

Review

Recent advances in the functional applications of conducting metallopolymer

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ABSTRACT

As promising optoelectronic materials, conducting metallopolymer (CMPs), which are hybrid polymers based on a π -conjugated organic backbone combined with a metal complex, have attracted rapidly increasing interest in recent years. In addition to the properties directly introduced to the materials by incorporating a metal complex into an organic backbone, the optical and electronic properties of CMPs can rationally be tuned by varying the strength of electronic interactions between the two components. These tunable and varied functionalities have led to applications of CMPs in many different fields, including chemical sensors, memory devices, catalysis, photovoltaics, and light-emitting diodes. Recent advances in the development of CMPs are reviewed herein along with current challenges in these fields and how the use of CMPs could potentially fulfill the requirements.

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1. Introduction

The development of π -conjugated conducting polymers (CPs) has progressed tremendously over the past several decades [1–3]. Semiconducting behavior is a key feature of the materials to be used in, but not limited to, optoelectronics (e.g., photovoltaics, light-emitting diodes, etc.) and traditional electronic devices (e.g., conductors, field-effect transistors, memory devices, etc.) [3]. Driven by many advances including the development of organic synthetic methods, there have been numerous works on structural modification of CPs in order to increase the functionality of these materials, not only by changing the polymer main-chain structures but also by attaching new components to the polymer chains [1]. Among the incorporated functionalities, metal complexes have been one of the most common and most promising moieties as a result of the various practical and complimentary applications the metal complexes provide, including but not limited to: catalysis [4], sensing [5], and pure-colored light-emission [6]. Material properties, e.g., optical and electronic, of metal-containing CPs, dubbed conducting metallopolymer (CMPs), are not only inherited from the individual components (i.e., polymer backbone and metal complexes), but are also affected by the interaction between the two components and can be tuned by varying the strength of the inter-influences between the organic backbone and the metal centers [7]. As the two components are covalently bound to each other, electron and/or energy transfers between the conjugated polymer segments and the metal centers in CMPs become much more effective, especially when they are in direct electronic communication, than those in blended metal complex/conducting polymer materials, which often suffer from heterogeneity and materials segregation over time. These close-distance interactions result in various novel properties, such as redox-enhancement [7,8], small-molecule attenuations [9], and direct charge transfer in hybrid semiconductors [10–12], in addition to the multifunctional characteristics of both metal complexes and organic conducting polymers, opening up the potential utilization of CMP materials in various applications.

A well-accepted classification of CMPs was established by Wolf and is based on how the metal centers are attached to the polymer backbones [13,14]. It has become clear as the field has developed, however, that the arrangements in which metal ions coordinate to the ligands are also important to the polymer structures and strongly affects the properties of CMPs. Thus, subclasses of each Wolf Type I–III CMPs have been introduced as presented in Fig. 1. In Wolf Type-I CMPs, the metal centers are tethered to the polymer backbone by insulating linker(s), commonly with alkyl chains, resulting in little to no direct electronic interactions between the metal center and the organic backbone. From a coordination aspect, the metal center could coordinate to the ligands via either one or multiple organic linkers, accompanied with or without auxiliary ligands to complete the coordination spheres (Fig. 1). The former case is commonly found for CMPs containing lanthanide ions [15] while the latter subclass is often seen in materials used for metal cation separation and/or sensing [16,17].

In Wolf Type-II CMPs, metal centers are covalently bound to the conjugated backbone of the polymers and the intrinsic properties of the two components are directly affected by each other. The metal-backbone interactions become less significant when there

is a conjugated-buffer linker between the metal and the polymer main chain (Fig. 1), which could be beneficial for controlling the strength of interactions while maintaining their electronic communication for effective electron and/or energy transfers.

In Wolf Type-III CMPs, the metal centers act as parts of the polymer conjugated backbone. In addition to structurally supporting the CMPs, the metal centers have a strong electronic interaction with the organic bridges. Therefore, optical and electronic properties of these metal centers are highly sensitive to the electronic changes of the polymer backbone. Additionally, the properties of CMPs are dependent on the number of coordination contacts and the geometry around the metal centers. The metal centers can directly bind to the conjugated backbone by covalent bonding or *via* coordination within ligand pockets presented with or without auxiliary ligands (Fig. 1). In most cases, a square planar geometry around a metal center helps to extend the π -conjugated system. For octahedral metal complexes and other coordination geometries, the metal centers can either extend or interrupt the conjugation of the polymer backbone depending on the arrangement of the ligands around these metal centers. Owing to the strong electronic interaction and extensive tunability of Wolf Type-III CMPs, this class has received a great deal of interest and has been extensively studied. Fig. 2 shows examples of Wolf Type-III CMPs classified into the subclasses introduced here.

There have been several reviews [7,13,14,22–29] on the development of metallopolymer with both conjugated and non-conjugated polymer chains and some specific functionalities, i.e., metallopolyynes [30]. The scope of this review is focused on the multifunctional applications of π -conjugated conducting metallopolymer (CMPs), in which the electrical conductivity of CMPs

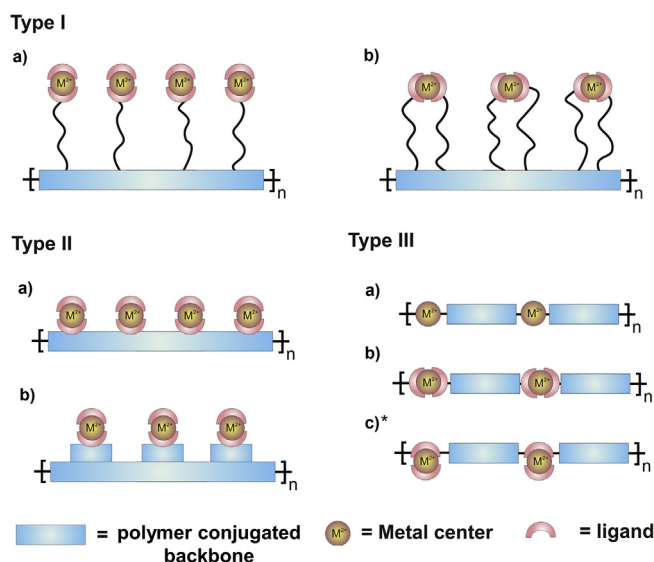


Fig. 1. Illustration of Wolf Type I–III CMPs based on the interaction between the metal centers and the conjugated backbone. Subclasses of each type are introduced based on metal–ligand coordination. This subclass can be considered as Type II if the ligand centers are in full conjugated with the polymer backbone and as Type III if the ligand centers are non-conjugated leading to the involvement of metal centers in polymer conjugation.

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