Self-Organized Kagomé-Lattice in a Conductive Metal-Organic Monolayer

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The on-surface synthesis of metal-organic covalent coordination networks with a dense Kagomé lattice of metallic centers is reported. Tetrahydroxyquinone and metal atoms (M = Cu or Mn) are codeposited on Ag(111) substrate to build well-ordered 2D lattices M₃C₆O₆. The surface is studied by scanning tunneling microscopy, low-energy electron diffraction, and X-ray photoelectron spectroscopy (XPS). Density functional theory (DFT) reveals a Cu⁺ charge state and no local magnetic moments for the Cu-organic network. For the Mn-organic network, the charge state Mn³⁺ and a local spin S = 5/2 are found. Charge transfer stabilizes the Cu⁺ and Mn³⁺ charge states. DFT calculations show a Dirac point, i.e., a band crossing with linear electron dispersion at the K-point ((2/3)gₓ + (1/3)gᵧ) of the Brillouin zone. This Dirac point is at the Fermi level without charge transfer but drops by 100 meV if electron doping of Cu₃C₆O₆ on Ag(111) surface is acknowledged. The magnetic couplings of an isolated Mn₃C₆O₆ monolayer to be short range and antiferromagnetic leading to high frustration at the Kagomé lattice and a tendency toward a spin-liquid ground state are predicted. In the case of hole transfer from the substrate, ferromagnetic ordering is introduced, making Mn₃C₆O₆ an interesting candidate for the quantum anomalous Hall effect.

1. Introduction

The discovery of graphene by exfoliation of graphite in 2004 initiated the experimental study of truly 2D materials. Since then, 2D materials have become an extremely fruitful field of research, with hundreds of newly isolated or synthesized artificial monolayers each year, and a multitude of techniques like, e.g., molecular beam epitaxy, chemical deposition on surfaces, synthesis in wet environment and many others. Initially mainly studied for their fundamentally new and exotic properties, 2D materials have now attracted widespread interest due to their high potential for novel nanotechnological applications. In this context, 2D materials composed of metal atoms and organic linkers have emerged as promising candidates to combine the advantages of both realms, also called 2D metal-organic frameworks (MOFs). For potential applications, we may cite, for example, their abilities in molecular recognition and functionalities for heterogeneous asymmetric catalysis, while their peculiar topological properties are interesting for new spintronic devices. Most of the 2D metal-organic frameworks (MOFs) synthesized so far are almost perfect insulators but there is a major exception, namely the subclass of conductive MOFs or c-MOFs which are either metallic or at least semiconducting. The development of these c-MOFs is an important challenge for future decades due to their novel electronic, optical, mechanical, and catalytic properties.
of massless Dirac fermions. But in graphene local magnetic moments are missing which excludes all interesting applications depending on magnetic effects or spin-dependent transport. Here, we report on the successful on-surface synthesis of a dense 2D metal-organic covalent coordination network with a Kagomé lattice of metal ions, thus opening a window to the unconventional electronic and magnetic properties of Kagomé lattices. So, the Kagomé lattice antiferromagnet shows an unconventional spin chirality on a 2D frustrated lattice.\textsuperscript{[24–26]} On the electronic side, the Kagomé lattice combines Dirac fermions with flat bands. The combination with ferromagnetic order then allows for the quantum anomalous Hall, i.e., a quantum Hall effect without an external magnetic field. This was recently observed in the quasi-2D Kagomé metal Fe\textsubscript{3}Sn\textsubscript{2}.\textsuperscript{[27]} a metallic compound with ferromagnetic order and a band crossing at the highly symmetric K point slightly below the Fermi level. In a ferromagnetic material with only one spin species, the band crossing is also called the Weyl point (what was the Dirac point in graphene) with concomitant massless quasiparticles. The spin–orbit coupling—which is crucial for the quantum Hall effect—opens a gap at the crossing point and leads to the observed massive quasiparticles in Fe\textsubscript{3}Sn\textsubscript{2}.\textsuperscript{[27]} The quantum Hall effect was also predicted for 2D metal-organic systems.\textsuperscript{[28]} In the present paper, we discuss a possible route to obtain that goal in synthesizing a metal-organic monolayer whose electronic structure possesses all the required features for the quantum Hall to occur.

