Abstract: Immobilization of two single transition metal (TM) atoms on a substrate host opens numerous possibilities for catalyst design. If the substrate contains more than one vacancy site, the combination of TMs along with their distribution patterns becomes a design parameter potentially complementary to the substrate itself and the bi-metal composition. By means of DFT calculations, we modeled three dissimilar bi-metal atoms (Ti, Mn, and Cu) doped into the six porphyrin-like cavities of porous C_{24}N_{24} fullerene, considering different bi-metal distribution patterns for each binary complex, \( \text{Ti}_x\text{Cu}_y@C_{24}N_{24} \), \( \text{Ti}_x\text{Mn}_y@C_{24}N_{24} \), and \( \text{Mn}_x\text{Cu}_y@C_{24}N_{24} \) (with \( x, y, z = 0-6 \)). We elucidate whether controlling the distribution of bi-metal atoms into the C_{24}N_{24} cavities can alter their catalytic activity toward CO\(_2\), NO\(_2\), H\(_2\), and N\(_2\) gas capture. Interestingly, Ti\(_2\)Mn\(_4@C_{24}N_{24}\) and Ti\(_2\)Cu\(_4@C_{24}N_{24}\) complexes showed the highest activity and selectively toward gas capture. Our findings provide useful information for further design of novel few-atom carbon-nitride-based catalysts.

Keywords: C_{24}N_{24}; porphyrin-like; porous fullerene; bi-metal doping; gas adsorption; nanocage

1. Introduction

Porous carbon-based catalysts are widely used as sorbents and support materials in heterogeneous catalysis [1–3]. The archetypical example is C\(_{60}\) fullerene, which has a closed-cage structure and can be synthesized with a highly defective surface and abundant holes [4,5]. It has high thermal stability, unique mechanical properties, high electron negativity, and high electron affinity [6]. Therefore, both pure and metal-doped C\(_{60}\) show promising applications in energy conversion [7,8], fuel cells [9,10], and for biomedical applications [11].

Recently, the adsorption and conversion of gas molecules on doped C\(_{60}\) fullerene by single transition metal (TM) or heteroatoms, especially nitrogen atoms, has gained significant interest [12,13]. Upon N-doping, carbon \( \pi \) electrons are activated by conjugating with the lone-pair electrons from N. Thus, the C atoms neighboring N become active centers for catalytic reactions. For instance, Chen et al. [14] theoretically investigated the oxygen reduction reaction (ORR) mechanisms and catalytic abilities of pure and N-doped fullerenes of various sizes (C\(_{20}\), C\(_{40}\), C\(_{60}\), and C\(_{180}\)). They found that the two pure and N-doped C\(_{20}\) and C\(_{180}\) structures are not active toward the adsorption of common intermediates produced during the ORR process. In contrast, C\(_{30}\)N showed the largest decrease in reaction energy of the rate-determining step in the relative energy profile, suggesting its ORR activity is the best among all the different sizes of fullerenes. Experimentally, N-doped carbon materials are prepared using chemical vapor deposition (CVD) or reactive magnetron sputtering [15,16]. For example, Usachov et al. [17] synthesized a N-doped graphene nanosheet from triazine molecules. Recently, Zhai et al. [18] for the first time synthesized metal-free N-doped graphene films on glass through plasma-assisted hot filament CVD using N\(_2\) gas as dopant. They found that both the hot filament and plasma
source are essential for growing N-doped graphene of high quality. By adjusting the N2 flow, the authors could easily modulate the N content, transmittance, and electrical properties of the graphene films.

The chemical inertness of pure fullerenes prevents their possible application for gas capture. Single metal doping (M-C60), like C58Pt and C59Pt [19], significantly modifies the electronic structure of C60, rendering it chemically active. However, one of the main challenges in the synthesis of M-C60 is the often-observed aggregation of metal atoms [8,20]. Recently, extensive efforts have been put into developing single-site catalysts such as pyrolyzed TM-modified porphyrin complexes (TM = Fe, Co, Mn, Cr, Ni) [21–31], which can be used in various applications like ORR and batteries [24,32–36]. The single TM atom doped in these porphyrin units was firmly fixed, preventing metal aggregation. Recently, the porphyrin-like porous C24N24 has been of great interest as truncated N-doped C60 nanocage. The C24N24 fullerene has six N4 cavities with eight s-triazine rings, which are connected via C-C bonds. Each porphyrin-like N4 cavity of C24N24 can host a single TM atom. Recently, TM-doped C24N24 and C24B24 fullerenes were studied for hydrogen storage [37–39], ORR [40], and gas conversion [41].

