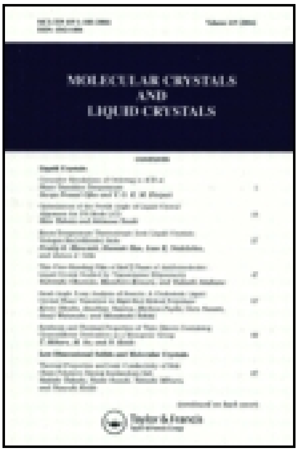

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Jean-Pierre Launay (1994): New Molecules for Intramolecular Electron Transfer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 255:1, 1-6

To link to this article: http://dx.doi.org/10.1080/10587259408029770

Mol. Cryst. Liq. Cryst. 1994, Vol. 255, pp. 1–6
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Printed in the United States of America

NEW MOLECULES FOR INTRAMOLECULAR ELECTRON TRANSFER

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Abstract. New molecules allowing long-range electron transfer and switching processes are described. The electron transfer is experimentally probed by measurement of the so-called "intervalence transition" which occurs in mixed valence binuclear coordination complexes of the general type M-L-M (M = metal site, L = bridging ligand). This allows the determination of the effective coupling parameter between metal sites.
For molecular switching, we consider systems in which the bridging ligand L can be modified by an external perturbation. Several examples are presented: control by photonic perturbation with the Twisted Internal Charge Transfer (TICT) effect, control by H^+ ion through a pH induced redox reaction, and control by reversible alkaline ion complexation.
The final goal is to use these molecules as bridges in ultrasmall metallic structures.

INTRODUCTION

Molecules with several redox sites can exhibit interesting properties due to an intramolecular electron transfer process. In the general field of Molecular Electronics, such molecules can be used in two ways : (i) as building blocks for molecular materials, which can be useful for electronic or optoelectronic devices, or (ii) as molecular components which could be used at the single molecule level. The latter is the option followed in the present review of the work performed in the Molecular Electronics Group in Toulouse. Thus we shall describe molecules allowing electron transmission and switching. The characterization will be achieved in a statistical sense, i.e. by spectroscopic experiments in solution, but the final goal and motivation of our activity is to work in the future at the truly unimolecular level.

INTERVALENCE TRANSITIONS AS PROBES OF ELECTRONIC INTERACTION

When a binuclear coordination compound is oxidized or reduced, it is in some cases possible to get a mixed valence compound in which the two terminal sites bear different formal charges (oxidation states). A typical example is given by pentaammine ruthenium complexes bridged by bipyridylpolyenes of general formula $[(NH_3)_5Ru$ py - $(CH = CH)_n$ - py $Ru(NH_3)_5]^{5+}$ (n = 2, 3, 4), where ruthenium is present in the II and III oxidation states. These compounds usually exhibit a special transition in the near infrared, called the intervalence transition, corresponding to a vertical (Franck Condon) process in which one electron is transferred from one end of the molecule to the other [1]. The interesting point is that the intervalence transition carries some information on the amount of electronic coupling between the two metal sites, denoted as V_{ab}. However, before recording intervalence transitions one has to worry about the problem raised by the chemical equivalence of sites.

The most classical way to generate a mixed valence compound is to start from the homovalent form, here ruthenium(II)-ruthenium(II) [abbreviated as II-II in the following], and to perform a partial oxidation. But due to the chemical equivalence of sites, they are oxidized together, so that one obtains a mixture of homovalent II-II and III-III forms as well as the desired mixed valence II-III form. These forms satisfy the so called comproportionation equilibrium :

$$\text{II-II} + \text{III-III} \rightleftarrows 2\ \text{II-III} \qquad \text{for which } K_c = [\text{II-III}]^2 / [\text{II-II}]\,[\text{III-III}]$$

