

Competitive Adsorption Between Nitrogen and Hydrogen

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1. Introduction

Since the 1900s, the global human population has seen an incredible period of growth, increasing from 1.5 to 8 billion people. This exponential growth is unprecedented in the context of human history and can be attributed to a variety of factors. One of the most significant developments in the last century that has enabled this growth is the Haber-Bosch process.

The Haber-Bosch process is the industrial procedure by which atmospheric nitrogen and gaseous hydrogen react using a metal catalyst at high pressures and temperatures. There are three proposed mechanisms for this catalysis reaction as shown in **Figure 1**¹.

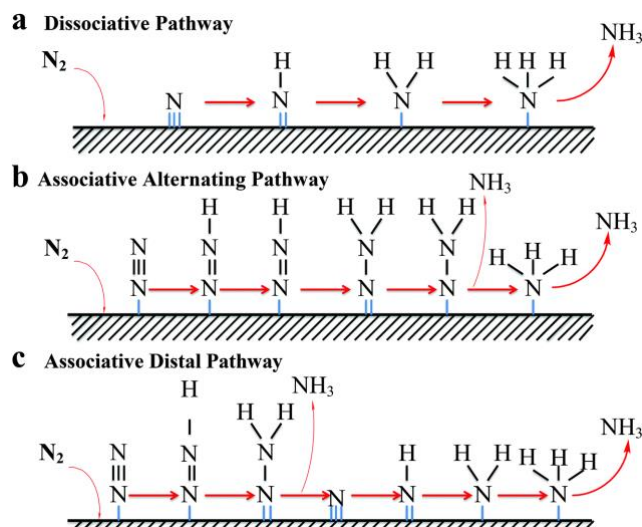


Figure 1. Possible mechanisms for ammonia synthesis in the Haber-Bosch process.

For each mechanism, the process begins with the adsorption of nitrogen. This means the overall reaction will be slowed down by hydrogen molecules that have adsorbed to the catalyst. Adsorbed hydrogens take up active reaction sites and prevent the synthesis of ammonia on that site until they have desorbed from the catalyst. Therefore, the efficiency of the Haber-Bosch process depends on the competitive adsorption for active sites between nitrogen and hydrogen.

Since the competitive adsorption on the catalyst surface depends on the reaction conditions, the conditions can be optimized to promote nitrogen adsorption and thereby increase the efficiency of the overall process. In this report, the adsorption behavior of nitrogen and hydrogen on a 2-D lattice surface as a function of chemical potential, interaction energies, and temperature is simulated and analyzed to broaden understanding of the competitive adsorption and determine the conditions that optimize nitrogen adsorption.

2. Methods

A Grand Canonical Monte Carlo (GCMC) simulation was used to study the competitive adsorption between nitrogen and hydrogen. A 4 x 4 lattice was initialized to represent a square surface with 16 empty sites. The size of the sites was such that only one molecule could be adsorbed to a site at once. A Metropolis algorithm was used to choose a random site and propose the addition or removal of a particle. The probability of proposing either an addition or removal of a particle was 50%. The probability of accepting the addition or removal of a particle depended on the change in energy (**Eq. 1**) that would occur if the move was accepted, where n_i^A and n_i^B are the number of hydrogen and nitrogen adsorbates at site i , respectively, μ_H is the adsorption energy of hydrogen, μ_N is the adsorption energy of nitrogen, and ϵ_{HH} , ϵ_{NN} , and

ϵ_{HN} are the interaction energies between two hydrogen particles, two nitrogen particles, and one hydrogen and one nitrogen particle, respectively.

$$E = \sum_i (n_i^H \epsilon_H + n_i^N \epsilon_N) + \frac{1}{2} \sum_{i,j} (n_i^H n_j^H \epsilon_{HH} + n_i^N n_j^N \epsilon_{NN} + n_i^H n_j^N \epsilon_{HN} + n_i^N n_j^H \epsilon_{HN}) \quad (1)$$

The functions used to accept the addition or removal of a particle are shown in **(Eq. 2)** and **(Eq. 3)** respectively, where N_A is the number of empty sites, N_s is the number of sites occupied by particle s (nitrogen or hydrogen), and μ_s is the chemical potential of particle s .

$$\text{acc} = \min \left[1, \frac{N_a - N_s}{N_s + 1} \exp(-\beta [\Delta E - \mu_s]) \right] \quad (2)$$

$$\text{acc} = \min \left[1, \frac{N_s}{N_a - N_s + 1} \exp(-\beta [\Delta E + \mu_s]) \right] \quad (3)$$

This simulation was run to investigate five sets of parameters which varied in ϵ_{HH} , ϵ_{NN} , and ϵ_{HN} .

