Hydrogen-bond aromaticity coupling in supramolecular polymers

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The coupling of aromatic gain and hydrogen bonding in a supramolecular polymer is examined. Partially aromatic bis(squaramide) bolaamphiphiles were designed to self-assemble through a combination of hydrophobic, hydrogen-bonding and aromatic effects into stiff, high-aspect-ratio fibers. UV and IR spectroscopy display electronic and geometric changes within the squaramide ring indicative of strong hydrogen bonding and aromatic gain of the monomer units. The contribution of aromaticity to the interaction energy was further supported computationally through nucleus-independent chemical shift (NICS) and harmonic oscillator model of aromaticity (HOMA) indices, showing greater aromatic character upon polymerization: at least 30 % in a pentamer. The aromatic gain-hydrogen bonding synergy results in a significant increase in thermodynamic stability and a striking difference in aggregate morphology of the bis(squaramide) bolaamiphile compared to isosteres that cannot engage in this effect.