

Localized π Surface States on 2D Molybdenum Disulfide from Carbene-Functionalization as a Qubit Design Strategy

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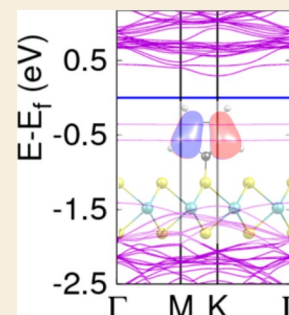


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Supporting Information

ABSTRACT: Surface chemistry is increasingly important for a number of applications, from catalysis to molecular qubits. For the qubit application, it is imperative that the energy levels of surface species involved in the process of interest are energetically distinct—that is addressable and not buried below or coincident with the substrate energy levels. One way to afford this is through chemical functionalization with derivatives that impart the property of choice to the interface. In this Letter, we report on the nature of the bond between a carbene moiety and an MoS₂ surface. With density functional theory (DFT) and spin-polarized calculations, we first observe states in the band structure that pertain to the carbene group and then prove their origin. Importantly, we find localized π -states in the band gap that are due to π -electrons that are part of a diene attached to the carbene carbon and are not available in bonding configurations without the π conjugation. These lead to open-shell monocationic structures involving midgap HOMOs with densities on the carbene moiety. Both neutral and cationic forms of the carbenes are energetically separate from the MoS₂ substrate, thus useful for optical manipulation. We explore several different choices of the carbene moieties, and show that those based on fused thiophene and bithiophene structures are the most favorable for localization, while purely carbon-based aromatic structures lead to states that are delocalized onto the MoS₂ and thus less useful. These findings are potentially of interest to the design and synthesis of future molecular qubit candidates for device fabrication.



KEYWORDS: carbene, band structure, molybdenum disulfide, spin, qubit, design, electronic states, functionalization

Molecular qubits¹ hold promise for future quantum computation,² yet their chemical engineering is highly challenging due to the limited design strategies at the molecular level.³ Functional 2D materials^{4,5} have long been a platform of choice for these technologies with significant development recorded in the literature over the last couple of decades.^{6,7} One key challenge is the synthesis of a molecular component that has its active electronic states both physically and energetically separate from the basal plane,^{8,9} yet localized and stable toward electron or spin transfer.¹⁰ Hence the rational design of molecular qubits and the 2D material support need to be considered together, not separate.

To this end, we previously reported¹¹ a range of derivatives covalently bonded to the surface sulfur of a 2D monolayer of molybdenum disulfide (MoS₂) that exhibited midgap electronic states which could lead to optically addressable molecular qubit systems. Derivatives with single electron donors such as hydrogen, halogen, methyl, and phenyl have a nonzero spin density due to the nature of the bonding, which involves covalency between the bonding derivative atom and a surface sulfur that is closed shell before functionalization. One derivative, a carbene (1,3 cyclopentadiene carbene), sits in a triplet state in free form, but becomes a singlet state when bound to the surface. In this case, the carbene is bonded to one sulfur atom and the band structure shows four electrons (two α and two β) in addition to the bands of the MoS₂, with no net spin as the α and β exactly cancel. The localized states¹² appear

as horizontal (flat) bands in contrast to the curved bands of the 2D material. Although two of these states are due to the two carbene electrons, as expected for a single bond, the nature of the other two was not determined.

Here, we study the origins of these states by probing an initial set of carbene derivatives (cyclopentadiene, cyclopentene, and cyclopentane) that contain a varied amount of π -electrons, where we can classify them as being unsaturated 1, half saturated 2, or fully saturated 3. With density functional theory (DFT) calculations, we show the origin of those unknown bands to be π -electrons and that they are not delocalized onto the MoS₂ surface. Additional carbenes are then considered to optimize localization for both the neutral and cationic states of the carbene/MoS₂ system.