Table 1. Interaction energies used for each parameter set (PS)

	PS1	PS2	PS3	PS4	PS5
ϵ_{HH} (eV)	0	0.05	-0.05	-0.05	0.05
ϵ_{NN} (eV)	0	0.05	-0.05	-0.05	0.05
ϵ_{HN} (eV)	0	0.05	-0.05	0.05	-0.05

For each set of conditions, the simulation was run for 10,000 steps, corresponding to 10,000 moves in the Metropolis algorithm. The systems sampled a range of μ_H from -0.2 to 0 eV.

μ_N was fixed at -0.1 eV because it was assumed that nitrogen was in excess. The systems also sampled a range of temperatures T from 0.001 to 0.019 K.

3. Results

3.1 Ideal Gas Mixture (PS1)

In the first parameter set, all the interaction energies were set to 0 eV (**Table 1**). This was done to reflect non-interacting particles in an ideal gas. **Figure 2a** shows the fraction of sites occupied by hydrogen over the total number of sites, which will be referred to as hydrogen

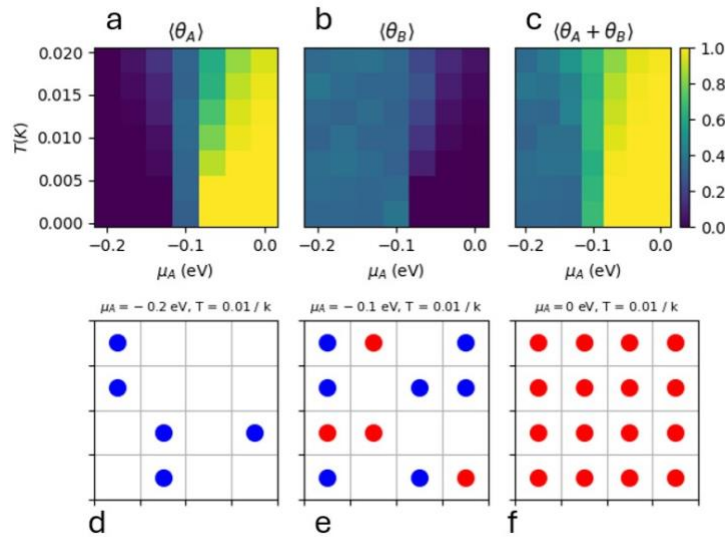


Figure 2. Phase and lattice diagrams for **PS1**. **a)** Hydrogen coverage as a function of μ_H and T . **b)** Nitrogen coverage as a function of μ_H and T . **c)** Combined nitrogen and hydrogen coverage as a function of μ_H and T . Lattice configuration at **d)** $\mu_H = -0.2$ eV, **e)** $\mu_H = -0.1$, **f)** $\mu_H = 0$ eV.

coverage (and analogously referred to as nitrogen coverage for nitrogen particles), increases as μ_H becomes more positive. Within the context of this study, chemical potential can be interpreted as the energy change when a particle is added to the system from a reservoir at constant temperature. A negative chemical potential indicates that a particle prefers to *desorb* from the surface while a positive chemical potential indicates that a particle prefers to *adsorb* from the surface. For $\mu_H < -0.1$ eV, hydrogen does not adsorb to the surface at all, but for $\mu_H > -0.1$ eV, hydrogen occupies most of the sites on the square lattice, reaching full coverage at $\mu_H = 0$ eV. Hydrogen coverage has different dependencies on T depending on the μ_H . For $\mu_H < -0.1$ eV, the fraction of sites occupied by hydrogen has a small but direct relationship with T . This relationship reverses for $\mu_H > -0.1$ eV, with hydrogen coverage decreasing for increasing T .