In the search for novel states of matter, the occurrence of a Kitaev spin liquid was predicted in a metal-organic magnetic system with a honeycomb lattice.\textsuperscript{[29]} Such metal-organic honeycomb lattices were indeed synthesized, but rather to look for applications as c-MOFs.\textsuperscript{[30,31]} The spin-liquid state can also be obtained on the Kagomé lattice with antiferromagnetic nearest-neighbor couplings like, e.g., in the naturally occurring quasi-2D Herbertsmithite.\textsuperscript{[32]} In this article, we report on the successful synthesis of a $S = 5/2$ Kagomé lattice arising as a self-organized metal-organic monolayer on the Ag(111) surface. Investigating the magnetic couplings by ab initio calculations we find the interesting phenomena that these couplings can be tuned, with antiferromagnetic couplings arising for an isolated layer, and ferromagnetic couplings for the layer on the substrate. To synthesize such a Kagomé lattice, tetrahydroxyquinone (THQ) is particularly attractive because of its ability to form stable complexes with various metal ions in a variety of coordination modes using its four hydroxyl groups.\textsuperscript{[33,34]} Here, we report the surface reaction between transition metal atoms (copper Cu and manganese Mn) and THQ on silver Ag (111) under ultrahigh vacuum conditions and at an appropriate temperature—which contrasts with the previously reported synthesis of the c-MOF Cu\textsubscript{4}(C\textsubscript{6}O\textsubscript{6})\textsubscript{2} in aqueous solution.\textsuperscript{[35]} The deposition of C\textsubscript{6}O\textsubscript{6}H\textsubscript{4} on Cu(111) with an appropriate thermal treatment leads to a dense 2D Cu\textsubscript{3}C\textsubscript{6}O\textsubscript{6} lattice whose properties differ significantly from the traditional porous MOFs. In our lattice, the Cu ions form a Kagomé network, but similar lattices were synthesized with Fe\textsuperscript{[37,38]} The adsorption of THQ molecules alone,\textsuperscript{[39]} without metallic linker, leads to an ordered arrangement of organic molecules with no chemical reaction, i.e., no real chemical binding. The organic molecules stack together only via hydrogen bonds.
photoemission spectroscopy (XPS) measurements. In the case of XPS experiments, Shirley background was subtracted on the spectra and data were fitted by Gaussian Lorentzian (30%) components. Figure 2a displays the STM image recorded after deposition of THQ on Ag(111) at room temperature. The lattice parameter is 7.65 Å in agreement with a previous study. The LEED diagram (Figure 2b) indicates the well-known ($\sqrt{7} \times \sqrt{7}$)R20° superstructure of THQ on Ag(111) rotated by ±20° with respect to the Ag(111) close packed directions.

The codeposition of THQ molecules and Cu atoms on the Ag (111) surface at 150 °C allows the formation of large and well-ordered domains of the metal-organic coordination network whereas the desorption temperature of the THQ molecule alone is around 120 °C. The deposition of THQ molecules on the substrate kept at 150 °C is only possible thanks to the presence of the codeposited Cu atoms. The STM image (Figure 3a) shows a well-organized domain of (8.17 ± 0.4) Å with a very slight modulation of the corrugation. This can be rationalized as a Moiré pattern with a lattice parameter of 5.5 ± 0.2 nm oriented at 10° from the [1–10] direction. Within these domains, the molecules are organized in a centered hexagonal network with 6 copper atoms surrounding each molecule. The mesh parameter of this lattice obtained by LEED is (8.10 ± 0.2) Å (Figure 3c). It is important to note that this lattice parameter is larger than the ($\sqrt{7} \times \sqrt{7}$) lattice substrate (i.e., 7.65 Å). This is at the origin of the appearance of a large-scale coincidence (5.5 nm Moiré) resulting from a Cu3C6O6 lattice parameter of 8.056 Å (see S5, Supporting Information).