In this work, we investigate the catalytic activity of bi-metal atom doping in C24N24, using Ti, Mn, and Cu as metals. In particular, we here focus on the influence of the metal atom distribution in the catalytic activity of the modified structures. We carefully investigated the adsorption characteristics, electronic properties, and charge transfer properties of our novel catalysts. We found that varying the TM ratio indeed has an important effect on the properties and catalytic activities of the catalysts toward adsorption of gas species. Our calculations can provide the fundamental adsorption mechanism of such a novel material, supporting its possible exploitation to be applied as a green catalyst for gas detection.

2. Computational Details

All quantum chemical DFT computations are performed using the Gaussian16 package [42]. We first tested fourteen DFT functional/basis set combinations (including GGA, meta-GGA, and hybrid functionals) for geometry optimization (see Table S1 of Supplementary Materials). As can be seen in Table S1, the obtained E_b values calculated with the B3LYP-D3/6-311G* are in close agreement with the reported E_b for H2 (−4.52 eV) [43,44], formation energy (E_f) of pristine C24N24 (−7.40 eV), and E_b of Ti6@C24N24 (−8.14 eV), as well as the geometry values for C-C (1.55 Å) and C-N (1.34 Å) bond length [45].

The cohesive energy (per atom) of C24N24 is defined as:

\[ E_{coh} = \frac{1}{48}(E_{C24N24} - 24E_C - 24E_N) \]  

where the E_C24N24, E_C, and E_N are the calculated total energy of the pure nanocage, carbon, and nitrogen atom, respectively. The E_b of each doped TM in C24N24 for a homogeneous TM-doped C24N24 (TM6@C24N24) and with different metal ratios (x, y, z = 0–6) was calculated using Equations (2) and (3), respectively:

\[ E_b(TM6@C24N24) = \frac{1}{6}(E_{TM6@C24N24} - 6E_{TM} - E_{C24N24}) \]  

\[ E_b(TixMnyCuZ@C24N24) = \frac{1}{6}(E_{TixMnyCuZ-C24N24} - xE_{Ti} - yE_{Mn} - zE_{Cu}), (x, y, z = 0–6) \]

where, in Equation (2), the E_{TM6@C24N24} and E_{TM} refers to the total energy of one type TM-doped C24N24 (Ti, Mn, or Cu) and the TM atom, respectively. In Equation (3), the E_{TixMnyCuZ@C24N24} is the total energy of the doped C24N24 complex and xE_{Ti}, yE_{Mn}, and zE_{Cu} are defined as the total energy of Ti, Mn, and Cu metal atoms times the number of doped Ti atoms (x), Mn atoms (y), and Cu atoms (z) into the six porphyrin cavities of C24N24 nanocage, respectively.

The adsorption energy (E_ads) of each gas moiety over the modified cage is defined as:

\[ E_{ads} = E_{ads@TixMnyCuZ-C24N24} - E_{TixMnyCuZ-C24N24} - E_{adsorbate} \]
where $E_{\text{ads}@TixMnyCuz-C24N24}$, $E_{\text{TixMnyCuz-C24N24}}$, and $E_{\text{adsorbate}}$ are the total energy of the adsorbate on the complex, pure complex, and the adsorbate molecule, respectively. The $x$, $y$, $z$ values represent the number of each TM atom doped into the porphyrin-like C$_{24}$N$_{24}$ cavities and are in the range of 0 to 6.

For each system, the zero-point energy ($E_{\text{ZPE}}$) is calculated by summing vibrational frequencies over all (real) normal modes. Enthalpy and Gibbs energy changes are calculated at 298.15 K following the standard procedure outlined in the reference [46]. To follow the nature of the adsorption process, the Wiberg bond indices (WBIs) were computed using NBO analysis. The WBIs are known as a better measure of bond strength relative to the overlap population, which is basis-set-dependent and often does not correlate well to bond strength. The WBIs are often similar in magnitude to the bond order expected from valence bond theory and have been used to propose trigger bonds in various energetic materials.