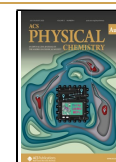
The covalently bound carbene structures 1–3 on the MoS₂ surface are shown in Figure 1A (hydrogen atoms not shown) and their spin-polarized band structures in Figure 1B. These were computed at the PBE/DZP level in the Spanish Initiative for Electronic Simulations with Thousands of Atoms

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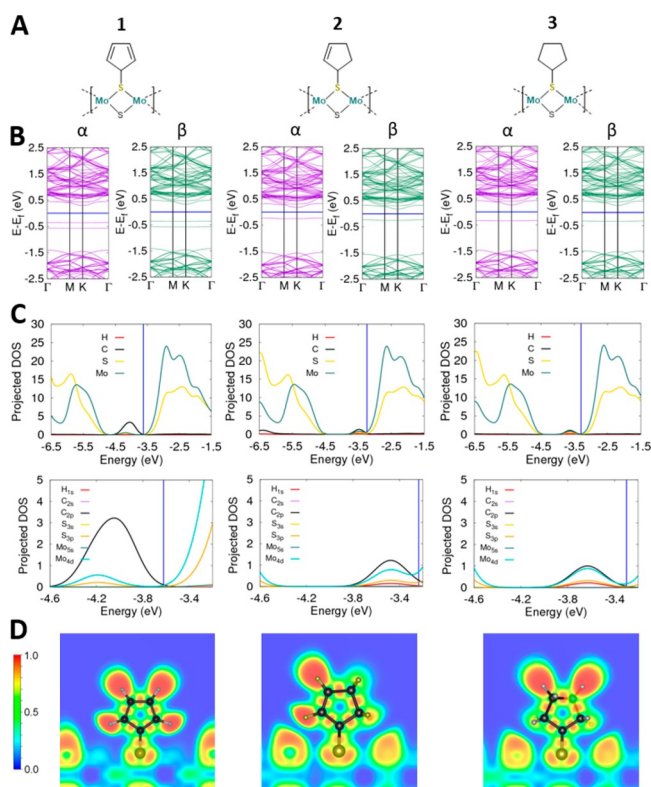


Figure 1. (A) Structures of three carbene derivatives that are functionalized to the surface sulfur of a 2D monolayer MoS₂; (B) their spin-polarized band structure; (C) projected density of states across the band gap and a zoomed-in region around the midgap states; (D) the electron localization function (ELF) plots.

(SIESTA) program¹³ (version 4.1 b3) and confirmed at the same level in the Vienna Ab Initio Simulation Package¹⁴ (VASP, version 5.4.4), Figure S1; for completeness, the plots were also computed at the HSE06 level with and without spin orbit coupling (Figure S2), and although they showed some shifting of the states as well as valence band splitting, no significant differences in terms of the number or position of the midgap states are apparent. For complete details, see the Methods section in the Supporting Information. Structure 1 has four occupied midgap states, while 2 and 3 have two each, one α and one β . Those of 2 and 3 are relatively the same energy from the Fermi level as to the highest energy states of 1, with the second states in 1 being only <200 meV lower. Metal atoms adsorbed onto the surface of MoS₂ have also been found to produce localized spins and midgap states,¹⁵ but through p-d orbital hybridization. These are potentially of interest for device applications but do not offer synthetic tunability.

The projected density of states (PDOS) are presented in Figure 1C, where the top three panels are the full spectra and the lower three are a zoomed in region around the midgap states. For 1, we can see a broad asymmetric DOS for the carbon atoms, and some states arising from both sulfur and molybdenum. In all three cases, these are associated with p orbitals. The carbon DOS peak is shifted away from the molybdenum and sulfur DOS, which situate around -4.2 eV, but still covers the same region. Therefore, the carbon DOS of 1 contributes to both the localized states in the band structure, but the molybdenum and sulfur do not and only contribute to lower energy states. This implies that the states from the higher energy band arise from the carbon atoms with the double

bonds and not other atoms. The DOS for the midgap states of both 2 and 3 shows significant amounts of carbon, molybdenum, and sulfur.

To check the covalent nature of the carbenes on the surface, electron localization function (ELF) calculations were conducted and are presented in Figure 1D. The red and blue colored regions show the presence and absence of electron density, respectively. The 1s-like orbitals of the hydrogen atoms are immediately seen for all structures 1–3, although those for the 2 and 3 are diminished for some atoms because the hydrogens are sitting either in front of or behind the plane of the ELF plot. The densities around the sulfur atom that the carbene is bound to are split into three small regions, where two are for bonding to adjacent molybdenum and the third is to the bonded-carbon, the presence of which implies a covalent bond.

