Tetraoxa[8]circulene-Based Nanosheets as a New Family of Two-Dimensional Covalent Metal-Free Organic Frameworks

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The structural and electronic properties of a new family of two-dimensional (2D) covalent metal-free organic frameworks based on tetraoxa[8]circulene (TOC) with different types of fusing have been studied. All nanosheets demonstrate high thermodynamic stability and unique electronic properties depending on the fusing type. Among three types of nanosheets, only two of them demonstrate semiconducting properties exhibiting 1.37 and 1.84 eV direct band gaps, while another one was found to be a semimetal, which possess strong topological states. We have found that spin-orbit coupling effects enhance the band gap (~87 meV) for the studied material and this effect exceeds by several orders of magnitude relative to the graphene analogue. Tetraoxa[8]circulene-based nanosheets are also predicted to be good organic semiconductors due to a clearly observable quantum-confinement effect on the band gap size in oligomers and relatively low effective masses, which result in high carrier mobility. Owing to the versatility of chemical design, these materials have the potential to expand applications beyond those of graphene.

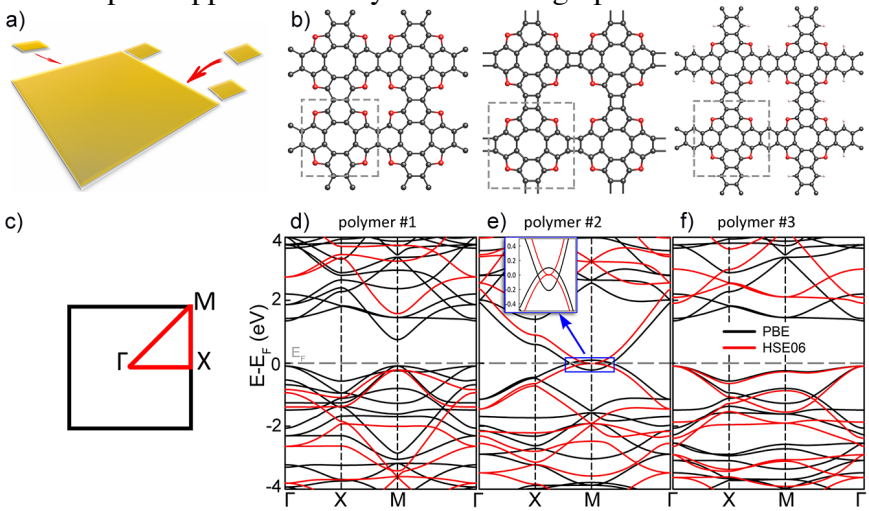

Figure 1: Illustration of 2D TOC formation (a) via attaching the same monomers in different ways (from left to right: polymer#1, polymer#2, and polymer#3 (b). Unit cells are marked by dashed gray lines. Carbon, oxygen, and hydrogen atoms are presented in black, red, and beige, respectively. The high-symmetry k-points (c) in the Brillouin zone and corresponding electronic band structures calculated by GGA-PBE (black lines) and HSE06 hybrid functional (red lines) for polymers#1 (d);#2 (e); and#3 (f). The inset shows the frontier states behavior near the Fermi level in polymer#2.

References

1. A. V. Kuklin, G. V. Baryshnikov, B. F. Minaev, N. Ignatova, H. Ågren, *J. Phys. Chem. C*, **122** (2018), 22216.