Quantum materials hold huge technological promise but challenge the fundamental understanding of complex electronic interactions in solids. The Mott metal–insulator transition on half-filled lattices is an archetypal demonstration of how quantum states can be driven by electronic correlation. Twisted bilayers of 2D materials provide an experimentally accessible means to probe such transitions, but these seemingly simple systems belie high complexity due to the myriad of possible interactions. Herein, it is shown that electron correlation can be simply tuned in experimentally viable 2D hexagonally ordered covalent organic radical frameworks (2D hex-CORFs) based on single layers of half-filled stable radical nodes. The presented carefully procured theoretical analysis predicts that 2D hex-CORFs can be varied between a correlated antiferromagnetic Mott insulator state and a semimetallic state by modest out-of-plane compressive pressure. This work establishes 2D hex-CORFs as a class of versatile single-layer quantum materials to advance the understanding of low dimensional correlated electronic systems.

1. Introduction

Hexagonally ordered single layers (SLs) of threefold connected sp² carbon sites (αC centers) possess one singly occupied nonhybridized 2p orbital per site. For weak intersite interactions these 2p electrons tend to form a gapless semimetallic state with Dirac-like linear dispersive bands, as exemplified by SL graphene. The ability to tune the electron–electron coupling in graphene would permit access to correlated gapped electronic states, which could be finely tuned in experimentally viable hexagonal SL carbon-based systems via application of relatively modest (<0.5 GPa) out-of-plane pressure to induce transitions to new states (e.g., superconducting and magnetic). Although the underlying physics is not yet fully understood, the tunability of twisted 2D hexagonal systems offers hope that analogous behavior could be found in simpler, potentially easier to analyze, SL systems. Herein, we show how correlated electronic states could be finely tuned in experimentally viable hexagonal SL carbon-based systems via application of relatively modest (<0.5 GPa) out-of-plane compressive pressure.

Recently, we proposed a new class of sp² carbon-based SL materials based on linking trivalent triarylmethyl (TAM) αC-containing radical molecules to form 2D covalent organic radical frameworks (CORFs). Since our prediction, some example 2D CORFs have been experimentally prepared. Herein, we focus on 2D CORFs with hexagonal connectivity based on the graphene-like honeycomb lattice (2D hex-CORFs), which we predicted to exhibit spin-polarized antiferromagnetic (AF) ground states and low energy valence bond quinoidal gapped states, linked by an intervening semimetallic transition state. Compared to the delocalized semimetallic state, the more stable AF and valence bond states have lower space group symmetries and thus can be described as emerging through symmetry breaking. The first experimental examples of a 2D hex-CORF were indeed found to exhibit an AF ground state. 2D hex-CORFs can be seen as expanded graphene lattices where chemical linkers, rather than external strain, increase the distance between the threefold connected carbon sites. In this respect, 2D hex-CORFs are similar to the hypothetical α-graphyne and α-graphdiyne, where the relatively
increased distance between sp² carbon nodes leads to a reduction in the internode electronic coupling. Unlike these hypothetical planar carbon allotropes, 2D hex-CORFs are based on sterically protected sp² carbon nodes (e.g., TAMs) leading to more experimentally realizable materials. TAMs are stable and versatile open-shell species, which exhibit the Kondo effect in molecular junctions, and have been employed as building blocks for molecular spintronics, nonvolatile memory platforms, and nanoporous magnets. The experimentally synthesized TAM building blocks we consider are also not planar, but exhibit twisted aryl rings whose twist angle largely determines their electronic properties. In turn, SL TAM-based 2D hex-CORFs exhibit out-of-plane atoms and thus have a small finite thickness. In this computational work, we show that the twist angles of aryl ring linkers in 2D hex-CORFs are highly sensitive to out-of-plane compression, which can thus be used to modulate the internode electronic coupling and thereby tune the electrical, magnetic, and optical properties. We show that these SL materials are 2D correlated systems in which applied out-of-plane pressure can shift the AFMI state towards a transition to a semimetallic state.

