

PORPHENE – A REGULAR HETEROCYCLIC TWO-DIMENSIONAL POLYMER

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Surface-constrained oxidative coupling of zinc porphyrin on an aqueous subphase containing a strong oxidant yields a bilayer of porphene in the form of sheets up to 0.1 mm across, which can be transferred to various solid substrates. The structure of this fully conjugated two-dimensional polymer with fourfold symmetry was proven by diffraction on the aqueous surface using a synchrotron grazing incidence X-ray beam. It was examined also by non-contact atomic force microscopy after transfer to highly ordered pyrolytic graphite. It is analogous to that of graphene, but is composed of fused free-base porphyrin rings instead of fused benzene rings. The absence of Zn ions has been demonstrated by X-ray photoelectron spectroscopy. Investigations of porphene formation mechanism and its spectroscopic, structural, electrical, chemical, and mechanical properties, as well as exfoliation to single sheets and construction of twisted multilayer sheets using bidentate ligands, are currently underway. The ability of the porphyrin macrocycle to bind many different kinds of metal cations carrying two, one, or no additional ligands promises that porphene has the potential for being not be a single polymer but rather, a large family of two-dimensional polymers with tunable properties. Here, porphene differs from graphene in that its functionalization does not require taking any of its π -electron centers out of conjugation, and merely involves insertion of metal ions into its macrocycles and attachment of arbitrary ligands. It is therefore expected that it will be at least as versatile as graphene.