Figure 2b shows that nitrogen has partial coverage when $\mu_H = -0.2$ eV but decreases sharply to minimal coverage at $\mu_H = -0.1$ eV. In the regime of partial nitrogen coverage, temperature has little to no effect on the number of adsorbed nitrogen molecules. In the regime of little to no nitrogen coverage, temperature has a very slight but direct relationship with the number of adsorbed nitrogen molecules at $\mu_H = -0.1$ eV. Above this chemical potential, temperature has a negligible effect on nitrogen coverage. **Figure 2c** succinctly shows that the surface lattice is slightly populated by nitrogen molecules only at low μ_H and is fully populated by hydrogen molecules only at high μ_H . **Figures 2d-f** pictorially show the coverage trends of nitrogen and hydrogen described above.

3.2 Repulsive Interactions between Nitrogen and Hydrogen (PS2)

The interaction energies used in **PS2** reflect a system where interactions between all particles are set to 0.05 eV, indicating a repulsive relationship between all particles (**Table 1**).

Figures 3a-c shows that **PS2** follows the same trends as **Figures 2a-c**, but the overall coverage is significantly lower for all μ_H . At $\mu_H = -0.2$ eV, the lattice has minimal nitrogen coverage and no hydrogen coverage. Interestingly, at $\mu_H = -0.1$ eV, there is more nitrogen coverage than observed at -0.2 eV, but this might be a statistical artifact arising from short sampling times. At $\mu_H = 0$ eV, the lattice is half filled with hydrogen. The impact of T on both nitrogen and hydrogen coverage is the same as in **PS1**. The lattice at $\mu_H = 0$ eV is too vacant to form a structure, but at $\mu_H \geq -0.1$ eV, a checkerboard pattern emerges, alternating between molecules and empty sites.

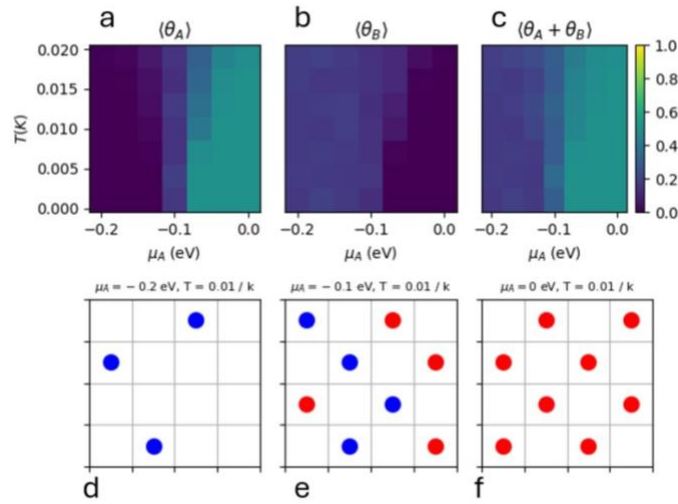


Figure 3. Phase and lattice diagrams for **PS2**. **a)** Hydrogen coverage as a function of μ_H and T . **b)** Nitrogen coverage as a function of μ_H and T . **c)** Combined nitrogen and hydrogen coverage as a function of μ_H and T . Lattice configuration at **d)** $\mu_H = -0.2$ eV., **e)** $\mu_H = -0.1$, **f)** $\mu_H = 0$ eV.

3.3 Attractive Interactions between Nitrogen and Hydrogen (PS3)

The interaction energies used in **PS3** reflect a system where interactions between all particles are set to -0.05 eV, indicating an attractive interaction between all particles (**Table 1**). Unlike **PS1** and **PS2**, hydrogen coverage is present for all μ_H in **PS3** (**Figure 4a**), although **PS3** exhibits the same relationship between hydrogen and nitrogen coverage and μ_H as **PS1** and **PS2** (**Figure 4**). For all μ_H , the lattice is completely covered with a mixture of hydrogen and nitrogen (**Figures 4d-f**). In this system, both hydrogen and nitrogen coverage have a negligible dependence on T .

