Electrochemical and optical experiments and DFT calculations for an allyl-thiophene substituted azulene

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Ethene-2,1-diyltetrathiophene azulene (L2064) was obtained and used to prepare modified electrodes, based on our results on the electrochemical behaviour of other azulene-based push-pull organic systems [1]. L2064 belongs to azulene compounds, with potential nonlinear optical responses, and staining properties [2,3]. Its electrochemical and optical properties were evaluated, in connection with the heavy metal (HM) ions complexation. The main structural characteristics and the molecular descriptors of the investigated ligand have been predicted by means of computational tools using B3LYP method [4] with 6-31(d, p) basis set [5]. Estimation of relevant global reactivity parameters according to Koopmans' theorem [6] was also carried out starting from calculated energies levels of frontier molecular orbitals, as in our previous works [7].

Novel chemically modified electrodes (CMEs) were prepared by electrooxidation of L2064. To evaluate their electrochemical behaviour, CMEs based on L2064 were characterized by ferrocene redox probe. They were also tested for the analysis of synthetic samples of HMs (Cd, Pb, Cu, Hg) ions. The influence of preparation conditions (ligand concentration, solvent, electric charge and potential) on the properties of these CMEs was examined. This study is relevant for further design and development of advanced materials based on this azulene derivative for the HMs analysis in polluted water samples. Electrochemical experiments and DFT computer-aided calculations recommended L2064 as a new suitable ligand for electrode surface modification in view of HMs ions analysis.

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References

1. S. Hunig, B. Ort, *Ann. Chem*. **1984(12)** (1984) 1905-1935 https://doi.org/10.1002/jlac.198419841203.
2. G. Iftime, P .G. Lacroix, K. Nakatani, A .C. Razus, *Tetrahedron Lett*. **39** (1998) 6853-6856 https://doi.org/10.1016/S0040-4039(98)01495-6.
3. P. G. Lacroix, I. Malfant, G. Iftime, A. C. Razus, K. Nakatani, J. A. Delaire, *Chem Eur. J.* **6(14)** (2006) 2599-2608 https://doi.org/10.1002/1521-3765(20000717)6:14<2599::AID-CHEM2599>3.0.CO;2-G.
4. C. Lee, W. Yang, R.G. Parr, Phys. *Rev. B* **37 (**1988) 785-789 https://link.aps.org/doi/10.1103/PhysRevB.37.785.
5. W. J. Hehre, A Guide to Molecular Mechanics and Quantum Chemical Calculations, Wavefunction, Inc. Irvine, CA, USA, 2003.
6. R. G. Pearson, *Inorg. Chem.***27** (1988) 734-740 https://doi.org/10.1021/ic00277a030.
7. A.-A. Vasile (Corbei), E.-M. Ungureanu, G. Stanciu, M. Cristea, A. Stefaniu, *Symmetry* **13** (2021) 1462 https://doi.org/10.3390/sym13081462.