Our theoretical exploration of 2D hex-CORFs upon out-of-plane compression has been carried out by means of all-electron density functional theory (DFT) based calculations and a mapping of the DFT results onto a Hubbard-like model Hamiltonian. Previously, we have confirmed that the linked TAMs and structural properties of individual TAMs can be well captured by DFT-based calculations. Building on previous work, we further confirm that the properties of TAM-based 2D hex-CORFs can be well captured by suitable DFT calculations, and thereby show how their electronic states can be tuned by compression. DFT is a formally exact method to determine the electron density of quantum systems without the need for an explicit many body treatment. In practical implementations, DFT-based calculations depend on a description of electron correlation through an approximate exchange–correlation potential (Vxc). To improve the accuracy of DFT-based treatments of the electronic structure of correlated systems, it is well established that Vxc can be significantly improved through incorporation of exact nonlocal Hartree–Fock exchange (HFE). The resulting hybrid DFT-based methods have become very effective approaches to investigate the electronic structure of different types of systems, ranging through strongly correlated transition metal oxides, organic radicals, and polyradicals, with a remarkable reliability in describing their ground states and magnetic properties. Hybrid functionals provide a computationally effective approach that can be applied in periodic schemes, and which give a good description of magnetic properties for many classes of compounds. Although quantitative results can be sensitive to the exact percentage of HFE employed, most hybrid functionals use between 20% and 50% HFE and tend to provide qualitatively similar results. Our DFT-based calculations employ 25% HFE through use of the PBE0 functional, to provide a self-consistent description of all electrons in our studied systems.

The use of model Hamiltonians to describe interactions between only those electrons in the system that are thought to be most important is a complementary approach to DFT. The half-filled (i.e., one electron per site) Hubbard model on the honeycomb lattice can thus be used to describe the essential electronic structure of SL hexagonal frameworks of sp² carbon sites. This model describes the interplay between: i) a localization effective short-range electrostatic repulsion between electrons on single sites (U), and ii) a kinetic energy term (t), which describes the capacity of electrons to move between sites. Due to the formal simplicity of such models, they are more amenable to being solved through accurate many body methods. Such approaches have revealed that the ground state phase diagram of this model exhibits graphene-like semimetallicity for smaller U/t ratios, and a continuous quantum transition to a correlated AFMI state when U/t is increased. Generally, the Hubbard model is a useful generic model for the essential physics of half-filled 2D systems, but extensions to the model are likely to be necessary for more precise descriptions of specific experimental systems. For example, extended Hubbard-like models with both short- and long-range components of the electron–electron repulsion can improve the description of different physical realizations of SL half-filled 2D Dirac fermionic systems on the honeycomb lattice (e.g., graphene on different substrates and artificial graphene made from quantum corrals). However, the presence of heteroatoms or different kinds of hybridized sites (such as in 2D hex-CORFs) leads to highly complex models that are only solvable approximately using mean field or limited correlated schemes.

In this work, we make a link between the DFT-based model Hamiltonian approaches by extracting approximate U and t values from our PBE0 calculations. In the extreme case of a molecular crystalline lattice of isolated (i.e., nonlinked) TAMs, t is extremely small and U is high leading to a highly robust AFMI state that has been experimentally shown to be resistant to pressures of over 20 GPa. In ref. relatively high U/t ratios (6.3–16.0) were obtained from DFT calculations of a few unstrained 2D hex-CORF structures. According to the Hubbard model for the 2D honeycomb lattice, these linked structures also have ground states that are firmly within the AFMI part of the phase diagram, for U/t > 3.8. This result is in line with the calculated and experimentally observed stability of AF phases reported for unstrained 2D hex-CORFs. Due to the approximations in both DFT and model Hamiltonian approaches outlined above, one should be careful not to overinterpret the physical significance of theoretically derived t and U values with respect to any specific material. However, the consistency between the stable states predicted by DFT-based calculations and the Hubbard model phase diagram for high U/t ratios indicate that taking both descriptions into account could be useful for exploring the electronic structure of 2D hex-CORFs with lower U/t ratios. Following the experimentally demonstrated compression-induced tunability of correlated states in twisted BL graphene, we show that application of out-of-plane compression to 2D hex-CORFs can dramatically reduce their U/t values. We further note that unlike typical magnitudes of out-of-plane compressive pressures used to observe effects in experiments on other 2D materials (e.g., 1–2.5 GPa for graphene), 0.5–5 GPa for SL MoS₂, we predict that relatively small out-of-plane pressures (<0.5 GPa) would be needed for 2D hex-CORFs. Specifically, we show that such modest out-of-plane pressure should enable an AFMI-to-semimetallic transition in suitably fabricated 2D hex-CORFs, thus highlighting
the potential of this class of SL materials for improving our understanding of 2D correlated electronic systems.