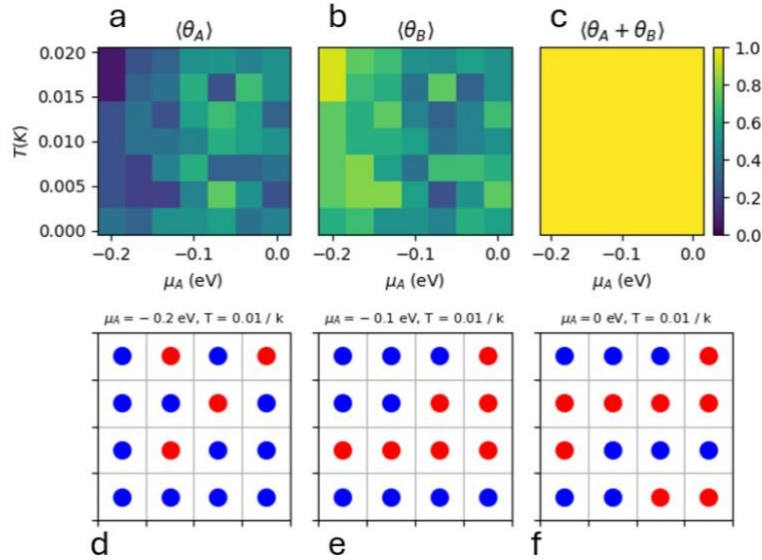


Figure 4. Phase and lattice diagrams for **PS3**. **a)** Hydrogen coverage as a function of μ_H and T . **b)** Nitrogen coverage as a function of μ_H and T . **c)** Combined nitrogen and hydrogen coverage as a function of μ_H and T . Lattice configuration at **d)** $\mu_H = -0.2$ eV., **e)** $\mu_H = -0.1$, **f)** $\mu_H = 0$ eV.

3.4 Immiscible Nitrogen and Hydrogen (PS4)

Both attractive and repulsive interaction energies were used in **PS4**. Specifically, the interaction energies between like molecules were attractive while the interaction energies between dislike molecules were repulsive (**Table 1**). These parameters reflect a situation in which nitrogen and hydrogen have starkly different polarities. **Figures 5a-c** show much more

intense phase shifts as a function of μ_H in comparison to other systems. At $\mu_H = -0.2$ eV, the lattice is completely occupied with nitrogen molecules. At $\mu_H = -0.1$ eV, the lattice is split into alternating 2×4 domains filled with either hydrogen or nitrogen (**Figures 5d-f**). At $\mu_H = 0$ eV, the lattice is completely occupied with hydrogen molecules. For both molecules, temperature influences adsorption rates near $\mu_H = -0.1$ eV, but the trend is inconsistent relative to the trends observed in previous parameter sets.

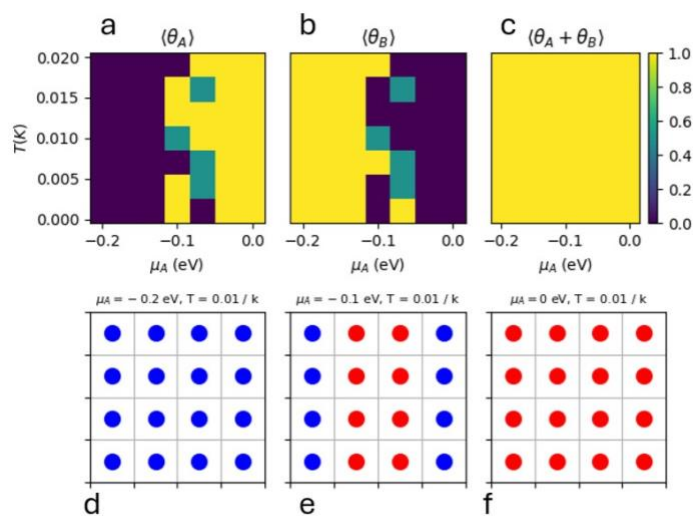


Figure 5. Phase and lattice diagrams for **PS4**. **a)** Hydrogen coverage as a function of μ_H and T . **b)** Nitrogen coverage as a function of μ_H and T . **c)** Combined nitrogen and hydrogen coverage as a function of μ_H and T . Lattice configuration at **d)** $\mu_H = -0.2$ eV., **e)** $\mu_H = -0.1$, **f)** $\mu_H = 0$ eV.

3.5 “Like Dissolves Unlike” Scenario (PS5)

PS5 contains attractive interaction energies between dislike molecules and repulsive interaction energies between like molecules, making it the inverse of **PS4** (**Table 1**). Instead of forming hydrogen or nitrogen only domains like **PS4**, **PS5** exhibits a perfect mixing of nitrogen

and hydrogen adsorbed sites (**Figure 6**). This parameter set gives rise to the only system studied in which adsorption is completely independent of both μ_H and T . For all μ_H and T , the lattice is filled with an equal amount of hydrogen and nitrogen.

