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Review

Design, synthesis and photophysics of ruthenium and osmium complexes through 20 years of collaboration

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Dedicated to Professor Vincenzo Balzani.

Abstract

In this article we report some results obtained during 20 years of collaboration with the group of Prof. Balzani. The small review covers Ruthenium and some Osmium compounds, from cage to multinuclear complexes and molecular switches. The review does not intend to be comprehensive but it is only a general overview of the most important achievements in the field of photophysics and photochemistry of luminescent metal complexes.

Keywords: Ruthenium complexes; Molecular switches; Luminescence; Cage-complexes; Multinuclear systems

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1. Introduction

This paper is a short account of a long standing and enjoyable collaboration amongst the Bologna, Bonn and Fribourg groups, and later on of the Amsterdam team due to the move of Luisa De Cola to the Netherlands. The work done together is scientifically documented in about 50 publications, and in this mini review. We wish to highlight some of the research topics, dealing with metal complexes, which have been developed in this cooperation.

Such a contribution is written in an informal style and perhaps follows an unusual pathway in order to let the reader participate to our development. For this reason we

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have devoted a small section to the history of such a network. The other chapters are only a short and a non-comprehensive report of some of our joint achievements.

2. The emergence of a transalpine collaboration

The collaboration between the Bologna and the Fribourg group was "ignited", when Alex von Zelewsky met Vincenzo for the first time at a conference in Firenze in early 1980. At that time Peter Belser had just synthesized, during his Ph.D. thesis in Fribourg, a number of ruthenium complexes with diimine ligands that could have had interesting photophysical properties. This first approach was corroborated by the visit of Vincenzo Balzani to Fribourg in 1981 arranged in the frame of the "3e cycle" and which offered a short but full immersion into the photochemistry of coordination compounds. This event changed many things in the Fribourg group, and after few months the interaction of the two teams was already well established. The samples of compounds synthesized in Fribourg were sent to Bologna and the first common publication appeared within months in late 1981 [1]. The cooperation strongly and rapidly intensified during the coming years and resulted in a first highly cited review [2]. Not only samples traveled across the Alps, but also members of both groups visited their colleagues on the other side in order to discuss problems personally. In 1987 Vincenzo located a research group even further north than Fribourg, where new and attractive ligands had been prepared in the Kekulé Institute of Bonn University. Vincenzo had encountered Professor Fritz Vögtle during this year, and he proposed to enlarge our cooperation to a three center institution. Luisa De Cola, at that time post-doctoral fellow, went to Fribourg at the end of 1987 to formally establish such a cooperation and develop together with Peter Belser a series of hemi- and caged complexes [3–5]. All of us were quite excited to have the possibilities of cooperation extended. The first three center meeting was organized in 1988 in Fribourg and it was a great success. In due course, an intensive exchange of ideas, persons, and samples took place between the three centers Bologna, Bonn, and Fribourg. Three-center meetings were organized at least once per year at various locations and today, several off-springs of this cooperation go on. All these collaborations were true bottom up events, which needed only little seed money that was often provided either by the local Universities or by funding institutions. The scientific highlights, which follow, are only a small example of what has been achieved.

3. Ruthenium caged-type complexes and dendrimers

The starting point of the Bonn collaboration with Vincenzo Balzani and Alex von Zelewsky was a new macrobicyclic trisbipyridine compound, the "cage" **10** that had been published in 1986 [6]. It is remarkable in this respect that it took the Bonn group quite some time (months) to recognize that this cage compound really had been obtained. It was isolated in a 3% yield after the cyclisation under dilution conditions at room temperature of the open tripod precursor **9d** with tris-amine **8** in chlorobenzene/dimethylacetamide as a solvent mixture. One batch yielded ≈200 mg of the wanted **10** in a high purity after recrystallisation from chloroform/methanol, see Figs. 1 and 2 for synthetic procedure. It is interesting to report that the ^{1}H NMR spectrum of pure sample at room temperature did not look nice, as it showed broad absorptions, so that at first sight we did not correlate this spectrum to cage **10** (Fig. 2), but rather to a polycondensed high molecular weight substance.

Only several weeks later upon heating of the NMR sample at 120° the benzylic signals sharpened. In the aromatic region there was a sharpening (and splitting of signals) too. The barrier of the underlying conformational flexibility of **10** was calculated to be about 60 kJ/mol (with a coalescence temperature of 20 °C and $\Delta\nu \approx 20$ Hz). The unclear correlation of structure and ^{1}H NMR had hindered the characterization of this key substance **10** and delayed its publication by months.

The desired Ru^{2+}-complex **12** (Fig. 3), however, could not be prepared by direct complex formation from cage **10** and Ruthenium salts because of the geometric strict requirements and inertness of the ruthenium ion. However, Peter Belser and Luisa De Cola were able to prepare it by a Ru^{2+}-metal templated macrocyclisation reaction starting from the open tripod system **9** via its Ru^{2+}-complex **11** (as the tris (acid chloride **11b**)) [3].

Complex **12** showed a great photostability due to the cage structure which confers an enhanced kinetic stability and improve the emission properties [4,5]. Furthermore, the dioxygen quenching of the ruthenium unit is strongly reduced and the complex exhibits a long excited state lifetime even in an aereated solution. Also the hemicaged structure **9** upon complexation with Ru(II) showed interesting properties and flexibility in terms of synthesis and purification.

Due to the difficult preparation and purification of compound **12** we did not pursue further this topic, but the lack of dioxygen quenching and improved photophysical properties conferred by the caged system, triggered the interest of the team which started the design of shielding ligands and in particular of dendritic structures.

Dendrimers containing ruthenium ions as the luminescent core have been prepared, using both the convergent and divergent approach, and showed an unusual solubility and photophysical behavior. Some representative examples [7,8] are depicted in Fig. 4.

The shielding from the environment provided by the branches of the dendritic structures, assures long excited state lifetimes of the complexes (up to 1.5 μs for complex **15**) in aereated solution and the peripheral groups confer solubility in any desired solvent. We have observed that the properties, luminescence quantum yields, excited state lifetimes, redox behavior, change with increasing dendrimer generation, showing that a real, measurable dendritic effect can be achieved. Furthermore, some of the compounds (see