In this report, we study the ordering of C_{60}, Sc_{3}N@C_{80}, and Dy_{2}ScN@C_{80} molecules on different metallic and dielectric surfaces such as Ag(100), Au(111), and MgO(100). By using DFT techniques, we can classify different types of cage-to-surface arrangements and their relative energies. Using a proposed homogenous sampling of the conformational space for the M_{3}N cluster, we determine a potential energy map that is capable of providing a structural distribution for a given energy window. We find that Coulomb interaction is a dominant force that governs the system's stability and order. However, a deep analysis of the charge density rearrangements reveals that even though the integral charges may be considered as a qualitative control parameter, it fails to provide quantitative data due to the importance of spatial characteristics of charge densities.
relative orientations and the charge density separation between the DyScN@C80 (MOI, stands for Molecule of Interest, later in the text) and surfaces. Moreover, by analyzing the real space charge densities in these systems, we concluded that localized charge pictures, for example, Bader charges, can be very misleading in the interpretation of charge rearrangements.

2 | METHODS

In the following, unless otherwise stated, the level of theory is DFT/PBE-D3/PAW, as implemented in VASP 5.0 with f-shell in core treatment for Dy atom. For all optimizations the Γ-point approximation is used with \( 5 \times 5 \times 6 \) metal supercells and \( 3 \times 3 \times 2 \) for MgO, which accounts for the next neighbor distances between fullerene cages of 14.4 Å—metals and 12.6 Å—MgO. We would like to emphasize that even though the whole system is considered in G-point, for the surfaces, due to supercell construction (\( 5 \times 5 \) in our case for the metals), the momentum space is sampled beyond G-point through real space integration for surface-based electrons. To generate a complete set of possible orientations of the \( 3N \) cluster inside the \( C_{80} \) cage the Fibonacci spherical grid is used to accomplish maximum homogeneous and most uniform sampling on a sphere. In this study, 120 original conformers are used. All in all 360 optimized structures are analyzed in these studies.

3 | RESULTS AND DISCUSSIONS

First, we outline the scope of the problem and thereby emphasize some obvious shortcomings in common strategies of similar research, and thus formulate an approach that we will use to accomplish the reproducibility goal of obtaining theoretical data.

Here, our aim is to construct potential energy surface (PES) fold that is complex enough to track and select thermodynamically stable conformational isomers within a certain energy range. As the system of interest consists of MOI and a surface, from a whole set of available degrees of freedom the angle between positive normal to the DySc plane and z-axis will be used. Such a single control parameter is sufficient to follow the conformational changes in the system due to cluster rotation. We have employed a similar strategy while studying \( 3N \) hosted by Ni(OEP) with great success. However, there are many more important unknowns capable of affecting the solution. Probably the most important are the following two. First, how far the molecule is positioned above the surface? Within local optimization algorithms, a few local minima are possible. Second, how the fullerene itself is oriented toward the surfaces? Although the \( C_{80} \) cage is a high symmetry cage, there are still quite a few options. Besides, with a low symmetry cluster inside, the amount of possible cage orientations grows dramatically. However obvious these questions are, they are often overlooked or simply ignored as less of importance. Nevertheless, both these questions would affect the accuracy and reproducibility of the theoretical data.

Thus, before a conformational analysis of the inner cluster, we have to position the MOI optimally next to the surfaces. To limit the number of possible cases some assumptions have to be made. Here, we use the fact that the cage and surfaces interact stronger than the cluster and cage. This assumption is easy to justify, as it is known that in the isolated \( 3N@C_{60} \), \( 3N \) rotates freely. This allows focusing solely on one nonspecific orientation of the cluster while studying the relative positions of MOI on the atomic grid.

