

*Low-molecular-weight amino-acid-based derivatives: from organogels to single crystals and mesocrystals*

Florencia Di Salvo<sup>1</sup>, Federico Movilla<sup>1</sup>, Juan Manuel Rey<sup>1</sup>, Olga Carolina Sánchez Montilva<sup>1</sup>  
<sup>1</sup>DQIAQF/INQUIMAE-CONICET, FCEN, University Of Buenos Aires, Buenos Aires, Argentina  
 E-mail: flor@qi.fcen.uba.ar

Amino acids are able to self-assemble into ordered superstructures, also called mesocrystals, when they are subjected to certain crystallisation conditions such as, pH, supersaturation level and the use of additives, being the last one the most popular strategy [1, 2]. Besides, self-assembly strategies applied to low-molecular weight building blocks can conduct to supramolecular gels. Their properties can be modulated by variation of temperature or solvent, since these changes directly affect the strength of the non-covalent interactions within the gel network [3]. The obtaining of both, supramolecular gels or crystalline materials, is governed by the presence of non-covalent interactions, resulting in spanning network that can immobilise solvents for the first ones or, the self-assembly between the building blocks, to give place to the others. Thus, there is a delicate balance for a low-weight molecule to behave as a gelator or crystal.

Herein, we present a new family of chiral L-amino-acid-based low-weight molecules which behave as excellent building blocks for the construction of supramolecular gels or crystalline structures. Compounds 1-3 are obtained as zwitterions after the reaction between piperonal and L-Alanine, L-Phenylalanine and L-Tyrosine, respectively. Crystallisation experiments using organic solvents are only possible with dilute solutions of the amino acid derivatives due to their low solubility. Compounds 1 and 3 conduct mainly to polycrystalline materials and 2 gives place to crystalline superstructures with spherical morphologies, results attributed to the different solubility and supramolecular properties conferred by the amino acid bone. All derivatives are soluble in basic media after the deprotonation of the zwitterion. After a slow evaporation of the solvent of the basic solutions, spherical-like mesocrystals are obtained. Due to their structural features, compounds 1-3 are also soluble in acids. After slow diffusion of hydrogen chloride vapours in basic solutions of 2, single crystals suitable for XRD studies are obtained. The crystallographic results confirm the presence of the protonated derivative. Although 1 and 3 do not give place to crystals of suitable quality under the same conditions, experiments using other acids are in progress. In order to increase the solubility of compounds 1-3 in their zwitterionic form in organic solvents, the temperature of the solutions can be increased. Only the derivative of phenylalanine is soluble in higher concentrations after increasing the temperature and then after cooling, it gives place to supramolecular gels. The reversibility of the gelification process with temperature is also observed. In conclusion, it is possible to suggest that the presence and directionality of certain functional groups and the intermolecular interactions developed, such as the existence or not of the OH and the phenyl group, are key factors in the mechanism of self-assembly into hierarchical structures, single crystals or even supramolecular organogels. Furthermore, the strong pH dependence allows the obtaining of single crystals or the assembly to crystalline superstructures. This new family of low-molecular-mass derivatives shows a huge versatility regarding supramolecular properties. Varying the aldehyde and/or the amino acid opens a broad perspective for the design of novel self-assembly architectures for the further development of functional soft and/or crystalline materials.

[1] Jiang, H. et al. (2011). *Cryst. Growth Des.*, 11, 3243–3249, and references therein.

[2] Ejgenberg, M. & Mastai, Y. (2012). *Cryst. Growth Des.*, 12, 4995–5001.

[3] Buerkle, L.E. & Rowan, S.J. (2012). *Chem. Soc. Rev.*, 41, 6089–6102.



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