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# Two-dimensional Kagome Lattices Made of Hetero Triangulenes are Dirac Semimetals or Single-Band Semiconductors

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*Supporting Information Placeholder*

**ABSTRACT:** Here we discuss, based on first-principles calculations, two-dimensional (2D) kagome lattices composed of polymerized hetero-triangulene units, planar molecules with  $D_{3h}$  point group containing a B, C or N center atom and  $CH_2$ , O or CO bridges. We explore the design principles for a functional lattice made of 2D polymers, which involves control of  $\pi$ -conjugation and electronic structure of the knots. The former is achieved by the chemical potential of the bridge groups, while the latter is controlled by the heteroatom. The resulting 2D kagome polymers have a characteristic electronic structure with a Dirac band sandwiched by two flat bands and are either Dirac semimetals (C center), or single-band semiconductors - materials with either exclusively electrons (B center) or holes (N center) as charge carriers of very high mobility, reaching values of up to  $\sim 8 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is comparable to crystalline silicon.

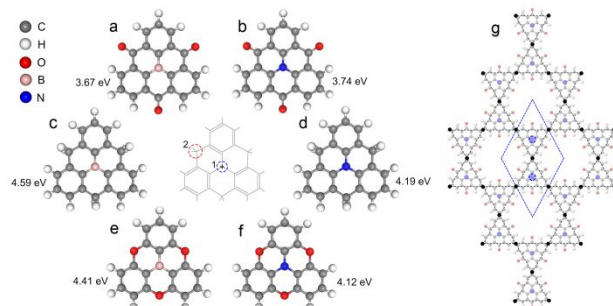
The properties of a crystalline material are governed by both its lattice geometry and chemical composition. A typical example highlighting the importance of the lattice is the two-dimensional (2D) honeycomb structure of graphene,<sup>1</sup> where the characteristic Dirac cones emerge due to the two hexagonal sub-lattices. Already in 1619 Johannes Kepler reported that only 13 nets with identical knots are possible in two dimensions (as 2 of them are enantiomeric we talk about 11 Kepler nets).<sup>2</sup> Various derivatives of these Kepler nets are possible.<sup>3</sup> However, even fewer than the 11 Kepler nets occur in single-layers exfoliated from natural layered crystals, or on surfaces. As the importance of topology is evident, e.g. from the graphene example, it is intriguing to explore the properties of the remaining Kepler nets and of their derivatives.

It is relatively straight-forward to computationally characterize these artificial lattices,<sup>4</sup> and many interesting properties have been predicted.<sup>5</sup> Enormous efforts were devoted to realize such lattices experimentally,<sup>6</sup> most prominently in photonic lattices.<sup>7</sup> For example, recent experiments confirm the intriguing predicted properties of the Lieb lattice in a challenging ultracold environment,<sup>8</sup> which is a show stopper for real-world applications.

Molecular framework materials, such as metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs), offer new possibilities to form exotic nets,<sup>9</sup> because molecules, acting as knots, can be designed in such way that their bridging sites reflect the required topology of the net. 2D polymers offer the opportunity to create exotic lattices which are stable at ambient conditions, including square,<sup>10</sup> rectangular,<sup>11</sup>

honeycomb,<sup>9b,12</sup> and kagome (**kgm**)<sup>13</sup>. 2D polymers have been fabricated by using surface or interface polymerization,<sup>14</sup> and mechanical exfoliation of the layered bulk sometimes is possible.<sup>15</sup> However, in order to realize the desired topological properties of the exotic nets present in the 2D polymers, the molecules marking the knots need to interact electronically with each other. In most cases, the bonds created by the coupling reaction electronically separate the  $\pi$  systems of the monomer units and thus block ballistic charge transport. Full  $sp^2$  conjugation can be achieved if a C=C bond connects the extended monomers to form 2D polymers.<sup>16</sup> Also for the recently reported 2D polymers realized by surface calcination or solution synthesis of hetero-triangulenes (HTs),<sup>17</sup> which form the exotic **kgm** 2D net, intermolecular  $\pi$  conjugation can be expected due to their reported band dispersion.