The distance between MOI and the surfaces is defined as the difference between the maximum of the \( z \) component of the surface and the minimum of MOI. This distance is used to set 10 initial geometries with step 0.25 from the surfaces up to 5.0 Å, and then optimized down to selected optimization criteria with no constraints attached. Although it might come as an unconventional approach, not a regular PES scan along a selected degree of freedom, this exercise is very illustrative all the same and allows recovery of the true minima in these systems. It is very difficult to make a proper scan as PES appeared to be relatively smooth within the same set of optimization thresholds, having only one minimum on a wide energy and distance range. Nevertheless, for Ag(100) and Au(111), the proposed distance analysis has revealed a minimum at 2.1 Å, and for MgO at 2.6 Å. Hereinafter all initial geometries are positioned at these optimal distances for the respective surface as derived from this exercise.

Now, we can consider the essential question of the relative orientations of the MOI next to surfaces. Here, MOI = Sc3N@C_{60} and C_{60} are representative trial cases. Both cases have multiple orientation options (Table 1). Edges [6] and [5, 6] of the cages were selected as reference points—the C–C bonds through which two hexagons and hexagon and pentagon faces are joined. Other reference points include vertices [6] and [5, 6], with a transparent logic behind the names. Furthermore, the surfaces also provide additional options like the void or metal sites for the Ag, Au surfaces, and Mg or O sites for the MgO case. Overall, 12 systems for Sc3N@C_{60} and 6 for C_{60} were considered as initial guesses, which are summarized in Table 1. Also, the inner cluster orientation initially was parallel to the surfaces but free to change during optimization.

Figure 1AB show the energy distribution following the complete optimizations of MOI/Surfaces systems with ID geometries (Table 1) as initial guesses. As mentioned before, due to the local nature of the optimization procedure, most of the minima are found in close proximity to the starting geometry. Also, the inner DyScN cluster remained in the same relative orientation. Thus, almost all 12 distinct cases can be seen with just some little twist to the original geometries (Figure 2). Among them, ID = E12 where the pentagon is next to the void in Ag(100), and Au(111), and O site in case of MgO. This configuration along with E1, E5, and E10 are the most stable for all the types of the surface. Same as E2, E9, and E11 cases are least energetically stable for all the surfaces. It is important to note that the total energy spreads over 0.6–0.7 eV for metals and 0.3 eV MgO. Also, we find that for the same cluster orientation toward the surface, the energy difference between the most stable cage orientation and the median energy from other orientations is \( \delta \varepsilon \sim 0.25 \) eV for metals and 0.15 eV for MgO. Thus, if conformational changes of the cluster would lead to the energy change greater than \( \delta \varepsilon \).
As it was already affirmed the initial geometries for Sc$_3$N@C$_{80}$ were set on the optimal distance. After the optimization process the molecule-surfaces gap—dz, and the distance between the two closest atoms from MOI and a surface d(M—C) were evaluated again and provided in Table 2. We also analyzed Bader charges$^{27,28}$ accumulated on the MOI. It is worth pointing out, though, that the charge transfer is affected little by relative molecular orientations, but by the distance to the surface. Furthermore, in the case of C$_{60}$, the charge transfer appears to be bigger which could be seen in the case of Ag(100) or MgO(100) surfaces (Table 2). These charge transfer values for the Ag(100) are in good agreement with other calculations.$^{29}$ The values reported for Ag(100) and Au(111) and defined by direct integration lay relatively close to those given in Table 2.$^{24}$

To have a better perception of the connection between the charge transfer intensity and the type of the surface, the same study was conducted for the trial MOIs on the different surface faces (Table 3). We find that within the same surface type an amount of charge transfer remains very close for different faces. Also, the results (Tables 2 and 3) demonstrate that the empty cage has slightly higher electron acceptor properties, while the Au surfaces are quite inert.