2. Results

We consider three examples of TAM-based 2D hex-CORFs based on: a) ring-sharing (rs) triphenylmethyl (TPM) radicals\[^9\] - TPM\(_{\text{rs}}\), b) ring-sharing perchlorotriphenylmethyl (PTM) radicals\[^9\] - PTM\(_{\text{rs}}\), and c) acetylenic linked PTM radicals as found in a recently synthesized and experimentally characterized material (PTM\(_{\text{acetylenic}}\))\[^10,11\] (see Figure 1). We note that although TPM\(_{\text{rs}}\) and PTM\(_{\text{rs}}\) have not yet been synthesized as extended materials, recently, it has been experimentally demonstrated that one can connect TPMs via ring-sharing in molecules containing a ring of six \(\alpha\)C centers (i.e., a TPM\(_{\text{rs}}\) fragment)\[^40\]. This breakthrough opens the door to the possibility of synthesizing extended 2D hex-CORFs based on ring-sharing TAMs. The structures of all three 2D hex-CORFs are shown in Figure 1.

We note that, at variance with purely planar SL systems such as graphene, out-of-plane hydrostatic compression significantly affects the dihedral angles and bond distances in 2D hex-CORFs. These changes govern electron localization in the hexagonal lattice of \(\alpha\)C centers in these materials, which remains planar throughout. Other materials with nonplanar layers (e.g., black phosphorus) have attracted interest due to their electronic response upon compression\[^41\]. In black phosphorus, compression affects the coordinates of all atoms in the puckered layers, which affect band dispersion/ordering, which, in turn, can cause a semiconductor–metal transition at 1.2 GPa. Unlike in 2D hex-CORFs, however, this transition is not due to electron correlation effects.

For each of our considered 2D hex-CORFs, we first optimize the cell parameters and all atomic positions of each system to obtain an unstrained reference point. Using an approach established in other studies modeling compressed SL materials\[^19,42\] we apply compressive stress to each 2D hex-CORF by employing selected out-of-plane (i.e., \(z\)-direction) structural constraints while allowing for full relaxation of the 2D lattice and unconstrained atoms (see the Experimental Section and the Supporting Information for details). With respect to the original \(z\)-direction thickness, we apply compression to each system such that each 2D hex-CORF is compressed by a maximum of 60% (i.e., to 40% of the original thickness). For each material, we have calculated the perpendicular (i.e., in a direction normal to the plane of the layer)\[^43\] Young’s modulus (see the Supporting Information for details) thus enabling us to provide an estimate of the required out-of-plane pressure to induce any percentage of compression. We find that the perpendicular Young’s moduli (TPM\(_{\text{rs}}\): 5.1 GPa; PTM\(_{\text{rs}}\): 13.8 GPa; PTM\(_{\text{acetylenic}}\): 0.74 GPa) imply that modest pressures (i.e., 0.9, 1.2 and 0.07 GPa respectively) would be needed to achieve the full range of reported compressions (see Figure 2b).

In Figure 2a,b the main compression-induced structural responses are shown for each 2D hex-CORF. Upon compressing the unstrained materials, the dihedral angles of the aryl rings with respect to the \(\alpha\)C centers decrease (i.e., ring flattening) in a linear manner, in line with the applied constraints. The main effect of ring flattening is to increase \(\pi–\pi\) orbital overlap between \(\alpha\)C centers and nearest neighbor carbon (nnC) atoms. The increased \(\pi–\pi\) overlap also leads to an associated increase in spin delocalization\[^8,20\] which we show for PTM\(_{\text{rs}}\) in a FM state in Figure 2c. The in-plane \(\alpha\)C–nnC bond distances show more complicated nonlinear dependence on out-of-plane compression, although in all cases tend to increase (i.e., bond stretching) for higher compressions due to increasing steric hindrance between aryl rings. In summary, during out-of-plane compression, there is a competition between increased \(\alpha\)C–nnC bond strength due to ring flattening and associated...
increased π–π overlap, and increasing steric hindrance between aryl rings, which tends to expand the in-plane αC–nnC bonds.

