1,2,4-triazole being discussed in a later section. Figure 6 shows the structures obtained for this dopant: it was found that two structures could indeed be obtained for this case, one where the proton was stable on the cage and the other where the proton (circled in red in the figure) was stable on the nitrogen of the 1,2,3-triazole. Hence, the calculations suggest that, of the three dopants, it is triazole that would be most effective in participating in proton exchange with $[\text{N-cage-H}_2]$ to make an effective proton-exchange membrane.

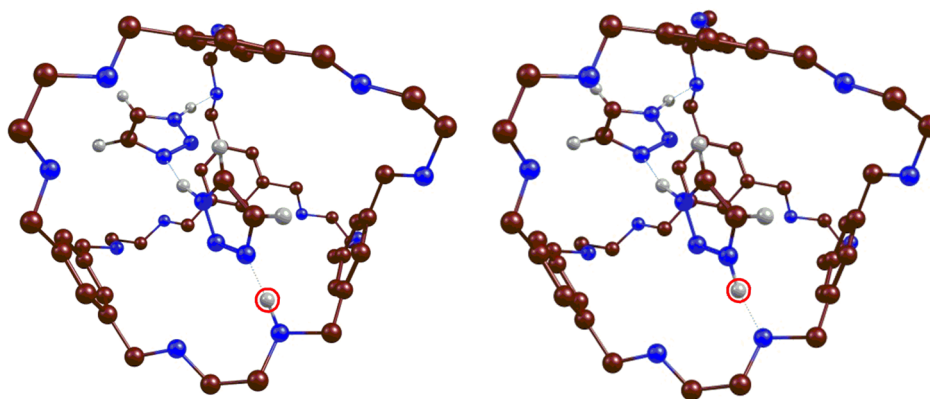


Figure 6. Two optimized structures that have been obtained for the cage doped with 1,2,3-triazole, with the proton, circled in red, present on both the cage and the dopant; the color scheme is as follows: carbon, brown; nitrogen, blue; hydrogen, gray; only a few hydrogen atoms that take part in the hydrogen-bonding network have been shown, for the purpose of clarity.

The reason for the difference in the proton abstraction behavior of the three dopants in the $[\text{N-cage-H}_2][2\text{X}][\text{H}]^+$ model lies in the difference in the ability of the dopant molecule to stabilize the positive charge of the proton. The following calculation makes this point more clear: the structures X and $[\text{XH}]^+$ were optimized for $\text{X} = \text{phosphoric acid}$, imidazole and 1,2,3-triazole, and the difference in the stability between the protonated and neutral species is shown in Figure 7. As the

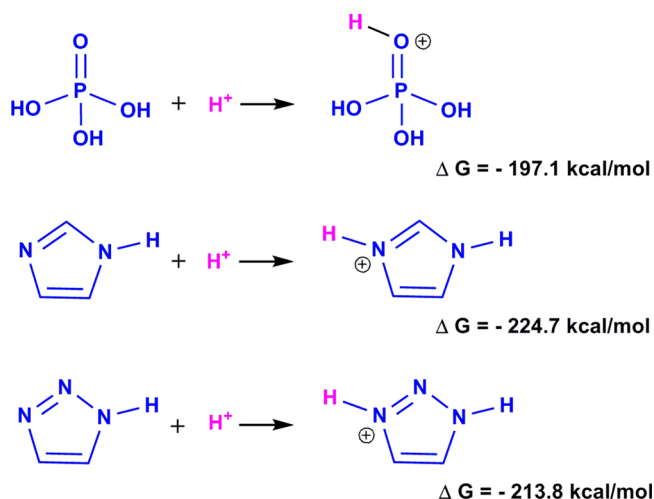


Figure 7. Free energies for the protonated phosphoric acid, imidazole, and 1,2,3-triazole dopants.