The WBI is a measure of the density between two atoms A and B. It determines by

$$WBI_{AB} = \sum_{i} \sum_{q} P_{pq}^2$$

(5)

3. Results
3.1. Geometry of Pristine C$_{24}$N$_{24}$

The porous C$_{24}$N$_{24}$ is formed by first removing the 12 C atoms in C$_{60}$ that connect two pentagons, thus creating six di-vacancies, as shown with a red circle in Figure 1, and subsequently substituting four undercoordinated C-atoms with N-atoms, thus creating six porphyrin-like N$_4$ cavities and eight connected s-triazine rings (see Figure 1). The calculated C-C and C-N bond lengths are 1.55 Å and 1.34 Å, respectively. The calculated cohesive energy per atom in C$_{24}$N$_{24}$ is $E_{\text{coh}} = -7.81$ eV, which is close to that reported by Ghosh et al. ($-7.40$ eV) [45] but significantly higher than the value of Tang et al. ($-5.78$ eV) [38].

![Figure 1. The optimized structure of porous C$_{24}$N$_{24}$ originated from fullerene. Color code: C, gray; N, blue.](image)

The HOMO-LUMO gap of C$_{24}$N$_{24}$ is calculated to be to be $E_g = 2.82$ eV, which is similar to the value reported by Ma et al. [39] and Song et al. [48] and is higher than the value reported in other investigations [40,45].

3.2. Metal Distribution Patterns
3.2.1. Geometry and Electronic Properties of Bi-Metal Complexes

The agglomeration of catalytically active TMs into clusters is a major challenge. This can be prevented by the strong interaction between TMs and support. C$_{24}$N$_{24}$ fullerene possesses natural N$_4$ rings that can host TM atoms (see Figure 1). We considered a combination of two metal atoms for the selected Ti, Mn, and Cu TMs with 3d$^2$4s$^2$, 3d$^5$4s$^2$, and 3d$^{10}$4s$^1$ valence electrons, respectively, i.e., TiCu, TiMn, and MnCu. Then, various distribution patterns of these dissimilar bi-metal atoms into the six porphyrin-like C$_{24}$N$_{24}$

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cavities were studied. Due to the presence of six cavities, the TM ratios will vary between zero to six. Therefore, we have Ti₆Cuₓ, TiₓMn₉, and Mn₉Cuₓ doped C₂₄N₂₄ fullerene (TiₓCuₓ@C₂₄N₂₄, TiₓMnₓ@C₂₄N₂₄, Mn₉Cuₓ@C₂₄N₂₄) with x, y, z = 0–6. Figure 2a–j shows a schematic presentation of possible bi-metal distribution patterns in the N₄ cavities of C₂₄N₂₄ cage. There are two main doping sites available in the C₂₄N₂₄ cavities: equatorial (green dashed line) and axial (red and black dashed lines), and z (green dashed line) axis directions, respectively. Two metal atoms in a complex can be distributed into the C₂₄N₂₄ cavities through seven different distribution patterns, as listed in Table 1.

![Figure 2](image)

**Figure 2.** A schematic representative of possible distribution patterns of two dissimilar TMs (TM₁:TM₂) in N₄-pyridinic cavities of the C₂₄N₂₄ nanocage: (a) 6:0, (b) 5:1, (c,d) 4:2, (e,f) 3:3, (g,h) 2:4, (i) 1:5, (j) 0:6. Color code: white, Ti; orange, Cu.

| Complex/Metal-Ratio | 6:0 | 5:1 | 4:2 | 3:3 | 2:4 | 1:5 | 0:6 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|
| Ti₆Cuₓ@C₂₄N₂₄       | a   | b   | c,d | e,f | g,h | i   | j   |
| TiₓMn₉@C₂₄N₂₄       | Ti₆ | Ti₅Cu | Ti₄Cu₂ | Ti₃Cu₃ | Ti₂Cu₄ | TiCu₅ | Cu₆ |
| Mn₉Cuₓ@C₂₄N₂₄       | Mn₆ | Mn₅Cu | Mn₄Cu₂ | Mn₃Cu₃ | Mn₂Cu₄ | MnCu₅ | Cu₆ |

