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Synthesis and photovoltaic properties of new ruthenium(II)-bis(aryleneethynylene) complexes

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ABSTRACT

A new series of small-molecular ruthenium(II)-diynes *trans*-Ru(dppe)$_2$(C≡CAr)$_2$ (**D1**–**D4**) (dppe = $Ph_2CH_2CH_2Ph_2$; Ar = aromatic moiety) have been successfully designed, synthesized and characterized by photophysical, electrochemical and computational methods, and complexes **D1** and **D3** were crystallographically characterized. The optical and time-dependent density functional theory studies showed that the absorption ability of these complexes was significantly enhanced by incorporating the stronger electron-donor groups. The effect of different electron-donor groups in these metallo-organic complexes on the optoelectronic and photovoltaic properties was also examined. In this work, benzothiadiazole as the electron acceptor and triphenylamine and/or thiophene as the electron donor were introduced in these complexes, which were found to have optimal energy bandgaps spanning from 1.70 to 1.83 eV and broad absorption bands within 300–700 nm, rendering them good electron donor materials to blend with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{70}BM$) in the fabrication of the solution-processed bulk heterojunction (BHJ) solar cells. The best power conversion efficiency (PCE) of 0.66% was achieved, which is the highest PCE in ruthenium(II)-containing BHJ solar cells to date.

1. Introduction

The demand for organic photovoltaic (OPV) cell [1] as a promising cost-effective alternative and potentially sustainably renewable energy is increasing steadily to deal with various economic and environmental issues [2,3]. As a new competitor to silicon-based solar cells, OPV cells possess light-weight, low-cost, and flexibility advantages [4,5]. Besides, the chemical structure and optical spectra of organic molecules can be modulated. In particular, OPV cells with bulk heterojunction (BHJ) architecture [6], in which the photoactive layer consists of a bicontinuous blend of an electron donor and an electron acceptor, has been extensively studied due to their great potential for cost-effective photovoltaic devices. Furthermore, they have been proven to be the successful device structure for OPVs so far [7]. The photoactive materials play a key role in the whole photovoltaic process and great efforts have been made to improve energy conversion efficiency (PCE), which in turn determines the electrical characteristics of the solar cell, such as short circuit current (J_{sc}), open circuit voltage (V_{oc}), and fill factor (*FF*). The J_{sc} depends on the wavelengths of the absorption bands and charge carrier mobilities of the donor and accepter materials, whereas V_{oc} is proportional to the difference between the lowest

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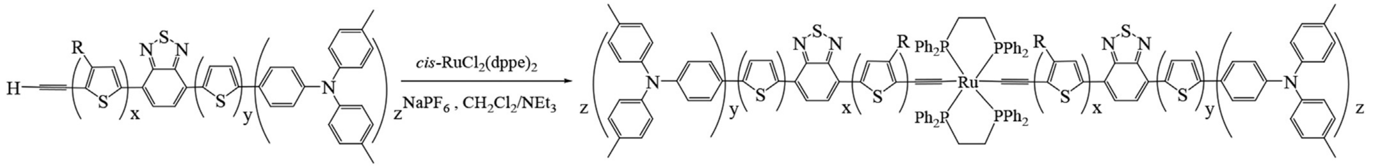
unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor, and *FF* is related to the charge carrier mobilities and device fabrication conditions [8,9]. Therefore, it is a challenge to design and synthesize an organic material that simultaneously possesses good film-forming properties, strong absorption ability, high hole mobility and suitable energy gap between the HOMO and the LUMO energy levels. Recently, the PCEs of single BHJ solar cells over 8% have been reported based on solution-processible polymers or small molecules [10,11]. However, knowledge is still limited on how to further improve solar cell efficiency through polymer development. Therefore, it is necessary to carry out detailed research to elucidate the structure-property relationship. A general guideline for the design of p-type material is a donor-acceptor (D-A) alternating molecular structure, which leads to a low bandgap suitable for efficient light harvesting. It is important that the HOMO of the donor polymers and the LUMO of the acceptors should match to achieve fast charge separation and high V_{oc}, thus a high PCE. On the other hand, one possible approach which has not been commonly explored involves the use of metal-containing polymers or small molecules [12,13]. In this context, our group has succeeded in developing a series of low bandgap metallopolyynes suitable for the application of OPV cells [14,15]. Their photovoltaic responses and PCEs depend to a large extent on the number of thienyl rings along the main chain. Although still in its infancy, the use of metallopolyynes and their oligomers represents an innovative and challenging research area for the development of BHJ solar cells. Compared to the BHJ solar cells based on polymers, solution-processed small-molecule (SM) BHJ solar cells have received less attention, and their efficiencies have remained below those of their polymeric counterparts [16,17]. However, optimizing the photovoltaic performance of a new polymer is complex because the process involves controlling the regioregularity, polydispersity, and molecular weight of the polymer during synthesis. Small molecules are easy to synthesize in high purity and possess well-defined structures [18]. In general, to address the issue of the low PCE for SM BHJ solar cells, several requirements should be considered, including wide and efficient absorption, matched energy levels with acceptors, planar structure for high hole mobility, good solubility and film formation ability.

