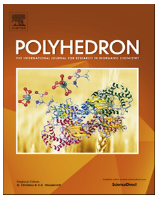
Polyhedron xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Ruthenium(II) σ-arylacetylide complexes as redox active units for (multi-)functional molecular devices

Xiaoyan He, Corinne Lagrost, Lucie Norel *, Stéphane Rigaut *

UMR 6226 CNRS-Université de Rennes 1, Institut des Sciences Chimiques de Rennes, Campus de Beaulieu, F-35042 Rennes Cedex, France

ARTICLE INFO

Article history:
Received 24 July 2017
Accepted 22 August 2017
Available online xxxx

Keywords:
Ruthenium complexes
Molecular switch
Molecular wire
Photochromism
Interfacial electron transfer

ABSTRACT

In this account, we present our contribution towards the building of molecular devices with the use of ruthenium organometallic complexes of the type Ru(dppe)$_2$(—C≡C-Aryl)$_2$ (dppe = 1,2-bis(diphenylphosphanyl)ethane). In the first part, we report that these systems are appropriate for the building of switchable functional surfaces. They allow (i) fast and discrete electron transfers required for the development of redox controlled surfaces and memories, and (ii) in association with a photochromic unit, the achievement of multifunctional surfaces triggered by an electrochemical potential and/or light. In the second part, we show that those complexes also allow the building of metal-molecule-metal junctions with attractive features, including coulomb blockade or weak resistance length dependence, and the reaching of the very first multifunctional molecular junction by light/electro triggering of its electrical conductivity.

1. Introduction

Following the "bottom-up" approach expressed by Feynman in 1959 proposing that atoms can be arranged in a manner to build circuits of a few thousands of Angströms across [1], single molecules as active elements have been considered as potential building blocks for future nanoelectronic systems because of their advantages on cost, scalability, component density, and power consumption [2–10]. In addition, the characteristics of the devices should be easily controllable by choosing the appropriate chemical design, a feature which allows infinite possibilities of developments.

Therefore, designing and preparing molecular wires with efficient charge transport performance is of primary interest. A molecular wire consists in a molecular chain that provides strong coupling between two electrodes attached to its chain ends in order to promote electron transfer through this bridge. Exploration of charge transport with a wide range of more or less complex molecules using various techniques (mechanical break junctions, scanning probe microscopies, nanogaps...) have been carried out to understand the dependence of molecular conduction, *ie*. of transport mechanism, on bonding architecture and molecular energy levels [2,5,11,12]. During the past decades oligo(phenyleneethynylene) (OPE) derivatives have emerged as benchmark molecules for studying charge transport in molecular junctions [7,8,13,14]. They are rigid, rod-like molecules with extended π-conjugation through the backbone and they display high conductivity and other electrical properties such as negative differential resistance or molecular switching that can be systematically tuned by chemical design. We and others participated to further studies on such molecules by probing the electrical conductivity of metal containing OPE derivatives [15–24]. In particular, these studies established that metal arylacetylides, with direct carbon rich metal σ-bonds display attractive characteristics over organic OPEs.

Another great challenge is to develop molecular-based switching devices in which one or several key physical properties can be modulated with external stimuli such as light or electricity [25,26] for the realization of logical functions [25,27]. In that respect, multifunctional molecules are susceptible to perform new properties or operations unattainable by conventional semiconductor technology. Color, luminescence, optical nonlinearity, magnetic and electrochemical properties, as well as changes in electrical conductivity are frequently proposed for memory or sensing applications. To this purpose, metal acetylides, particularly ruthenium acetylide, with direct σ-bond connection of the carbon-rich ligands with the metal are attractive redox active building blocks [28–32]. They present fast and discrete interfacial electron transfers that make them a valuable alternative to ferrocene centres [33–36]. Recently, they allowed redox modulation of different features such as NLO [37–39], luminescence [40–42], or other

---

* Corresponding authors.

E-mail addresses: lucie.norel@univ-rennes1.fr (L. Norel), stephane.rigaut@univ-rennes1.fr (S. Rigaut).

http://dx.doi.org/10.1016/j.poly.2017.08.025
0277-5387/© 2017 Elsevier Ltd. All rights reserved.

optical properties [43–47], as well as magnetism [44,48–52] and conductivity [53,54].

Our contribution towards the building of molecular devices focuses on the use of ruthenium acetylides with a *trans* ditopic structure to achieve molecular wires and switches. Such ruthenium systems are well suited for these purposes owing to their unique ability to operate as connectors allowing electron flow to occur through different elements in multi-component systems [49,55–58] and over very large distances [55]. This behavior results from the substantial carbon-chain ligand character of the highest occupied molecular orbital (HOMO) due to the overlap of a metal d(π) orbital and of a delocalized π-orbital of the carbon-rich ligand. As an example, with ethynyl ruthenium complexes of the type ClRu(dppe)$_2$(—C≡C-Aryl) (dppe = 1,2-bis(diphenylphosphanyl)ethane), the level of involvement of the carbon rich ligand in the redox processes is found to be major, with a reduced metal contribution [59]. This feature also explains why functional organic units undergo strong modification of their specific properties upon incorporation within such ruthenium complexes. For example, in the case of the photo- and electro- switchable dithienylethene (DTE) unit, low potential switching is obtained for the resulting complexes in solution, making them ideal multi-functional switches [44,60,61].

