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257

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Molecular Wires

From Design to Properties

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Molecular Wires

From Design to Properties

Volume Editor: Luisa De Cola

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D. K. James · M. A. Ratner · F. Scandola · L. D. A. Siebbeles ·
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Westfälische Wilhelms-Universität
Physikalisches Institut
Mendelstr. 7
D-48149 Münster,
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decola@uni-muenster.de

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Dipartimento di Chimica „G. Ciamician“
University of Bologna
via Selmi 2,
I-40126 Bologna, Italy
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Institut für Organische Chemie
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37077 Göttingen, Germany
ameijer1@uni-goettingen.de

Prof. Dr. Kendall N. Houk
University of California
Department of Chemistry and
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405 Hilgard Avenue
Los Angeles, CA 90024-1589
USA
houk@chem.ucla.edu

Prof. Dr. Horst Kessler
Institut für Organische Chemie
TU München
Lichtenbergstraße 4
86747 Garching, Germany
kessler@ch.tum.de

Prof. Jean-Marie Lehn
ISIS
8, allée Gaspard Monge
BP 70028
67083 Strasbourg Cedex, France
lehn@isis.u-strasbg.fr

Prof. Steven V. Ley
University Chemical Laboratory
Lensfield Road
Cambridge CB2 1EW
Great Britain
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Prof. Stuart Schreiber
Chemical Laboratories
Harvard University
12 Oxford Street
Cambridge, MA 02138-2902
USA
sls@slsiris.harvard.edu

Prof. Dr. Joachim Thiem
Institut für Organische Chemie
Universität Hamburg
Martin-Luther-King-Platz 6
20146 Hamburg, Germany
thiem@chemie.uni-hamburg.de

Prof. Barry M. Trost
Department of Chemistry
Stanford University
Stanford, CA 94305-5080
USA
bmtrost@leland.stanford.edu

Prof. Dr. F. Vögtle
Kekulé-Institut für Organische Chemie
und Biochemie
der Universität Bonn
Gerhard-Domagk-Str. 1
53121 Bonn, Germany
voegtle@uni-bonn.de

Prof. Dr. Hisashi Yamamoto
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The University of Chicago
5735 South Ellis Avenue
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Preface

In the emerging field of nanoscience the desire to construct objects which in the molecular scale can resemble and act as macroscopic devices is a constant trend. Amongst the simplest but also most attractive functional component *molecular wires* are surely the most investigated. The reason for such interest is quite obvious since wires, in today world, are used all around us and are the most indispensable unit to assemble any type of electronic devices. But at this point the question is what is a molecular wire? Amongst the several definitions the one which will be addressed in this issue and which in my opinion best describes the discrete molecular systems dealt with in this issue is: a molecular wire is a molecule or an assembly of molecules able to strongly electronically couple the terminal sites in order to mediate energy and charge transport over long distance. Since many years several scientist have attempted to synthesize unidimensional molecular systems able to vectorially transport energy or charge from one terminal site to the other one. Often the terminal units have been donor and acceptor groups, and light has been used as energy source to promote the energy or charge migration. More recently a lot of attention has focused on the possibility to interface molecular structures between electrodes of conductive materials, enabling a direct measurement of the *conductivity* of the system. Despite the differences in experimental set-up and the conditions applied, it is clear that there is a good agreement on the insulating or conductive properties of the molecules obtained by the various methods. However, in the construction of a multicomponent system great attention must be paid on the terminal units since the electronic coupling between these terminal groups and what is in between can dramatically influence the overall behavior.

The misuse of the words *molecular wire* has lead to confusion in the definition and many rod-like systems, just because their linear and rigid structure, have been labeled as wires. I would like to stress that in many cases the loss in the transport is dramatic and an exponential decrease of the conductivity is observed with increasing distance between the terminal sites resulting in a few nanometer conductance which cannot be addressed as a wired behavior.

I believe that effort in connecting, with molecular wires, components possessing different properties and address them with different inputs can lead to a much more interesting way to conceive nanoelectronics which goes far behind than just trying to interconnect macro and nanoworld. The possibility

to have a complete electronic or photo-addressable circuit which requires no external *physical* interface to be operational is just a vision at the moment but the realization of components self-consistent and molecularly connected is reality.

