Supporting Information for:

Design Elements for Enhanced Hydrogen Isotope Separations in Barely Porous Organic Cages

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In the non-functionalized CC3-S the average pore areas range from ~26.7 to ~26.9 Å². In the functionalized 6ET-RCC3, the pore areas are much smaller and range from ~7.9 to ~8.2 Å². This large difference in pore area is the direct result of the functionalization of 6ET-RCC3.

**Figure S1.** Three CC3 POCs of CC3 (left), RCC3 (middle), and 6ET-RCC3 (right). Functionalization, or lack thereof, are highlighted in each POC. For CC3, two bridging N atoms
have been highlighted (dashed blue circles) showing lack of functionalization. In RCC3 the bridging N atoms are reduced via H addition (dashed green circles). Functionalization of 6ET-RCC3 results from the addition of 6 equivalents of acetaldehyde to CC3 (red dashed circle) resulting in pore functionalization. In all POCs the elements are represented by C (brown), N (blue), and H (white).

**Determination of pore window areas and average pore window distances.**

Each pore window can be defined by three locations using the bridging N atoms of the POCs. For RCC3 and CC3-S the average between each set of neighboring N atoms provides a window point, Figure S3. These average points are used to calculate the area of the pore window via the cross product, $S = \frac{\|a \times b\|}{2}$, where the area of the pore triangle, $S$, is calculated by the vectors $a$ and $b$ which correspond to two sides of the pore triangle in three dimensions.
**Figure S2.** The pore window (red triangle) in RCC3 and CC3-S is defined by average neighboring N atom positions (green circle) with the two vectors, a and b, used to calculated the cross product area. The atoms in the POC are shown as C (brown), N (blue), and H (white).

The use of bridging N atoms is valuable as the RCC3 and CC3-S POC have either minimal or no functionalization of the pore window and are well represented by the average N positions. However, for 6ET-RCC3, the windows are functionalized and the pore is defined using either the methyl or H functional group. One example of pore defining atoms are identified in Figure S4 below.
Figure S3. The atoms used to define the pore windows in the functionalized 6ET-RCC3 have been highlighted with yellow (left). A visualization of the chosen atoms and resulting pore window is shown for the chosen functional atoms (green circles) and pore window (red triangle). The atomic elements in the POC are represented as C (brown), N (blue), and H (white).

Each POC has four pore windows that a gas molecule can pass through. In both RCC3 and CC3-S each pore is identical as there is either minimal or no pore functionalization. In the 6ET-RCC3 the pore windows are different as the window area is determined by the position of both
methyl and H functional groups. The increased steric hindrance due to multiple methyl groups in a pore window result in a higher energy barrier. The average pore window area for both CC3-S and 6ET-RCC3 have been calculated along the varying temperature AIMD trajectories, Table S5.

**Selectivity Dependence on POC flexibility**

Investigation of POC flexibility was modeled using a completely flexible RCC3 POC and a semi-fixed RCC3 POC. The semi-fixed RCC3 POC included two fixed C atoms on the ends of the terminal benzene groups, for a total of 12 fixed C atoms per simulation. The result is a POC that is unable to rotate in response to varying temperature, but with pore apertures that are not fixed in place. These semi-fixed RCC3 POC structures were used to approximate a covalently bonded POC structure and test the hypothesis that the rotation of the POC cage due to weak van der Waals bonding is a factor in controlling hydrogen isotope separation.

A unique feature of the POC framework is that weak van der Waals bonds between POCs form the extended structure, which allows for rotation of the POC due to thermal vibrations. Even at the low temperatures studied here, the entire cage is noted to rotate over the course of the AIMD simulation. Given the narrow pore opening in the POC, it is unclear if the movement of the pore
window, and the H\textsubscript{2} or D\textsubscript{2} molecule, change the escape mechanisms. If a fixed cage structure is advantageous to hydrogen separation, then a fully crystalline POC could be synthesized to improve selectivity of the material. To test this hypothesis, twelve carbon atoms located on the outer benzene rings in the RCC3 POC were frozen to limit cage rotation. From the modeled flexible POCs, it is apparent that the primary change in aperture size is due to thermal motion. The semi-fixed RCC3 still allows flexibility of the pore apertures, being indirectly reduced due to the fixed terminal C atoms. In larger systems interactions between neighboring POCs play a role in the ability of a gas to pass from one to another. To begin to address the known dependent behavior between neighboring POCs, this model simulates a single cage behavior and intends to identify response of H\textsubscript{2} and D\textsubscript{2} molecules to a single cage.

