The first members of covalent organic frameworks (COF) have been designed and successfully synthesized by condensation reactions of phenyl diboronic acid C₆H₄[B(OH)₂]₂ and hexahydroxytriphenylene C₁₈H₆(OH)₆. The high crystallinity of the products (C₃H₂BO)₆ (C₉H₁₂)₁ (COF-1) and C₉H₄BO₂ (COF-5) has allowed definitive resolution of their structure by powder X-ray diffraction methods which reveal expanded porous graphitic layers that are either staggered (COF-1, P6₃/mmc) or eclipsed (COF-5, P6/mmm). They exhibit high thermal stability (to temperatures up to 500- to 600-C), permanent porosity, and high surface areas (711 and 1590 m²/g, respectively) surpassing those of related inorganic frameworks. A similar approach has been used for the design of other extended structures.