In this issue the synthesis and characterization of molecular wires based on organic or metal complexes components, their properties and some theoretical background will be illustrated. It is clear that we are very far for a full overview but I hope that the readers will find the field as much exciting as it is for me.

Münster, 15 July 2005

Luisa De Cola

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Luminescent Molecular Rods – Transition-Metal Alkynyl Complexes

Vivian Wing-Wah Yam (✉) · Keith Man-Chung Wong

Centre for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research, and
Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong,
P.R. China
wwyam@hku.hk

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Abstract A number of transition-metal complexes have been reported to exhibit rich luminescence, usually originating from phosphorescence. Such luminescence properties of the triplet excited state with a large Stoke's shift, long lifetime, high luminescence quantum yield as well as lower excitation energy, are envisaged to serve as an ideal candidate in the area of potential applications for chemosensors, dye-sensitized solar cells, flat panel displays, optics, new materials and biological sciences. Organic alkynes (poly-yne)s, with extended or conjugated π -systems and rigid structure with linear geometry, have become a significant research area due to their novel electronic and physical properties and their potential applications in nanotechnology. Owing to the presence of unsaturated sp -hybridized carbon atoms, the alkynyl unit can serve as a versatile building block in the construction of alkynyl transition-metal complexes, not only through σ -bonding but also via π -bonding interactions. By incorporation of linear alkynyl groups into luminescent transition-metal complexes, the alkynyl moiety with good σ -donor, π -donor and π -acceptor abilities is envisaged to tune or perturb the emission behaviors, including emission energy (color), intensity and lifetime by its role as an auxiliary ligand as well as

to govern the emission origin from its direct involvement. This review summarizes recent efforts on the synthesis of luminescent rod-like alkynyl complexes with different classes of transition metals and details the effects of the introduction of alkynyl groups on the luminescence properties of the complexes.

Keywords Luminescence · Alkynyl · Metal–metal interaction · Phosphorescence

Abbreviations

^t Bu ₂ bpy	4,4'-di- <i>tert</i> -butyl-2,2'-bipyridine
Bpy	2,2'-bipyridine
Fc	ferrocene
Np	naphthylene
Me ₂ bpy	4,4'-dimethyl-2,2'-bipyridine
(CF ₃) ₂ bpy	4,4'-bis(trifluoromethyl)-2,2'-bipyridine
Phen	1,10-phenanthroline
Dppm	bis(diphenylphosphino)methane
Dppa	<i>N,N</i> -bis(diphenylphosphino)amine
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital

1

Introduction

Luminescent transition-metal complexes, in particular those with triplet excited states that show emission of a phosphorescence nature arising from the enhanced intersystem crossing as a result of the larger spin-orbit coupling due to the presence of the heavy metal center, have attracted considerable attention in recent years. In addition to studies that provide the fundamental information for the elucidation of electronic structures and examination of photoinduced electron or energy transfer processes [1–4], extensive studies on such luminescent complexes have also led to their potential applications in the area of chemosensing, dye-sensitized solar cells, flat panel displays, organic light-emitting devices (OLEDs), optical materials and biological applications. For example, a number of ruthenium(II) complexes have been utilized as dyes, which were immobilized on a TiO₂ surface via anchoring groups. Photoexcitation of the metal-to-ligand charge transfer (MLCT) leads to injection of electrons into the conduction band of the TiO₂ for the conversion of solar energy into electricity [5–8]. Due to the triplet phosphorescence nature, a number of luminescent transition-metal complexes have been employed as the emitting layer for OLED fabrication with improvements in the electroluminescence (EL) intensity, quantum efficiency as well as the tuning of EL color [9–14].