HTs are nearly planar molecules that have been studied intensively.<sup>18</sup> Our selection for this work is displayed in **Figure 1a-f**. We note that Dirac cones can be anticipated (we confirm them here) in the reported band structures,<sup>17b, 19</sup> even though the HT center atoms, which mark the knots of a honeycomb sublattice, are separated by distances of more than 1 nm.



**Figure 1.** Schematic representation of cationic triangulene (centre) and its HTs derivatives by replacing the centered  $C^+$  (1) with B or N, and the  $-CH_2$  bridge (2) with  $C=O$ , or O, respectively, which are (a) carbonyl-bridged triphenylborane (CTPB), (b) carbonyl-bridged triphenylamine (CTPA),<sup>18a</sup> (c) methylene-bridged triphenylborane (MTPB), (d) methylene-bridged triphenylamine (MTPA),<sup>17b</sup> (e) oxygen-bridged triphenylborane (OTPB),<sup>18d</sup> and (f) oxygen-bridged triphenylamine (OTPA).<sup>18e</sup> (g) scheme of the **kgm** lattice that combines a regular hexagonal tiling (blue lattice for the unit cell) and a regular triangular tiling (black lattice).

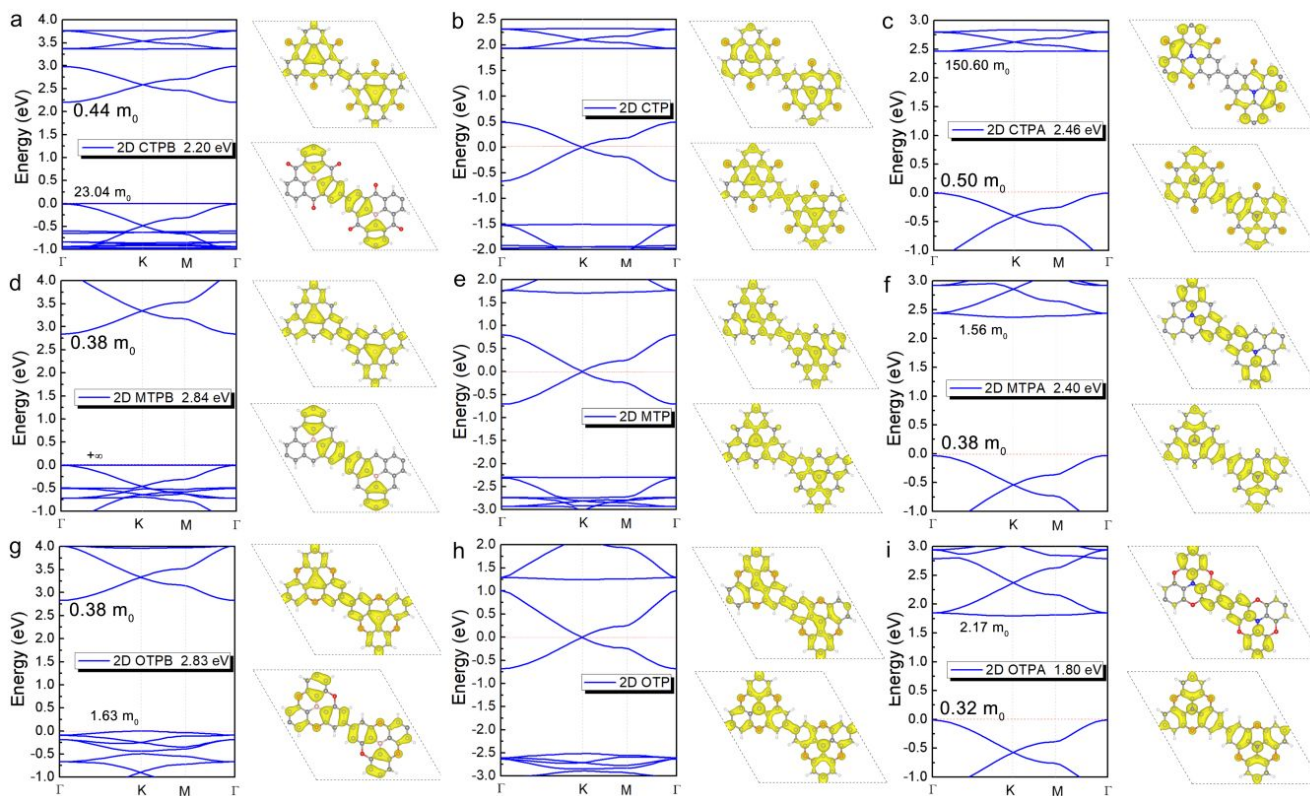
By using density functional theory (DFT, VASP code,<sup>20a</sup> PAW approach,<sup>20b</sup> cutoff energy of 450 eV, PBE functional,<sup>20c</sup> electronic structure refined by HSE06<sup>20d</sup>, details see SI) based