In TPMrs, the initial average aryl ring dihedral angle ⟨θ⟩ is the lowest of all considered materials (≈32.6°) due to the relatively low steric hindrance between the H-functionalized aryl rings.[20] At the maximum considered compression, ring flattening leads to a ⟨θ⟩ value of only 12.9°. The in-plane αC–nnC bond lengths in TPMrs start at just below 1.44 Å. This value is slightly higher than C–C bond length in graphene (1.42 Å), in line with the conjugated C–C bonding throughout the TPMrs network. With increasing compression, this bond length increases monotonically with a gradually increasing rate up to 1.458 Å at 60% compression.

For PTMrs, the more sterically hindered Cl-functionalized aryl rings induce an initial ⟨θ⟩ value of 45.7°, which reduces to 17.5° at maximum compression. PTMrs has the same topologically connected carbon network but with higher ⟨θ⟩ values that reduce the π–π overlap, leading to longer average αC–nnC bond lengths than in TPMrs. However, unlike TPMrs, for 0–25% compression, the αC–nnC distances first decrease and then increase with increasing aryl ring flattening. This nonmonotonic behavior can be understood due to the relatively reduced π–π overlap in the longer relatively strained αC–nnC bonds in uncompressed PTMrs. Unlike in uncompressed TPMrs, where the conjugation is relatively high and the initial αC–nnC bonds are quite short, in PTMrs, ring flattening significantly increases the π–π overlap leading to a strengthening and shortening of these bonds. For PTMacetylenic, the aryl rings are also Cl-functionalized and the initial ⟨θ⟩ value (48.2°) is thus very similar to that of PTMrs. However, the π-conjugation through the longer acetylenic linkers is relatively lower and the initial average αC–nnC bond lengths are considerably longer (1.468 Å). Like
PTMr, compression also leads to an initial increase in $\pi-\pi$ overlap and a corresponding dip in the average $\alpha C$-nnC distances. At higher compression PTM$_{acetylenic}$ also shows significant fluctuations in the average $\alpha C$-nnC distances. These C-C bond distance fluctuations are observed throughout the conjugated in-plane bonded carbon network of this material (see the Supporting Information) and are thus likely to be linked to variations in $\pi-\pi$ overlap. We note that energetically competing spiral conjugated $\pi-\pi$ overlap possibilities have been reported in acetylenic chains,$^{[44]}$ which would sensitively depend on $\langle \theta \rangle$. We also note that these small bond length fluctuations do not appear to indicate that the material is failing structurally, as can be confirmed through the small effect they have on the near-harmonic energy versus compression relation, implying elastic behavior for this compression range (see the Supporting Information).

The structural changes arising from compression induce a significant electronic response in the three 2D hex-CORFs. In all cases and for all considered compressions, our DFT calculations predict a gapped AF ground state. However, with increasing compression for all 2D hex-CORFs the AF state is progressively energetically destabilized with respect to the semimetallic state (see Figure 3a). This tendency can also be measured by the average absolute spin moment per $\alpha C$, the AF coupling constant ($J$), and the electronic bandgap ($\Delta E$), see the Experimental Section and the Supporting Information for details. In all three 2D hex-CORFs, we find that these three indicators decrease with increasing compression (see Figure 3b–d).

With respect to the parameters plotted in Figure 3a–d, TPMrs shows the mildest changes of all three 2D materials with respect to compression. Although TPMrs is the closest energetically to being semimetallic for most of the compression range, with correspondingly smaller spin densities and a relatively small bandgap, the AF magnetic coupling in TPMrs is the largest of all considered materials. In unstrained TPMrs, our PBE0 calculations predict a $J$ value of $-318$ meV. We note that this value appears to be fairly robust with respect to the percent of HFE used in the functional (see Table S2 in the Supporting Information). At 60% compression, $J$ reaches $-386$ meV (see also Table 1 for selected J values for each 2D hex-CORF). Recently, a singlet–triplet energy gap of 248 meV was measured for a synthesized molecular fragment of the TPMrs structure containing six spin $\frac{1}{2} \alpha C$ sites in a ring. Using the exact solution for an AF hexagonal Heisenberg system of $S = \frac{1}{2}$
spin particles in a 6-membered ring, in which \((E_S-E_I) = 1.369\ J\)\(^{[45]}\) we obtain \(J = -197\ \text{meV}\) for this experimental system. We note that the average dihedral angle in this molecule is \(\approx 7^\circ\) higher than in our extended TPM\(_{rs}\) material. In previous work, we showed that the average dihedral angle of aryl rings in TAM-based 2D CORFs determines the energy difference between AF and FM solutions.\(^{[8]}\) In order to compare with experiment, we linearly extrapolate the \(J\) versus compression curve for TPM\(_{rs}\) (to \(\approx -20\%\) compression), to better match the average dihedral angle value of the TPM-based ring molecule. In line with experiment, we find \(J = -200\ \text{meV}\) for TPM\(_{rs}\) under these conditions providing support for the suitability of our hybrid DFT approach for treating these systems.

