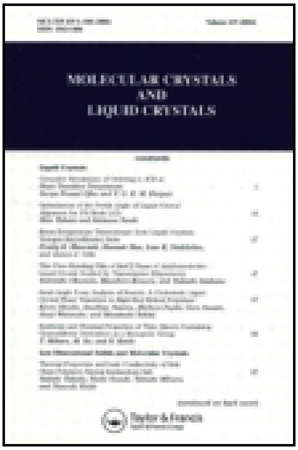

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Incorporation of a Photochromic Moiety in a Mixed-Valent Complex: Switching “On” and “Off” an Intervalence Electron Transfer

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Incorporation of a Photochromic Moiety in a Mixed-Valent Complex: Switching "On" and "Off" an Intervalence Electron Transfer

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A dinuclear ruthenium photochromic complex, based on the dithienylperfluorocyclopentene unit, has been prepared following a building block approach, by palladium-catalyzed Sonogashira-Hagihara cross-couplings. At 254 nm, a photostationary state occurs, characterized by 75 % of ring closure. Upon oxidation to mixed-valence species, the *open* isomer displays no intervalence (IV) band, while for the *closed* one, an IV band corresponding to a 0.025 eV electronic coupling parameter is observed, as well as a thermal reopening of the cyclohexadiene moiety. Extended Hückel calculations have been performed on model complexes in order to rationalize this efficient switching effect, and also the unexpected unstability of the oxidized *closed* isomer.

Keywords: Mixed valence complexes; dithienylperfluorocyclopentene; cyclometallated complexes; molecular switch; molecular electronics; extended Hückel calculations

Photochromic compounds undergo large changes in their electronic structure upon irradiation. Such a change has been used in several examples to switch ON and OFF physico-chemical properties with the aim to make macroscopic devices.[1,2] However, a monomolecular approach is needed if nanometric devices have to be prepared. In order to get a quantitative insight on a light-triggered switch, we have recently prepared a dinuclear complex of ruthenium, combining our knowledge of mixed valence species[3] with the amount of experimental data on the dithienylethylene core.[1,2] In the present study, as for a conventional electrical switch, "switching" will mean a change in the intramolecular properties, especially its "transparency" toward electron transfer. From a theoretical point of view, it will be shown that an Extended Hückel analysis of the system can give details on the origin of the switching effect, as well as on the stability of the various species.

Synthesis

Our synthetic route to dinuclear complex **1** relies on the use of Sonogashira-Hagihara cross-couplings to graft "building-blocks"[4,5] together. Hence, the bridging photochromic ligand is never prepared in its uncomplexed form. Our results are summarized in Figure 1, and full experimental details will be reported elsewhere.[6]

Photoisomerisation

Despite the visible absorption of the bright red dinuclear complex **1** due to low energy MLCT transitions, no sensitization of the isomerisation was observed, and optimal ring-closure wavelength was found to be 254 nm[1,2]. At the photostationary equilibrium, the proportion of the *closed* isomer was found to be *ca.* 75 %. Both isomers were separated on a KPF_6-impregnated TLC plate, the *open* isomer migrating faster than the *closed* one. The deep blue *closed* form reverts to the *open* red one by a mere irradiation with visible light above 600 nm. As expected, the Ru(III)/Ru(II) redox couples were found to be reversible for both *open* and *closed* photoisomers, giving a *pseudo*-bielectronic wave respectively at 0.53 and 0.52 V/SCE (cyclic voltammetry in MeCN, nBu_4PF_6 0.1M, Pt, 0.1V/s).

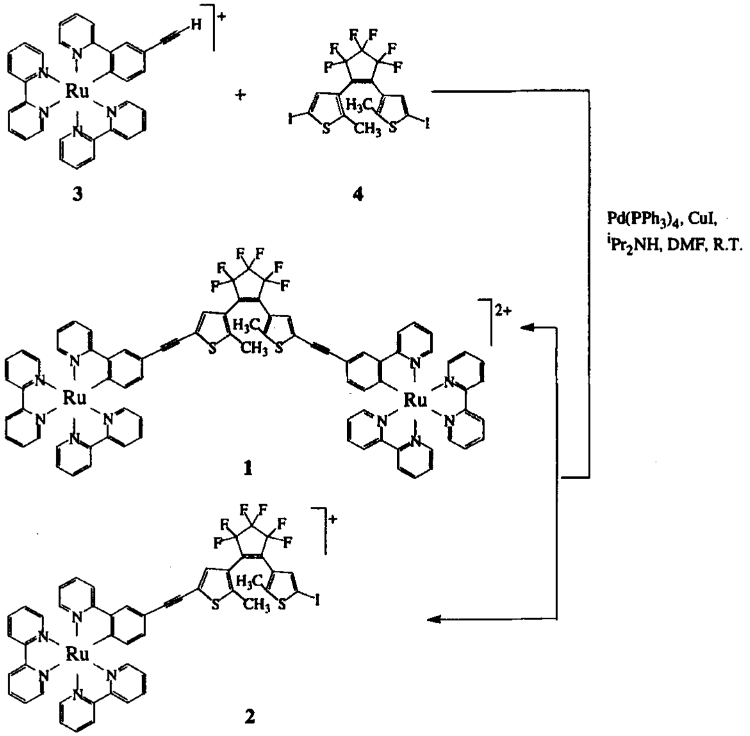
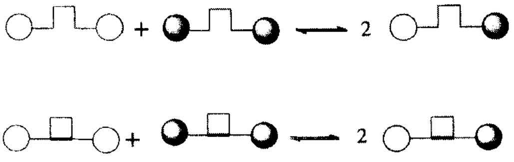


FIGURE 1. Synthesis of the photochromic dinuclear complex.