Furthermore, the direction of charge transfer on Au is rather curious and requires deeper consideration. Therefore the real space charge density redistribution (depletion and accumulation) was computed by subtracting from the total densities the densities of isolated MOIs and surfaces:

\[
\delta \rho (r) = \rho_{\text{MOI}}(r) - \rho_{\text{MOI}}(r) - \rho_S(r).
\]

These difference electron densities for most stable C$_{60}$ Surfaces and Sc$_3$N@C$_{80}$ Surfaces on Au(111) are shown in Figure 3. Expectedly, the density rearrangement is more prominent in the contact area (in the gap) of MOI and the surface. In both cases, MOIs accumulate positive fragment density while the surface regions host most of the negative parts of $\delta \rho (r)$. But in the case of C$_{60}$ on Au(111), $\delta \rho (r)$ forms an intertwined net with alternating pockets of density depletion and accumulation. Thus, although the overall picture is consistent with the direction of the charge transfer from the integral values of Bader charges Tables 2 and 3, one can see that the exact values of the atom properties would vary significantly by choice of the integration basin. Therefore, it is always beneficial and more instructive to follow the exact $\delta \rho (r)$ topology rather than integrated values. Having all these in mind, we further analyzed conformational ordering and charge distribution preferences in the promising SMM candidate— Dy$_2$ScNC$_{80}$ Surfaces.

### 3.1 Conformation trends of Dy$_2$ScN$_2$ Surfaces

The optimal configurations EG1, EU1, and EM1 (see Figure 1) were used as frameworks for the subsequent analysis of Dy$_2$ScN cluster rotation along with the Fibonacci nodes. The resulting energy distributions are provided in ESI, Figure 4. The most stable geometries from this set helped us rationalize experimental observables in Krylov et al.$^{16}$ The effect of the surfaces is very pronounced. There relative
FIGURE 2  Four of most important binding motifs predicted for C_{60} (left) and Sc_{3}N@C_{80} (right) on Ag(100), Au(111), and MgO(100) surfaces. The corresponding names and relative energy is given below each conformer in meV. A lower part of a carbon cage and the closest segment of the upper layer of a surface are displayed.

TABLE 2  Intermolecular distances and charge characteristics for the most stable orientational configurations of C_{60} and Sc_{3}N@C_{80} on Ag(100), Au(111), and MgO

|       | C_{60} | Sc_{3}N@C_{80} |
|-------|--------|----------------|
|       | ID     | dz, Å          | d(M-C), Å | Q_{mol}, e | ID     | dz, Å          | d(M-C), Å | Q_{mol}, e |
| BG1   | 2.27   | 2.41           | −0.55     |            | EG1   | 2.11   | 2.44           | −0.24     |            |
| BG2   | 2.23   | 2.46           | −0.47     |            | EG2   | 2.18   | 2.39           | −0.27     |            |
| BG3   | 2.00   | 2.42           | −0.52     |            | EG3   | 2.04   | 2.43           | −0.26     |            |
| BG4   | 2.10   | 2.31           | −0.41     |            | EG4   | 2.02   | 2.43           | −0.23     |            |
| BU1   | 2.10   | 2.29           | −0.00     |            | EU1   | 1.99   | 2.30           | +0.23     |            |
| BU2   | 1.88   | 2.26           | +0.03     |            | EU2   | 2.01   | 2.37           | +0.26     |            |
| BU3   | 1.85   | 2.23           | +0.09     |            | EU3   | 1.93   | 2.27           | +0.28     |            |
| BU4   | 2.07   | 2.33           | +0.09     |            | EU4   | 1.98   | 2.35           | +0.23     |            |
| BM1   | 2.38   | 2.51           | −0.18     |            | EM1   | 2.69   | 2.96           | −0.13     |            |
| BM2   | 2.30   | 2.42           | −0.24     |            | EM2   | 2.55   | 2.64           | −0.13     |            |
| BM3   | 2.53   | 2.75           | −0.21     |            | EM3   | 2.58   | 2.70           | −0.12     |            |
| BM4   | 2.50   | 2.78           | −0.19     |            | EM4   | 2.59   | 2.78           | −0.12     |            |