Then AIMD simulations were run to compare differences in pore aperture size, Figure S4, number of exit and entrance events, Figure S5, time outside the pore, Figure S5, and H\textsubscript{2} and D\textsubscript{2} velocities, Figure S6. The results can be used to compare between the original flexible POC structure and the frozen POC structure.
Figure S4. Average pore aperture areas calculated for the fixed RCC3 POC across all temperatures (30, 50, 77, and 100 K) for D$_2$ (blue) and H$_2$ (red) containing models.

The pore aperture area of the semi-fixed RCC3 shows a small variation for the D$_2$ systems across all temperature ranges ranging from 26.683 Å$^2$ to 27.059 Å$^2$. This is reduced compared to the flexible RCC3 which had aperture areas with D$_2$ range between 25.578 Å$^2$ to 26.847 Å$^2$. The values of the semi-fixed RCC3 are higher than the respective flexible values, indicating a reduction of pore flexibility. The semi-fixed H$_2$ RCC3 shows a larger dispersion in aperture area, with the calculated values at 100K to show greater flexibility compared to the D$_2$ system. The dispersion at 100 K of the H$_2$ system follows the trend identified in the flexible system. The size of the pore
aperture and the area fluctuation relate to the ability for H\textsubscript{2} and D\textsubscript{2} to pass through the pore openings.

**Figure S5.** Averaged number of exit or entrance events per AIMD trajectory (left) and averaged time D\textsubscript{2} (blue) or H\textsubscript{2} (red) spends outside the POC pore (right) for the fixed RCC3 POC at temperatures of 30, 50, 77, and 100 K.

The average number of events across three trajectories at each temperature indicate non-trending events for D\textsubscript{2} and H\textsubscript{2}, Figure S5 (left). The standard error shows significant overlap at temperatures of 30 and 77 K, while 50 and 100K show some distinction of D\textsubscript{2} having lower exit and entrance events than H\textsubscript{2}. The relative time outside the pore, Figure S5 (right), also shows minimal distinction between D\textsubscript{2} and H\textsubscript{2} at temperatures of 30, 50, and 100 K. At 50 K the H\textsubscript{2} was observed to spend
~2x more time outside the pore compared to D$_2$, indicating preferential capture of D$_2$ within the semi-fixed RCC3.

**Figure S6.** Calculated average isotope velocities for D$_2$ (left) and H$_2$ (right) in the fixed RCC3 at varying positions of the simulation cell. Velocities are plotted for regions where the isotope is in the POC ($V_{in}$, blue), outside the POC ($V_{out}$, red), and when exiting or entering the POC ($V_{exit}$, green).

The calculated velocities of D$_2$ and H$_2$ in the semi-fixed RCC3, Figure S6, indicate similar trends in response to temperature. Both isotopes show increasing velocities up to 77 K before lowering at 100 K. The average velocity values of H$_2$ are calculated to be minimally greater than those of D$_2$ across the temperature range.
Functionalized Pore Aperture Areas in 6ET-RCC3

**Figure S7.** Pore areas in 6ET-RCC3 are averaged at temperatures of 30, 50, 77, and 100 K for all four pores in D$_2$ and H$_2$ loaded trajectories, represented by blue, red, green, and cyan, respectively.

In 6ET-RCC3 two sizes of pores are available for exit and entrance into the POC. Figure S7 provides the averaged pore aperture area over each temperature trajectory. Pores one and three have two methyl groups and one H in the pore opening, while pores two and four have one methyl and two H.

**Mixed gas trajectories.**
Beyond individual behavior of single isotope molecules inside the POC cages, AIMD trajectories were simulated with mixed isotopes inside RCC3, CC3-S, and 6ET-RCC3 POCs. The inclusion of both H$_2$ and D$_2$ molecules inside the POCs provide direct competitive interactions and increases the relative pressure inside the pore.

**Figure S8.** Average pore aperture areas and standard error calculated during the mixed H$_2$ and D$_2$ AIMD trajectory for CC3-S (left, blue), RCC3 (left, red), and 6ET-RCC3 (right, green).