The use of line shape analysis of a pulsed differential voltammogram allowed us to determine the comproportionation constants for the two equilibria (scheme below).[7]



$K_c^{open} = 11$

$K_c^{closed} = 12$

No intervalence band was detected by electrochemical oxidation of the *open* isomer as the half-oxidation was reached, indicating the bad electronic coupling in the initial material. Very different results were obtained for the *closed* isomer, since a moderately fast chemical process was observed under similar conditions. If a reducing agent was added to the resulting solution, the *open* isomer's absorption spectrum was restored suggesting a reopening of the photochromic moiety. Eventually, we have found that a fast chemical oxidation[8] allowed us to observe an intervalence band in the NIR region which, after deconvolution from the other absorption bands (ν_{max} = 7400 cm^{-1}; ε = 1400 $mol^{-1}.L.cm^{-1}$, band width: 5000 cm^{-1}), yielded an experimental V_{ab} value of 0.025 eV, by using Hush's equation,[9] with a metal-to-metal distance of 23.4 Å.

Theoretical model

The electronic interaction in symmetrical mixed valence complexes can be simply described using Molecular Orbital theory, thanks to the so-called dimer splitting model.[10] All molecular orbitals are either symmetric or antisymmetric with respect to the symmetry element. The splitting between a conveniently chosen pair of molecular orbitals (orbitals with predominant metal contributions and opposite symmetries[10]) is a measure of the electronic interaction, and equals 2 V_{ab}. In the present case, after a geometrical optimization by Molecular Mechanics,[11] followed by an Extended Hückel calculation,[12] the analysis of the orbitals energies along these lines gives V_{ab} = 0.003 eV for the open form (OFF) and 0.021 eV for the closed form (ON). This large change in the electronic coupling is in qualitative agreement with the experimental observations. To go further in the understanding and help visualize the pathway for the propagation of electronic effects, we have performed calculations on a *monometallic* model compound, in which one of the terminal ruthenium site is replaced by a simple phenyl group. In such a system, the orbitals with high weights on the ruthenium atoms are very similar to the diabatic orbitals involved in electron transfer.[10b,13] In particular their spatial extension, i.e. the "tails" of the wave function on the bridging ligand, show how and to what extent the two metal atoms can communicate in the bimetallic species. In the *open* form, the three highest occupied orbitals are mostly metallic, and correspond to the doubly occupied t_{2g} set of ruthenium(II) in a pseudo-octahedral coordination. They are well separated from the ligand orbitals, especially from MO n° 152 , mostly centered on the photochromic core (Figure 2).

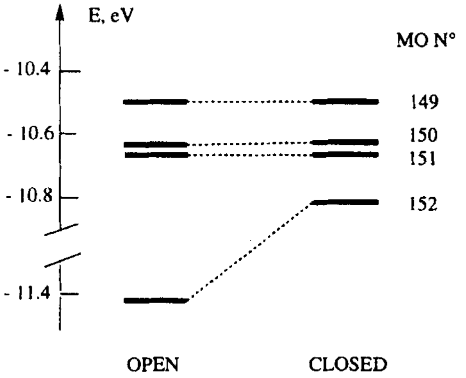


FIGURE 2. Highest occupied levels in the model monometallic compounds (open form and closed form)

One of those frontier orbitals penetrates the bridge up to the first thiophene ring only (Figure 3). Since a similar result is obtained by symmetry for the other metallic center, one can understand why the coupling within the starting *open* form remains weak despite apparent conjugation.

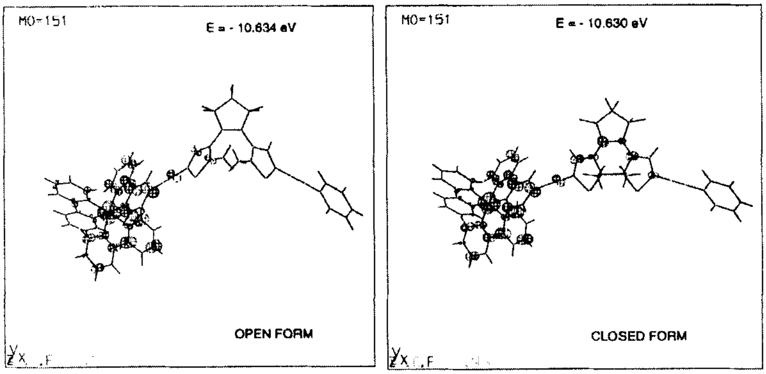


FIGURE 3. Shape of metal orbitals in the model monometallic compound (open form and closed form)