In this account, we emphasis our efforts to build functional surfaces and molecular junctions using ruthenium σ-arylacetylide complex based molecular wires and switches, thanks to *ad hoc* collaborations. In the first part, we cover the development of redox switchable surface with self-assembled monolayers (SAMs) of mono- and poly-metallic systems allowing fast and discrete electron transfers. Such transfers are required for the development of surface confined redox control of multiple properties, and the development of multibit memories. Further incorporation of DTE photochromic units affords multifunctional surfaces with the possibility of combining switching events triggered by an electrochemical oxidation at low potential and by light.

In the second part, we focus on charge transport devices and show how ruthenium organometallics permit the building of metal-molecule-metal junctions with attractive features, including coulomb blockade or weak resistance length dependence. This work ultimately led to the achievement of the very first multifunctional molecular junction which electrical conductivity can be triggered with two orthogonal stimuli, *ie.* light and redox potential, a stunning illustration of the potential of these complexes in the context of molecular electronics.

2. Ruthenium organometallics for functional surfaces

2.1. Fast electron transfer exchange at self-assembled monolayers on gold

Surface functionalization through self-assembled monolayers (SAMs) onto metallic substrates has been extensively investigated in the past decade [62–64]. Using this strategy, redox-active building blocks could be positioned in proximity to the surface of an electrode with control akin to molecular level [65]. This constitutes a powerful approach to design functional materials for use as data storage and transfer in integrated devices. Ferrocene is often used as a redox center for its attractive electrochemical characteristics including low oxidation potential that is compatible with the SAM stability, along with its fast electron transfer rate and the stability of the two redox states. Indeed, the write/erase performance of such molecular memory component is governed by the electron-transfer rates of the attached molecules.

Carbon-rich ruthenium complexes have been recently identified as other valuable candidates for fast and reversible charge storage and electron transport, when immobilized on silicon [66,67]. In order to broaden their scope and potential applications, we built the new series of ruthenium organometallic carbon-rich complexes displayed on Chart 1 for further formation of self-assembled monolayers (SAMs) on gold surfaces [35]. The molecules consist of highly conjugated ruthenium(II) mono(σ-arylacetylide) or bis(σ-arylacetylide) complexes functionalized with different bridge units with specific (protected) anchoring groups that possess high affinity for gold, such as thiol, carbodithioate, and isocyanide. While the thiol anchoring group is ubiquitous in the field, other anchoring groups to metal such as dithiocarboxylic acid or isocyanide have been proved to be efficient [68,69]. Apart from the stability and the organization of the SAMs, a particular concern for applications in molecular electronics is the electronic state mixing between the gold substrate and the anchoring group. It is then of fundamental interest to develop and to study the influence of different anchoring groups. Saturated aliphatic short groups —CH$_2$— and —O-(CH$_2$)$_6$— were also inserted between the Ru(II) σ-arylacetylide complex and the thiol anchoring group, allowing a structural tuning of the bridging unit which might have a significant impact on the quality of the SAMs and on the electronic coupling.

For all the different Ru(II) organometallics, both single component SAMs and mixed SAMs, prepared by coadsorption with benzylthioacetate, were formed on gold surfaces and studied in order to optimize the SAMs qualities. They were fully characterized by wettability studies, infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), and electrochemical analyses. With the use of high-speed cyclic voltammetry, we could systematically address the possible influence of the different parameters on the electronic transfer kinetics within the SAMs. A well-resolved redox signal corresponding to the reversible mono-electronic oxidation of the ruthenium-acetylide system is observed for all surfaces with E^0 = 0.3–0.5 V/SCE (Fig. 1). Remarkably, large surface concentrations are obtained for the mixed layers which are almost equal to those obtained for their single component analogues (0.5–2.8 $\times$ 10^{-11} mol. cm^{-2}). The steric hindrance and tilt of the ruthenium organometallics lead to loosely packed submonolayers. Then, the diluents act as a template matrix that allows a better organization and packing of the bulky compounds onto the surface, and probably help for self-patching the surface coverage.

By applying the Laviron's formalism, fast electron transfer kinetics ($\approx$10^4 s^{-1}) were found at the derived self-assemblies with

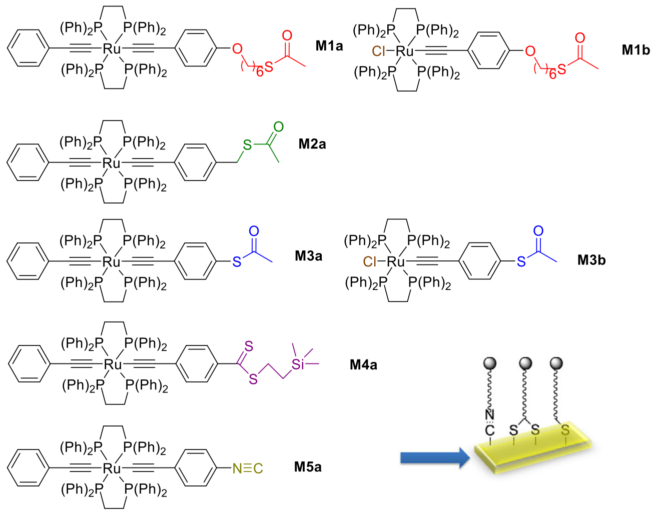


Chart 1. Molecular structures of the studied organometallic complexes (reprinted with permission from Ref. [35]. Copyright 2015 American Chemical Society).

Please cite this article in press as: X. He et al., Polyhedron (2017), http://dx.doi.org/10.1016/j.poly.2017.08.025