figure indicates, the protonated structure is more stable in all the three cases. However, the dopant that is most effective in stabilizing the proton is imidazole, followed by 1,2,3-triazole, with phosphoric acid predicted to be the least effective. The reason for this trend is the difference in the basicities of the three moieties. As has been experimentally determined by Meotner et al.,²⁹ triazoles have lower proton affinity as compared to imidazole. This difference in the proton affinity, and therefore the basicity between imidazole and triazole, explains why the proton is too stabilized with imidazole as the base and cannot be “recaptured” by the nitrogen of the cage, while the lower basicity of triazole allows the proton to be stabilized by both the cage and the triazole moiety. It is noted here that there are several other bases whose proton affinities (ΔH values) have also been experimentally determined.²⁹ As

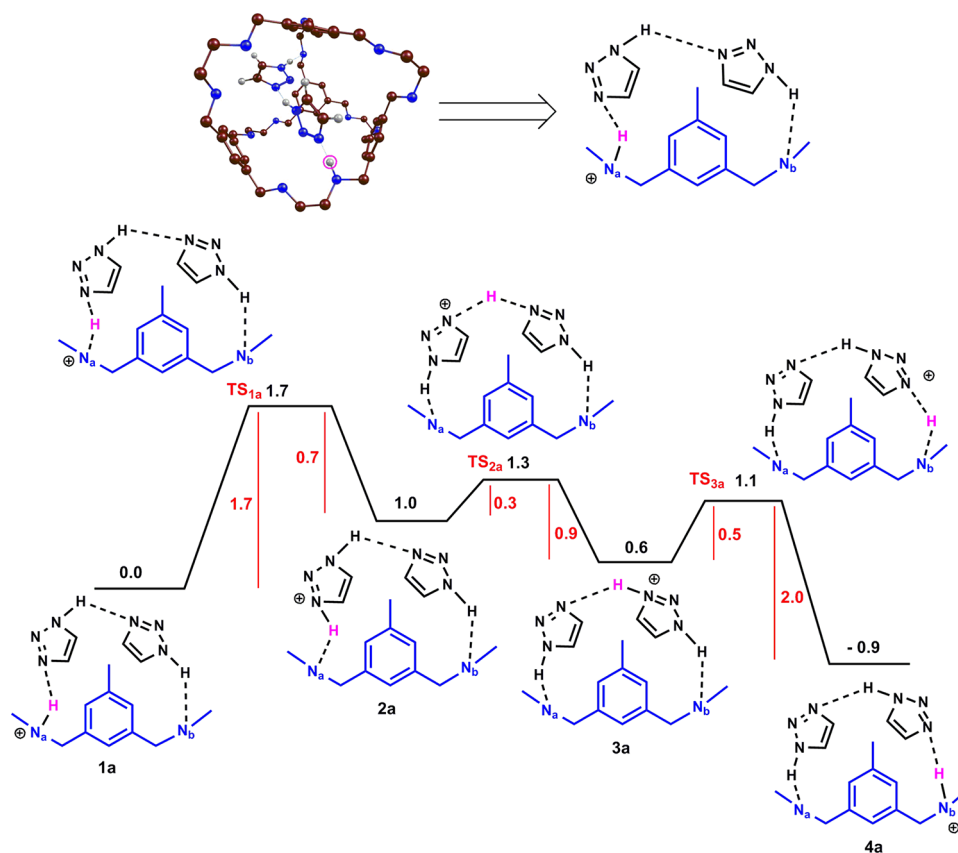


Figure 8. Potential energy for the transfer of the proton through the hydrogen-bonded network from one end of the cage to the other, and the dopant employed in 1,2,3-triazole. All values (ΔE) are in kcal/mol.

Table S2 in the Supporting Information indicates, the current calculations provide values close to the experimentally obtained ΔH values, in addition to faithfully reproducing the observed experimental trend in the proton affinities.