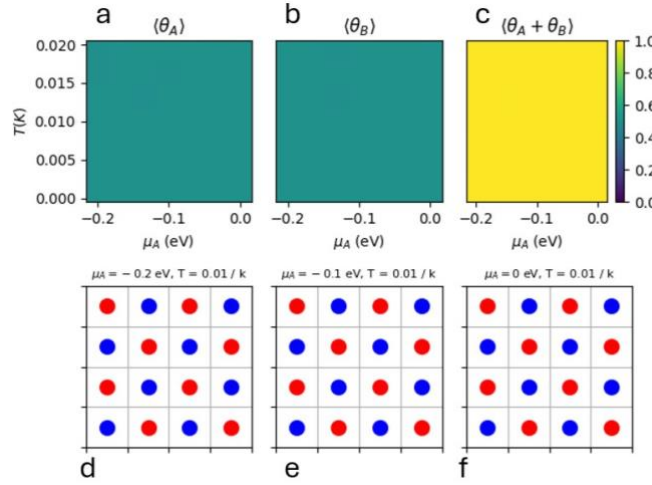


Figure 6. Phase and lattice diagrams for **PS5**. **a)** Hydrogen coverage as a function of μ_H and T . **b)** Nitrogen coverage as a function of μ_H and T . **c)** Combined nitrogen and hydrogen coverage as a function of μ_H and T . Lattice configuration at **d)** $\mu_H = -0.2$ eV., **e)** $\mu_H = -0.1$, **f)** $\mu_H = 0$ eV.

4. Discussion

4.1 Adsorption Trends as a Function of μ_H

For all systems besides **PS5**, the hydrogen coverage increases as μ_H increases, although the amount of change varies per system. **PS5** was characterized by attractive interaction between unlike molecules and repulsive interaction between like molecules. At low μ_H , nitrogen is expected to be the primary adsorbed particle given the low μ_H promote hydrogen desorption. However, the repulsive interactions between nitrogen molecules prevents the adsorption of neighboring nitrogens. Additionally, since there is an attractive interaction between nitrogen and

hydrogen, the hydrogen molecules adsorb to the sites where repulsive interactions prevent nitrogen occupancy, even at low μ_H . This suggests that systems with attractive interaction energies between nitrogen and hydrogen begin with one or a few nitrogen particles adsorbing to the surface. Once nitrogen is present on the surface, the attractive forces promote the adsorption of hydrogen, even though hydrogen would prefer to desorb according to μ_H . This also explains why **PS3** exhibits hydrogen adsorption at low μ_H . Therefore, systems with attractive interactions between nitrogen and hydrogen can promote hydrogen adsorption even at low μ_H with an initial adsorption of a few nitrogen molecules that then promote hydrogen adsorption.

Conversely, nitrogen has an inverse relationship with μ_H for all systems except for **PS5**. The decrease in nitrogen coverage stems from competition between the favorable adsorption of hydrogen molecules at high μ_H . Like the case described above, **PS5** does not exhibit a dependence on μ_H . At most, hydrogen can only occupy half of the surface, forming a checkerboard pattern in which hydrogen and empty sites alternate. Consequently, the attractive interactions between hydrogen and nitrogen in **PS5** promote the adsorption of nitrogen in these empty sites, even at high μ_H where competition between molecules is present in other systems.

As mentioned before, besides **PS5**, all systems have the same general trends of coverage as a function of μ_H . However, there are differences in the compositions, spatial distributions and the intensities of coverage across the systems that reveal interesting dynamics in the competitive adsorption of nitrogen and hydrogen. **PS1** and **PS2** are the only systems where the surface is not fully adsorbed for all μ_H . This is due to the lack of attractive interactions between particles in these systems (**Table 1**). Therefore, the total coverage of a surface increases as attractive interactions are introduced into a system. Similarly, the introduction of repulsive forces in **PS2** reduces the total coverage of the system. Interestingly, the impact of attractive forces on the total

coverage of a system outweighs the impact of repulsive forces on the total coverage of the system. Even though **PS4** and **PS5** contain repulsive interaction energies, they also contain attractive interactions, resulting in the occupation of all surface sites.

