

A brilhante eletroquímica de corantes fluorescentes derivados de BODIPY

The brilliant electrochemistry of BODIPY-based fluorescent dyes

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4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) is an outstanding class of fluorescent dyes with wide applications in biological/analytical/environment research. As a first example, a fluorescent lapachone-based BODIPY was synthesized and characterized by computational and electrochemical aspects, which helped understanding its molecular mechanism of action. A second example comes from new nitrosyl-6-phenyl-BODIPY dyes. Electrochemical studies, useful in understanding the redox properties of these materials, in finding structure stability relations for the radical ions and for electrogenerated chemical luminescence are reported. Special emphasis is put on the *meso*-phenyl substituted BODIPYs **1** and new nitrosyl derivatives (**2** and **3**). They were electrochemically investigated, using CV, in degassed DMF + n-Bu₄NPF₆ and ACN + n-Bu₄NPF₆, vs. Ag/AgCl, Cl⁻ (sat) and the couple Fc⁺/Fc (Fig. 1A-B). The CVs of compound **1** display two reduction waves, the first one, related to a one-electron, quasi-reversible, diffusion-controlled electron transfer and the second, with lower intensity and irreversible. The anodic counterpart is represented by a 2 e⁻, irreversible peak. The addition of the acceptor nitrosyl group, in compounds **2** (in position α) (Fig. 1B) and **3** (in position β), leads to a different profile. The reduction is much easier, ca 300 mV more positive. For compound **2**, based on spectroelectrochemistry and DFT calculations, the first to be reduced is the nitroso group, due to the proximity to the positively charged N (E_{plc3} = -0.673 V), and effects of the spatially close fluorine, on the BODIPY moiety, differently from compound **3**, where the reduction occurs in the BODIPY core. Computational studies corroborated present findings. These compounds show promise as thiol sensors.

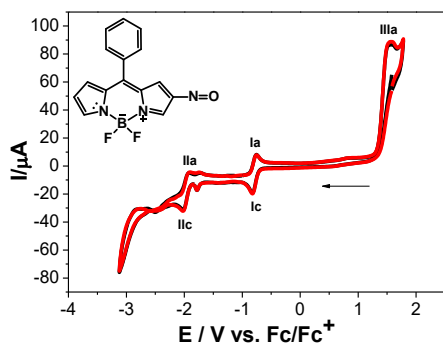


Fig 1A: CV of compound 3..

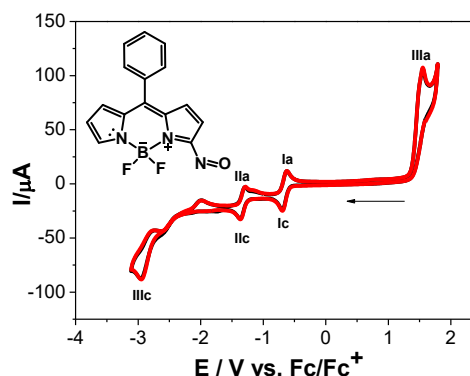


Fig 1B: CV of compound 2.

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