Hence, the above discussion indicates that bases with intermediate basicities such as 1,2,3-triazole would be the best choice as a dopant for $[\text{N-cage-H}_2]$: they can abstract the proton from the nitrogen of the cage, while not binding too strongly to it so as to allow the cage to abstract it back, thereby making for a good proton-exchange pair with the cage. This intermediate value obtained for 1,2,3-triazole also suggests a guide for choosing other dopants in the future: if a base is to be considered as the counterpart to hydrogenated zero-dimensional cage structures such as $[\text{N-cage-H}_2]$, then the difference in the stability between the protonated and neutral species for such a molecule should fall in the range indicated by 1,2,3-triazole: $\Delta G = -213.8$ kcal/mol for the reaction: $\text{X} + \text{H}^+ \rightarrow [\text{XH}]^+$. Since our calculations indicate that the ΔG and the ΔH values for the reaction $\text{X} + \text{H}^+ \rightarrow [\text{XH}]^+$ are quite similar, as the entropic change in adding a proton is very small, ΔH values, that is the proton affinity, of bases in the vicinity of -213.8 kcal/mol would be a good guide as to which bases would act as good dopants for the zero-dimensional cages such as $[\text{N-cage-H}_2]$ for the purposes of proton transfer in fuel cell membranes. A perusal of the proton affinity values determined experimentally²⁹ therefore indicates that 4-methylimidazole (-224.8 kcal/mol), 1-methylimidazole (-228.0 kcal/mol), pyrazole (-212.8 kcal/mol), and others with similar proton affinities would also be good dopants for $[\text{N-cage-H}_2]$.

Having identified the triazoles as good dopants for the zero-dimensional cages, it was also necessary to determine the ease with which the proton could move between the cage and the base, since that would determine the efficiency of the proton conduction process if such doped cages were to be employed as fuel cells. Discussed in the next section is the potential energy surface obtained for the proton-transfer process from the cage to the hydrogen-bonded triazole network and back to the cage.

Proton Conduction Studies. Figure 8 shows the energy profile (ΔE values) for the transfer of a proton from a nitrogen of $[\text{N-cage-H}_2]$ to the hydrogen-bonded 1,2,3-triazole, from that triazole molecule to the adjoining hydrogen-bonded triazole moiety and then from the second triazole back to another nitrogen atom of $[\text{N-cage-H}_2]$. The barriers for these three proton-transfer processes have been calculated using transition state theory. Frequency calculations were done in order to ensure that the obtained transition-state structures contained only one negative frequency corresponding to the correct normal mode.

As Figure 8 indicates, all the three transition states obtained corresponded to very low barrier reactions. TS_{1a} , which corresponds to the first transfer of the proton from the nitrogen of $[\text{N-cage-H}_2]$ (structure 1a, see Figure 8) to the nitrogen of 1,2,3-triazole (leading to the structure 2a, see Figure 8), has the highest barrier for the entire proton transfer cycle. This barrier is found to be only 1.7 kcal/mol (ΔE value), which indicates that the proton transfer would be facile, with the efficiency for the process likely to be high at higher temperatures. The other two barriers, TS_{2a} and TS_{3a} , corresponding to the transfer of the proton from one 1,2,3-