### 3.2.2. Binding Energy (Eₐ)

To assess the stability of the modified complexes, the binding energy of each configuration was calculated (see Tables S2–S4). The computed Eₐ for each complex changes in the range of −3.35 eV to −8.11 eV. The lowest and highest Eₐ values correspond to the homogeneous doping with Cu (Cu₆@C₂₄N₂₄) and Ti (Ti₆@C₂₄N₂₄), respectively. The calculated Eₐ for Ti₆@C₂₄N₂₄ is in good agreement with previous studies (−8.61 eV and −8.14 eV) [39,45]. The binding energy of Ti₆Cuₓ@C₂₄N₂₄, TiₓMn₉@C₂₄N₂₄, and Mn₉Cuₓ@C₂₄N₂₄ (x, y, z = 0–6) configurations is plotted and compared in Figure 3.

The high Eₐ values indicate a strong chemisorption of two dissimilar TMs at six N₄ cavities of C₂₃N₂₃, which inhibits the diffusion of TMs into the C₂₄N₂₄ fullerene, increasing the stability of nanocages by metal doping. Due to the higher binding energy of Ti₆@C₂₃N₂₃ and Mn₆@C₂₄N₂₄ than the cohesive energy of bulk Ti (4.85 eV/atom) and Mn (2.92 eV/atom) [49], TM aggregation is not expected, and these materials are likely to be...
stable enough to be used in catalytic processes. In contrast, Cu6@C24N24 shows an Eb of –3.55 eV, slightly higher than the cohesive energy of bulk Cu (3.49 eV/atom) [50], such that homogeneously Cu-doped C24N24 is much less stable against TM agglomeration.

Figure 3. The calculated binding energy (Eb) of TixCu2@C24N24, TixMny@C24N24, and Mn6Cu@C24N24 (x, y, z = 0–6). a–j refer to the bi-metal configurations with different metal ratios listed in Table 1. All values are in eV.

One can see from Figure 3 and Tables S2–S4 that by increasing the ratio of Cu-to-Ti, Mn-to-Ti, and Cu-to-Mn atoms in TixCu2@C24N24, TixMny@C24N24, and Mn6Cu@C24N24, the Eb decreases (i.e., becomes less negative).

3.2.3. NBO Charge Analysis

Figure 4 shows the NBO charge accumulation on individual TMs in different configurations (a–j) for each complex. The precise values are reported in Tables S2–S4. Ti and Cu atoms in TixCu2@C24N24 and MnCu@C24N24 complexes have the highest charge transfer values from the metal atom to the nanocage, in the range of 1.34 to 1.44 |e| and 0.67 to 0.69 |e|, respectively. The high charge on the metal atoms corresponds to the high electron donation induced by the four surrounding N atoms in each porphyrin-like cavity where the d orbitals of Ti, Mn, and Cu atoms overlap with the neighboring nitrogen sp2 orbitals of the cavity to form a sp2d hybridization. The charge transfer leads to the elongation of the average C-C bond (≈1.55 Å) compared to that of pristine C60 (1.45 Å), indicating the activation of C24N24 fullerene upon bi-metal doping.

3.2.4. Thermodynamic Properties and Energy Gap (Eg)

Figure 5 shows the changes in Gibbs free energy for each doped configuration, showing that bi-metallic doping is exothermic and exergonic at room temperature. The values are reported in Tables S2–S4.

Doping C24N24 with various Ti, Mn, or Cu distributions significantly narrows the HOMO–LUMO gap of the C24N24, leading to a noticeable energy gap (Eg) reduction. The highest Eg reduction occurs in Ti2Mn4@C24N24, where the calculated Eg is reduced from 2.82 eV in pure C24N24 to 0.13 eV, making the complex act as a semi-conductor (see Figure 5b, complex g, purple line). The calculated HOMO–LUMO gap for doped configurations does not follow any particular order but in general is less than <1.58 eV, and thus all configurations can be classified as semiconductors. Since the electrical conductivity is exponentially related to Eg, we expect that Ti2Mn4@C24N24 may show good electrical conductivity.
3.2.4. Thermodynamic Properties and Energy Gap (Eg)

Figure 5 shows the changes in Gibbs free energy for each doped configuration, showing different possible positions for the adsorbents to adsorb on the TM sites of each complex and their subgroup configurations. As shown in previous investigations, the existence of two dissimilar TM atoms in a catalyst induces various active sites [51–54].}

Besides the effects of doping on the geometric, thermodynamic, and electronic properties of the complexes as described above, we find that the location of the second introduced TM atom in axial or equatorial positions has little effect. Therefore, we expect that the complexes c and d, e and f, and g and h exhibit similar catalytic activities.

