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Making 2D Topological Polymers a reality

First-principle calculations predicted electronic topological properties for 2D honeycomb-kagome polymers, which have been now confirmed experimentally thanks to improvements in on-surface synthesis.

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With the discovery of graphene, the connection between lattice and electronic topologies became evident. As direct consequence of the honeycomb lattice (a superposition of two hexagonal lattices), the famous Dirac cones in the electronic band structure emerge (Figure 1a), where massless electrons reside at the Fermi level.¹ Many more lattice types exist in 2D, and despite their geometry was already known since the classical period (some are known as Archimedean lattices), and have been categorized by Kepler during late Renaissance (known as Kepler² or Kepler-Shubnikov nets³), only few of them have been found as atomic lattices in nature.

Now, writing in Nature Materials Gianluca Galeotti and colleagues demonstrated how on-surface chemical reactions can be optimized⁴ to realize artificial 2D lattices whose electronic characterization reveal intriguing topological features, thus confirming earlier predictions on grounds of first-principles calculations.⁵

In chemistry, it became recently possible to create virtually any lattice topology by stitching molecular building blocks of suitable symmetry together. Coupled via interlinkage bonds, crystalline frameworks, for example metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), or crystalline polymers, can be formed. However, in most cases the electronic structure of the constituting molecules remains preserved in the crystal, as electronic interaction across the interlinking bonds is hindered. Thus, electronically, the impact of the lattice topology on the electronic structure is not pronounced.

The discovery of fully conjugated 2D polymers^{6,7} triggered the possibility to create such lattice topologies with electronic structures that disperse across the building blocks – at least in 2D. In fact, many 2D lattices feature electronic structures with non-trivial topology.⁸ One particularly interesting example is the kagome lattice, with a flat band and a Dirac cone (Figure 1b). Furthermore, first-principles calculations² have shown that 2D polymers based on hetero-triangulene building blocks (referred to as P²TANG polymers by Galeotti and colleagues) form 2D honeycomb-kagome lattices that show the same electronic characteristics as their underlying fundamental nets (Figure 1c,d). For example, as in graphene P²TANG shows a Dirac cone which emerges due to the honeycomb sublattice formed by the nitrogen atoms, although the nitrogen atoms in P²TANG are about 7 times further apart than the carbon atoms in graphene. This research strongly suggests that lattice

topology in 2D polymers can control their electronic structure, yet till date, these findings remained the exotic hypothesis of theorists. In fact, although such 2D honeycomb-kagome polymers have been realized by surface calcination in previous works^{9,10}, their intriguing electronic properties could not be measured.

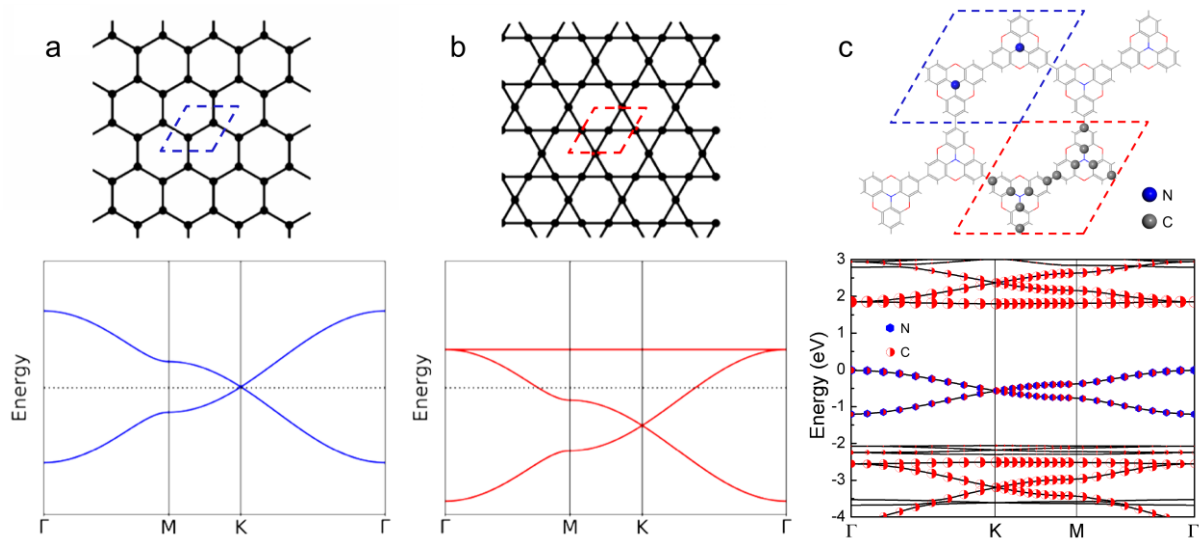


Figure. 1 Structure-electronic topology relation of honeycomb-kagome 2D polymer P²TANG.

Structure (top) and Tight-Binding band structure (bottom) of (a) a honeycomb lattice⁸ and (b) a kagome lattice.⁸ (c) Optimized structure with the unit cell indicated twice, highlighting the honeycomb (blue) and kagome (red) sublattices (top), and first-principles band structure (bottom) of the honeycomb-kagome P²TANG conjugated 2D polymer,^{Fehler! Textmarke nicht definiert.} with band contributions arising from the nitrogen honeycomb sublattice (blue solid hexagons) and the π -conjugated carbon atoms to the kagome and honeycomb sublattices (red half-filled circles)..a,b, adapted from ref.8 by Maximilian A. Springer.

Galeotti and coworkers delivered the experimental proof that puts the research on conjugated 2D polymers on solid grounds. They managed to experimentally prove the predicted electronic structure for these low-density 2D polymers, and thus confirm that indeed the lattice topology features the electronic band structure. This proof was possible only by overcoming two challenges: first, a highly crystalline flake of sufficiently large domain size and with low defect density had to be grown. This was possible by introducing a new technique, the so-called hot dosing approach combined with rigid precursors, where a hot substrate temperature allows defect healing during the growth process. With this approach, it was possible to prepare large, highly crystalline domains of 100 x 100 nm² size. The second challenge was to probe the electronic structure. Angle-resolved photoelectron spectroscopy (ARPES) is the standard technique for this purpose. ARPES signals typically are somewhat fuzzy, even for well-ordered solids. Therefore, a large area of the substrate (~100 x 100 μm^2) with long-range homogeneity in the domain direction had to be covered with the polymer. The presence of first-principles data strongly supported the analysis of the ARPES data, which revealed both the Dirac cone and the flat bands in the so-called P²TANG 2D conjugated polymer.

These results show that the rational design of electronic structures, so-called band-structure engineering, is feasible also for 2D polymers, even though their lattice vectors exceed 1 nm. Importantly, although the 2D polymers have been obtained by an on-surface reaction, they can be detached and transferred to any other substrate, such as silicon oxide or mica, and thus be incorporated in electronic devices. Hence, not only theorists but also experimentalists will be

motivated to explore new electronic topologies that emerge from the wide range of 2D lattice types.⁸ Given the manifold of conjugated molecular building blocks known from organic chemistry, it can be expected that many of the possible 2D nets can be realized as conjugated 2D polymers, opening a new playground for condensed matter physicists who are interested in implementing and studying exotic quasiparticles such as Majorana fermions, superconductivity, and correlated phenomena.

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