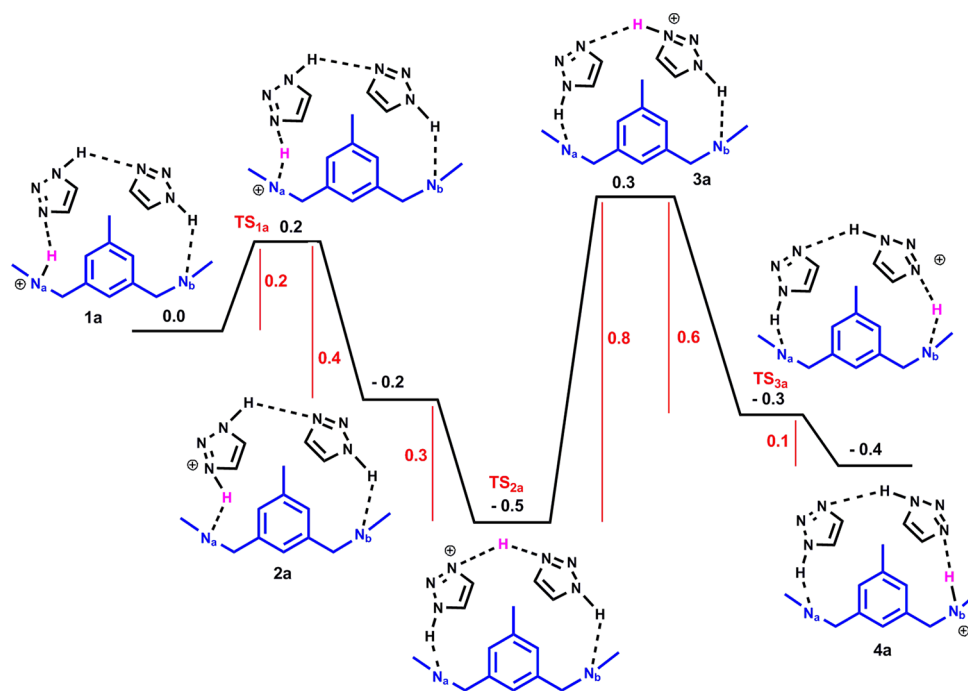


Figure 9. Free energy surface for the transfer of the proton through the hydrogen-bonded network from one end of the cage to the other, and the dopant employed in 1,2,3-triazole. All values (ΔG) are in kcal/mol.

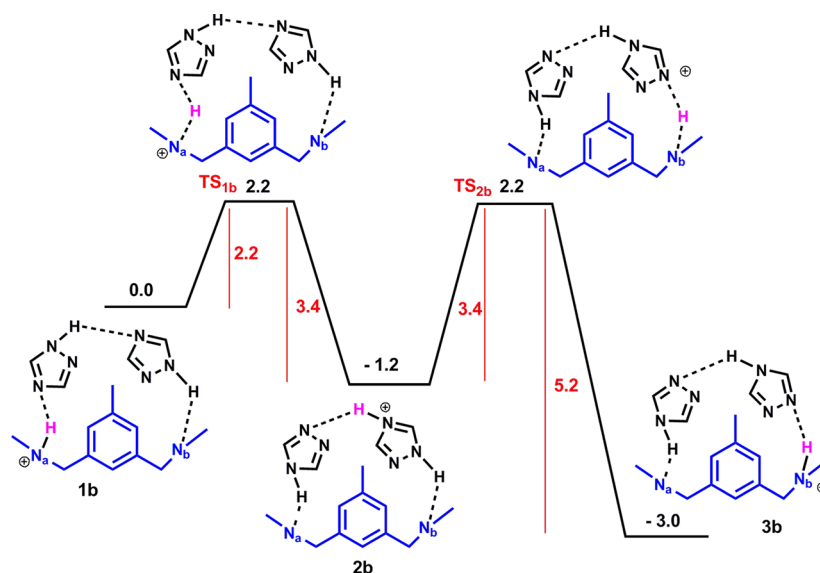


Figure 10. Potential energy for the transfer of the proton through the hydrogen-bonded network from one end of the cage to the other, and the dopant employed in 1,2,4-triazole. All values (ΔE) are in kcal/mol.

triazole molecule to the other (forming 3a, see Figure 8), and then back to another nitrogen of the cage (structure 4a, see Figure 8) are found to be even lower, 0.3 and 0.5 kcal/mol, respectively, thereby indicating the facility of the proton transfer for the $[\text{N-cage-H}_2][\text{X}][\text{H}^+]$ case where $\text{X} = 1,2,3$ -triazole. Figure 9 shows the corresponding ΔG values for the same proton-transfer cycle. The reason the ΔE and the ΔG values have been shown in separate figures is to highlight the fact that the incorporation of entropic effects renders the proton-transfer process even more facile, with the rate-determining barrier for the process (corresponding to the transition state TS_{1a}) reduced to only 0.2 kcal/mol. It is noted that the other two transition states are actually found to lie

slightly lower in energy than the corresponding reactants (see Figure 9) because the original positive difference in the ΔE terms is so small that the favorable addition of entropic and other terms leaves the free energy of the transition-state structures lower than the free energy of the corresponding reactant structures. The net result of the ΔG calculations is therefore to indicate that the proton-transfer process for the $[\text{N-cage-H}_2][2\text{X}][\text{H}^+]$ system, where $\text{X} = 1,2,3$ -triazole, is likely to be a highly facile one. Since many such proton-transfer pathways will be likely to exist in the doped system due to the possibility of more dopant molecules being housed in the porous cages and thus being able to transfer protons through other routes between different nitrogens of $[\text{N-cage-H}_2]$, the