Note: The right picture visualizes the geometrical parameters, where dz is the minimal difference between z components of MOI and a surface, d(M-C) is the distance between the closest atoms of MOI and a surface, Q_{mol} is a Bader-defined accumulated charge on a molecule.
energy spread for different conformers (Dy$_2$ScNC$_{80}$Au) on metals is 6 times bigger compared to isolate molecule (Dy$_2$ScNC$_{80}$). With max ($\Delta E$)~50 meV it indicates a strong interaction between the metallic surfaces and the MOI leading to a spatial extension of the PES. The same effect, but to a smaller extent is observed on MgO(100). To be less interactive is quite intuitive behavior for a self-saturated insulator. Thus, in this case, the energy spread is twice as small (~25 meV) if compared to the metal surfaces.

These scatter plots show the position of distinct minima of PES along the $\Theta$ degree of freedom. The small energy differences between neighboring pairs of the optimized conformers indicate the possibility of the cluster rotation (assuming the Bell-Evans-Polanyi principle is valid and the barriers between the nearest conformers are proportional to the enthalpy). Nevertheless, these folded PESs (Figure 4) have a visible clustering along the $\Theta$ coordinate with energy preference of certain angles of Dy$_2$ScN clusters relative to an underlying surface. Therefore, if employed experimental techniques have sufficiently high energy resolution ($\delta \epsilon$) and the system is under thermodynamic control, we can separate conformers $\Theta_i$ and $\Theta_{i+1}$, if $\Delta E_i = E(\Theta_i) - E(\Theta_{i+1}) < \delta \epsilon$.

From the data in Figure 4, we find that $\delta \epsilon$ border value should be below 50 meV (which corresponds to $2k_BT$ at room temperature) so the system Dy$_2$ScNC$_{80}$ order would be distinguishable on different surfaces.

Thus, for metals, the conformers closer to $\Theta = 0^\circ$ value would dominate the sampling. At the same time, for the MgO surfaces, there are 2 preferential orientations at nearly $40^\circ$ and $75^\circ$. On a whole, both these findings are consistent with experimental observation.

Also, we find the energy overlap between cage location isomers and cluster conformers for a given cage orientation—Figures 1A and 4. As mentioned, it leads to a formal necessity to consider the conformational transformations of the cage and the cluster together. At this time such a problem would be unfeasible. However, the obtained patterns would likely be preserved through the variation of the cage position.

### TABLE 3  Bader charge values accumulated on the optimally positioned individual C$_{60}$ or Sc$_3$N@C$_{80}$ molecule deposited on different surface faces

| Surface     | C$_{60}$ | Sc$_3$N@C$_{80}$ |
|-------------|---------|-----------------|
| Ag(100)     | -0.56   | -0.24           |
| Ag(110)     | -0.65   | -0.37           |
| Ag(111)     | -0.40   | -0.17           |
| Au(100)     | -0.06   | 0.19            |
| Au(110)     | -0.08   | 0.13            |
| Au(111)     | 0.04    | 0.23            |
| Cu(100)     | -0.72   | -0.42           |
| Cu(110)     | -0.82   | -0.41           |
| Cu(111)     | -0.54   | -0.28           |
| MgO(100)    | -0.20   | -0.13           |

### FIGURE 3  Difference electron densities as defined by Equation (1), for four most stable configurations of C$_{60}$Au(111) (top row) and Sc$_3$N@C$_{80}$Au(111) (bottom row). Here, the red isosurfaces (isovalue = XYZ e/Å$^3$) correspond to accumulation of electron densities and while the blue ones correspond electron density depletion. The intermixed nature of charge separation in the system makes it difficult to rely on integrated values and on-site (atomic) properties

#### 3.2  Difference densities in Dy$_2$ScNC$_{80}$Surfaces

Further, the Bader analysis has revealed the correlation between the charge transfer value and the relative cluster orientation toward the
surfaces (the charge transfer is color-coded in the scatter plot in Figure 4). Even though the spread of the charge transfer values \( \max_{\text{MOI}} |\sum_{i \in \text{MOI}} \phi_i| - \min_{\text{MOI}} |\sum_{i \in \text{MOI}} \phi_i| \) is humble 0.1 \( \text{e} \), one can read the trend clearly. This correlation is more pronounced in the case of the Au(111) surface, where the charge transfer gradually decreases with \( \Theta \) and destabilizes the system.