4. Catalytic Behavior of Bi-Metal Complexes toward Adsorption of Gas Species

4.1. Geometric Properties

To explore the effect of bi-metal-doping on the catalytic behavior of each complex, we investigated the individual adsorption of four gas molecules (CO₂, NO₂, H₂, and N₂) on each complex and their subgroup configurations. As shown in previous investigations, the existence of two dissimilar TM atoms in a catalyst induces various active sites [51–54]. Thus, it is important to first determine the available active sites in each substrate (see Figure S1). Considering each complex as a sphere, TM atoms are placed in x, y, and z directions. In homogeneous doping with one TM atom, one active site will be available (Figure S1a–j). By adding the second TM atom to the complex, it can be doped into one of the porphyrin vacancies along the x, y, or z direction, forming the complexes that are shown in Figure S1b. With two different TM atoms present in the complex, one would expect to have two different active sites available. However, for the adsorbent, there are not only two sites. We have labeled the TM atoms in Figure S1 (denoted as i, j, and k) to show different possible positions for the adsorbents to adsorb on the TM sites of each complex.
catalyst. It is clear that \( i, k/j \) sites are located on the axial (perpendicular to the plane of the ring) or equatorial (in the plane of the ring) axis of the catalyst, respectively. Depending on the TM ratio, the adsorbent can adsorb on either \( i, j \), or \( k \) positions. One can see that for each configuration, two active sites are available except in configurations \( b \) and \( i \), in which, depending on the adsorption position of the adsorbent in the equatorial \((j)\) or axial \((i \text{ and } k)\) axis, three possible active sites are available. In addition, each adsorbent adopts mainly three adsorption modes on each active site of the substrates: parallel (side-on) or vertical (end-on) to the surface, and bridge positions.

Our results reveal that \( \text{CO}_2 \), \( \text{H}_2 \), and \( \text{N}_2 \) adsorb strongly on \( \text{Ti}_x\text{Cu}_y@\text{C}_{24}\text{N}_{24} \) and \( \text{Ti}_y\text{Mn}_y@\text{C}_{24}\text{N}_{24} \) and weakly on \( \text{Mn}_y\text{Cu}_x@\text{C}_{24}\text{N}_{24} \), while \( \text{NO}_2 \) adsorbs quite strongly with \(|E_{\text{ads}}| > 6 \text{ eV}\) on all three complexes (see Figure 6 and Table S5). The adsorption behavior of each set of configurations is discussed below.

![Figure 6](image)

**Figure 6.** The more active bi-metal configurations of \( \text{Ti}_x\text{Cu}_y@\text{C}_{24}\text{N}_{24} \), \( \text{Ti}_y\text{Mn}_y@\text{C}_{24}\text{N}_{24} \), and \( \text{Mn}_y\text{Cu}_x@\text{C}_{24}\text{N}_{24} \) \((x, y, z = 0–6)\) toward \( \text{CO}_2 \), \( \text{NO}_2 \), \( \text{H}_2 \), and \( \text{N}_2 \) gas capture.