first-principles calculations, we show that 2D HT-based **kgm** lattices exhibit unprecedented electronic features that are accessible by chemical modification of the building units. The HTs act as “superatoms” with local  $D_{3h}$  symmetry, in analogy to  $sp^2$  hybridized C atoms. If the center atom is chosen to be carbon (HT(C)), the monomers also electronically act like  $sp^2$  hybridized carbon atoms. Arranging six of them in a “super benzene” structure, we obtain  $D_{3h}$  (HT)<sub>6</sub> (**Figure S1a**). The frontier  $\pi$  orbitals that resemble the characteristic electronic structure of benzene are prototypic for aromatic molecules. Arranged in an extended 2D **kgm** lattice (**Figure S1b**), the electronic structure includes the expected half-filled Dirac cones at the K points of the Brillouin zone which emerge from the honeycomb sublattice (**Figure S1c**). If the heteroatoms are changed to B or N, the resulting **kgm** lattices show a peculiar combination of two apparently mutually exclusive characteristics: one of the bands next to the Fermi level is flat and does not contribute to charge transport, the other one is strongly dispersed, with highly mobile charge carriers (reaching mobility of  $8 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  in the case of **kgm** CTPB-polymer), and thus determines the electric conductivity. The **kgm** HT-polymers become either n-type (only electrons as mobile charge carriers) or p-type (only holes as mobile charge carriers) single band (intrinsic) semiconductors, by either completely emptying (B) or filling (N) the strongly dispersed Dirac bands (**Figure S1c**).

Highly reactive triangulene is a  $\pi$  radical with two unpaired electrons.<sup>21</sup> Stable cationic closed-shell derivatives are obtained by substitution of outer CH groups with CO, O, or CH<sub>2</sub> bridges (**Figure 1**). Such molecular ions have been widely used as dyes.<sup>22</sup> As neutral, single radical species, their  $D_{3h}$  symmetry allows the arrangement in a **kgm** lattice as shown in **Figure 1g**, thus forming a **kgm** 2D polymer with a honeycomb sublattice that carries the

HT center atoms. The frontier orbital of the HT(C)s has  $\pi$  character with one unpaired electron and resembles the electronic features of  $sp^2$  carbons in aromatic molecules, illustrated for the benzene-analogue of CTP in **Figure S1a**. The HT(C) atoms forming the honeycomb sublattice yield a band resembling the graphene electronic structure with Dirac cones at the K points of the Brillouin zone (**Figure 2 b, e, h**), even though their distance is  $\sim 1 \text{ nm}$ , seven times larger than in graphene. In free-standing form, for steric reasons, the monomers are slightly twisted with respect to one another, which results in the opening of a small band gap of 29–58 meV (**Figure S2**).

On the other hand, the substituted HTs resemble the electronic analogues of 2D nitrogen (N-substituted) and 2D boron (B-substituted), both in the honeycomb sublattice. The six substituted HT(N/B) structures are shown in **Figure 1a-f**, all of these molecules being nearly planar and with HOMO-LUMO gaps in the range of 3.7–4.6 eV. The resulting **kgm** HT(N/B)-polymers are stable (two have been reported experimentally),<sup>17a,b</sup> and for all others the reaction energy is very similar, ranging from 1.36...1.86 eV/unit (see **Equation S1**, **Table S1** and **Figure S3**). They all have similar lattice vectors (17.07...17.62 Å) and pore sizes (11.75...13.10 Å) (**Table S1**). In free-standing form, the **kgm** HT(N/B)-polymers are slightly twisted. In the remainder, however, we assume them to adopt flat geometries in agreement with a suspended structure as expected in experiment (see refs. 17a,b). However, even if they are slightly twisted, their electronic characteristics are maintained and the twisting has negligible impact on the results presented and discussed here (for details, see **Figure S4** and **Table S1** and **S2**).



