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Insights into Physical Interactions and Structuration in Self-Assembled Azapeptide Hydrogels Through Spectroscopy Techniques

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Self-assembly is a captivating phenomenon within supramolecular chemistry, triggering the formation of hydrogels stabilized by non-covalent interactions including hydrogen bonding, π-π stacking, electrostatic interactions, and hydrophobic forces. Supramolecular gels-based low molecular weight molecules find applications in tissue engineering, drug delivery, biosensing, and catalysis [1]. Azapeptides, characterized by their nitrogen atoms, offer unique functionalities and stability, rendering them ideal for the fabrication of supramolecular hydrogels [2, 3]. In this study, two hydrogelator molecules derived from azapeptide family were designed, and structurally elucidated using various spectroscopic techniques. NMR, FTIR, UV-Vis, fluorescence, SEM, and rheology experiments were conducted to explore molecular, supramolecular, mechanical features. In solution, both molecules exhibit monomeric states adopting β-turn conformation stabilized by intramolecular hydrogen bonding, while the supramolecular structure (as revealed by X-ray crystallography) is stabilized mainly through intermolecular hydrogen bonding and π-π stacking (data is not shown). In the gel state, circular dichroism (CD) spectroscopy, is crucial for understanding the secondary structure and self-assembly of azapeptide-based hydrogels [4]. This study sheds light on the conformational changes occurring during the self-assembly process. For example, the temperature dependent experiment revealed the gel-sol transition associated with conformational changes (see **Figure 1**). By integrating principles from supramolecular chemistry, innovative azapeptide design strategies, and sophisticated spectroscopic methodologies, the development of functional hydrogels with tailored properties for diverse applications becomes achievable.

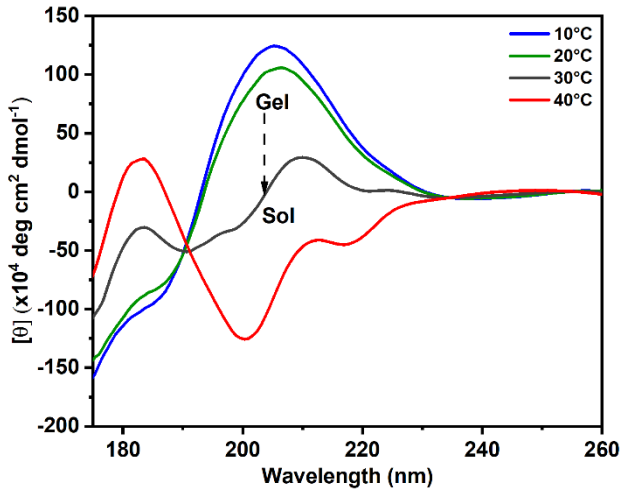

FIGURE 1. Temperature-dependent SRCD spectrum of azapeptide hydrogel (c = 0.8 w/w%, pH = 7.0).

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