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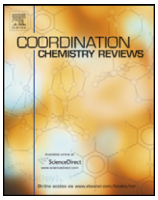

Review

Twists and turns: Studies of the complexes and properties of bimetallic complexes featuring phenylene ethynylene and related bridging ligands

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Contents

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ABSTRACT

The concept of a molecular-based electronic technology has been evolving for over 50 years, and the development of molecular designs for such components over this period has drawn heavily on studies of intramolecular charge transfer in mixed-valence complexes and related systems. Recent advances in methods for the assembly and measurement of device characteristics of metal|molecule|metal junctions have brought the realisation of the considerable promise of the area within a tantalisingly close reach. This review presents a selective summary of the chemistry, spectroscopic properties and electronic structures of bimetallic complexes $[\{L_xM\}(\mu\text{-bridge})\{ML_x\}]^{n+}$ based primarily, but not exclusively, on the Ru(PP)Cp' and $Mo(dppe)(\eta\text{-}C_7H_7)$ fragments and alkynyl based bridging ligands. The molecular design strategies that lead to a wide spectrum of electronic characteristics in these systems are described. Examples range from weakly coupled mixed-valance complexes through more strongly coupled systems in which the electronic states of the bridging ligand are intimately involved in electron transfer processes to complexes. An argument is made that the latter are better described in terms of redox non-innocent bridging ligands supported by metal-based donor substituents rather than strongly coupled mixed-valence complexes. The significance of these results on the further development of metal complexes for use as components within a hybrid molecular electronics technology are discussed.

1. Introduction

Electron transfer reactions are arguably the simplest subset of all chemical reactions, yet they underpin essentially every aspect of chemistry and biology [1–4]. In relatively recent times the understanding of these elementary processes has been exploited in the design of advanced optoelectronic materials [5] and devices for solar energy harvesting and conversion [6–8], as well as serving to stimulate further exploration of electron exchange in a wider variety of molecular and nanoscale frameworks [9–12]. Although earlier enthusiasm for single molecule electronics from the mid 1970s and 1980s waned with the realisation of the magnitude of the challenges associated with developing this technology, the success of plastic electronics (e.g. OLED devices) and development of ever more reliable and accessible methods for measurements of single molecule conductance properties in metal|molecule|metal junctions [13,14] and methods for the assembly of molecules within device-type platforms has led to another dramatic surge in

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Abbreviations: ap, 2-anilinopyridinate; pz, pyrazine; DBU, 1,8-diazabicycloundec-7-ene.

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interest in the topic [15]. The near-future potential for molecular electronics is now widely recognised, and the International Technology Roadmap for Semiconductors (ITRS) has begun to include molecular targets within its future materials agenda [16]. The integration of functional molecular components within electronic devices is a paradigm shift from conventional CMOS technology [17]. Consequently, exploration of the science which underpins this emerging high technology sector provides opportunities for the design and synthesis of novel molecular products en route to future industrial processes. In recognition of the importance of this area, major manufacturers have now established research programmes encompassing molecular electronic concepts [see, for example, [18–22]].

Whilst the vast majority of studies with molecular junctions conducted to date have concentrated on studies of surface binding and trans-molecule conductance of short chain organic oligo(arylene ethynylene) systems [23–25], metal complexes are beginning to migrate from the prototypical systems with which to study intramolecular electron transfer in solution towards functional molecular materials in hybrid solid-state/molecule assemblies [see, for example, [26–37]]. As has been noted elsewhere [38,39], metal complexes offer numerous advantages in the design of molecules for use in single molecule electronics. These include the synthetic flexibility in terms of molecular length, conformational rigidity, steric bulk through appropriate choice of ancillary ligands, and control over the orbital energy and spin state at the metal center(s) through redox processes (Fig. 1) [40]. The modular construction of metal complexes on surfaces has been elegantly demonstrated [41], which provided an interesting counter-point to the assembly of organic molecules in a junction in situ [42], and demonstrated an alternative method for the assembly of metal complexes within device structures to assembly strategies based on pre-preparation of the entire molecular component.

Perhaps the most fascinating prospect for metal complexes in molecular electronics lies in the capacity to bring frontier orbitals in and out of resonance with the contacting electrodes either through bias or change of molecular redox state at moderate potentials, or through the introduction of spin or Coulomb blockades [34,43]. Nevertheless, many challenges still remain for molecular electronics in general, and organometallic moltronics in particular. High amongst the list of these challenges lies the development of chemical structure/device electronic property maps and the engineering challenges associated with fabrication of three-terminal device platforms that permit the full range of electrochemically accessible molecular redox states to be utilised to enhance junction characteristics [44,45].

