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Photosensitization of novel ruthenium-functionalized photoconductive polymers: Effect of ruthenium complex as photosensitizer

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ABSTRACT

Owing to their efficient photo-charge generation, ruthenium derivatives are emerging as an important class of photosensitizers. Despite their promising characteristics, several deficiencies, such as the relatively low quantum yield and short lifetime of the lowest energy metal-ligand charge transfer, have limited their applications. Here, we present new photoconducting polymers that contain ruthenium complexes as a photosensitizer. $Ru(phen)_2(m\text{-}COOH)(PF_6)_2$ complexes, which covalently bind the poly(*N*-vinyl carbazole) (PVK) side chain, provided a high quantum yield and sufficient lifetime of the lowest energy metal-ligand charge transfer state for photo-charge generation. A series of PVK–$Ru(phen)_2(m\text{-}COOH)(PF_6)_2$ complexes were thus prepared with various concentrations of Ru. We employed a helium-neon (HeNe) laser (633 nm) and a xenon lamp to measure the photo-charge generation efficiency and photoconductivity of the studied complexes. The wavelength dependence of the photo-charge generation efficiency and photoconductivity was found to be similar to their metal-ligand charge transfer absorption spectra. This suggests that the Ru complexes can extend the photosensitivity of the conductive polymers to longer wavelengths due to the lowest metal-ligand charge transfer energy. The photo-charge generation efficiency and photoconductivity of these polymers was found to be greater than those of PVK–Ru-complex composites.

1. Introduction

On account of their significant optical nonlinearity, low permittivity, and low cost, polymeric photorefractive materials are potentially useful in a variety of areas, including xerographic layers and large-area solar cells. Consequently, several studies have focused on the development of photogenerating charge carriers in photoconducting polymers [1–5]. Despite these promising properties, the low charge-generation efficiency and poor charge-carrier mobility of the traditional photosensitizers often limit their application in photodiodes and polymeric solar cells [6–9]. TNF (2,4,7-trinitro-9-fluorene) [10], TNFM (2,4,7-trinitro-9-fluorenylidene) malononitrile)) [11], TCBQ (tetracloro-1,4-benzoquinone) [12], TCNQ (7,7,8,8,-tetracyano-quinnodimethane) [13], TCNE (tetracyanoethylene) [14], and fullerene [15] have been recently employed as photosensitizers in poly(*N*-vinyl carbazole) (PVK), which is a photoconducting polymer with a well characterized hole-transporting capability. However, these organic materials provide a lower quantum yield compared to that of inorganic materials such as CdSe and PbSe [16,17]. In order to address this issue, the fundamental mechanisms involved in the photo-charge generation and charge transport must be understood, and, to achieve this, innovative methods are required. In this regard, transition-metal complexes, such as metal-phthalocyanine, are considered promising systems that may promote the efficiency of photosensitizers [18–20].