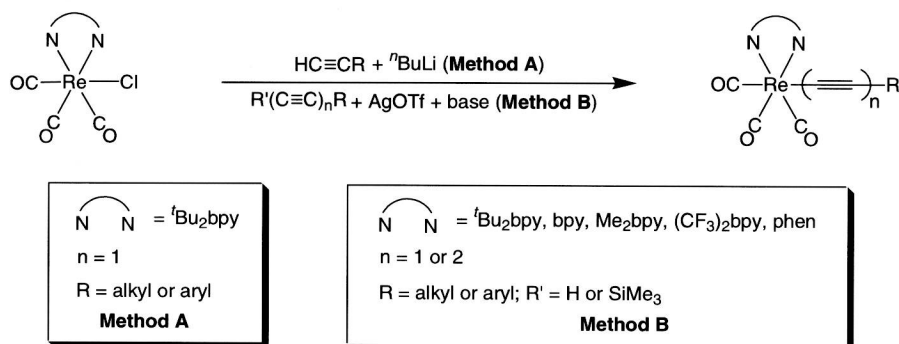
Organic alkynyl compounds (poly-ynes) with extended π -conjugated systems, rigid structure and linear geometry have attracted enormous attention due to their novel electronic and physical properties as well as their ability to serve as potential candidates for development in nanotechnology [15–17]. In view of this, incorporation of alkynyl groups into transition-metal complexes may lead to systems with unique optical, electronic and physical properties that may find potential applications as non-linear optical materials, liquid crystals, molecular electronics and wires [18–25]. Owing to the presence of unsaturated sp -hybridized C-atoms, the alkynyl group can serve as a versatile building block in the construction of alkynyl transition-metal complexes in the σ -bonding and π -bonding modes. By introduction of the linear alkynyl group with the unique properties of having good σ -donor, π -acceptor and π -donor abilities into luminescent transition-metal complexes, fine-tuning and perturbation of emission behaviors, in the sense of energy (color), emission intensity and lifetime could be envisaged through their role as an auxiliary ligand. In some cases, the alkynyl groups may exert their influence in perturbing the emission properties by their direct involvement in the emission origin. The introduction of heavy metal atoms into the alkynyl backbone in metal-containing oligo- and poly-ynes also provided a versatile method to improve the chances of producing triplet emitters, leading to long-lived triplet emission, as a result of a larger spin-orbit coupling constant and an enhanced intersystem crossing efficiency.

In several classes of transition-metal complexes, the presence of a non-emissive low-lying $d-d$ state would quench the luminescence excited state via thermal equilibration or electron/energy transfer [26, 27]. Coupling of a strong σ -donating alkynyl ligand to such a system is anticipated to raise the $d-d$ state, resulting in improvement or enhancement of the luminescence by increasing the population of the luminescence excited state. On the other hand, the sp -hybridized unsaturated $C \equiv C$ group is capable of interacting with other metal centers, for example copper(I), silver(I) or gold(I), through π -bonding fashion [22, 28–32]. Therefore, introduction of such metal centers into the rigid rod-like metal alkynyl complex would alter the structural and luminescence properties. Elongation of the alkynyl group has also been reported to vary the linearity and electronic communications of the metal alkynyl complexes [25, 33]. It is envisaged that such an extension of the conjugated π -system would lead to perturbation of the luminescence properties.

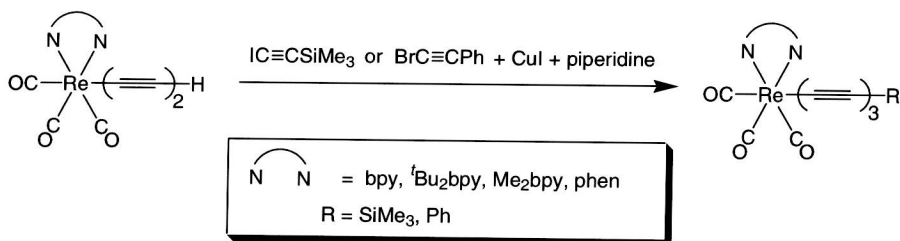
2 Rhenium(I) and Ruthenium(II)