For PTM\(_{acetylenic}\), the AF state shows the largest energy difference with respect to the semimetallic state for all considered compressions, but with relatively weak AF coupling. For unstrained PTM\(_{acetylenic}\) we obtain \(J = -15\ \text{meV}\). We note that our PTM\(_{acetylenic}\) model is an infinite symmetric SL with an unpinned spin at every \(\alpha\)C site. However, experimental PTM\(_{acetylenic}\) samples consist of a few finite-sized layers, each with a proportion of nonspin carrying sites and each likely to exhibit some structural defects. These differences may explain why the fitting of experimental susceptibility data leads to a relatively larger \(J\) value (\(-46.5\ \text{meV}\)) than we obtain.\(^{[30]}\) For this system, the highest considered compression destabilizes the dominant AF state by \(0.18\ \text{eV per atom}\) at \(\alpha\)C site. Recently, it was proposed that by replacing the PTM\(_{rs}\) nodes in the PTM\(_{acetylenic}\) structure with oxo-bridged planar TAMs, one could increase the calculated AF coupling strength by approximately four times.\(^{[36]}\) We note that oxo-bridged planar TAMs are relatively unstable to reaction with oxygen,\(^{[46]}\) unlike TAMs, which are kinetically stabilized by sterically hindering access to the central \(\alpha\)C (e.g., PTMs and TPMs). As such, 2D hex-CORFs based on oxo-bridged planar TAMs are unlikely to be amenable to experimental synthesis. Herein, we predict that application of small out-of-plane compressive pressures (0–0.07 GPa) to the stable as-synthesized PTM\(_{acetylenic}\) structure could achieve a \(2.5\times\) increase in AF magnetic coupling strength (\(J = -37\ \text{meV}\)) together with a significant decrease (\(>0.5\ \text{eV}\)) in the magnitude of the electronic bandgap (see Figure 3). For PTM\(_{acetylenic}\) at high compression, we observe some fluctuations in all the measured electronic parameters (Figure 3a–d), which is also observed in the in-plane C–C bond distances (see Figure 2 and the Supporting Information).

As noted above, these variations are likely linked to different \(\theta\)-dependent \(\pi-\pi\) overlap possibilities in the acetylenic bridges. Of the three considered 2D hex-CORFs, PTM\(_{rs}\) shows the most dramatic electronic response with respect to compression. For no strain, our calculations predict PTM\(_{rs}\) to exhibit an AF state with a slightly larger energy gap than PTM\(_{acetylenic}\). With increasing strain, the PTM\(_{rs}\) energy gap rapidly decreases to eventually be lower than that of both TPM\(_{rs}\) and PTM\(_{acetylenic}\) for \(>50\%\) compression. Moreover, for this high compression, PTM\(_{rs}\) has the lowest spin density per atom and energetically is the closest to being semimetallic. As for TPM\(_{rs}\), the AF coupling is significant in this material, with \(J = -365\ \text{meV}\) for the highest compression. The evolution of the electronic band structure of PTM\(_{rs}\) with increasing compression is shown in Figure 3e, where the decrease in the energy gap and increase in overall band dispersion is clearly seen. For high compression, the difference in energy between the AF and the semimetallic state for both TPM\(_{rs}\) and PTM\(_{rs}\) is calculated to be only \(\approx 30\ \text{meV per atom}\). Such marginal energy differences between distinct electronic states should be treated with caution within a single determinantal picture such as DFT. These results suggest that compression of 2D hex-CORFs can make the semimetallic and AFMI states almost degenerate in energy, and both would contribute to the true ground state.

