PÔSTER - RESUMO - MATERIAIS E BIOMATERIAIS

SELF-ASSEMBLY OF E AND Z ARYLAZOPYRAZOLE PHOTOSWITCHES AS RESPONSIVE MATERIALS

Ranylson Marcello L. Savedra (ranylson.savedra@gmail.com)

Camile Contarini Freitas (camile.freitas@aluno.ufop.edu.br)

Priscila F. Silva (Ic) (priscila.fs@aluno.ufop.edu.br)

Melissa F. Siqueira (melissa@ufop.edu.br)

The ability of photoswitchable molecules to reversibly change their structure and properties under light makes them powerful, dynamic tools [1]. This unique characteristic is driving innovation across diverse domains, including next-generation energy storage, targeted photopharmacology, and the development of smart biotechnological materials [1,2]. Traditionally, azobenzenes have set the standard for light-induced isomerization. However, arylazopyrazoles are redefining these limits by enabling near-total E to Z conversion, overcoming the incomplete switching often observed with conventional derivatives [2]. Furthermore, in aqueous media, these molecules exhibit surfactant behavior and undergo supramolecular self-assembly. In this work, we investigated the self-assembly of Z and E arylazopyrazole molecules in water independently. This study was conducted by employing molecular modeling methods based on Quantum Mechanics (QM) and Molecular Dynamics (MD). The electronic structure calculations were carried out with the DFT approach, at the PBE0/cc-pVTZ level. To investigate molecular self-assemblies, we employed the all-atom OPLS-AA force field over 260 ns simulation trajectories, following previously

reported methodologies [3]. Despite starting from random distributions, the isomers assumed distinct self-assemblies. The Z isomer condensed into a quasi-spherical aggregate, whereas the E isomer yielded an ellipsoidal configuration and showed a significantly slower rate of stabilization. The radial distribution functions (RDF) plots show that both final structures adopted micellar morphologies, characterized by a dense hydrophobic core and a well-defined hydration shell at the interface. QM data further demonstrate that the isomeric configuration modulates the distribution of the LUMO, impacting the molecule's overall electronic properties.

Acknowledgments:

CNPq, FAPEMIG, INEO/INCT, FIMAT and UFOP.

FAPESP - processo nº 2025/27044-5 e CNPq - processo: 408449/2024-1

References

[1] M. Gao, D. Kwaria, Y. Norikane, and Y. Yue, Nat. Sci. 3, e220020 (2023).

[2] G. Tyagi, J. L. Greenfield, B. E. Jones, W. N. Sharratt, K. Khan, D. Seddon, L. A. Malone, N. Cowieson, R. C. Evans, M. J. Fuchter, and J. T. Cabral, JACS Au 2, 2670 (2022).

[3] R. M. L. Savedra and M. F. Siqueira, J. Mol. Liq. 398, 124255 (2024).

Palavras-chave: arylazopyrazole; molecular modeling; photoswitches.