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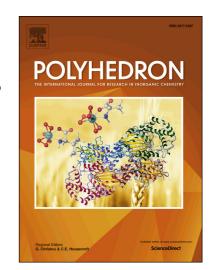
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A New Molecular Switch based on a Symmetrical Dinuclear Complex of Two Tricarbonylrhenium(I) moieties bridged by 4,4"-azobis-(2,2'-bipyridine)

Pedro O. Abate, [a] Gaston Pourrieux, [a] Faustino E. Morán Vieyra, [b] Mauricio Cattaneo, [a] Mónica M. Vergara [a], Néstor E. Katz*[a]

Abstract

A new symmetrical dinuclear complex of two tricarbonylrhenium(I) moieties, of formula $[(CH_3CN)(CO)_3Re(4,4"-azobpy)]$ $Re(CO)_3(CH_3CN)](PF_6)_2$, with 4,4"-azobpy = 4,4"-azobis-(2,2'-bipyridine), has been synthesized and characterized by spectroscopic, electrochemical, spectroelectrochemical, photophysical and computational techniques. The bridging azo group in the bipyridyl ring decreases the emission quantum yield of the 3MLCT lowest-lying excited state respect to similar Re(I) complexes and introduces a new emissive excited state with a longer lifetime, due to increased electronic delocalization in the bridging ligand. When reducing the azo group in CH_3CN/H_2O mixtures with sodium dithionite, the emission is enhanced by an order of magnitude. Therefore, this complex can be used as a "molecular switch" with electron and proton additions. Besides, changes in the absorption spectrum on addition of L-Cysteine can be applied for sensing aminoacids with reducing thiol groups. The electronic structures calculated by DFT methods agree reasonably well with experimental results.

Keywords: Rhenium carbonyls; Azobipyridines; L-Cysteine sensing; Molecular switches

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