In addition to directly inspecting the nature of the lowest energy state predicted by DFT calculations, we can also extract \(U\) and \(t\) parameters from our calculations (see the Experimental Section and the Supporting Information for details), which we can use to compare with predictions from the Hubbard model on the honeycomb lattice. In Figure 4, we plot the extracted values of \(U\), \(t\), and \(U/t\) for all three 2D hex-CORFs for all considered degrees of compression (see also Table 1 for selected values). For TPM\(_{rs}\), and PTM\(_{acetylenic}\), compressing the unstrained structures up to \(60\%\) leads to a decrease in \(U\) of 0.28 and 0.57 eV, respectively. For both these 2D hex-CORFs this compression also leads to a similar increase in \(t\) (0.3–0.5 eV). For PTM\(_{acetylenic}\), the extracted \(U\) values are relatively high compared to the \(t\) values and this entails a corresponding increased sensitivity of the \(U/t\) values, which vary from 12.8 to 7.4. In ref. [24], the smallest reported \(U/t\) ratio of 6.3 was obtained in a proposed structure based on oxo-bridged planar-TAMs with vinylene linkers. In both cases, these \(U/t\) ratios firmly place these materials in the AFMI regime according to the Hubbard model phase diagram. For PTM\(_{acetylenic}\), this picture is fully consistent with a direct inspection of our DFT results (see Figure 3). Ideally, for exploring transitions between the AFMI and semimetallic phases in half-filled 2D-hexagonally ordered systems, one should be able to tuneably access the regimes above and below \(U/t = 3.8\)\(^{[31,32]}\).

For TPM, the \(t\) values are relatively larger than the \(U\) values and the corresponding \(U/t\) ratio does not change significantly with compression (from 2.75 to 2.15), which places TPM\(_{rs}\) in the semimetallic region of the Hubbard phase diagram. Direct inspection of our DFT results for TPM\(_{rs}\) indicates that the semimetallic state is always within 48.5 meV per \(\alpha\)C of the AF state.

### Table 1. Extracted values of \(J\), \(U\), and \(t\) for PTM\(_{acetylenic}\), PTM\(_{rs}\), and TPM\(_{rs}\) for selected compressions. The \(U/t\) values are shaded according to the corresponding ground state on the Hubbard model phase diagram for the 2D half-filled hexagonal lattice: AFMI: orange; semimetallic: blue.

|          | \(J\) [meV] | \(U\) [eV] | \(t\) [eV] | \(U/t\) |
|----------|-------------|------------|------------|---------|
|          | 0% | 20% | 60% | 0% | 20% | 60% | 0% | 20% | 60% |
| PTM\(_{acetylenic}\) | -15 | -24 | -37 | 2.23 | 1.96 | 1.66 | 0.17 | 0.20 | 0.22 |
| PTM\(_{rs}\) | -157 | -259 | -365 | 2.27 | 1.76 | 1.26 | 0.50 | 0.50 | 0.28 |
| TPM\(_{rs}\) | -318 | -362 | -386 | 1.65 | 1.48 | 1.37 | 0.60 | 0.62 | 0.64 |

For no strain, our calculations predict PTM\(_{rs}\) to exhibit an AF state by \(0.18\ \text{eV per atom}\) with respect to the semimetallic state with a slightly larger energy gap than PTM\(_{acetylenic}\). With higher \(t\) values of 12.8, 9.63, and 7.39, the semimetallic and AFMI states almost degenerate in energy, and both would contribute to the true ground state.
and that this energy difference slightly decreases with compression. Although, the quantitative picture provided by these two perspectives differs somewhat, both suggest that TPMrs has a ground state that is quite close to the boundary between AFMI and semimetallic phases and which is only slightly affected by compression.