### 4.2 Adsorption of \( \text{CO}_2 \) and \( \text{H}_2 \)

\( \text{Ti}_2\text{Cu}_4@\text{C}_{24}\text{N}_{24} \) and \( \text{Ti}_2\text{Mn}_4@\text{C}_{24}\text{N}_{24} \) tend to chemisorb \( \text{CO}_2 \) and \( \text{H}_2 \) species with high adsorption energies (see Figure 7). The covalent nature of the adsorbed species is confirmed by the calculated WBIs. As a result, the structure of \( \text{CO}_2 \) is drastically distorted upon its adsorption on these complexes. It is bent over the Ti atom binding via its C and O and forms a triangular ring above the nanocage. The O-C-O angle is bent to 131.12° in its adsorbed form and the C=O bond length is elongated to 1.35 Å, which we attribute to the significant charge transfer of 0.49 |e| from the complex to the 2π* orbitals of the \( \text{CO}_2 \) molecule. The obtained adsorption energies for \( \text{CO}_2 \) are lower than those reported on \( \text{B}_{80} \) fullerene \((-3.49 \text{ eV}) \) [55] and higher than those of N-S dual doped graphene \((-0.25 \text{ eV}) \) [56] and Ti-doped \( \text{C}_2\text{N} \) \((E_{\text{ads}} = -0.95 \text{ eV}) \) [57]. The WBIs of both Ti-C and Ti-O bonds in \( \text{Ti}_2\text{Cu}_4@\text{C}_{24}\text{N}_{24} \) and \( \text{Ti}_2\text{Mn}_4@\text{C}_{24}\text{N}_{24} \) are 0.84, confirming the covalent bond between TM and \( \text{CO}_2 \) atoms and therefore its chemisorption over these substrates. \( \text{H}_2 \) adsorbs dissociatively in a barrierless reaction, forming two covalent Ti-H bonds above the Ti atom with H-H bond length of >2.0 Å (see Figure 7). The NBO charge analysis (see Table S5) along with the calculated WBIs for both Ti-H bond lengths (0.89) confirms the covalent binding between Ti and H atoms and consequently the \( \text{H}_2 \) chemisorption. Interestingly, we find that the adsorption energy of one hydrogen molecule on these complexes is higher than the adsorption of six \( \text{H}_2 \) molecules on \( \text{Ti}_6@\text{C}_{24}\text{N}_{24} \) \((E_{\text{ads}} = -0.48 \text{ eV}) \) [39] \[39\], \( \text{Fe-B}_{38} \) \((E_{\text{ads}} = -0.42 \text{ eV}) \), \( \text{Co-B}_{38} \) \((E_{\text{ads}} = -0.72 \text{ eV}) \), \( \text{Ni-B}_{38} \) \((E_{\text{ads}} = -0.89 \text{ eV}) \) [58], and 2D carbon allotrope \( \Psi \) graphene \((E_{\text{ads}} = -0.34 \text{ eV}) \) [59].
Due to the lower activity of the Cu6@C24N24 complex, CO2 and H2 physisorb on this structure in their gas-phase form. The calculated E_{ads} of H2 on Cu6@C24N24 is lower than that reported on Ti2C- and Ti2CN-Mxenes (E_{ads} in the range of −0.99 to −1.4 eV) [60]. A negligible charge transfer from CO2 (H2) to Cu6@C24N24, the large Cu-C (Cu-H) bond length, and the low WBIs value of 0.12 (0.2) confirm physisorption of these CO2 (H2) species on Cu6@C24N24.

4.3. Adsorption of N2 and NO2

Two different orientations were considered for N2 adsorption on each structure: side-on or end-on. The ideal catalyst would provide strong binding sites for the N2 molecule and thus weaken the N−N bond. Our results indicate that the ideal orientation for N2 adsorption on Ti2Cu4@C24N24 and Ti2Mn4@C24N24 and Mn3Cu3@C24N24 is the end-on (see Figure 8). Upon N2 adsorption, the N-N bond length increases from 1.09 Å in the gas phase to 1.11 and 1.12 Å in its adsorbed form on Ti2Cu4@C24N24 and Ti2Mn4@C24N24 complexes, respectively. These values are in between the double and triple bond lengths, indicating the activation of N2 upon adsorption on Ti sites. The empty d orbitals of the Ti atom can accept the lone-pair electrons of N2. In turn, the Ti’s capacity to donate electrons to the antibonding π* orbital of N2 is also significant for N2 binding to Ti. Therefore, this electron acceptance/donation process between the nanocage and N2 plays an important role in N2 activation (see Table S5). Ti2Mn4@C24N24 has a greater tendency for N2 activation with higher adsorption energy than that reported on Co-doped graphitic carbon nitride (−1.63 eV) [61] and Fe doped phosphorene (−0.81 eV) [62].

Figure 7. The optimized configurations of CO2 and H2 on bi-metal complexes. All bond distances are in Å. Color code: white, Ti; orange, Cu; purple, Mn; red, O; grey, C; blue, N.

Figure 8. The optimized configurations of N2 and N2O on bi-metal complexes. All bond distances are in Å. Color code: white, Ti; orange, Cu; purple, Mn; red, O; grey, C; blue, N.