The wave functions of these states are plotted in Figure 2. The lowest unoccupied molecular orbital (LUMO) corre-

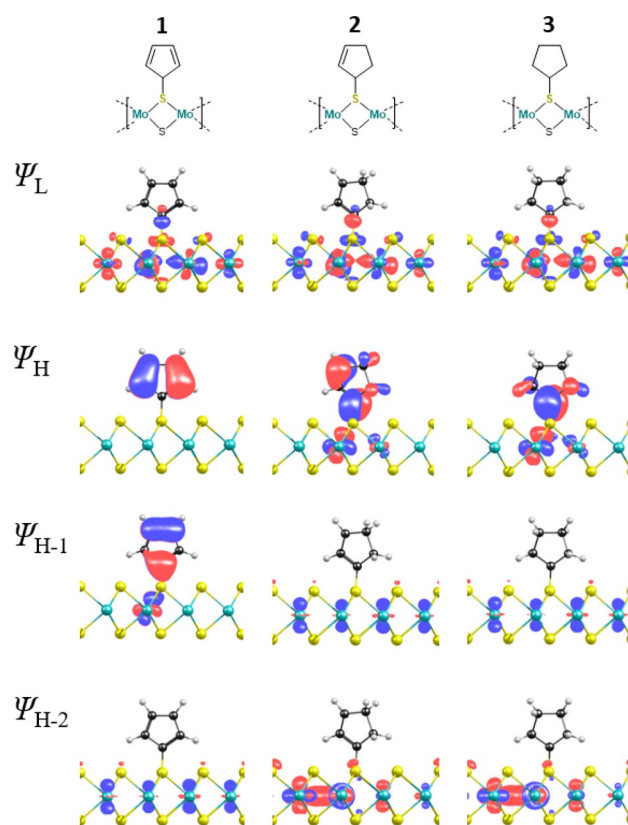


Figure 2. Plots of the FMO wave functions for the covalently bound carbene derivatives 1–3.

sponds to the lowest energy conduction band, and the highest occupied molecular orbital (HOMO) corresponds to the highest energy midgap state. The HOMO–1 level for 1 is the second midgap state, and for 2 and 3, it involves the valence band maxima inherent from MoS₂; the equivalent level in 1 is the HOMO–2. The π density can be seen in the HOMO level of 1, and as this wave function is localized around only the carbon atoms, it also corresponds well to the carbon DOS. 2 presents a more interesting case, where the HOMO wave function has densities on both the double bonds and thus π electrons, as well as around the carbon atom bound to the sulfur. This implies a wave function of mixed σ and π character.

The HOMO of **3** shows mostly carbene-like character. The hydrogen atoms of **2** and **3** are involved in some of the HOMO wave functions and explain the presence of H DOS in Figure 1C.

We expand the scope of this Letter by looking at the effects of the π electrons from fused-ring derivatives **4**–**7**, two of which are fully unsaturated (**4**, **6**), while two have saturated bonds on the right side of the original carbene ring (**5**, **7**). As before, midgap flat bands are seen in their spin-polarized band structure (Figure 3); structures **4** and **6** have two, while **5** and

