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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)

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## Abstract

A new symmetrical dinuclear complex of two tricarbonylrhenium(I) moieties, of formula  $[(\text{CH}_3\text{CN})(\text{CO})_3\text{Re}(4,4''\text{-azobpy}) \text{Re}(\text{CO})_3(\text{CH}_3\text{CN})](\text{PF}_6)_2$ , 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  $^3\text{MLCT}$  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  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  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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