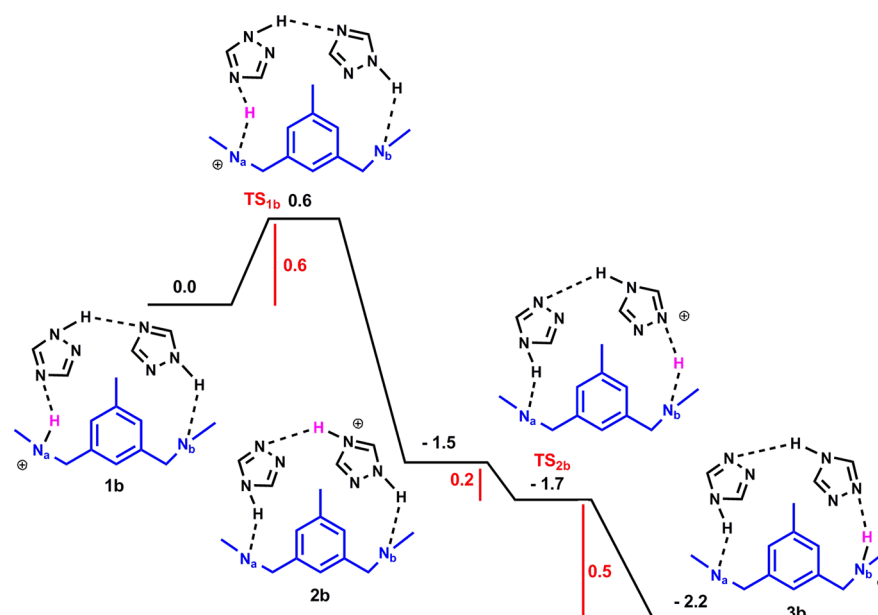


Figure 11. Free energy for the transfer of the proton through the hydrogen-bonded network from one end of the cage to the other, and the dopant employed in 1,2,4-triazole. All values (ΔG) are in kcal/mol.

results indicate that the $[\text{N-cage-H}_2]$ system doped with 1,2,3-triazole would be likely to perform in a highly efficient manner as a proton-exchange membrane.

Proton Transfer with 1,2,4-Triazole. Discussed in the previous section was the proton-transfer pathway for $[\text{N-cage-H}_2][2\text{X}][\text{H}^+]$, where X is 1,2,3-triazole. The corresponding potential energy surface has also been determined for X = 1,2,4-triazole, the other triazole isomer. Figure 10 shows the potential energy surface calculated as the difference in the ΔE values between the different reactants, intermediates, and transition states along the proton-transfer route. Only two transition states were obtained: after the first proton transfer from the cage (structure **1b**, see Figure 10) to the hydrogen-bonded dopant, going through the transition state TS_{1b} (see Figure 10), the intermediate obtained has the proton already transferred to the second 1,2,4-triazole molecule (structure **2b**, see Figure 10); that is, the transfer of the proton from the first 1,2,4-triazole molecule to the second is a barrierless process. The second transition state, TS_{2b} , connects this intermediate to the final structure, **3b**, along the potential energy surface (see Figure 10). The barrier heights are found to be higher for this case in comparison to $[\text{N-cage-H}_2][2\text{X}][\text{H}^+]$, where X = 1,2,3-triazole. These values are reduced, as in the earlier case, when ΔG values are considered: the slowest step of the proton-transfer pathway considered is 0.6 kcal/mol (corresponding to the transition state TS_{1b} , see Figure 11), 0.4 kcal/mol higher than the slowest step for X = 1,2,3-triazole case. However, the smallness of the barrier heights indicates that 1,2,4-triazole can also be a good dopant for $[\text{N-cage-H}_2]$ in order to make the zero-dimensional cage an effective proton-exchange membrane.