The XPS measurements (Figure 4) allow to analyze the chemical state of the different species. Core level spectra of O1s, C1s and Cu2p3/2 were recorded and compared to as-deposited molecules and copper atoms alone to confirm the reaction between the copper atoms and THQ. This indicates that all the molecules are dehydrogenated as demonstrated by Zhang et al. in the case of C6O6H6 on Cu(111). The analysis of Cu2p (cf Figure S4, Supporting Information) reveals the presence of Cu2p3/2 and Cu2p1/2 without the presence of shake-up peaks,
and moreover Cu2p3/2 is measured at 931.7 eV in the case of Cu-THQ deposition whereas it is found at 932 eV in the case of Cu deposited alone on Ag(111). This small shift of 0.3 eV as well as the absence of satellite peaks allows to deduce that the Cu atoms are not in Cu(II) configuration, as expected from the reaction between hexahydrobenzene and Cu atoms in solution, but in Cu(I) or Cu(0) configuration.\cite{37-40} In the case of Cu(I) a small satellite peak should be obtained between Cu2p3/2 and Cu2p1/2 but the resolution is not accurate to discriminate Cu(I) from Cu(0) configuration. DFT calculations allows to conclude on this chemical state.

In the case of THQ and Mn codeposition, the Moiré pattern is not present and all the molecules are on equivalent adsorption sites thanks to a smaller mesh size than in the previous case with copper. As deduced from the STM and LEED data the lattice parameter is (7.62 ± 0.2) Å (Figure 5) corresponding to the (√7 × √7)R20°. The deconvolution by Gaussian-Lorentzian (30%) components of the XPS spectrum of Mn2p shows two main peaks at 641.1 and 651.1 eV corresponding to Mn2p3/2 and Mn2p1/2. From these positions, it is not possible to determine the oxidation state of Mn but the presence of two satellite peaks at 645.7 and 657.4 eV are the spectroscopic signature of Mn (II) (Figure 5.d). Therefore, it is concluded that the Mn is in a chemical state (II).\cite{41}

2.1. Theoretical Results

To supplement and interpret the experimental findings, several ab initio calculations were performed. The Vienna Ab-initio Simulation Package (VASP) and density functional theory were used in the form of the spin unpolarized generalized gradient approximation (GGA) for Cu3C6O6 and using the spin-polarized version (SGGA) for Mn3C6O6. The influence of the Hubbard U correction (SGGA+U functional) on the incompletely filled 3d shell was also investigated, which is found in Mn3C6O6 (see Supporting Information for more details on the method). Isolated M3C6O6 layers (M = Cu or Mn) in two different configurations as a function of the lattice constant, as well as adsorbed layers on the Ag(111) surface of the substrate were modeled.

The results for isolated monolayers and start with Cu3C6O6 (Figure 6a) are first discussed. Here, results are shown by using the GGA functional without spin splitting. It should be remarked that there exists a ferromagnetic solution which is nearly degenerated with the nonmagnetic one. As is explained below, this ferromagnetic solution is not relevant for Cu3C6O6 since it becomes unstable due to the charge transfer from the Ag substrate. The crystal structure where each Cu would have 4 equivalent O neighbors (which is denoted as structure A) is that one which is realized for Mn3C6O6 as shown in Figure 1. It leads to the energy minimum at 7.75 Å of the red curve in Figure 6a. However, the Bader charge analysis, whose details are given in the Supporting Information, points to a completely filled d-shell, implying that the GGA solution should display a copper charge closer to Cu2+ than to Cu+. In analogy to the difference between the crystal structures of CuO and Cu2O, it can be expected that Cu2+ will prefer just two oxygen neighbors over a configuration with four. This preference can be met by rotating the C6O6 rings while keeping the Kagomé lattice for the metal ions fixed (oxygen ions are so tightly bound to the C6 ring that they will rotate with the carbon ring). In the following, structure B is denoted the configuration with only two O neighbors as depicted in Figure 1 for Cu3C6O6. Ab-initio calculations allow to distinguish between structures A and B by differently choosing the initial atomic positions. For structure B, the rotation angle of the C6O6 rings converges toward an optimal angle for each fixed lattice constant. At that lattice constant where the energy minimum for structure B, with a larger lattice constant of 8.25 Å, which is energetically almost degenerate with structure A. The result coincides with previous ab initio calculations.\cite{36}