During the mixed gas trajectories, the pore aperture areas of CC3-S (left, blue) and 6ET-RCC3 (right, green) were observed to match the values identified during the single H$_2$ or D$_2$ gas trajectories. The values of RCC3 at 30 and 50 K also agreed with values calculated along single
gas trajectories. However, the values at 77 K and 100 K showed significant deviation from the expected values. Upon visual analysis of the trajectories, the RCC3 framework became unstable at 77 and 100 K. The final framework geometry no longer retained the expected porosity as a portion of the POC had collapsed within itself, leading to the large deviation of pore aperture area at 77 and 100 K. Moving forward the data from the 77 and 100 K trajectories for RCC3 are presented but will not be discussed.

**Figure S9.** Time outside the POC pore of H\textsubscript{2} (filled squares) and D\textsubscript{2} (open diamonds) along the mixed H\textsubscript{2}+D\textsubscript{2} AIMD trajectories for CC3-S (blue), RCC3 (red), and 6ET-RCC3 (green).

The time outside the pore for H\textsubscript{2} and D\textsubscript{2} along the mixed trajectories show a high frequency of large amounts of time outside the pore. This is the result of either the H\textsubscript{2} or D\textsubscript{2} exiting the pore early along the AIMD trajectory. The early exits are in agreement with the DFT calculated change in energy as a function of gas loading. Even with only two gases in the POC pores, it is favorable for one to exit upon start of the dynamic trajectory.
**Figure S10.** Number of exit and entrance events for $\text{D}_2$ (left, diamonds) and $\text{H}_2$ (right, squares) along the mixed $\text{H}_2$ and $\text{D}_2$ trajectories in CC3-S (blue), RCC3 (red) and 6ET-RCC3 (green).

**Figure S11.** Velocities of $\text{D}_2$ (left) and $\text{H}_2$ (right) at varying positions in the simulation cell for CC3-S (blue), RCC3 (red), 6ET-RCC3 (green) at temperatures of 30, 50, 77, and 100 K. The areas of the model are in the pore, $V_{\text{in}}$ (squares), outside the pore, $V_{\text{out}}$ (circles), and exiting or entering the pore, $V_{\text{exit}}$ (diamond).
For both D\textsubscript{2} and H\textsubscript{2} the highest velocities at 100 K are observed for the non-functionalized CC3-S, with the lowest velocities observed in the functionalized 6ET-RCC3, matching experimental trends. At the lowest temperature of 30 K the highest calculated velocities for both D\textsubscript{2} and H\textsubscript{2} are observed in the RCC3 POC. However, for D\textsubscript{2} the lowest velocity at 30 K is in RCC3 whereas for H\textsubscript{2} the lowest velocity is in 6ET-RCC3. This result mirrors the calculated trend of the individual gases and supports the ability of D\textsubscript{2} to move more easily through highly functionalized pore apertures. Overall, the identification of strong trends is difficult given the reduced information for RCC3 at the two higher temperatures. However, for D\textsubscript{2} a clear trend of high calculated velocities is seen at 30 and 50 K of RCC3. To further identify clear trends triplicate trajectories should be simulated in future work in studying pressurized gas environments on these POC systems.
**Figure S12.** Visualization of $\text{H}_2$ (left) and $\text{D}_2$ (right) as they break the plane to exit the CC3-S POC.

The pore aperture is highlighted with a red dashed circle and the atomic elements are represented as N (blue), C (gray), and H (white).

**Table S1.** Total energies of empty and gas loaded 6ET-RCC3. Change in energy of gas loaded vs empty POC and change in energy per $\text{H}_2$ molecule loaded.

| # of $\text{H}_2$ | Total Energy (eV) | dE vs Empty (eV) | dE/$\text{H}_2$ (eV) |
|-------------------|-------------------|------------------|-------------------|
| 0                 | -1307.27          | -                | -                 |
| 3                 | -1327.91          | -20.64           | -6.88             |
The total energy values of the 6ET-RCC3 + n(H_2), Table S1, are the calculated results of the entire system. The results in Table 1 of the manuscript provide the change in energy of the POC cage framework in response to gas loading. The dE/H2 results in Table S1 indicate that the energy of each H_2 molecule contribute an average energy of 6.845±0.024 eV, across all gas loadings.