New Self-Healable Materials by Supramolecular Chemistry

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Expanding the range of healable materials is an important challenge for sustainable societies. Noncrystalline, high molecular weight polymers generally form mechanically robust materials, which, however, are difficult to repair once they are fractured. This is because their polymer chains are heavily entangled and diffuse too sluggishly to unite fractured surfaces within reasonable timescales. Here, we report that low molecular weight polymers, when crosslinked by dense hydrogen bonds, give mechanically robust yet readily repairable materials, despite their extremely slow diffusion dynamics [1]. A key was to utilize thiourea, which anomalously forms a zigzag hydrogen-bonded array that does not induce unfavorable crystallization. Another key was to incorporate a structural element for activating the exchange of hydrogen-bonded pairs, which enables the fractured portions to rejoin readily upon compression.

We also report here heat-resistance, self-healable porous crystal. This crystal is an anomalous porous molecular crystal built of ‘C–H···N-bonded double-layered roof/floor components’ and ‘wall components of a segregatively interdigitated architecture’ [2]. This complicated porous structure consists of only one type of fully aromatic multi-joint molecule carrying three identical dipyridylphenyl wedges. Despite its high symmetry, this molecule accomplishes difficult tasks by employing two of its three wedges for roof/floor formation and employing its other wedge for wall formation. Although a C–H···N bond is extremely labile, the porous crystal maintains its porosity until thermal breakdown of the C–H···N bonds at 202 °C to afford a non-porous polymorph. While this non-porous crystal survives even at 325 °C, it can retrieve the parent porosity under acetonitrile vapor. These findings show how one can translate simplicity into ultrahigh complexity.

References