The situation for Mn3C6O6 is completely different. First of all, the magnetic solution is several electron volts deeper in energy than the nonmagnetic one. That is visible in Table 1, where the energy difference is presented between the high spin solution (S = 5/2) and the intermediate spin solution (S = 3/2). The difference with the nonmagnetic one is even larger. It is also seen that the inclusion of the Hubbard U correction prefers the high spin solution even more and leads to the appearance of a gap in the electronic spectrum. Furthermore, only structure A (4 oxygen neighbors) is stable (see Figure 6c) and there is no second minimum for structure B. For larger lattice constants, structure A simply goes over into structure B and there is no second minimum. Without the Hubbard U correction, half-metallic behavior with a magnetic moment of M = 5μB is found. This corresponds to S = 5/2, a spin state which is only possible in the case of Mn3C6O6 oxidation state. However, in analogy to ab initio results for similar metal-organic monolayers\cite{32,43} or for other 3d transition metal compounds in general, the half-metallic behavior of the simple SGGA func-
tional is not believed. On the contrary, the SGGA+U functional is used, which gives a gap of 1.22 eV for a U parameter of 5 eV, to be much more realistic. The magnetic state (\(S = 5/2\)) does not change by including the Hubbard U correction. In the Supporting Information, results between \(U = 4\) and 5 eV are also compared showing that a small change of \(U\) is not essential and there more details on the electronic structures of Cu\(\text{C}_6\text{O}_6\) and Mn\(\text{C}_6\text{O}_6\) are given.

However, simple monolayer calculations are not sufficient to understand the electronic structure of Mn\(\text{C}_6\text{O}_6\) on the Ag-substrate. For that reason, the Ag substrate was introduced in the ab initio study by six Ag layers. After relaxing the atomic positions, the structures presented in Figure 7 are found. There the results for the Mn system are shown where the experimental lattice constant of Ag was used to which the Mn\(\text{C}_6\text{O}_6\) monolayer adapts perfectly (in the \((\sqrt{7} \times \sqrt{7})\) superstructure) leading to a lattice constant of 7.65 Å. Also, the SGGA+U functional with \(U = 5\) eV for Mn\(\text{C}_6\text{O}_6\) was used. To take into account the larger lattice constant of the Cu\(\text{C}_6\text{O}_6\) monolayer being visible in the Moiré pattern, the underlying Ag substrate was expanded resulting in a lattice constant of 8.10 Å (see Supporting Information). The ab initio simulation of the Moiré pattern would be too difficult for an ab initio simulation and is practically impossible. Also, a nonmagnetic state was simulated for the Cu system and the GGA functional was used.

In the case of the Mn-THQ network (see Figure 7) as well for Cu-THQ (see Supporting Information), the adsorbed monolayers are not fully planar. The metal ions are closer to the Ag substrate than the \text{C}_6\text{O}_6\) rings. More important than these structural details are the charge transfers from the substrate to the Mn\(\text{C}_6\text{O}_6\) (M = Cu or Mn) monolayers. The substrate dopes 0.43 electron to the Cu\(\text{C}_6\text{O}_6\) network but removes 0.59 electron from the Mn-organic monolayer. The charge transfer is visible in the Bader charge analysis presented in the Supporting Information.

The charge transfer is also the key element to resolve two problems of the monolayer calculation for Cu\(\text{C}_6\text{O}_6\) without charge transfer (Figure 6a), namely the near degeneracy between the two minima for structures A and B and between magnetic and nonmagnetic solution. If structures A and B would indeed be energetically degenerate, phase separation and the presence of phase A also for Cu\(\text{C}_6\text{O}_6\) would be expected. However, as it is presented in Figure 6b, taking into account a

**Table 1.** Energy difference \(\Delta e_{\text{HS}}-e_{\text{IS}}\) between high spin (\(S = 5/2\)) and intermediate spin (\(S = 3/2\)) solutions for isolated monolayers of Mn\(\text{C}_6\text{O}_6\) within the SGGA (\(U = 0\) eV) and SGGA+U functionals. Also given are the distance between Mn and O (\(d_{\text{Mn-O}}\)), the lattice constant (\(a\)), the exchange energies (\(E_{\text{ex-1}/2} = E_{\text{AF}(1/2)}-E_{\text{FM}}\) per Mn atom) and coupling constants (\(J_1\) and \(J_2\)), as well as the total energy gap (\(E_g\)).

|          | \(U = 0\) eV | \(U = 5\) eV |
|----------|--------------|--------------|
| \(\Delta e_{\text{HS}}-e_{\text{IS}}\) [eV] | –1.96        | –4.38        |
| \(d_{\text{Mn-O}}\) [Å] | 2.10         | 2.10         |
| \(a\) [Å] | 7.941        | 7.975        |
| \(E_{\text{ex-1}}\) [meV] | –26.07       | –6.08        |
| \(E_{\text{ex-2}}\) [meV] | –46.35       | –10.87       |
| \(J_1\) [meV] | 2.43         | 0.57         |
| \(J_2\) [meV] | 0.35         | 0.08         |
| \(E_g\) [eV] | 0            | 1.22         |

Figure 6. Total energies as a function of lattice constant for Cu\(\text{C}_6\text{O}_6\) a) without and b) with charge transfer, as well as for c) Mn\(\text{C}_6\text{O}_6\) using GGA or SGGA.