Although the Mn3Cu3@C24N24 complex adsorbs N2 molecule with lower E_{ads}, due to its lower catalytic activity toward gas adsorption, this value is still higher than that on Mn-Fe bi-metal atoms anchored pyridinic nitrogen-doped graphene (E_{ads} = −0.53 eV) [63]. The calculated WBIs (≈0.0001) and charge transfer confirm the N2 physisorption on Mn3Cu3@C24N24.

Regardless of all possible bi-metal distributions into the porphyrin C24N24 cavities, the three Ti3Cu6@C24N24, Ti2Mn4@C24N24, and Mn3Cu3@C24N24 (x, y = 0–6) complexes with
all the metal ratios exhibit an outstanding activity toward NO\textsubscript{2} adsorption and activation. However, the more stable configurations are shown in Figure 8. One can see that the NO\textsubscript{2} molecule binds via two O atoms with the Ti atom in Ti\textsubscript{6}@C\textsubscript{24}N\textsubscript{24} and Ti\textsubscript{2}Mn\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} and with the Mn atom in the Mn\textsubscript{3}Cu@C\textsubscript{24}N\textsubscript{24} complex, respectively. Owing to the great NBO charge transfer from the nanocage to the NO\textsubscript{2} molecule (0.46 |e|) reported in Table S5, the N-O bond length increases compared to that of the gas phase (1.19 Å).

4.4. Electronic and Thermodynamic Properties

To see if the adsorption of CO\textsubscript{2}, NO\textsubscript{2}, H\textsubscript{2}, and N\textsubscript{2} gas species on the selected twelve more energetically stable complexes affects their electronic properties, we also investigated the LUMO-HOMO energy gap of each structure and compared our results with those of pristine bi-metal doped nanocages reported in Figure 5. The obtained \( E_g \) values for adsorption structures are listed in Table S5, showing that \( E_g \) indeed increases upon gas adsorption. This confirms the tunable electronic properties of C\textsubscript{24}N\textsubscript{24} nanocage induced by hosting six dissimilar bi-metals doping into its N\textsubscript{4} cavities with various distribution patterns. All adsorption reactions are exothermic and exergonic, except for H\textsubscript{2} adsorbed on the Cu\textsubscript{6}@C\textsubscript{24}N\textsubscript{24} complex, which is slightly endergonic (see Table S5).

4.5. Lifetime of the Adsorbed Gas Species on Bi-Metal Complexes

The retention time of a molecule on a surface can be calculated with the Frenkel equation [64]:

\[
\tau = \tau_0 e^{Q/RT}
\]

where \( \tau_0 \) is \( 10^{-12} \) to \( 10^{-13} \) s and \( Q \) is the adsorption energy. We calculated the lifetime of each adsorbent over each configuration from which the energetically more favorable structures were chosen and plotted versus temperature. Figure 9 shows the computed lifetime vs. temperature for adsorbed CO\textsubscript{2}, NO\textsubscript{2}, H\textsubscript{2}, and N\textsubscript{2} on the twelve nanocages discussed above. As can be seen in Figure 9, the lifetime of gas species on Ti\textsubscript{6}Cu\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} and Ti\textsubscript{6}Mn\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} at 400 K is higher than that on Mn\textsubscript{4}Cu\textsubscript{6}@C\textsubscript{24}N\textsubscript{24} (x, y, z = 0–6), indicating that Ti\textsubscript{6}Cu\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} and Ti\textsubscript{6}Mn\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} are likely to be more efficient for gas capture. Obviously, increasing the temperature reduces the lifetime leading. However, Ti\textsubscript{6}Cu\textsubscript{4}@C\textsubscript{24}N\textsubscript{24}, Ti\textsubscript{6}Mn\textsubscript{4}@C\textsubscript{24}N\textsubscript{24}, and Mn\textsubscript{4}Cu\textsubscript{6}@C\textsubscript{24}N\textsubscript{24} catalysts capture NO\textsubscript{2} so actively that it will not desorb from the catalyst even at high temperatures. Therefore, we can conclude that, except for NO\textsubscript{2}, which effectively adsorbs and is retained on the catalysts, the gas species adsorb and remain on the Ti active site of Ti\textsubscript{6}Cu\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} and Ti\textsubscript{6}Mn\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} fullerene at room temperature, whereas they are not retained on Mn\textsubscript{4}Cu\textsubscript{6}@C\textsubscript{24}N\textsubscript{24} sufficiently for gas capture.

