

Cyclable Photomodulation of Supramolecular Gels in Deep Eutectic Solvents

Ramón Rial^a, Isabella M.V. Ewell^b, Miguel No-Gomez^b, Javier Montenegro^b, A. Sánchez-Fernández^c

^a Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Física Aplicada, Universidade de Santiago de Compostela, Santiago de Compostela, Spain.

^b Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago de Compostela, Spain.

^c Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Departamento de Enxeñaría Química, Universidade de Santiago de Compostela, Santiago de Compostela, Spain.

ramon.rial@usc.es

Deep eutectic solvents (DESs) are a class of designer solvents formed by the complexation of two or more components (e.g., a hydrogen-bond donor and an organic salt), yielding a mixture with a significantly depressed melting point. This cooperative hydrogen-bond network produces liquids with tunable physicochemical properties dictated by the specific combination of precursors [1].

Building on this versatility, DESs have emerged as compelling media for directing soft-matter organization. Specifically, DES-based gels (eutectogels) offer a paradigm shift in the design of functional soft materials [2], enabling macroscopic properties that emerge fundamentally from solvent–solute interplay rather than isolated molecular design [3].

In this contribution, we present a flexible methodology for the preparation of photo-responsive eutectogels that display inherent capabilities for mechanical tuning. To accomplish this, we targeted supramolecular co-assembly process pairing an amphiphilic molecule with a custom-synthesized azobenzene derivative, which was specifically optimized to dissolve readily in anhydrous DES environments. Analysis at both the molecular and mesoscale levels sheds light on the molecular interactions responsible for generating elongated, one-dimensional networks. Importantly, our findings reveal how molecular-level photoisomerization propagate into mesoscopic morphological changes, ultimately switching macroscopic behavior. When exposed to ultraviolet light, the assemblies contract, which triggers a distinct transition from a gel to a fluid state and effectively erases its solid-like properties. Conversely, exposure to visible light regenerates strong, stable gel networks that display remarkable stability to prolonged storage. These light-driven phase shifts demonstrate excellent reversibility, allowing for numerous cycles with virtually no degradation in mechanical strength or structural integrity. Overall, our findings provide a broad, adaptable framework for creating advanced, dynamic smart materials using DES platforms.

Keywords:

Deep Eutectic Solvents, Eutectogels, Photo-responsive Materials, Self-Assembly

References:

- [1] Hansen, B. *et al.*, Chem. Rev. **2021**, *101*, 1232-1285.
- [2] P. A. Mercadal, A. González, A. Beloqui, L. C. Tomé, D. Mecerreyes, M. Calderón and M. L. Picchio, *JACS Au*, **2024**, *4*, 3744-3758.
- [3] A. Sanchez-Fernandez, J. F. Poon, A. E. Leung, S. F. Prevost and C. Dicko, *ACS Nano*, **2024**, *18*, 18314-18326.

Acknowledgements:

The authors acknowledge financial support from MCIN/AEI (RYC2022-037909-I and PID2022-141673OA-I00).