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Review

Metal-organic complexes-towards promising organic thermoelectric materials

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A B S T R A C T

Recent research progress has drawn the attention to thermoelectric (TE) property of Poly(M-ett) (M = metal, ett = ethylenetetrathiolate), which provides the best performance of n-type organic thermoelectric (OTE) materials. Metal-organic complexes have been extensively studied for their applications in magnetism, catalysis, molecular storage, and luminescence etc. Now their potential for thermoelectric conversion technology is being explored. The research on thermoelectric effect of metal-organic complexes has a history of over 50 years, efforts were mainly focused on small molecular complexes in early studies, such as metal phthalocyanine complexes. Related research on Poly(M-ett) injects fresh vitality to the field of OTE materials. In this article, TE properties of metal-organic complexes are reviewed, including small molecular complexes and coordination polymers (CPs), empirical guidelines for OTE research on metal-organic complexes are discussed.

Contents

1. Introduction

In the 1820s, Thomas Johann Seebeck noticed an interesting phenomenon what is called Seebeck effect nowadays: he found a magnetized needle can be deflected by a closed circuit composed of two metals, when the circuit was placed in a temperature gradient. In other words, an electric potential difference was formed when temperature difference existed. It was the first time thermoelectric phenomenon was noticed on record. Then Peltier effect and Thomson effect was discovered by Charles Peltier and William Thomson respectively. Peltier effect is the heating or cooling at an electrified junction of two different conductors, and Thomson effect refers to the heating or cooling of a current-carrying conductor with a temperature gradient. These three effects are referred to thermoelectric (TE) effect nowadays.

For a long time, TE effect was just regarded as a physical issue, research on TE properties was performed to investigate the electronic structure and charge transport mechanism. For

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example, measurement of Seebeck coefficient was often used to determine the conduction type of organic materials in early studies [1]. In those days, the performance of TE materials remained at a fairly low level, even the capability of thermoelectric conversion couldn't be evaluated exactly. The concept of thermoelectric figure of merit *ZT* was established in the mid-20th century, the dimensionless *ZT* can be expressed as the following equation: $ZT = S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature. It quantifies the TE effect and clarifies the basic rule to improve the performance: enhance the Seebeck coefficient as well as electrical conductivity and reduce the thermal conductivity. For inorganics, more efforts are devoted to reducing the thermal conductivity to obtain higher *ZT* value. By contrast, organics' thermal conductivity and electrical conductivity are both much lower than inorganics', so the main strategy for organic materials is enhancing the power factor *PF*, $PF = S^2\sigma$.

As the potential in energy harvesting was recognized, more chemists and material scientists participated in the field of TE effect and TE materials. The wide application prospects of TE effect in energy harvesting and green refrigeration have been well explored, so the related contents will not be discussed here, readers can find out information about applications of thermoelectric conversion technology in some review articles [2–6]. There are two facts have to be pointed out. First, applications of TE effect do not just remain at theoretical level, but have already played a role in daily life even in the military field and space technology which demand technologies to be efficient and reliable. One typical example is that Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) designed by U.S. Department of Energy has already worked in NASA space missions [7]. Second, the market value of TE technology is growing rapidly. According to the commercial report by IDTechEx, the market of TE energy harvesters is less than $60 million in 2015, the valuation is over $90 million in 2016 and $1.1 billion by 2026. It's reasonable to believe that the future of TE technology is bright. High-speed development of TE market benefits from the achievements in fundamental research over the past years, but more efforts are needed to make TE technology more efficient and practical, the central issue is enhancing *ZT* value and improving the applicability of TE devices.