Figure 7. Top view (top figure) and side view (bottom figure) of Mn\(\text{C}_6\text{O}_6\) with the substrate as obtained from a SGGA+U calculation with \(U = 5\) eV.
realistic charge transfer of 0.43 electron doping for the Cu$_3$C$_6$O$_6$ monolayer leads to a considerable lowering of the energy for structure B with respect to structure A explaining the experimental findings. Also, the charge transfer stabilizes the non-magnetic solution with respect to the magnetic one (not shown) and moves the Cu charge closer to Cu$^{+}$.

Finally, the band structures close to the Fermi-level are discussed which are especially promising for a Kagomé lattice. Since it allows for a band crossing and a linear electron dispersion at the K point in close analogy to the Dirac point in graphene which is at the origin of all the exceptional electronic properties of graphene or other Dirac systems. As shown in Figure 8a,b, a similar Dirac point is predicted to exist in Cu$_3$C$_6$O$_6$ at the K point. It is located exactly at the Fermi-level for the undoped situation but 100 meV below in the electron-doped case realized on the Ag(111) substrate.

In contrast to the metallic behavior of the Cu$_3$C$_6$O$_6$ monolayer (without or with charge transfer), a magnetic, insulating state is predicted for Mn$_3$C$_6$O$_6$ if there is no charge transfer. However, the hole doping that is discovered in the ab initio calculation with the Ag substrate leads to a metallic state with the Fermi-level lying in the valence band with majority spin and being of predominantly oxygen character (see Figure 8 and Supporting Information). For this calculation, a ferromagnetic ordering of the magnetic moment was chosen which was the ground-state for the adsorbed monolayer as is discussed more in detail below. Now, the band crossing at the K point below the Fermi-level has no spin degeneracy and describes Weyl quasiparticles. It should be noted, however, that the inclusion of spin–orbit coupling would open a small gap at the K point.

It is highly interesting that the magnetic moments at the Mn sites build a Kagomé lattice. The exchange couplings $J_1$ and $J_2$ to nearest and second nearest neighbors on the Kagomé lattice in the Heisenberg Hamiltonian are determined

$$H = \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2} \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_{i+\mathbf{g}}$$

(1) where $\langle i,j \rangle$ means that each bond is summed only once. Similar to the linear metal-organic polymer chains,[42,43] the energy difference is taken between ferromagnetic $E_{\text{FM}}$ and antiferromagnetic $E_{\text{AF}}$ spin arrangements to calculate $E_{\text{ex}} = E_{\text{AF}} - E_{\text{FM}}$ which is defined per magnetic ion. For a 1D Heisenberg chain with only nearest neighbor exchange $J_1$ and taking the approximation of classical spins $\mathbf{S}_i \cdot \mathbf{S}_j = \pm \frac{1}{2}$ for parallel or antiparallel arrangement $E_{\text{ex}} = -2J_1S^2$ is obtained, where a factor of 2 in the formulas used in refs. [42, 43] is corrected (As a consequence of this mistake all the exchange couplings given in refs. [42, 43] have to be multiplied by a factor of 2). For a ferromagnetic arrangement of the spins $S = 5/2$ on the Kagomé lattice, $E_{\text{FM}} = 2(J_1 + J_2)S^2$ is obtained whereas the two antiferromagnetic arrangements (see Supporting Information) give

$$E_{\text{AF1}} = \frac{2}{3} (J_1 - J_2)S^2$$

(2)

$$E_{\text{AF2}} = -\frac{2}{3} (J_1 + J_2)S^2$$

(3)

