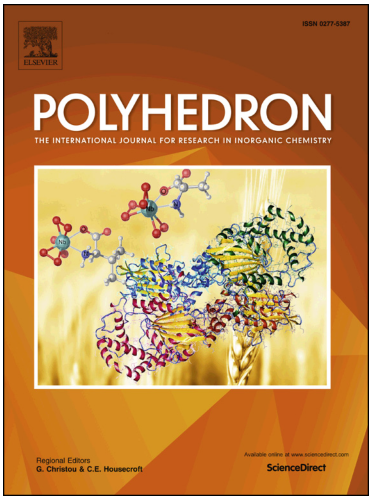

A New Molecular Switch based on a Symmetrical Dinuclear Complex of Two Tricarbonylrhenium(I) moieties bridged by 4,4''-azobis-(2,2'-bipyridine)

Pedro O. Abate, Gaston Pourrieux, Faustino E. Morán Vieyra, Mauricio Cattaneo, Mónica M. Vergara, Néstor E. Katz

PII: S0277-5387(18)30206-7
DOI: https://doi.org/10.1016/j.poly.2018.04.029
Reference: POLY 13131

To appear in: *Polyhedron*

Received Date: 14 December 2017
Accepted Date: 20 April 2018

Please cite this article as: P.O. Abate, G. Pourrieux, F.E. Morán Vieyra, M. Cattaneo, M.M. Vergara, N.E. Katz, A New Molecular Switch based on a Symmetrical Dinuclear Complex of Two Tricarbonylrhenium(I) moieties bridged by 4,4''-azobis-(2,2'-bipyridine), *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.04.029

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 $[(CH_3CN)(CO)_3Re(4,4''\text{-azobpy})\ Re(CO)_3(CH_3CN)](PF_6)_2$, 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 ^{3}MLCT 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

[a] *INQUINOA-UNT-CONICET, Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 471, T4000INI San Miguel de Tucumán, Argentina*

[b] *INBIONATEC-UNSE-CONICET, Universidad Nacional de Santiago del Estero, RN9, Km 1125 (G4206XCP) Santiago del Estero, Argentina*