

## Novel Thiolate Ni(II) complexes for hydrogen evolution photocatalytically and electrocatalytically

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Photocatalytic production of hydrogen has been investigated with particular emphasis on the development of an efficient method of converting solar energy into renewable and sustainable fuel. This is due not only to the effort to reduce environmental pollution from fossil fuels but also because solar energy is by far the largest resource among the various renewable energy sources.<sup>1–3</sup> Many different approaches have been used to achieve this goal, with the most auspicious being the use of catalytic systems based on complexes with transition metals.<sup>4–6</sup> The oxidative mechanism involves the oxidation of the excited photosensitizer from PS' to PS<sup>+</sup>, from an electron receptor R.<sup>7</sup> In contrast to the oxidative mechanism, the reductive quenching mechanism involves the reduction of the photosensitizer through the excited state of PS 'by the electron donor D.<sup>7</sup>

In this project, three thiolate Ni(II) complexes were synthesized carrying as a ligand 2-aminothiophenol. The complexes were analyzed and characterized with various spectroscopical (UV-Vis, IR, NMR, HRMS) and electrochemical methods (Cyclic Voltammetry). Furthermore, the complexes were examined for their stability and their catalytic properties both for light-driven and electrocatalytically hydrogen production. The photocatalytic activity was tested in systems containing a sacrificial donor (Triethanolamine), a photosensitizer (Fluorescein) and our complexes as catalysts. All three complexes are active electrocatalysts but only two are good homogeneous catalysts that reach almost 1000 TONs in photocatalytic systems.

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### Acknowledgment:

The authors wish to thank the Special Research Account of NKUA for financial support. F. K. also thanks the co-funding by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Strengthening Human Resources Research Potential via Doctorate Research” (MIS-5000432), implemented by the State Scholarships Foundation (IKY).