It is to be noted that all the calculations discussed in the previous sections have focused on *static* quantum chemical calculations on zero-dimensional cage structures, and it is also important to note that the calculations have been done with a *model system* consisting of a single zero-dimensional cage doped with imidazole, triazole, or phosphoric acid molecules. Were this system to be employed as a membrane in a fuel cell, it would consist of a stacking of several doped 0-D cage

molecules, and its performance as a fuel cell membrane could therefore be influenced by other factors such as local concentration effects wherein dopant molecules might cluster more around certain regions of the porous membrane and less in other regions. Such effects are not captured by the current computational model employed and might require further investigations in the future.

Furthermore, it is also possible that thermal fluctuations, which cannot be captured by the static nature of the quantum chemical calculations described here, can have effects such as the distortion of the cage due to elongation/fluctuation of the C–C and N–C bonds in the cage. Zhang et al.,³⁰ for instance, have observed that *ab initio* molecular dynamics simulations done on the zero-dimensional C_{60} cage structure resulted in distortion of the cage at high temperatures (up to 1800 K), though the cage structure was still preserved. Sun et al.³¹ observed, through *ab initio* molecular dynamics simulations done at 300 K, that the presence of H_2 molecules in B–N cage structures led to distortion of B–N bonds in the cage due to the asymmetric distribution of the H_2 molecules in the cage. Joshi et al.³² have observed an increase in bond length fluctuations in small gallium clusters, Ga_{30} and Ga_{31} , upon conducting *ab initio* molecular dynamics simulations and increasing the temperature from 0 to 900 K in such systems. Chandrachud et al.³³ have investigated the behavior of small sized gold cages (Au_{16} and Au_{17}) through *ab initio* molecular dynamics simulations and found that the increase in temperature from 0 to 600 K led to distortions in the cage structure, as well as to a degree of isomerization for both the gold cages considered. While it is clear that the behavior of different cage structures, in the presence and absence of dopants, is likely to be dependent on its chemical constitution, the examples of the different cage structures cited here indicate that regardless of the chemical nature of the cage, thermal effects, captured by *ab initio* molecular dynamics simulations, would lead to the distortion of the cage, though the cage structure would remain intact up to high temperatures. The static calculations discussed in the work presented here cannot account for the thermal

distortions that are likely in the doped N-cage structures at the temperatures under which the fuel cell would operate, and this is a limitation of the current work. It is, however, also clear that the N-cage structure should remain intact even at high temperatures, and the ease of proton transfer from the cage to the dopant base and back to the cage should be even more facilitated at higher temperatures, due to the greater ease with which the barrier to proton transfer can be surmounted. Therefore, it is likely that (a) the doped N-cage structure would persist at fuel cell operating temperatures, even though distortions in the cage structure would be likely and (b) the efficiency of the proton transfer, and therefore the effectiveness of the proposed fuel cell membrane, would also be high at the higher temperatures.

CONCLUSIONS

The recently synthesized and characterized zero-dimensional nitrogen-based (N-cage) structures have been experimentally found to be stable up to temperatures well above 300 °C.¹⁷ Such cages structures are also porous and can thus be easily doped with hydrogen-bonding bases such as phosphoric acid, imidazole, and 1,2,3- and 1,2,4-triazoles. Since it has been demonstrated¹⁸ that formation of dynamic hydrogen bond networks within the membrane is an important prerequisite to high proton conductivity,¹⁸ such zero dimensional doped N-cage structures have the potential to be excellent proton-exchange membranes in fuel cells. This potential has been explored through full quantum mechanical calculations with DFT and MP2 methods. The results indicate that the hydrogenated zero-dimensional cages (N-cage-H₂) would perform very efficiently as PEMs in combination with two hydrogen-bonding 1,2,3- and 1,2,4-triazole molecules ([N-cage-H₂][2X], where X = 1,2,3- and 1,2,4-triazole). The process of transferring a proton from one nitrogen in the cage to another through the network of triazole molecules was found to be nearly barrierless—the slowest step in the proton-transfer process studied had a barrier of 0.2 kcal/mol (ΔG value) for X = 1,2,3-triazole. The corresponding barrier in 1,2,4-triazole was 0.6 kcal/mol. The results thus highlight the possibility of the existence of highly efficient proton-conducting channels in the proposed [N-cage-H₂][2X] PEMs. The results are significant due to the need for developing new, efficient PEMs that can perform in the absence of water at high temperatures.