where the quantities inside brackets designate the concentrations. Fortunately, there are two favorable circumstances : (i) In the worst case of a vanishingly small interaction between sites, the proportion of the mixed valence compound at half oxidation is still 50%, from simple statistical arguments; this proportion is higher if there is some kind of interaction. (ii) It is possible to determine the comproportionation constant K_c from an accurate redox titration. This allows us to compute the corrected spectrum of the mixed valence form, although these species is never obtained quantitatively in the solution. When this is done, the effective coupling between metal sites can be obtained from the following equation [2] :

$$V_{ab} = 2.05\ 10^{-2}\ (\varepsilon_{max}\ \bar{\nu}_{max}\ \Delta\bar{\nu}_{1/2})^{1/2} / R_{MM}$$

where V_{ab} is the coupling (in cm^{-1}), ε_{max} is the maximum extinction coefficient, $\bar{\nu}_{max}$ is the band position in cm^{-1}, $\Delta\bar{\nu}_{1/2}$ is the full width at half maximum (cm^{-1}) and R_{MM} is the metal-metal distance in Å.

EXAMPLES OF "MOLECULAR WIRES"

We have first studied pentaammineruthenium (II/III) complexes bridged by ligands of the type py - $(CH = CH)_n$ - py with n = 2, 3, 4. The results of V_{ab} determinations show that the decay with distance is very slow and can be approximated by the following law [3]:

$V_{ab} = V_{ab}^{\circ} \exp(-\alpha R_{MM})$ with $\alpha = 0.08$ Å^{-1}

Theoretical calculations by the Extended Huckel method also give $\alpha = 0.08$ [4], while a CNDO calculation by Reimers and Hush gives $\alpha = 0.13$ [5]. To give an idea of the magnitude of this decay, 0.08 Å^{-1} corresponds to a decrease by a factor of 2 only for each 8.5 Å increase in the metal-metal distance. Since in the adiabatic regime, the electron transfer rate does not depend critically on the electronic coupling, this means that an efficient long-range electron transfer is possible. However, the uncertainty in the V_{ab} determination is rather large in the above example, owing to the poor band resolution. But we have recently expanded this work to other systems which give a much better resolution, such as α–ω biferrocenyl polyenes [6] and also bis-terpyridylruthenium compounds [7]. In the last case, the V_{ab} parameters decay according to almost the same law as for bipyridylpolyenes [7].

The replacement of the central polyene part by an heterocycle such as thiophene or furan has been also investigated [3]. Thus bipyridylthiophen and furan act as efficient bridges, with the advantage over bipyridyl polyenes of a good stability and a better resolution of the intervalence transitions.

Finally, it is interesting to notice that this kind of study is not limited to coordination complexes. Purely organic compounds can also give intervalence transitions if they contain several identical sites which can be oxidized or reduced. Thus polyaromatic amines used as hole-transport materials such as pEFTP can be partly oxidized to generate mixed valence cation radicals with coexistence of normal nitrogen sites and of oxidized ones [8]. In the same spirit, some stable chlorinated organic radicals can be partly reduced to yield mixed valence systems with a radical site and a carbanion site [9]. However organic systems present the disadvantage that the redox site cannot be identified with a single atom and is not as clearly defined as in coordination chemistry.

EXPERIMENTAL APPROACHES OF A MOLECULAR SWITCH

What we call a switch is an improvement of the previous metal-ligand-metal assembly by introducing a structural mobility, so that it is possible to change V_{ab} by an external perturbation. Three examples, currently being studied in our group, are given below.

Photochemical control.

We have used the so called TICT effect (Twisted Internal Charge Transfer). It arises in certain donor-acceptor molecules which are planar in the ground state, the most typical being dimethylaminobenzonitrile (DMABN). Upon photochemical excitation, two excited states are generated successively: first a planar Franck Condon state, which is weakly polar, and then a twisted and strongly polar state. These two states are usually characterized by a dual luminescence with two clearly resolved emission bands in the visible spectrum. The large conformational change associated with twisting strongly affects orbital overlaps and thus the electronic coupling between donor and acceptor, which makes this effect appealing for molecular switching.

