

Transformation between 2D and 3D Covalent Organic Frameworks via Reversible [2 + 2] Cycloaddition

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Abstract

We report the first transformation between crystalline vinylene-linked two-dimensional (2D) polymers and crystalline cyclobutane-linked three-dimensional (3D) polymers. Specifically, absorption-edge irradiation of the 2D poly(arylenevinylene) covalent organic frameworks (COFs) results in topological [2 + 2] cycloaddition cross-linking of the π -stacked layers in 3D COFs. The reaction is reversible, and heating to 200°C leads to a cycloreversion while retaining the COF crystallinity. The resulting difference in connectivity is manifested in the change of mechanical and electronic properties, including exfoliation, blueshifted UV-vis absorption, altered luminescence, modified band structure, and different acid-doping behavior. The Li-impregnated 2D and 3D COFs show a significant room-temperature ion conductivity of 1.8×10^{-4} S/cm and 3.5×10^{-5} S/cm, respectively. Even higher room-temperature proton conductivity of 1.7×10^{-2} S/cm and 2.2×10^{-3} S/cm was found for H₂SO₄-treated 2D and 3D COFs, respectively.

FIGURES