**Figure 2.** (a-i) band structures, at the HSE06 level and corresponding charge density distribution for CBM (above) and VBM (below), respectively, of **kgm** HT(B/C/N)-polymers (their monomers are introduced in **Figure 1a-f**). 2D MTP and OTP complete the **kgm** HT(C)-polymers built from MTP radical and OTP radical. The Fermi level is set at the VBM for the semiconductors, effective masses of the frontier bands are indicated, and the isosurface for all orbitals is set to be  $0.0013 \text{ e}\text{\AA}^{-3}$ . All structures are spin unpolarized.

**Table 1.** Calculated effective masses  $m^*$  for electrons and holes (italic values indicate low-mobility carriers) at the PBE level. For the mobile charge carriers, deformation potential (DP) constant  $E_1$ , in-plane stiffness  $C_{2D}$  and carrier mobility  $\mu$  for **k<sub>gm</sub>** HT(N/B)-polymers along the zigzag direction. Armchair values differ only slightly (see **Table S4**).

<b>k<sub>gm</sub></b> HT-polymers	CTPB	CTPA	MTPB	MTPA	OTPB	OTPA
$m_e^*/m_0$	0.44	<i>150.60</i>	0.34	<i>1.56</i>	0.35	2.17
$m_h^*/m_0$	<i>23.04</i>	0.47	$\infty$	0.30	<i>1.63</i>	0.27
$E_1$ /eV	0.72	2.21	2.09	3.87	2.97	4.78
$C_{2D}$ /Nm <sup>-1</sup>	59.32	63.25	59.79	62.73	65.05	63.72
$\mu$ / $\times 10^3$ cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	8.39	0.83	1.68	0.66	0.85	0.54

According to their band structures, the triangulene-based **k<sub>gm</sub>** polymers can be categorized in two classes (**Figure 2**): **k<sub>gm</sub>** HT(C)-polymers are Dirac semimetals, and the **k<sub>gm</sub>** HT(N/B)-polymers are intrinsic single-band semiconductors with electrons (HT(B)-polymers) and holes (HT(N)-polymers) as mobile charge carriers. Note that for **k<sub>gm</sub>** HT(C)-polymers a tiny band gap of ~0.05 meV is observed when spin-orbit coupling is included in the Hamiltonian, a value similar as found for graphene. This indicates a topological phase for 2D HT(C) polymers. The band gaps range from 1.8-2.8 eV, with the band edges being enclosed within the HOMO-LUMO region of their corresponding HT(N/B) monomers (**Figure S5**). In all cases, the flat bands have their extrema (if they can be specified) at the K point, while those of the strongly dispersed band are located at the  $\Gamma$  point. Even though the effective masses of the mobile charge carriers are similar, ranging from 0.32-0.5  $m_0$  (**Figure 2**, **Table S3**), the calculated charge carrier mobilities (see **Equation S2**, **Table 1**, **Figure S6**) differ strongly between the **k<sub>gm</sub>** HT(N)-polymers ( $0.5\text{-}0.9 \times 10^3$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) and their generally more mobile HT(B)-polymer counterparts ( $0.8\text{-}8.4 \times 10^3$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>). For the flat bands, the lowest effective masses are 1.6  $m_0$ , while for some structures the effective masses exceed 100  $m_0$ .

