Transition-Metal Cross-Linked Alginates: Domain Architecture and Structure as Seen by Paramagnetic ss-NMR Spectroscopy and Heterospectral Machine Learning

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Across chemistry and biology, a central limitation in understanding function is the lack of access to atomically resolved molecular structure under native, complex conditions. While spectroscopic probes such can isolate signals from specific molecules in such environments, they typically provide only fragmentary information. Due to the regenerative nature of metal-coordination bonds, transition-metal cross-linked alginates have become indispensable in addressing a range of technological challenges. However, as given by their amorphous character and the paramagnetic nature of many transition-metal ions, the crucial knowledge for optimizing their physicochemical properties – i.e. coordination geometry, and atomic-resolution structure – have long remained elusive to the conventional solid-state NMR and x-ray diffraction techniques. To overcome this problem, we have utilized an advanced strategy based on ultra-fast magic angle spinning (UF/MAS) NMR allowing to remove extreme signal broadening caused by the interactions of nuclear spins with unpaired electrons. Furthermore, we developed a heterospectral machine-learning approach that translates low-resolution or indirect spectroscopic data into high-resolution ^{13}C CP/MAS NMR spectra, enabling recovery of atomic-level structural information from fragmentary inputs. The method was validated on chemically distinct systems including a small organic molecule and a complex biomacromolecular network (alginate–pectin gels), demonstrating its robustness across molecular scales. This way we have focused on obtaining up to now unreported data on molecular structure, network density and domain architecture of multicomponent alginate systems cross-linked by paramagnetic Cu^{2+}/Fe^{3+} ions.

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