We have prepared a bridging TICT molecule, namely bis (4-cyanophenyl) piperazine (BCPPZ). The molecule consists of three parts, which are almost coplanar in the ground state: a central piperazine ring and two outer cyanophenyl groups. Time resolved luminescence and transient absorption studies show that the TICT effect occurs only on one side of the molecule, i.e. there is a symmetry breakdown in the excited state [10]. But the coupling efficiency of the molecule is very small, even in the almost planar ground state, because of a lack of conjugation through the central piperazine ring. Recent work on a conjugated version of a TICT molecule (N-imidazoyl-benzonitrile) appears more promising [11]. Returning now to BCPPZ, this molecule can be studied for its properties due to the symmetry breakdown in the excited state : thus Time Resolved Microwave Conductivity (TRMC) experiments show the polarity of the excited state [12], and even the dynamical exchange of the excitation between the two equivalent parts of the molecule [13].

Control by H^+ ions.

Starting from binuclear pentaammine ruthenium (II) complexes bridged by 4,4' azopyridine, we have investigated the effect of a protonation reaction. However, it turned out that we have in fact a pH induced redox reaction, i. e. upon H^+ addition the azopyridine ligand is reduced to bipyridyl hydrazine, while ruthenium is oxidized to the ruthenium (III) state [14]. It is nevertheless possible to demonstrate the control of the electron transfer by independently generating the two mixed valence compounds bridged by either azopyridine or bipyridyl hydrazine. They are found to differ markedly with respect to electron transfer properties. In a later study, the azopyridine bridging ligand has been incorporated in a polymeric structure with ruthenium porphyrins. Here again the intramolecular redox reaction is observed. Since it generates ruthenium (III) from ruthenium (II), it is even possible to switch ON or OFF the intervalence transition by action of H^+ ions [15].

In the same spirit, a control by H^+ has been elegantly demonstrated by Haga *et al* in a binuclear ruthenium complex [16], where protonation decreases the V_{ab} coupling by a factor of 4 to 6.

Control by Na^+ ions.

Here again we try to modify the angle between two parts of a molecule (as in the photochemical experiment), but in this case it is achieved through a reversible complexation reaction. The principle is to prepare a bridging ligand which is of the 4,4' bipyridine type, but in which the two pyridine rings have been connected by a crown ether chain [17]. Thus, it is possible to bridge two pentaammine ruthenium groups through the pyridine functions. In addition, the crown ether part can be complexed by an alkaline ion (typically sodium). This will change the chain geometry and thus indirectly the angle between the two pyridine rings, and finally the coupling. A detailed investigation of the consequences of this complexation on electron transfer is in progress.

CONCLUSION

It is clear that an increasing number of molecules with original properties are now available. However, a further step is necessary if we want to work at the truly unimolecular scale. Our final goal is to incorporate these molecules in an artificial structure made of two metallic nanowires, so the the molecule would bridge the gap. This would allow the measurement of an electron flux (a current) through the molecular structure. Experiments are in progress to realize ultrasmall gold wires buried in an insulating substrate [18] with less than 200 Å gaps, and simultaneously to synthesize giant bridging molecules.

ACKNOWLEDGMENTS.

This work has been made possible thanks to the contributions of C. Joachim, A.-C. Ribou, Ph. Lainé, V. Marvaud, J. Bonvoisin, A. Hatzidimitriou, S. Itoua and A. Gourdon in CEMES, Toulouse. In addition, fruitful collaborations are underway with, C. W. Spangler (de Kalb, Illinois), F. Heisel and J.-P. Sauvage (Strasbourg) E. Amouyal (Orsay), M. Van der Auweraer (Leuven), J. Veciana (Barcelona), J. Warman (Delft) and K. Takahashi (Sendai). Financial support has been provided by CNRS, Région Midi-Pyrénées and Alcatel-Alsthom Recherche.

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