Figure 8. Band-structures of Cu$_3$C$_6$O$_6$ (nonmagnetic) a) without and b) with charge transfer of 0.43 electron, as well as of Mn$_3$C$_6$O$_6$ (majority spin-up is black and minority spin-down is red) c) without and d) with charge transfer of 0.59 hole from the substrate. The nonmagnetic calculations were performed with the GGA functional, and the magnetic ones with SGGA+U functional and $U = 5$ eV.
Taking the two exchange energies $E_{\text{ex},1} = E_{\text{AF1}} - E_{\text{FM}}$ and $E_{\text{ex},2} = E_{\text{AF2}} - E_{\text{FM}}$ for $U = 5$ eV (see Table 1), a considerable antiferromagnetic exchange coupling $J_1 = 0.57$ meV to nearest neighbors but a roughly 10 times smaller (also antiferromagnetic) coupling $J_2 = 0.08$ meV to second neighbors is obtained. Table 1 also provides the $J$ values calculated without $U$ and in the Supporting Information the $J$ values with a $U$ of 4 eV.

The exchange couplings change if the substrate explicitly is taken into account and the adsorbed monolayer is considered. The energy difference between the two antiferromagnetic solutions remains nearly the same, but the ferromagnetic one goes drastically down in energy such that it becomes the ground-state ($E_{\text{ex},1} = 13.25$ meV and $E_{\text{ex},2} = 10.09$ meV). It means that the exchange coupling to nearest neighbors $J_1 = 0.38$ meV remains antiferromagnetic, but the ferromagnetic second neighbor exchange coupling $J_2 = -0.98$ meV dominates now the magnetic order. The main reason for that transition to a ferromagnetic state is the charge transfer which leads already to $E_{\text{ex},1} = 2.78$ meV and $E_{\text{ex},2} = -2.77$ meV ($J_1 = 0.67$ meV and $J_2 = -0.57$ meV) if an isolated monolayer with the 0.59 holes charge transfer is just calculated. A further stabilization of the ferromagnetic order occurs due to exchange paths which include the Ag substrate.

2.2. Perspectives and Discussion

A new synthesis route was demonstrated to achieve a dense 2D metal-organic polymer network of $\text{M}_3\text{C}_6\text{O}_6$ on Ag(111) which was worked out for the metals $\text{M} = \text{Cu}$ or Mn. But no principal reason was seen why it should not work for other metals also beyond the 3d transition metals or other substrates. So, a rather general way was found to synthesize Kagomé lattices of magnetic centers with different spin values. Also, the two examples showed that the substrate generally dopes the metal-organic monolayers (electron or hole doping) and may change an insulating monolayer into a metallic one. By choosing different substrates, the doping may eventually be tuned.

A principal difference between the newly synthesized structures to metal-organic frameworks (MOFs) was mentioned which were already known for several years. These MOFs (not necessarily 2D) are most commonly synthesized in aqueous solution and they are rather porous. In the case, after the on-site polymerization reaction, a rather dense 2D metal-organic network with small metal–metal distances was obtained. For instance, if the MOF $\text{Cu}_3(\text{C}_6\text{O}_6)\text{H}_2$ was compared to synthesized in aqueous solution with the c-MOF network $\text{Cu}_3\text{C}_6\text{O}_6$ due to on-surface polymerization, in both cases a Kagomé lattice of metal ions was observed. However, the nearest neighbor $\text{Cu}–\text{Cu}$ distance is 7.0 Å in $\text{Cu}_3(\text{C}_6\text{O}_6)\text{H}_2$ reducing to 4.1 Å in the newly synthesized c-MOF network $\text{Cu}_3\text{C}_6\text{O}_6$.

The Cu ions in the c-MOF network $\text{Cu}_3\text{C}_6\text{O}_6$ on Ag(111) are in the Cu$^+$ charge state with a completely filled d-shell and no magnetic moment. The charge transfer of 0.43 electron from the substrate to the monolayer stabilizes the Cu$^+$ charge state which is comparable with the situation on the Cu(111) surface where the charge transfer was found to be 0.66 electron. That c-MOF network is interesting as a highly conducting metal-organic layer. The ab initio calculations indicate metallic behavior for a free-standing Cu$_3$C$_6$O$_6$ monolayer with the Fermi level lying in a band of about 0.7 eV width. Interestingly, a Dirac point is exactly located at the Fermi level was found. The adsorption on Ag(111) leads to a down-shift of this band with respect to the Fermi level as it was also observed for Cu$_3$C$_6$O$_6$ on Cu(111).