4.2 Adsorption Trends as a Function of T

The temperatures used in the simulations have a less substantial impact on the competitive adsorption of nitrogen and hydrogen compared to μ_H . In **PS3**, **PS4**, and **PS5**, both hydrogen and nitrogen coverage have either little to no dependence on temperature or an inconsistent dependence. However, not only is the temperature dependence of adsorption clear in **PS1** and **PS2**, but they also follow the same trend.

As mentioned in the **Results** section, the effect of T depends on the phase of the molecule. When nitrogen is the dominantly adsorbing molecule, an increase in T has no effect on the nitrogen coverage, but it promotes hydrogen coverage. The increase in hydrogen adsorption stems from the increased energy of hydrogen molecules in response to higher temperatures, allowing them to “appose” the negative μ_H they feel. When hydrogen is the dominantly adsorbing molecule, an increase in T promotes nitrogen adsorption and hydrogen desorption. The increase in hydrogen desorption stems from the increased energy of hydrogen molecules in response to higher temperatures, allowing them to “appose” the positive μ_H they feel and escaping the surface. The same reasoning holds for nitrogen molecules. The reason why nitrogen coverage is independent of T at low μ_H for **PS1** and **PS2** requires a closer analysis.

4.3 Implications for the Haber-Bosch Process

For all proposed mechanisms of the Haber-Bosch process, the initial step is the adsorption of nitrogen. Therefore, competitive adsorption between nitrogen and hydrogen for surface sites on a catalyst causes efficiency loss through the reduction of empty sites available for nitrogen to adsorb to. However, it is desirable to keep hydrogen relatively close to the surface so that nitrogen and hydrogen can react to form ammonia. Therefore, the optimal experimental conditions for the Haber-Bosch process should maximize nitrogen adsorption while maintaining hydrogen near the surface. It must be noted that this claim only holds if the selected experimental conditions do not negatively affect the Haber-Bosch process in areas not captured by this simulation.

PS3 represents a system in which particles only experience an attractive interaction (**Table 1**). **Figure 4d** shows that at μ_H , the surface lattice is fully saturated with adsorbents and is primarily occupied by nitrogen molecules. **Figure 4b** also shows that nitrogen adsorption is maximized at low μ_H and high T . This suggests that the Haber-Bosch process would be most efficient when **1)** hydrogen and nitrogen have attractive interactions, **2)** the μ_H is lower than μ_N , and **3)** T is high. An increase in T and pressure can promote attractive interactions between hydrogen and nitrogen by increasing the number of interactions that occur between the molecules. To ensure that μ_H is lower than μ_N , the concentration of nitrogen should be in excess in the reactor.

5. Conclusion

The Haber-Bosch process is one of the most important processes that humanity has ever developed. Its role in sustaining the growing human population is paramount and utilizes a significant number of global resources. As a result, even the slightest optimization of the Haber-Bosch process can lead to huge increases in yield, cuts in production costs, and reduction in its contribution to climate change.

The synthesis of ammonia during the Haber-Bosch process has multiple mechanisms, but each starts with the adsorption of nitrogen to a catalyst surface. Hydrogen is a necessary reagent for ammonia but can compete with nitrogen for sites on the catalyst surface, creating an inherent efficiency loss resulting from the inability of ammonia synthesis to begin with an adsorbed hydrogen and limited surface sites. Therefore, it is possible to optimize the Haber-Bosch process by maximizing the number of adsorbed nitrogen molecules while maintaining an efficient reaction between nitrogen and hydrogen.

In this study, it was observed that the chemical potential of hydrogen, μ_H , significantly influences the competitive adsorption between nitrogen and hydrogen. Furthermore, although to a lesser extent, temperature, T , was found to affect the competitive adsorption between nitrogen and hydrogen. Specifically, nitrogen adsorption was maximized at low μ_H and high T . However, it is important to consider that hydrogen must remain close to the surface for desirable reaction rates. Therefore, this study suggests that a system that promotes attractive interaction between nitrogen and hydrogen at low μ_H and high T is optimal for the Haber-Bosch process.

References

1. Wen, X. and Guan, J. (2020) *Recent advancement in the electrocatalytic synthesis of ammonia*, *Nanoscale*. Available at: <https://doi.org/10.1039/D0NR01359E> (Accessed: 13 November 2024).