2.1 Rhenium(I) Polypyridines

In 1974, Wrighton and coworkers reported the photoluminescence studies of a new class of rhenium(I) tricarbonyl diimine complexes, $[\text{Re}(\text{CO})_3(\text{N}-\text{N})\text{Cl}]$ ($\text{N}-\text{N}$ = phen or related diimine ligand), exhibiting octahedral geometry with the three carbonyl groups arranged in a *facial* fashion [34]. The emission origin has been assigned to be derived from the triplet $d\pi(\text{Re}) \rightarrow \pi^*(\text{N}-\text{N})$ metal-to-ligand charge transfer (MLCT) excited state. Since then, numerous studies on the luminescence properties of related complexes, including derivatives of the chlororhenium(I) tricarbonyl diimine complexes such as those obtained by the replacement of the chloro ligand with pyridine, phosphine, nitrile or isonitrile ligands, have been reported [35–40]. In 1995, Yam and coworkers reported the first synthesis and photophysical properties of luminescent rhenium(I) complexes incorporating alkynyl ligands [41]. The treatment of the precursor complex, $[\text{Re}(\text{CO})_3(^t\text{Bu}_2\text{bpy})\text{Cl}]$ with a lithiated alkynyl reagent, prepared in situ from the reaction of $^n\text{BuLi}$ with the corresponding terminal alkyne, afforded the desired alkynyl-rhenium(I) products, $[\text{Re}(\text{CO})_3(^t\text{Bu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{R})]$ (R = alkyl or aryl; Scheme 1). Later on, a more general synthetic protocol was developed to enable the synthesis of a variety of luminescent alkynylrhenium(I) complexes with different diimine as well as diynyl ligands, with the general formula, $[\text{Re}(\text{CO})_3(\text{N}-\text{N})(\text{C}\equiv\text{C})_n-\text{R}]$ ($\text{N}-\text{N}$ = bpy, $^t\text{Bu}_2\text{bpy}$, Me_2bpy , $(\text{CF}_3)_2\text{bpy}$, phen; n = 1 or 2) (Scheme 1) [42–44]. Such a pathway has also opened up the possibility of employing the trimethylsilyl-protected alkynes instead of the terminal alkynes and extended the versatility and flexibility of the synthetic



Scheme 1 Synthetic routes of rhenium(I) monoylnyl and diynyl complexes



Scheme 2 Synthetic routes of rhenium(I) triynyl complexes

methodology. Depending on the nature of the diimine and alkynyl ligands, either reaction could be employed to give the desired target complexes. Extension of the work to the tri-ynyl system has been achieved by the reaction of the butadiynyl complex, $[\text{Re}(\text{CO})_3(\text{N}-\text{N})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]$, containing a terminal acetylenic proton, with an excess of the bromo- or iodo-alkyne reagent in the presence of copper(I) catalyst (Scheme 2) [44, 45]. In principle, elongation to higher order poly-ynyl complexes is feasible by the utilization of the above methodology in a series of stepwise reactions.

Upon excitation at $\lambda > 350 \text{ nm}$ in the solid state and in fluid solution, these rhenium(I) alkynyls exhibited intense orange phosphorescence, which generally occurs at lower energy compared to the chloro precursor, $[\text{Re}(\text{CO})_3(\text{N}-\text{N})\text{Cl}]$, attributed to the presence of the strong σ -donating alkynyl group. The luminescence energies have been found to be dependent on the nature of both the diimine and alkynyl ligands. The origin of such luminescence has been ascribed to a ${}^3\text{MLCT}$ [$d\pi(\text{Re}) \rightarrow \pi^*(\text{N}-\text{N})$] excited state, probably with some mixing of [$\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{N}-\text{N})$] ligand-to-ligand charge transfer (LLCT) character taking into consideration the relatively high-lying filled $\pi(\text{C}\equiv\text{C})$ orbital.