Figure 9. Cont.
5. Conclusions

In this work, the effect of dissimilar bi-metal doping into the six porphyrin-like cavities of a C\textsubscript{24}N\textsubscript{24} nanocage on the catalytic activity and adsorption characteristic of a number of greenhouse gases are investigated by means of DFT calculations. The binding energy and bulk cohesive energy calculations reveal that the selected TM atoms are stably trapped in the C\textsubscript{24}N\textsubscript{24} cavities, especially Ti/Cu atoms in Ti\textsubscript{x}Cu\textsubscript{y}@C\textsubscript{24}N\textsubscript{24} and Ti/Mn atoms in Ti\textsubscript{x}Mn\textsubscript{y}@C\textsubscript{24}N\textsubscript{24} (x, y, z = 0–6) complexes, suggesting the durability of the catalysts. Studying the adsorption behavior of these catalysts toward H\textsubscript{2}, CO\textsubscript{2}, NO\textsubscript{2}, and N\textsubscript{2} sensing show that the Ti\textsubscript{2}Mn\textsubscript{4}@C\textsubscript{24}N\textsubscript{24} is more active for adsorption of all species. Furthermore, the lifetime of each gas species on Ti\textsubscript{x}Cu\textsubscript{y}@C\textsubscript{24}N\textsubscript{24} and Ti\textsubscript{x}Mn\textsubscript{y}@C\textsubscript{24}N\textsubscript{24} at 400 K is higher than that on Mn\textsubscript{x}Cu\textsubscript{y}@C\textsubscript{24}N\textsubscript{24} (x, y, z = 0–6), indicating that Ti\textsubscript{x}Mn\textsubscript{y}@C\textsubscript{24}N\textsubscript{24} and Ti\textsubscript{x}Cu\textsubscript{y}@C\textsubscript{24}N\textsubscript{24} are likely to be more efficient for gas capture. Overall, this work systematically provides the unique fundamental understanding of catalytic properties of two dissimilar bi-metal atom catalysts that could open a way for the future design and development of novel few-atom catalysts.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/nano11071794/s1, Figure S1: A schematic representative of available active sites (shown with red stars) on various BM@C\textsubscript{24}N\textsubscript{24} configurations. Color code: white, Ti; orange, Cu, Table S1: The calculated cohesive energy (E\textsubscript{coh}) per atom of C\textsubscript{24}N\textsubscript{24}, binding energy (E\textsubscript{b}) of hydrogen molecule and Ti\textsubscript{x}-doped C\textsubscript{24}N\textsubscript{24} along the energy gap of pristine C\textsubscript{24}N\textsubscript{24} using different functional and basis sets, Table S2: The calculated binding energy (E\textsubscript{b}), change of enthalpy (\Delta H\textsubscript{298}), change of Gibbs free energy (\Delta G\textsubscript{298}), energy gap (E\textsubscript{g}), and the average NBO charge on Ti\textsubscript{x}Cu\textsubscript{y}@C\textsubscript{24}N\textsubscript{24}. All the values are in eV, Table S3: The calculated binding energy (E\textsubscript{b}), change of enthalpy (\Delta H\textsubscript{298}), change of Gibbs free energy (\Delta G\textsubscript{298}), energy gap (E\textsubscript{g}), and the average NBO charge on Ti\textsubscript{x}Mn\textsubscript{y}@C\textsubscript{24}N\textsubscript{24}. All the values are in eV, Table S4: The calculated binding energy (E\textsubscript{b}), change of enthalpy (\Delta H\textsubscript{298}), change of Gibbs free energy (\Delta G\textsubscript{298}), energy gap (E\textsubscript{g}), and the average NBO charge on Mn\textsubscript{x}Cu\textsubscript{y}@C\textsubscript{24}N\textsubscript{24}. All the values are in eV, Table S5: The calculated total adsorption energy (E\textsubscript{ads}), energy gap (E\textsubscript{g}), changes of enthalpy(\Delta H\textsubscript{298}), changes of free energy(\Delta G\textsubscript{298}), and NBO charge analysis for the energetically more stable adsorption configurations.

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