The challenges inherent in the fabrication and study of molecules contacted by even only two macroscopic contacts has led to a substantial interest in bimetallic model systems for molecular components in which charge transfer properties can be studied in solution using spectroscopic methods (Fig. 2). Since the earliest studies of the Creutz-Taube ion, $[\{Ru(NH_3)_5\}_2(\mu\text{-pz})]^{5+}$, mixed valence derivatives in particular have played a vital role in both fundamental and applied studies involving electron transfer reactions in metal complexes [2,46]. Consequently, transition metal complexes in which two (or more) metal atoms are linked through a common bridging ligand have been a target for synthetic chemists.

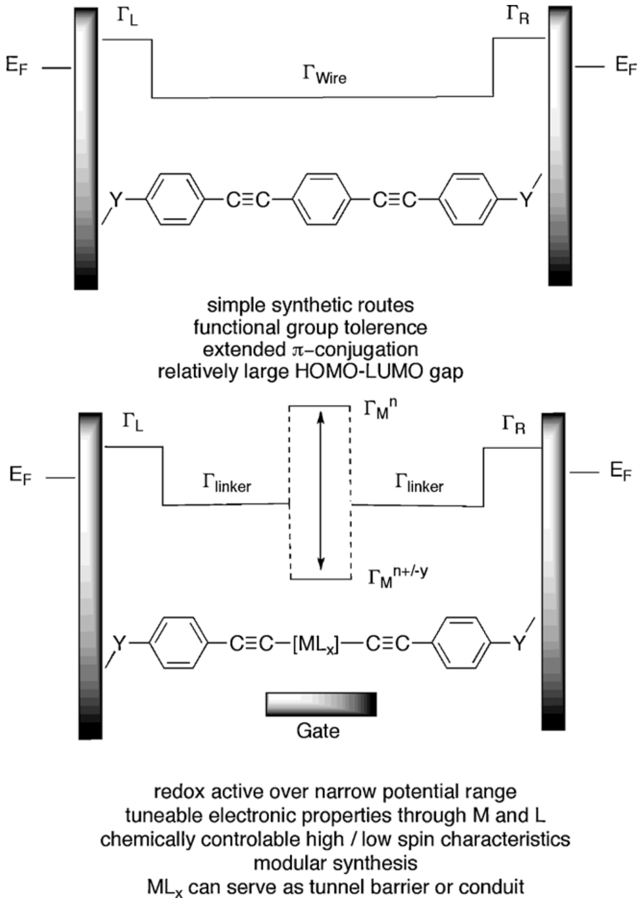

Fig. 1. A schematic showing a prototypical organic (top) and organometallic (bottom) component within two- (top) and three- (bottom) terminal junctions. The junction conductance can be described in terms of the Landauer formalism $G = (2e^2/h) \cdot \Gamma_L \cdot \Gamma_B \cdot \Gamma_R$ where e is the electron charge, h is Planck's constant and Γ_L, Γ_B and Γ_R are the transmission coefficient of the left contact, the molecular bridge and the right contact, respectively. The introduction of a redox active molecule and a gate electrode offers a mechanism through which to tune Γ_B.

However, the use of bimetallic complexes, $[\{L_xM^n\}(\mu\text{-bridge})\{M^nL_x\}]$, as precursors to mixed valence derivatives, $[\{L_xM^n\}(\mu\text{-bridge})\{M^{(n\pm y)}L_x\}]$, and hence models of molecular wires in device structures, lies alongside the growing body of work that has re-ignited awareness of the redox activity of supporting and bridging ligand [47]. Further complications arise in the middle ground of electronic structures where bridge and metal states mix, leading to significant deviations from the well-known Hush two-state model of electronic coupling in mixed valence systems, whilst retaining some spectroscopic characteristics associated with mixed valency [48–51]. Identifying the electronic characteristics of the redox products derived from $[\{L_xM^n\}(\mu\text{-bridge})\{M^nL_x\}]$ systems therefore requires application of a range of physical and spectroscopic methods which provide information across a range of timescales, often supported by computational investigations, and which precede discussions of the electron transfer characteristics of these species. The difficulties of using DFT based computations to model the electronic structure and charge transfer transitions in localised mixed valence systems is well documented [52], but there is considerable optimism regarding the potential for local hybrid and gradient functionals to satisfactorily model long-range charge transfer processes [53–55]. Nevertheless, the combination of DFT calculations with appropriately chosen functionals and spectroscopic data provides a powerful method

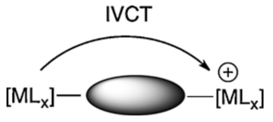

Fig. 2. A schematic of a mixed valence complex; the intervalence charge transfer (IVCT) transition contains information concerning the electronic structure (localised vs delocalised) and electronic coupling between the metal centers, and also provides information concerning the mixing of the bridge with the metallic states.