On the other hand, for the *closed* isomer, the situation has dramatically changed: First the previously well detached ligand-based orbital n° 152, has now come closer to the frontier metal-centered MOs. This favors an important mixing between metal-based and bridge-based orbitals, and promotes the metal-metal electronic coupling through superexchange. One of the metal-based frontier MO now penetrates inside the photochromic moiety up to the *second* thiophene ring, (Figure 3) so that the overlap with its counterpart coming from the other ruthenium atom is sufficient to give rise to an electronic coupling. The electronic interaction occurs mainly through the conjugated carbon backbone. No delocalization has been observed on the heteroatoms (S and F), but they could play an indirect role by subtle changes in the energy levels.

Returning to orbital N° 152 in the closed form, it has two interesting features: a small metallic contribution, and a bonding character on the newly created σ bond (Figure 4).

Although the experimental results show that the oxidation of the bimetallic complex is metal-centered,[6] the energetic proximity of the metal orbitals with orbital 152 suggests that an oxidation of the ruthenium ion must deplete the local electron density on the newly created σ bond. This may explain why the *closed* isomer reopens slowly upon oxidation.

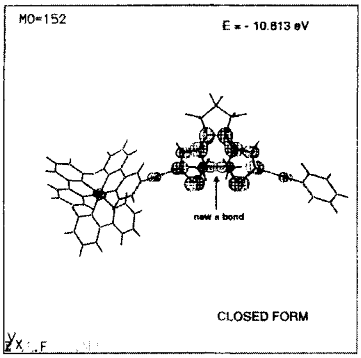


FIGURE 4. Shape of the MO N° 152 in the closed form.

Conclusion

The use of the dithienylethene core allowed us to switch reversibly from a weakly coupled to a non-coupled species, thus mimicking what would be a molecular switch *in the electrical sense of the term.* A simple Extended Hückel analysis gives further details of the process: during the photochemical ring closure, there is a partial saturation of two thiophene groups, allowing a better coupling of the metallic centers, but also mixing the σ skeleton of the molecule with the metal-centered frontier orbitals. This results in an interplay of redox reactions on the organometallic parts with photochemical reactions of the dithienylethene moiety, which could be used to prepare molecules with original properties.

References

[1] S. Kobatake, T. Yamada, K. Uchida, N. Kato, M. Irie, *J. Am. Chem. Soc.* **121,** 2380 (1999). M. Irie, K. Sakemura, M. Okinaka, K. Uchida, *J. Org.Chem.* **60,** 8305 (1995). M. Irie, K. Sayo, *J. Phys Chem.* **96,** 7671–7674 (1992). T. Saika, M. Irie, T. Shimidzu, *J. Chem. Soc., Chem. Commun.* 2123 (1994). S. Nakamura, M. Irie, *J. Org.Chem.* **53,** 6136 (1998).

[2] S. H. Kawai, S. L. Gilat, J.-M. Lehn, *Eur. J. Org. Chem.* 2359 (1999). G. M. Tsivgoulis, J.-M. Lehn, *Chem. Eur. J.* **2,** 1399 (1996). S. H. Kawai, S. L. Gilat, R. Ponsinet, J.-M. Lehn, *Chem. Eur. J.* **1,** 285 (1995). S. H. Kawai, S. L. Gilat, J.-M. Lehn, *Chem. Eur. J.* **1,** 275 (1995).

[3] C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, *Inorg. Chem.* **36,** 5037 (1997), and references therein. P. Lainé, V. Marvaud, A. Gourdon, J.-P. Launay, R. Argazzi, C.-A. Bignozzi, *Inorg.Chem.* **35,** 711 (1996).

[4] S. Fraysse, C. Coudret, J.-P. Launay, *Tetrahedron Lett.* **39,** 7873 (1998).

[5] C. Coudret, S. Fraysse, J.-P. Launay, *Chem. Commun.* 66 (1998).

[6] S. Fraysse, C. Coudret, J.-P. Launay, submitted for publication.

[7] D. E. Richardson, H. Taube, *Inorg. Chem.* **20,** 1278 (1981).

[8] R. Weiss, J. Seubert, *Angew. Chem. Int. Ed. Engl.* **33,** 891 (1994).

[9] N. S. Hush, *Progr. Inorg. Chem.* **8,** 391 (1967). N. S. Hush, *Coord. Chem. Rev.* **64,** 135 (1985).

[10] (a) S. Woitellier, J.-P. Launay, C. Joachim, *Chem. Phys.* **131,** 481 (1989). (b) C. Joachim, J.-P. Launay, S. Woitellier, *Chem. Phys.* **147,** 131 (1990).

[11] Cerius2, Biosym/Molecular Simulations, San Diego, CA, USA.

[12] CACAO PC Version 4.0, July 1994. C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **67,** 399 (1990).

[13] M. D. Newton, *Chem. Rev.* **91,** 767 (1991).