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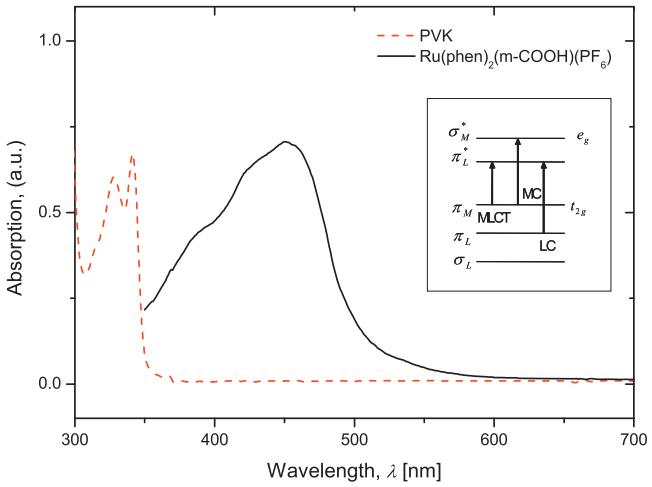
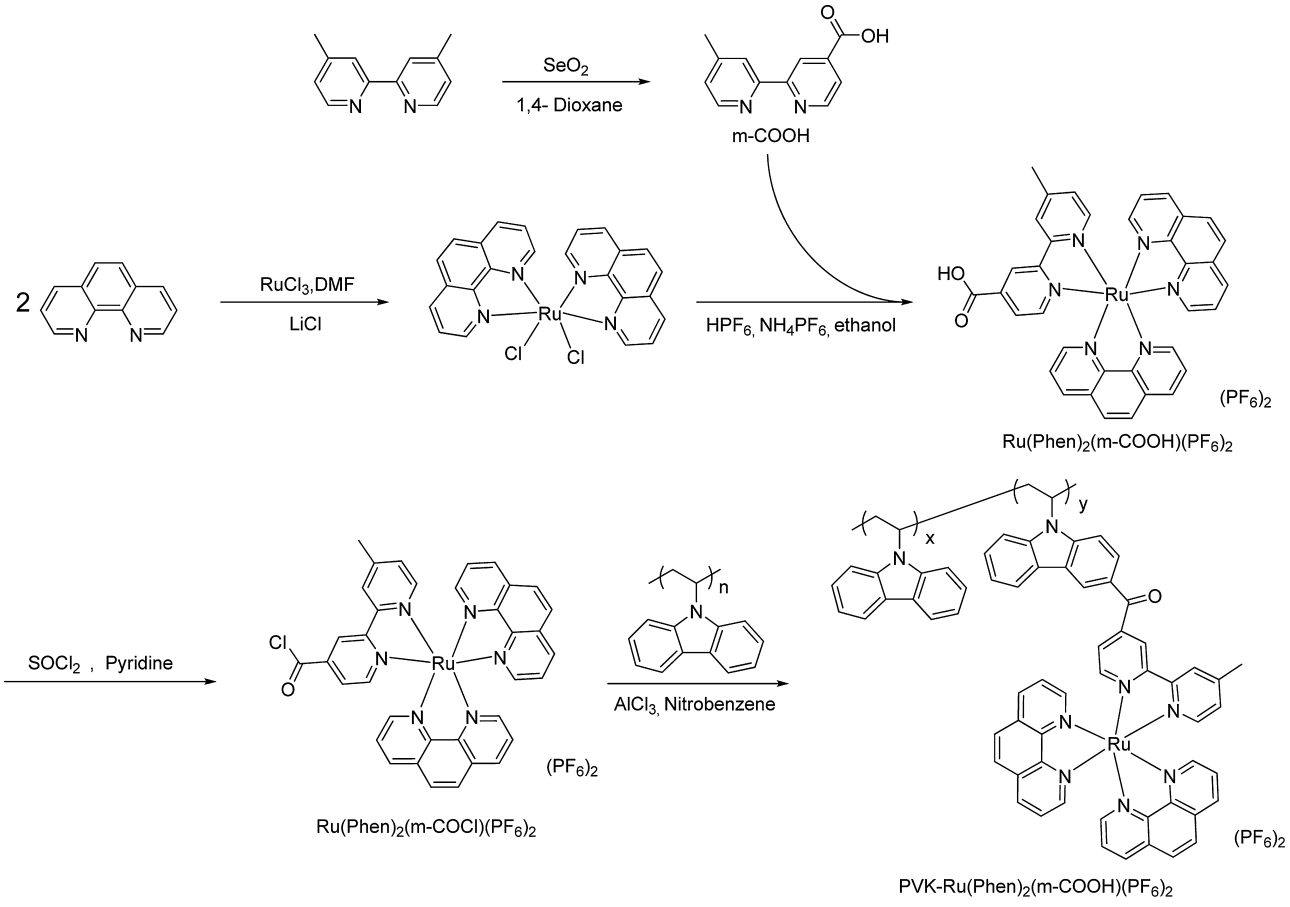


Fig. 1. Absorption spectra of PVK and $Ru(phen)_2(m\text{-}COOH)(PF_6)_2$ in $CHCl_3$ and schematic view of molecular orbitals.

One of the most widely used transition-metal complex photosensitizers is ruthenium(II)-trisphenanthroline [$Ru(phen)_3^{2+}$] (Fig. 1). $Ru(phen)_3^{2+}$ is an efficient photosensitizer because of its excellent electron-acceptor properties [21,22]. The efficient energy and electron-transfer process are associated with a durable excited state. In particular, $Ru(phen)_3^{2+}$ performs efficiently as energy-transfer, electron-transfer, and electron-acceptor material owing to its relatively long lifetime in the metal-ligand charge-transfer (MLCT) excited state [22–26]. Polymers doped with $Ru(phen)_3^{2+}$ have been recently developed for solar-energy conversion [27–29], metal-ion sensors [30,31], polymer-supported electrodes [32–35], nonlinear optics [36], photorefractivity [37], and electroluminescence [7,38].

In traditional composite systems, the significant phase separation of the dopant, which is caused by a concentration increase, limits a further investigation of the performance [39]. In an effort to improve the photoconducting properties of polymer-based systems, here we synthesized novel photoconductive ruthenium–polymer complexes. Unlike composite systems, polymer complexes are expected to have a higher phase stability owing to the covalent binding of the dopant in the polymer chain. The data presented in this study show that the introduction of a transition metal (Ru) complex may increase the charge-generation quantum efficiency and promote the formation of the charge carrier. In this study, the use of a Ru-complex (bearing a phenanthroline moiety instead of a bipyridine moiety) resulted in an improvement of the overall performance of the device compared to previous systems due to a lower band-gap and a delocalized π-conjugated backbone of the Ru complex [40]. The attachment of the Ru complex to the PVK branches was achieved under the Friedel–Crafts conditions. To characterize the photo-physical properties of the synthesized PVK–Ru complexes, xerography and conductivity experiments were carried out, and the results and implications discussed. In addition to providing crucial information about the synthesis of this class of materials, in this study an improvement in the charge-generation quantum efficiency was obtained. Moreover, the photoconductivity was measured to be 1.37 pS/cm. Thus, from our data, it is clear that the inclusion of the Ru complex results in a substantial improvement of the photo-physical properties. Finally,



Scheme 1. Synthetic routes of PVK–$Ru(phen)_2(m\text{-}COOH)(PF_6)_2$.