Local magnetic moments in Mn$_3$C$_6$O$_6$ and metallic behavior due to hole-doping by the Ag(111) substrate with the Fermi-level short above the band-crossing point at K were found. Without doping, the magnetic interactions are short range and mainly between nearest neighbors. However, doping brings the ferromagnetic spin arrangement down in energy with respect to the antiferromagnetic ones and leads to a ferromagnetic order. So, this Mn-monolayer on Ag(111) was predicted to be a ferromagnetic Kagomé metal similar to Fe$_3$Sn$_2$ and the anomalous Hall effect was expected. The spin–orbit coupling opens a small gap at the band-crossing point at K, and shifting the Fermi level into this small gap, the anomalous Hall effect would even be quantified. This prediction was checked by transport measurements in a magnetic field. Diminishing the magnetic field, the Hall effect should remain even for zero field.

Without charge transfer, i.e., for a free-standing Mn$_3$C$_6$O$_6$ monolayer, the antiferromagnetic exchange couplings are clearly dominant. For such a system, the magnetic couplings are highly frustrated on the Kagomé lattice and could lead to spin-liquid (SL) behavior. Please note also that the metal–oxygen network of the network is practically identical to that one realized in Herbertsmithite, a model material for SL behavior. There, the Cu ions build a spin 1/2 Kagomé network whereas a spin 5/2 lattice for Mn$_3$C$_6$O$_6$ is found here. Apparently, the Cu ions in Herbertsmithite are Cu$^{2+}$ in difference to the case due to different charge transfers. So, the synthesis route opens the way to prepare experimental systems representing antiferromagnetic Kagomé lattices with different values of spin.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The manuscript was written with the contributions of all authors. All authors have given approval to the final version of the manuscript. All the authors contributed equally.
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The data that support the findings of this study are available from the corresponding author upon reasonable request.

