

Synthesis of Porphene, an Antiaromatic Analog of Graphene

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Two-dimensional organic materials offer atomic precision for optoelectronics and energy-efficient nanoelectronics, but most are not easily patterned and tuned. The fully conjugated Zn-porphene, $(C_{20}N_4Zn)_\infty$ has now been prepared from Zn porphyrin by oxidative polymerization on aqueous surface and transferred to solid substrates. Its structure was established by imaging as well as in-situ and ex-situ spectroscopy. Reversible insertion of other metal ions is possible and promises an atomic canvas for painting with thousands of distinct metal ions and ligands without taking any π centers out of conjugation. Unlike earlier computational results, which predicted a $P4mm$ (D_{4h}) square unit cell and metallic conductivity, ours resemble those for antiaromatic molecules and predict Zn-porphene to be a two-dimensional antiaromatic semiconductor with a pair of $P2mm$ (D_{2h}) rectangular unit cells, rapidly interconverting via a $P4mm$ (D_{4h}) square structure by tunneling and/or thermal excitation. This result is supported by measurements of electrical conductivity and of N(1s) chemical shift in X-ray photoelectron spectra.