PTMrs, unlike PTM acetylenic and TPM rs, shows a large and nonmonotonic change in \( t \) with respect to increasing compression. The \( t \) values for PTM rs lay between those extracted for TPMrs and PTM acetylenic but first increase by 0.04 eV with a 0–10% compression increase and thereafter decrease by 0.26 eV as compression increases to 60%. This nonmonotonic behavior in \( t \) is related to the analogous behavior in the \( \alpha C \)–nnC bond distances (see Figure 2), which are a structural indicator of the electronic coupling between \( \alpha C \) centers. The value of \( U \) for uncompressed PTM rs is higher than the corresponding value for PTMacetylenic but rapidly decreases with increasing compression and becomes lower than that of TPM rs for 60% compression. Correspondingly, the \( U/t \) ratio for uncompressed PTM rs starts at 4.52, then decreases to a minimum value of 3.50 at 20% compression, and then gradually increases back up to 4.53 at the highest compression. From a Hubbard model perspective, the PTM rs would have an AFMI ground state, which could be tuned to be arbitrarily close to the AFMI–semimetallic phase transition boundary with out-of-plane compression above and below 20%. We note that to achieve 20% compression in PTM rs, we estimate that only 0.47 GPa of out-of-plane pressure would be required. A direct inspection of the DFT calculations also suggests that PTM rs exhibits an AF state that can be tuned to be energetically close to the semimetallic phase. However, the latter picture indicates a monotonic progression toward the semimetallic phase with increasing compression. These different tendencies are to be expected due to differences in the methodologies employed. The electronic states in the Hubbard model are derived from a subset of the actual electrons on a fixed lattice, and effects such as polarization/delocalization of non-\( \alpha C \)-based electrons and structural relaxations (e.g., of the linkers), which are described by DFT calculations, are inherently not included. On the other hand, Monte Carlo treatments of the Hubbard model Hamiltonian explicitly describe electronic correlation and attempts to solve it using mean field based approaches (e.g., pure HF) tend to yield lower effective \( U \) values than direct many body solutions. Hybrid DFT functionals attempt to partially bridge the gap between these approaches but results can be sensitive to the percent of HFE employed. In Figure 4c, we include shading to indicate tentative variations in \( U/t \) with respect to modest changes in HFE percent.

3. Conclusions

2D hex-CORFs are novel examples of the half-filled 2D honeycomb lattice and thus lie in the same class as graphene and hexagonal quantum corals. Theoretical studies using simple but exactly solvable many body model Hamiltonians are still revealing new fundamental physical insights regarding the AFMI–semimetallic transition in such systems. However, even for these structurally uncomplicated systems, such simplified descriptions of their electronic structure can fail to capture essential features found in experiment. 2D hex-CORFs are relatively chemically complex materials that have a highly nontrivial structural and electronic response to out-of-plane compression. To accurately describe such complexity using a many body Hamiltonian approach would likely require a highly complicated and intractable model. Here, we use an all-electron hybrid DFT approach to describe the full chemical structure and electronic response of our 2D hex-CORFs.
while also extracting parameters relevant to model Hamiltonian descriptions (i.e., $U$, $t$, and $J$). The complementary picture thus obtained shows that compressing suitable 2D hex-CORFs could provide a new means for probing the phase diagram of this important 2D correlated electron system. Specifically, we demonstrate that TAM-based 2D hex-CORFs, like twisted BL graphene, are correlated electronic materials with states that can be tuned by out-of-plane compression. The twistable aryl rings in the SL materials we consider mean that only modest out-of-plane pressures (<0.5 GPa) can significantly vary their electronic structure. This general result can be readily tested as we predict that such pressures applied to the experimentally synthesized PTM acetylenic material should lead to a significant increase in its observed AF magnetic coupling strength. Further, based on synthesized TPM molecular fragments, we propose that ring-sharing 2D hex-CORFs should be experimentally viable materials and would be particularly promising as they can: i) exhibit ground states laying close to the AFMI–semimetallic transition, and ii) have compression-tunable $U/t$ ratios for low out-of-plane pressures. 2D hex-CORFs are thus promising materials, both from a fundamental point of view to study correlation effects in low dimensional materials and for potential technological applications (e.g., sensors and spintronics/electronics). We hope that our work will inspire further experimental and theoretical work into this fascinating new class of 2D correlated electronic materials.

4. Experimental Section

Unstrained structures of each 2D hex-CORF were obtained via DFT-based optimizations of atomic positions and cell parameters using the PBE0[29] hybrid functional as implemented in the all-electron FHI-AIMS code. In all calculations, nonbonded dispersion interactions were included via the TS-vdW approach. A “light/Tier1” numerical atom-centered orbital (NAO) basis set was used throughout. This basis set provides results of a similar or higher quality to those obtained with valence triple-zeta plus polarization Gaussian type orbitals in line with the trends regarding the quality of these NAO basis sets. The 2D hex-CORF SLs were oriented so that the $\alpha$C plane was parallel to the $x$-$y$ plane (with $z = 0$ for the $\alpha$C plane) and were separated from their periodic images by a vacuum spacing of 40 Å in the $z$-direction. $6 \times 6 \times 1$ Monkhorst-Pack generated grid meshes of $k$-points were used for each 2D hex-CORF.

