

Chiral bis(amino acid)- and bis(amino alcohol)-oxalamide gelators. Gelation properties, self-assembly motifs and chirality effects

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Bis(amino acid)- and bis(amino alcohol)oxalamide gelators represent the class of versatile gelators whose gelation ability is a consequence of strong and directional intermolecular hydrogen bonding provided by oxalamide units and lack of molecular symmetry due to the presence of two chiral centres. Bis(amino acid)oxalamides exhibit ambidextrous gelation properties, being capable to form gels with apolar and also highly polar solvent systems and tend to organise into bilayers or inverse bilayers in hydrogel or organic solvent gel assemblies, respectively. ¹H NMR and FTIR studies of gels revealed the importance of the equilibrium between the assembled network and smaller dissolved gelator assemblies. The organisation in gel assemblies deduced from spectroscopic structural studies are in certain cases closely related to organisations found in the crystal structures of selected gelators, confirming similar organisations in gel assemblies and in the solid state. The pure enantiomer/racemate gelation controversy is addressed and the evidence provided that *rac*-**16** forms a stable toluene gel due to resolution into enantiomeric bilayers, which then interact giving gel fibres and a network of different morphology compared to its (*S,S*)-enantiomer gel. The TEM investigation of both gels confirmed distinctly different gel morphologies, which allowed the relationship between the stereochemical form of the gelator, the fibre and the network morphology and the network solvent immobilisation capacity to be proposed. Mixing of the constitutionally different bis(amino acid) and bis(amino alcohol)oxalamide gelators resulted in some cases in highly improved gelation efficiency denoted as synergic gelation effect (SGE), being highly dependent also on the stereochemistry of the component gelators. Examples of photo-induced gelation based on closely related bis(amino acid)-maleic acid amide and -fumaramide and stilbene derived oxalamides where gels form by irradiation of the solution of a non-gelling isomer and its photo-isomerisation into gelling isomer are provided, as well as examples of luminescent gels, gel-based fluoride sensors, LC-gels and nanoparticle-hydrogel composites.

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Introduction

In the past three decades, noncovalent interactions have been increasingly used as a powerful tool for construction of many



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Leo Frkanec studied biology and chemistry at the Faculty of Sciences, University of Zagreb (Croatia). He received his PhD for the work in supramolecular chemistry on amino acid derivatives of crown ethers and calixarenes in 2000 under the supervision of Prof. Mladen Žinić. He was a postdoctoral fellow with Raphael Darcy at the University College Dublin working on the synthesis and development of amphiphilic cyclodextrins as gene delivery vectors. He returned to Rudjer Bošković Institute in 2004 and presently holds the position of research associate. His scientific interest is focused on supramolecular chemistry, particularly on artificial ionophores, molecular recognition, and self-assembly of organogelators.



Mladen Žinić

Mladen Žinić received his PhD in Organic Chemistry from the Faculty of Pharmacy and Biochemistry (PBF) University of Zagreb. In 1978/79 he was postdoctoral fellow at ETH Zurich in the laboratory of the Nobel Prize laureate Vlado Prelog. He joined the Rudjer Boskovic Institute (RBI) in 1986 where he was promoted to the rank of senior research scientist 1998 and the Head of the Laboratory of Supramolecular and Nucleoside Chemistry in 1993. In 1999 he was elected as titled full professor of chemistry at the Faculty of Natural Sciences, Univ. of Zagreb and in 2009 at the Faculty of Medicine, Univ. of Rijeka. From 2005–2009 he was Director of RBI. His research interest lies in supramolecular chemistry with recent emphasis on the stereochemistry of organogels. In 2001, he received the State Award and in 2002 the Croatian Academy Award for Natural Sciences.