ASSOCIATED CONTENT

Supporting Information

Potential energy surface for proton transfer in triazole–triazolium dimers; barriers to proton transfer obtained from full MP2 calculations; comparison of the experimentally obtained H values for different bases; and optimized geometries of the structures reported in the paper. 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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REFERENCES

- (1) Appleby, A. J.; Foulkes, F. R. *Fuel cell handbook*; Van Nostrand Reinhold: New York, 1989; p 762.
- (2) Savadogo, O. Emerging membranes for electrochemical systems: Part I. Solid polymer electrolyte membranes for fuel cell systems. *J. New Mater. Electrochem. Syst.* **1998**, 1 (1), 47–66.
- (3) Steele, B. C. H.; Heinzel, A. Materials for fuel-cell technologies. *Nature* **2001**, 414 (6861), 345–352.
- (4) Kreuer, K.-D.; Paddison, S. J.; Spohr, E.; Schuster, M. Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology. *Chem. Rev.* **2004**, 104, 4637–4678.
- (5) Carla, H.-W. Recent advances in perfluorinated ionomer membranes: structure, properties and applications. *J. Membr. Sci.* **1996**, 120 (1), 1–33.
- (6) Kreuer, K.-D.; Rabenau, A.; Weppner, W. Vehicle Mechanism, A New Model for the Interpretation of the Conductivity of Fast Proton Conductors. *Angew. Chem. Int. Ed. Engl.* **1982**, 21 (3), 208–209.
- (7) Kreuer, K.-D. Proton Conductivity: Materials and Applications. *Chem. Mater.* **1996**, 8, 610–641.
- (8) Eikerling, M.; Kornyshev, A. A.; Kuznetsov, A. M.; Ulstrup, J.; Walbran, S. Mechanisms of Proton Conductance in Polymer Electrolyte Membranes. *J. Phys. Chem. B* **2001**, 105, 3646–3662.
- (9) Samuel, C. Et tu, Grotthuss! and other unfinished stories. *Biochim. Biophys. Acta (BBA)—Bioenerg.* **2006**, 1757 (8), 876–885.
- (10) Kreuer, K. D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J. Membr. Sci.* **2001**, 185 (1), 29–39.
- (11) Noam, A. The Grotthuss mechanism. *Chem. Phys. Lett.* **1995**, 244 (5–6), 456–462.
- (12) Tuckerman, M. Ab initio molecular dynamics simulation of the solvation and transport of hydronium and hydroxyl ions in water. *J. Chem. Phys.* **1995**, 103 (1), 150.
- (13) Tuckerman, M.; Laasonen, K.; Sprik, M.; Parrinello, M. Ab Initio Molecular Dynamics Simulation of the Solvation and Transport of H₃O⁺ and OH[−] Ions in Water. *J. Phys. Chem.* **1995**, 99, 5749–5752.
- (14) Allcock, H. R.; Hofmann, M. A.; Ambler, C. M.; Lvov, S. N.; Zhou, X. Y.; Chalkova, E.; Weston, J. Phenyl phosphonic acid functionalized poly[aryloxyphosphazenes] as proton-conducting membranes for direct methanol fuel cells. *J. Membr. Sci.* **2002**, 201 (1–2), 47–54.
- (15) Wainright, J. S.; Wang, J. T.; Weng, D.; Savinell, R. F.; Litt, M. Acid-Doped Polybenzimidazoles: A New Polymer Electrolyte. *J. Electrochem. Soc.* **1995**, 142 (7), L121–L123.
- (16) Glipa, X.; Bonnet, B.; Mula, B.; J. Jones, D.; Roziere, J. Investigation of the conduction properties of phosphoric and sulfuric acid doped polybenzimidazole. *J. Mater. Chem.* **1999**, 9 (12), 3045–3049.
- (17) Tozawa, T.; Jones, J. T. A.; Swamy, S. I.; Jiang, S.; Adams, D. J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S. Y.; Tang, C.; Thompson, S.; Parker, J.; Trewin, A.; Bacsá, J.; Slawin, A. M. Z.; Steiner, A.; Cooper, A. I. Porous organic cages. *Nat. Mater.* **2009**, 8 (12), 973–978.
- (18) Nagamani, C.; Viswanathan, U.; Versek, C.; Tuominen, M. T.; Auerbach, S. M.; Thayumanavan, S. Importance of dynamic hydrogen bonds and reorientation barriers in proton transport. *Chem. Commun.* **2011**, 47 (23), 6638–6640.

