
Abstract: Diphenylalanine is one of the most studied building blocks in organic supramolecular chemistry, forming ordered assemblies with unique mechanical, optical, piezoelectric, and semiconductive properties. These structures are being used for diverse applications, including energy storage, biosensing, light emission, drug delivery, artificial photosynthesis, and chemical propulsion. To increase the structural diversity of this dipeptide building block, three previously unreported analogues in which the aliphatic chain between the peptide backbone and the phenyl ring was gradually lengthened were synthesized. Each dipeptide self-assembled into unique microstructures, differing in morphology, which ranged from flat plates to long microrods to flattened microplanks. The structures were also found to possess distinctive optical properties. Furthermore, X-ray crystallography of each of the three diphenylalanine analogues presented distinctive molecular arrangements. The remarkable differences between each dipeptide in the intermolecular interactions they formed provide insight into the physicochemical mechanisms of self-assembly and, in addition, indicate the biological significance of the single methylene bridge of phenylalanine.