On the Ag(111) surface, the charge transfer reverses direction in terms of Bader analysis. However, as we have eluded before, these integral values may be deceptive and the real space density analysis may be more helpful. Accordingly, the difference electron densities were obtained (Equation (1)) and are shown in Figure 5 for the two most stable and most unstable conformers on these surfaces. The overall appearance of \( \delta \phi(r) \) is similar to one in cases of the trial MOIs and concentrate mostly in the contact area, or, more precisely, in the gap between MOI and the surface.

In the case of Au(111), two domains formed with most of density depletion on carbon cage and accumulation on the surface. In the Ag(100) case, \( \delta \phi(r) \) forms intertwined net with alternating pockets of density depletion and accumulation as we have seen before in the case of C_{60}/Au(111) system, which generalizes the observation.

Furthermore, we find a similar topology of \( \delta \phi(r) \) account for very different local properties. For example in Figure 5 (the gold surface case) the Bader charge predicted for the most stable and most unstable conformer have a two-fold difference in terms of Bader charges \( \sum_{i \in \text{MOI}} \phi_i = -0.14 \) and \( \sum_{i \in \text{MOI}} \phi_i = -0.26 \), however, the spatial order of \( \delta \phi(r) \) is identical. Thus, in this case, concluding the exact amount of charge transfer in terms of the localized model will be an inadequate approach. Nevertheless, it should be noted, that spatial ordering of \( \delta \phi(r) \) forces inner clusters to avoid the regions of \( \pi \)-systems distortion in the cage. For metals, it means the parallel orientation of the cluster toward the surfaces. For less electronically distorted MgO the small perturbation region surfaces as attractor instead, making perpendicular order more preferable (Figure 5).

### CONCLUSIONS

In conclusion, we provided an inclusive DFT study of the functional fullerene-based molecules (C_{60}, Sc_{3}N@C_{80}, Dy_{2}ScN@C_{80}) ordering next to metal (Au, Ag) and dielectric (MgO) surfaces—the MOI/Surface systems. We investigated systems stability as a function of the surface...
proximity, the fullerene cage orientations toward the surfaces and the cluster conformation. We found that the relative energy scale for surfaces positioning is roughly 0.5 eV and coincides with the energy scale of the inner cluster rotation \( \langle \cos \theta \rangle - E(\theta_{i+1}) \sim 0.4 \text{ eV} \). We find that cluster ordering in EMF is controlled by overall charge distribution in the systems. However, having analyzed the charge delocalization in terms of local properties and real space distributions, we found very similar topological trends in electron densities but very different local atomic properties. Thus, we conclude that the local atomic properties cannot be used as a guide and real space densities are more reliable properties.

**ACKNOWLEDGMENTS**

S.A. acknowledges funding German Research Foundation (DFG) Grant AV/169-3. Computational resources were provided by the centre for Information Services and High Performance Computing (ZIH) in TU Dresden. We thank Ulrike Nitzsche for technical assistance with computational resources in IFW Dresden. Open Access funding enabled and organized by Projekt DEAL.

**DATA AVAILABILITY STATEMENT**

All structural information that supports the findings of this study is available in the local database at IFW, Dresden, and will be provided upon request.

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**How to cite this article:** V. Dubrovin, S. M. Avdoshenko, J. Comput. Chem. 2022, 43(24), 1614. https://doi.org/10.1002/jcc.26962