For the complexes with the same alkynyl ligand, higher luminescence energy was observed for the complexes containing better electron-donating substituents on the diimine ligand, resulting in the order of ${}^3\text{MLCT}$ energy: $1 > 6 > 7$ (Fig. 1) [43–46]. On the other hand, 2, with a strongly electron-donating alkynyl group showed lower luminescence energy than 1, and even much lower than 3, in line with the energy level of the $d\pi(\text{Re})$ orbital. It is noteworthy that the longer the carbon chain of the alkynyl group is, the higher is the luminescence energy, i.e. $5 > 4 > 1$. Despite the fact that a better energy

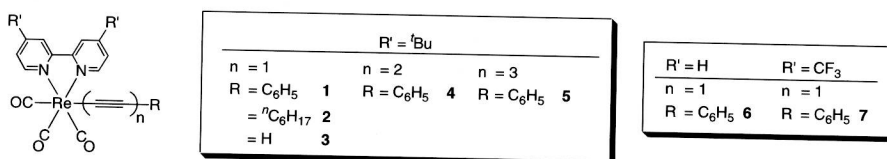
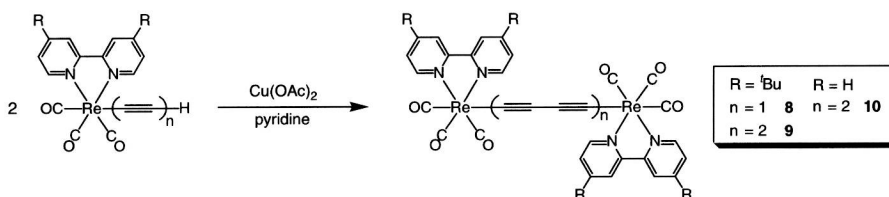


Fig. 1 Mononuclear alkynylrhenium(I) complexes of 1–7



Scheme 3 Synthetic routes of dinuclear alkynylrhenium(I) complexes 8–10

match with the $d\pi(\text{Re})$ orbital in the filled-filled $p\pi - d\pi$ overlap would be expected from the higher-lying $\pi(\text{C} \equiv \text{C})$ orbital of the longer alkynyl analogue, a poorer overlap integral actually would be resulted due to delocalization of the electron density across the alkynyl chain, as supported by molecular orbital calculations.

The synthesis of dinuclear luminescent rhenium(I) complexes tethered by a linear rod-like oligo-ynyl bridge has been accomplished by oxidative homo-coupling reaction in the presence of copper(II) catalyst (Scheme 3) [43, 44, 47, 48]. Owing to the absence of *tert*-butyl substituents on the bpy ligand, **10** is not soluble in common organic solvents. Complexes **8–10** showed intense luminescence, typical of $^3\text{MLCT}$ emission with some mixing of LLCT character. In the solid state at 77 K, the phosphorescence origins of **8** and **9** have been assigned as derived from the metal perturbed intra-ligand (IL) $[\pi(\text{C} \equiv \text{C}) \rightarrow \pi^*(\text{C} \equiv \text{C})]$ excited state, which has been supported by the observation of a structured emission band with vibrational progressional spacings of ca. 2100 cm^{-1} , characteristic of the $\nu(\text{C} \equiv \text{C})$ stretch.

2.2

Ruthenium(II) Polypyridines

The polypyridyl ruthenium(II) system, similar to the rhenium(I) diimine complexes, is another class of the most studied luminescent transition-metal complexes. While most studies on ruthenium alkynyl complexes were focused on the use of phosphine ligands, corresponding studies on nitrogen donor ligands are relatively rare. As an extension of the luminescence studies on alkynylrhenium(I), Yam and coworkers attempted to design and prepare the luminescent alkynylruthenium(II) complexes in 1998. Reaction of $\text{cis-}[\text{Ru}(\text{N}-\text{N})_2(\text{Me}_2\text{CO})_2]^{2+}$ with terminal alkyne yielded an unprecedented ruthenium(II) (aryl)-carbonyl complex, $\text{cis-}[\text{Ru}(\text{N}-\text{N})_2(\text{CO})(\eta\text{-CH}_2\text{-C}_6\text{H}_4\text{-R-4})]^+$. It was proposed that the terminal alkyne first coordinated to the ruthenium(II) metal center to form a vinylidene intermediate, with the electron-deficient α -carbon highly susceptible to nucleophilic attack. Finally, a ruthenium(II) (aryl)-carbonyl complex was obtained by the nucleophilic attack of a water molecule on the α -carbon of the vinylidene ligand via the hydroxycarbene complex intermediate