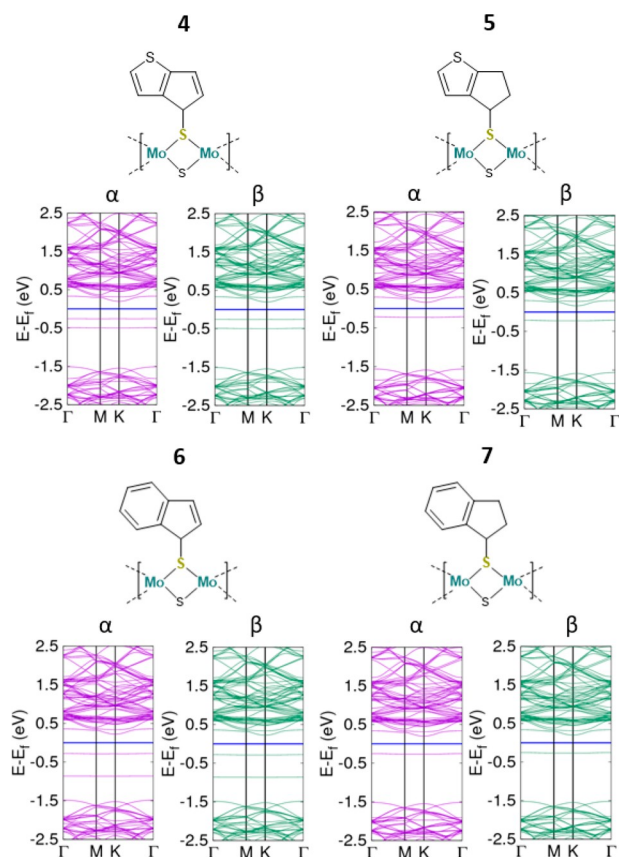


Figure 3. Structures and spin-polarized band structures of fused-ring thiophenyl- and phenyl- carbene derivatives **4**–**7**.

7 have one. The flat bands of the phenyl **6** have a larger energy difference between them than those of the thiophenyl **5**, and thus are stabilized by the extra aromatic delocalization.

The FMO wave functions of **4**–**7** are plotted in Figures S3 and S4.

For structures **5**–**7**, the upper band (HOMO) arises from the carbene electrons, while the lower bands are from π -electrons—this is akin to their nonfused counterparts **2** and **3**, with **6** being the exception. Some π states are only in the band gap if they are part of a diene configuration (with respect to the bonding carbene atom), such as with **1**, **4**, and **6**. The remaining π states are lower in energy than the valence band of the MoS₂ and thus difficult to see in the band structure, yet they can be determined by inspecting their FMOs.

Curiously, the addition of another thiophenyl (**8**) or phenyl (**9**) fused-ring to the other side of the cyclopentyl carbene generates band structures (Figure 5) and wave functions (Figure S5) akin to **4** and **6**. The only striking difference is the proximity of the two midgap states in **8**, where

the HOMO and HOMO–1 are almost degenerate, even if their orbitals show uniqueness.

Since they are localized on the adsorbate, and do not interact with the substrate, the surface π -states in **1**, **4**, and **6** have the potential for manipulation in an electronic device. Yet qubit devices and spintronics utilize the presence of spin, or unpaired electrons. To study this possibility, the derivatives **1**–**3** were optimized to their monocationic states, leaving one unpaired electron in their outer π shell. In practice, this could be achieved with electrochemical oxidation. The resulting band structures in Figure 4B show significant differences from the

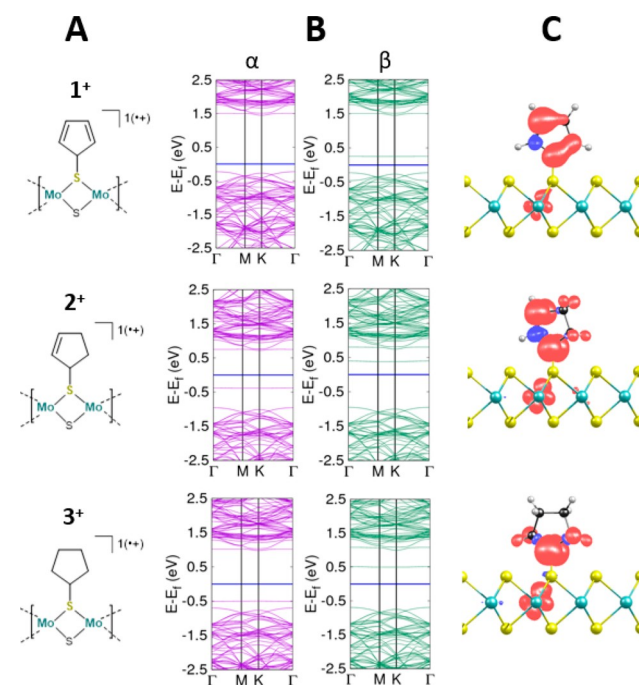


Figure 4. (A) Structures, (B) band structures, and (C) spin density wave function plots (both phases colored) of the optimized monocations of the carbene derivatives **1**–**3**.