The constrained atom method[39,42] was used to induce a $z$-directed out-of-plane compression on the 2D hex-CORFs. In ref. [39], the results from employing this method have been shown to compare very well with experimental results from uniaxial out-of-plane compression on SL MoS$_2$. Firstly, a set of $C$ atoms was selected both above and below the $\alpha$C plane for each structure (see the Supporting Information for specific atom sets in each case). To apply compression, the absolute value of the $z$-coordinates of these constrained atoms was adjusted according to incremental decreases of the dihedral angles of the aryl rings, and then fixed for each increment. The resulting $z$-constrained structures were then optimized again using the above setup allowing for full relaxation of the unit cell, positions of nonconstrained atoms, and the $x$ and $y$ coordinates of the $z$-constrained atoms. In the Supporting Information, it is shown that this constrained atom method produces the same structural response as when a 2D hex-CORF is sandwiched within a compressed layered 2D heterostructure. The perpendicularly Young’s moduli, and thus the external out-of-plane pressure required to induce these compressions, were extracted from the total energy versus unit cell volume curves (see the Supporting Information for details). From these curves, it could be verified that the 2D hex-CORFs were always in the elastic regime for all considered compressions.

The magnetic coupling constants, $J$, were evaluated assuming the Heisenberg Hamiltonian whereby the energy difference between AF and FM states is directly related to the Heisenberg spin exchange parameter $J_{ij}$ (see the Supporting Information for further details). The $t$ and $U$ values were extracted from the electronic band structures of each 2D hex-CORF following the procedure detailed in ref. [52] (see also the Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the following research grants: MICIUN/FEDER RTI2018-095460-B-I00, PID2019-109518CB-I00 and CTQ2017-87773-P/AEI/FEDER (Spanish government, MINECO), MDM-2017-0767 (“María de Maeztu” program for Spanish Structures of Excellence), and 2017SGR13 and 2017SGR348 (Generalitat de Catalunya, DURSI). R.S. acknowledges a predoctoral FI grant from MINECO under grant agreement CTQ2017-87773-P/AEI/FEDER. I.A. is grateful for support from the Alexander von Humboldt Foundation. The authors also acknowledge access to supercomputer resources as provided through grants from the Red Española de Supercomputación.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, compressive stress, correlated materials, density functional theory calculations, semimetal–insulator transition

Received: May 28, 2020
Revised: August 21, 2020
Published online: November 4, 2020

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 2004, 306, 666.
[2] S.-H. Lee, S. Kim, K. Kim, Phys. Rev. B 2012, 86, 155436.
[3] H.-K. Tang, E. Laksono, J. N. B. Rodrigues, P. Sengupta, F. F. Assaad, S. Adam, Phys. Rev. Lett. 2015, 115, 186602.
[4] S. Sorella, K. Seki, O. O. Brovko, T. Shirakawa, S. Miyakoshi, S. Yunoki, E. Tosatti, Phys. Rev. Lett. 2018, 121, 066402.
[5] S.-H. Lee, H.-J. Chung, J. Heo, H. Yang, J. Shin, U.-i. Chung, S. Seo, ACS Nano 2011, 5, 2964.
[6] Y. Cao, V. Fatemi, A. Demir, S. Fang, S. L. Tomarken, J. Y. Luo, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, E. Kaxiras, R. C. Ashoori, P. Jarillo-Herrero, Nature 2018, 556, 80.
[7] M. Yankowitz, S. Chen, H. Polshyn, Y. Zhang, K. Watanabe, T. Taniguchi, D. Graf, A. F. Young, C. R. Dean, Science 2019, 363, 1059.
[8] I. Alcón, D. Reta, I. de P. R. Moreira, S. T. Bromley, Chem. Sci. 2017, 8, 1027.
[9] I. Alcón, F. Viñes, I. de P. R. Moreira, S. T. Bromley, Nat. Commun. 2017, 8, 1957.