So far, inorganic TE materials receive more attention as a result of their superior performance. *ZT* value of SnSe single crystal reaches up to 2.62 at 923 K, which is the highest value ever reported [8]. But organic thermoelectric (OTE) materials are catching up, more efforts are devoted to the related research and encouraging developments have been achieved [9–15]. Number of publications and citations increased rapidly in the past 10 years, meanwhile, the highest *ZT* value of OTE materials rose scores of times, reached to 0.42 [16]. It's well known organic materials have many advantages, like light weight, stretchable, low-cost, solution-processable, low-toxic etc. For most inorganic TE materials, their best performance is generally achieved at high temperature. By contrast, OTE materials show their potential around the room temperature or lower. For these advantages, OTE materials could have wide application prospects, and they are supposed to be good supplements to inorganic TE materials. One of the greatest potentials of OTE materials may be the latent demand for flexible power supply devices in wearable products, which demands the materials to be light and flexible.

Although more efforts have been concentrating on traditional conducting polymers [12,13,15,17], like polyaniline, polypyrrole, polyacetylene and poly(3,4-ethylenedioxythiophene) etc., but the research on OTE effect is never limited to some particular material systems, scientists have always been studying different materials, to explore the great potential of OTE. In 2012, research work by Zhu et al. brought attention to coordination polymers, which provided the best performance of n-type OTE materials at the time [18].

High electrical conductivity can be achieved in metal-organic complexes, whether small molecules [19,20], 1D coordination polymers (CPs) [21], or 2D metal-organic frameworks (MOFs) [22]. It's an essential advantage for developing efficient OTE materials. A wide range of choices for central metals and organic ligands provide the rich possibilities of molecular design to obtain materials with unique properties. By the targeted design with proper metal and ligand, the Fermi level, band gap, and density of state etc. can be modified, which will significantly affect the charge transport properties of complexes. From another point of view, the TE properties can be improved utilizing various approaches at the molecular level. It will be another advantage for metal-organic complexes. So it's reasonable to believe the research on TE properties of metal-organic complexes will be greatly accelerated, by combining the accumulated experiences from previous works on OTE materials and coordination compounds.

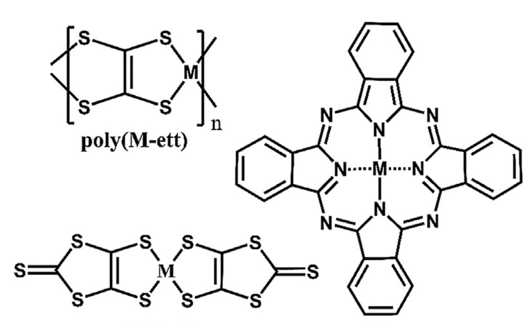
In this review, thermoelectric related research progress of metal-organic complexes will be presented, including small molecular complexes and coordination polymers. Chemical structures of some compounds mentioned in the review are presented in Scheme 1. Through the following retrospection, we expect to provide readers a brief overview of TE research on metal-organic complexes, stimulate the interest of exploring high performance OTE materials.

2. Thermoelectric properties of small molecular complexes

2.1. Metal-Phthalocyanine complexes

Phthalocyanine (Pc) was used as industrial dye in early days, then its advantages as organic semiconductor attracted more and more attention. Pc's good chemical and heat stability provide a powerful guarantee for its application. Study of Metal-Phthalocyanine (MPc)'s conduction can be traced to 1940s [23–25]. Like most organic semiconductors, charge transport behavior of MPc can be influenced by many factors, as chemical and electronic structure, temperature, pressure, even measurement method etc., it means attention should be paid to these aspects in related studies. TE properties of some typical MPc materials are given in Table 1.

In early studies, Hamman introduced measurement method for Seebeck coefficient of CuPc single crystal in details [26,27], and S was found to be the order of 1 $mV\,K^{-1}$. In addition, the values are quite different for α- and β-phase single crystal. For example, S of α- and β-phase ZnPc are $970 \pm 50\,\mu V\,K^{-1}$ and $1280 \pm 70\,\mu V\,K^{-1}$, while the S of α- and β-phase NiPc are $960 \pm 50\,\mu V\,K^{-1}$ and $1750 \pm 90\,\mu V\,K^{-1}$ respectively [28]. Schlettwein et al. made systematic research on charge transport properties of MPc derivatives [1,29–33]. They found the conduction type of MPc



Scheme 1. Structures of some metal-organic complexes mentioned in the article.