- (19) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic structure calculations on workstation computers: The program system turbomole. *Chem. Phys. Lett.* **1989**, *162* (3), 165–169.
- (20) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865.
- (21) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Auxiliary basis sets to approximate Coulomb potentials. *Chem. Phys. Lett.* **1995**, *240* (4), 283–289.
- (22) Sierka, M.; Hogekamp, A.; Ahlrichs, R. Fast evaluation of the Coulomb potential for electron densities using multipole accelerated resolution of identity approximation. *J. Chem. Phys.* **2003**, *118*, 9136.
- (23) Hattig, C.; Weigend, F. CC2 excitation energy calculations on large molecules using the resolution of the identity approximation. *J. Chem. Phys.* **2000**, *113* (13), 5154–5161.
- (24) Li, A.; Yan, T.; Shen, P. Exploring proton transfer in 1,2,3-triazole-triazolium dimer with ab initio method. *J. Power Sources* **2011**, *196* (3), 905–910.
- (25) Mangiatordi, G. F.; Hermet, J.; Adamo, C. Modeling Proton Transfer in Imidazole-like Dimers: A Density Functional Theory Study. *J. Phys. Chem. A* **2011**, *115*, 2627–2634.
- (26) Pal, A.; Vanka, K.; DFT, A investigation of the potential of porous cages for the catalysis of ammonia borane dehydrogenation. *Chem. Commun.* **2011**, *47* (41), 11417–11419.
- (27) Zhou, Z.; Li, S.; Zhang, Y.; Liu, M.; Li, W. Promotion of Proton Conduction in Polymer Electrolyte Membranes by 1H-1,2,3-Triazole. *J. Am. Chem. Soc.* **2005**, *127*, 10824–10825.
- (28) Li, S.; Zhou, Z.; Zhang, Y.; Liu, M.; Li, W. 1H-1,2,4-Triazole: An Effective Solvent for Proton-Conducting Electrolytes. *Chem. Mater.* **2005**, *17*, 5884–5886.
- (29) Meot-Ner, M.; Liebman, J. F.; Del Bene, J. E. Proton affinities of azoles: experimental and theoretical studies. *J. Org. Chem.* **1986**, *51*, 1105–1110.
- (30) Zhang, Q. M.; Yi, J.-Y.; Bernholc, J. Structure and dynamics of solid C₆₀. *Phys. Rev. Lett.* **1991**, *66* (20), 2633–2636.
- (31) Sun, Q.; Wang, Q.; Jena, P. Storage of Molecular Hydrogen in B-N Cage: Energetics and Thermal Stability. *Nano Lett.* **2005**, *5*, 1273–1277.
- (32) Joshi, K.; Krishnamurty, S.; Kanhere, D. G. “Magic Melters” Have Geometrical Origin. *Phys. Rev. Lett.* **2006**, *96* (13), 135703.
- (33) Chandrachud, P.; Joshi, K.; Krishnamurty, S.; Kanhere, D. Stability of gold cages (Au₁₆ and Au₁₇) at finite temperature. *Pramana* **2009**, *72* (5), 845–855.