closed-shell neutral states. For example, the midgap π -states are absent in the $1^{(\bullet+)}$ system, although they are likely shifted down to lower energies where they get mixed closer to the valence band. A new unoccupied β state is now present, due to the cation or hole in the system. $2^{(\bullet+)}$ and $3^{(\bullet+)}$ retain their midgap α state with the loss of the β electron. All systems have a net spin of 1 electron, where “spin” is in the SIESTA convention meaning the population of α electrons minus β electrons, rather than the actual spin of an electron (spin quantum number). This spin population is plotted from spin density difference calculations in Figure 4C. The spin populations appear similar to their closed-shell HOMO states yet the density of the unpaired electron undergoes some rearrangement, reflecting changes in orbital couplings when one electron is removed. It is important to note that the wave functions of these half-occupied monocationic states remain primarily on the carbene derivatives, similar to their closed-shell HOMO levels, and are not significantly delocalized onto the surface or below the valence bands. The observations for $[1-3]^{(\bullet+)}$ are the same for those of $[4-7]^{(\bullet+)}$ (Figure S5).

That said, one qualitative observation can be made, which is that some systems (**1**, **4**, **8**) exhibit π -character regardless of them being in either their neutral or monocationic states, while

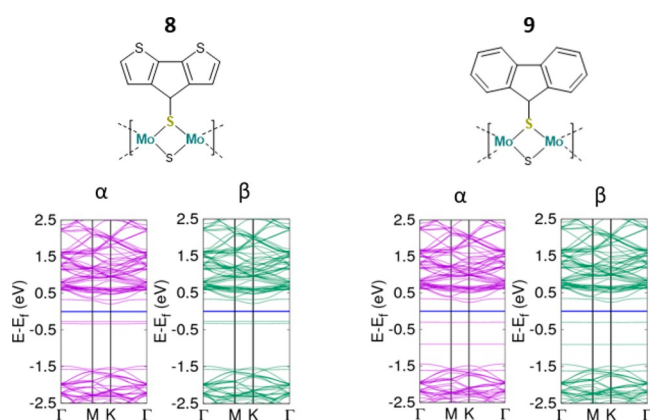


Figure 5. Structures and spin-polarized band structures of double fused-ring bithiophenyl- and biphenyl-carbene derivatives **8** and **9**.

others (**2**, **3**, **5–7**, **9**) retain more carbene-character, which is especially noticeable in the HOMO wave functions and also apparent in their spin densities. This is related to the first set of systems being fully unsaturated cyclopentyl and thiophenyl derivatives while the second set are either mixed saturation and/or phenyl derivatives. This phenomenon surrounding the combination of cyclopentyl and thiophenyl systems warrants a further in-depth study.

In conclusion, nine mono-, bi-, and tri-ring carbene systems have been studied as functionalized derivatives on 2D molybdenum disulfide. It was found that they exhibit midgap states that are readily distinguishable, and in some cases, localized as π states. In addition, monocationic states of all carbene-functionalized MoS₂ systems, regardless of having midgap π states or not, exhibit localized density on the carbene moiety, akin to their closed-shell counterparts. Both neutral and cationic systems have the potential to be optically addressable in molecular electronic devices, for applications such as molecular qubits¹⁶ or in quantum information.¹⁷ We also identified an interesting subset of fully unsaturated cyclopentyl and fused-ring thiophenyl carbenes that retain not just midgap π states but also strong π character in their monocationic spin densities, meaning they are excellent candidates for device applications. These findings should also be relevant for multilayer or bulk MoS₂, as the surface affects are semilocalized to the site of binding; because the important states are on the carbene, the results should be substrate independent, although calculations to determine this for graphene and borophene are underway. What is more, theoretical developments in quantum embedding^{18–20} and machine learning^{21,22} could significantly improve the efficiency of these endeavors toward a faster discovery of quantum spin materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acspchemau.1c00055>.

(The computational methods, band structures computed in VASP for **1–3**, molecular orbitals for **4–7**, and data for monocations of [4–7]^(•+) PDF)

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Notes

The authors declare no competing financial interest.

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