The honeycomb sublattice makes the HTs behave like “sp<sup>2</sup>-superatoms” B, C and N, where the sp<sup>2</sup>-like configuration is enforced by the D<sub>3h</sub> symmetry and planarity of the HTs, with a  $\pi$ -orbital (resembling the 2p<sub>z</sub>) that is either empty (B), half-filled (C) or filled (N). Orbitals of the flat bands (**Figure S7**) show no contribution of the HT center atoms (independent of C, N or B), but are delocalized on the remainder of the 2D lattice. Bridge functionalization controls the orbital shapes of the HT(N/B) molecules and thus the conjugation in the **k<sub>gm</sub>** HT(N/B)-polymers, in particular the curvature of the flat bands. In the case of very flat bands (VB of **k<sub>gm</sub>** CTPB-polymer and MTPB-polymer, CB of **k<sub>gm</sub>** CTPA-polymer) the  $\pi$  electron density is significant at the bridge groups, but reduces at the bonds connecting the monomers (**Figure 2**). Appreciable conjugation is observed for the more dispersed flat bands (VB of **k<sub>gm</sub>** OTPB-polymer, CB of **k<sub>gm</sub>** MTPA-polymer and OPA-polymer). Partial density-of-states analysis (**Figure S8**) indicates that the C=O bridge has significant contribution at the VBM of **k<sub>gm</sub>** CTPB-polymer and CBM of CTPA-polymer, contrary to CH<sub>2</sub> and O bridges. The conjugated band with the low-effective-mass charge carriers is less affected, but this picture changes for charge carrier mobilities, where both center atom and bridge group strongly affect the electron-phonon coupling via the deformation potential: the holes in **k<sub>gm</sub>** HT(N)-polymers are more prone to acoustic phonon scattering than the electrons of **k<sub>gm</sub>** HT(B)-polymers that possess the same bridge skeleton, while the C=O, CH<sub>2</sub> and O bridges reduce the carrier mobilities in that order, but with smaller impact. Note that due to neglect of coupling between optical phonons and electrons our predicted charge carrier mobilities are likely to be slightly overestimated.

To summarize, we have shown that hetero-triangulene derivatives form kagome lattices which show a peculiar electronic structure of a Dirac band sandwiched by two flat bands. The center atoms of the HTs mark a honeycomb sublattice, and act like sp<sup>2</sup> “superatoms” B, C or N. Although they are ~1 nm apart from

each other, they still interact considerably, which results in the highly dispersed Dirac band which contains the mobile charge carriers of the presented 2D polymers. The six **k<sub>gm</sub>** HT(B/N)-polymers are intrinsic semiconductors with band gaps in the range of 1.8-2.8 eV. The center atom (B or N) determines the type of mobile charge carrier, while the bridge functional group influences the flat band curvature via  $\pi$  conjugation, and the band gap. While one frontier band shows very high charge carrier mobility of up to  $8 \times 10^3$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, the other bands do not contribute to charge transport. Those flat bands contribute high peaks in the electronic density-of-states and may offer interesting phenomena, e.g. Lifshitz transitions,<sup>23</sup> if located at the Fermi level. Our observations suggest that the flat bands are inherent features of the **k<sub>gm</sub>** lattice, as their crystal orbitals are formed by all atoms except for the center ones, and as their dispersion is strongly influenced by the bridge groups which mark the edges of the triangles that characterize the **k<sub>gm</sub>** lattice structure.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Details of the DFT calculations, frontier orbitals of HTs oligomers, stability of **k<sub>gm</sub>** HT(N/B)-polymers, band structure of twisted **k<sub>gm</sub>** HT-polymers and details for the calculations of the carrier mobilities according to the DP theory, orbitals of the flat bands and density of states of **k<sub>gm</sub>** HT(N/B)-polymers are given in the Supporting information.

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### Notes

The authors declare no competing financial interests.

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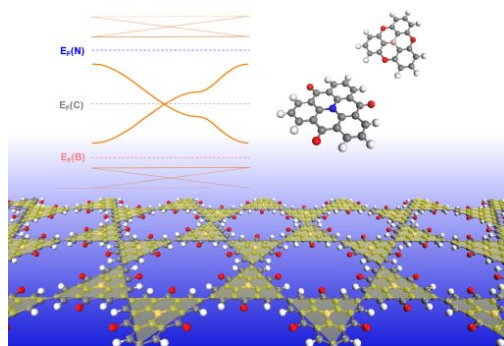
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