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[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] C. Xue, M. Gao, Y. Xue, L. Zhu, L. Dai, A. Urbas, Q. Li, J. Phys. Chem. C 2014, 118, 15332.
[3] R. Dong, Z. Zheng, D. C. Tranca, J. Zhang, N. Chandrasekhar, S. Liu, X. Zhuang, C. Seifert, X. Feng, Chem. - Eur. J. 2017, 23, 2255.
[4] H. K. Bisoiy, Q. Li, Prog. Mater. Sci. 2019, 104, 1.
[5] A. D. Oyedele, C. M. Rouleau, D. B. Geohegan, K. Xiao, Carbon 2018, 131, 246.
[6] K. Khan, A. K. Tareen, M. Aslam, R. Wang, Y. Zhang, A. Mahmood, Z. Ouyang, H. Zhang, Z. Guo, J. Mater. Chem. C 2020, 8, 387.
[7] F. Schwierz, J. Pezoldt, R. Granzner, Nanoscale 2015, 7, 8261.
[8] L. Wang, H. K. Bisoiy, Z. Zheng, K. G. Gutierrez-Cuevas, G. Singh, S. Kumar, T. J. Bunning, Q. Li, Mater. Today 2017, 20, 230.
[9] U. Mueller, M. Schubert, F. Teich, M. Puetter, K. Schierle-Arndt, J. Pastré, J. Mater. Chem. 2006, 626, 636.
[10] V. Stavila, A. A. Talin, M. D. Allendorf, Chem. Soc. Rev. 2014, 43, 5994.
[11] L. E. Kreno, K. Keong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, Chem. Rev. 2012, 112, 1105.
[12] G. S. Papaefstathiou, T. Fristeric, L. R. MacGillivray, J. Am. Chem. Soc. 2005, 127, 74160.
[13] A. J. Clough, J. W. Yoo, M. H. Mecklenburg, S. C. Marincusc, J. Am. Chem. Soc. 2015, 137, 118.
[14] G. Yang, C. Zhu, D. Du, J. Zhu, Y. Lin, Nanoscale 2015, 7, 14237.
[15] A. H. Khan, S. Chosh, B. Pradhan, A. Dalui, L. K. Shrestha, S. Acharya, K. Ariga, Bull. Chem. Soc. Jpn. 2017, 90, 627.
[16] Z. Liu, X. Zhang, C. Liu, D. Li, M. Zhang, F. Yin, C. Xin, G. Wang, J. Mater. Chem. A 2020, 8, 2777.
[17] A. Dhakshinamurthi, A. M. Asiri, H. Garcia, Chem. - Eur. J. 2016, 22, 8012.
[18] Y. Peng, Y. Li, Y. Ban, W. Yang, Angew. Chem., Int. Ed. 2017, 56, 9757.
[19] N. Lahiri, N. Lotfi,deh, R. Tsuchikawa, V. V. Deshpande, J. Louie, J. Am. Chem. Soc. 2017, 139, 19.
[20] M. G. Campbell, D. Sheberla, S. F. Liu, T. M. Swager, M. Dincă, Angew. Chem. 2015, 127, 4423.
[21] L. Sun, M. G. Campbell, M. Dincă, Angew. Chem., Int. Ed. 2016, 55, 3566.
[22] M. Ko, L. Mendecki, K. A. Mirica, Chem. Commun. 2018, 54, 7873.
[23] L. Yang, X. He, M. Dincă, J. Am. Chem. Soc. 2019, 141, 10475.
[24] A. L. Chernyshov, M. E. Zhitomirsky, Phys. Rev. Lett. 2014, 113, 237202.
[25] D. Grohol, E. H. Matan, J. H. Cho, S. H. Lee, J. W. Lynn, D. G. Nocera, Y. S. Lee, Nat. Mater. 2005, 4, 323.
[26] M. Nishiyama, S. Maegawa, T. Inami, Y. Oka, Phys. Rev. B 2003, 67, 224435.
[27] L. Ye, M. Kang, J. Liu, F. Von Cube, C. R. Wicker, T. Suzuki, C. Jozwiak, A. Bostwick, E. Rotenberg, D. C. Bella, L. Fu, R. Comin, J. G. Checkelsky, Nature 2018, 555, 638.
[28] Z. F. Wang, Z. Liu, F. Liu, Phys. Rev. Lett. 2013, 110, 196801.
[29] M. G. Yamada, H. Fujita, M. Oshikawa, Phys. Rev. Lett. 2017, 119, 057202.
[30] E. M. Miner, L. Wang, M. Dincă, Chem. Sci. 2018, 9, 6286.
[31] T. Chen, J. H. Dou, L. Yang, C. Sun, N. J. Libretto, G. Skorupski, J. T. Miller, M. Dincă, J. Am. Chem. Soc. 2020, 142, 12367.
[32] R. Broholm, R. J. Cava, S. A. Kivelson, D. G. Nocera, M. R. Norman, T. Senthil, Science 2020, 367, 263.
[33] D. Gupta, B. Shankar, P. Elumalai, R. Shanmugam, S. M. Mobin, F. Weisser, B. Sarkar, M. Thiyendiran, J. Organomet. Chem. 2014, 754, 59.
[34] A. W. Stubbs, M. Dincă, Inorg. Chem. 2019, 58, 13221.
[35] J. Park, A. C. Hinckley, Z. Huang, D. Feng, A. Yakovenko, M. Lee, S. Chen, X. Zou, Z. Bao, J. Am. Chem. Soc. 2018, 140, 14533.
[36] R. Zhang, J. Liu, Y. Gao, M. Hua, B. Xia, P. Knecht, A. C. Papageorgiou, J. Reichert, J. V. Barth, H. Xu, L. Huang, N. Lin, Angew. Chem., Int. Ed. 2019, 10, 13698.
[37] Z. Gao, Y. Gao, M. Hua, J. Liu, L. Huang, N. Lin, J. Phys. Chem. C 2020, 124, 27017.
[38] M. Hua, B. Xia, M. Wang, E. Li, J. Liu, T. Wu, Y. Wang, R. Li, H. Ding, J. Hu, Y. Wang, J. Zhu, H. Xu, W. Zhao, N. Lin, J. Phys. Chem. Lett. 2021, 12, 3733.
[39] M. Abel, V. Oison, M. Koudia, L. Porte, Phys. Rev. B 2008, 77, 085410.
[40] L. Martin, H. Martinez, D. Poinot, B. Pecquenard, F. Le Cras, J. Phys. Chem. C 2013, 117, 4421.
[41] E. S. Ilton, J. E. Post, P. J. Heaney, F. T. Ling, S. N. Kerisit, Appl. Surf. Sci. 2016, 366, 475.
[42] H. Denawi, M. Koudia, R. Hayn, O. Sirdi, M. Abel, J. Phys. Chem. C 2018, 122, 15033.
[43] H. Denawi, M. Abel, R. Hayn, J. Phys. Chem. C 2019, 123, 4582.