

# Electrochemical Study of a Family of Triazines: Cyclic Triimidazoles and their Halo Derivatives

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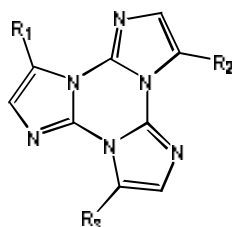
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Solid-state luminogens are required in many high-tech fields, with applications that spread from lighting to biology. Unfortunately their development is far from being an easy task, mainly due to the aggregation-caused quenching phenomenon; as a result weakly or even nonemissive materials in condensed phase are obtained from highly emissive molecules in solution. On the contrary, materials characterized by enhanced emission in the solid state (aggregation-induced emission, AIE) or, even better, molecules that are induced to emit by crystallization (crystallization-induced emission, CIE) are well desired. Even if organic emitting materials are preferred over their organometallic counterparts because of sustainability, chemical flexibility and economical reasons, intrinsic electronic properties hinder the isolation of new organic luminogens characterized by multicolored emission with lifetimes spanning from the nanosecond to the millisecond regime.

Moving into this context, some of us have recently proposed triimidazo[1,2-*a*:1',2'-*c*:1'',2''-*e*][1,3,5]triazine and its halo derivatives as efficient scaffolds for the development of fully organic emitters with a multifaceted photoluminescence behavior. In particular they exhibited CIE with room temperature ultralong phosphorescence (RTUP) under ambient conditions (up to the second regime), associated with H-aggregation [1,2]. Notwithstanding detailed photophysical studies, to the best of our knowledge, no electrochemical data have been still provided. In this work we have wanted to fill the gap. The ideal  $C_{3h}$  symmetry of the heterocyclic scaffold (Figure) is particularly appealing, providing an intriguing source of molecules with three equivalent redox sites. A suitable set of cyclic triimidazole compounds was selected (Figure), including both neutral and charged (*i.e.* salt) species, together with bromo- and iodo derivatives. For sake of uniformity, to avoid any possible misleading results due to a direct role of the solvent in the electron transfer processes, *N,N*-dimethylformamide (DMF) was chosen as the election solvent due to its good solubilizing ability. The forefather cyclic triimidazole exhibited a quite pure electroactivity on glassy carbon electrode in DMF with  $[(n\text{-Bu})_4\text{N}][\text{PF}_6]$  supporting electrolyte, in good agreement with its wide optical band gap, clues of a poor/absent conjugation between the three 5-member rings. Further experimental evidence points to imidazoles be almost perfectly independent redox sites in the aforementioned polar solvent.

Additionally, the possibility to functionalize the heterocyclic scaffold with halogen atoms makes these triazines an interesting springboard to study the dissociative electron transfer of C–X bonds (with X = Br or I). In this context the reactivity of some halo-triimidazoles was analyzed on glassy carbon (as an ideally inert electrode) and on two electrode surfaces (*i.e.* gold and silver) known to exhibit a catalytic behavior toward the electro-cleavage of C–X bond.



## References:

- [1] E. Lucenti, A. Forni, C. Botta, L. Carlucci, C. Giannini, D. Marinotto, A. Pavanello, A. Previtali, S. Righetto, E. Cariatì, *Angew. Chem. Int. Ed.*, **2017**, 56, 16302.
- [2] E. Lucenti, A. Forni, C. Botta, L. Carlucci, C. Giannini, D. Marinotto, A. Previtali, S. Righetto, E. Cariatì, *J. Phys. Chem. Lett.*, **2017**, 8, 1894.