In our previous work, after the synthesis of a series of platinum(II) acetylide donor complexes from our group, we found that the structures of ruthenium(II) acetylide donor complexes are rarely used in small molecule-based solar cells, which have attracted an increasing attention in recent years because they possess potential advantages over mainstream inorganic-based solar cells [19,20]. The incorporation of a ruthenium metal center instead of a relatively more expensive platinum in a conjugated backbone and the D-A structure applied in these complexes should give rise to some advantages, since a red shift of the absorption spectra and hence better solar light harvesting is anticipated in the case of ruthenium(II) species. In the literature, there are very few examples of the applications of ruthenium-containing complexes for solution-processed OPV cells. The use of simple mononuclear ruthenium(II) bis(acetylide) complexes for BHJ devices is still unprecedented. We report here the synthesis and characterization of ruthenium(II)-acetylide complexes simply by using aryleneethynylene ligands to form soluble and tractable symmetric ruthenium(II)-bis(aryleneethynylene) complexes **D1**–**D4** for SM BHJ solar cells. The benzothiadiazole unit was introduced as the electron-accepting group to tailor the energy levels of the frontier molecular orbitals for **D1**–**D4**. The synthetic processes are convenient and provide reasonably good yields. All of these products are easy to purify by flash column chromatography on Al_2O_3 using the appropriate eluent and recrystallization from hexane. These compounds have been applied in BHJ devices and the corresponding optical, electronic and photovoltaic properties have been carefully studied and their structure-photovoltaic property relationships with different spacers are also presented.

2. Results and discussion

2.1. Synthesis and chemical characterization

The key aryleneethynylene ligands **L1**–**L4** were prepared according to the procedures reported by our group [21], and the metal halide complex *cis*-[$RuCl_2(dppe)_2$] was prepared by the known methods [22]. The synthetic routes of the ruthenium-containing bis(aryleneethynylene) complexes **D1**–**D4** are illustrated in Scheme 1. Complexes **D1**–**D4** were obtained by $NaPF_6$-catalyzed dehydrohalogenation reaction between ligands **L1**–**L4** and *cis*-[$RuCl_2(dppe)_2$] in a ratio of 2:1, respectively. Purification of the reaction mixture by flash column chromatography furnished the complexes as air-stable solids in high purity and moderate yield. All the metal complexes **D1**–**D4** are air-stable and soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, THF and toluene. They were fully characterized by FTIR and NMR (^1H and ^{31}P) spectroscopies, MALDI-TOF mass spectrometry and, in some cases, X-ray crystallography. ^1H NMR analyses clearly demonstrate a well-defined structure for each of the compounds. All the proton signals of aromatic rings are in the downfield region (δ, above 6.30 ppm) and those of the dppe ($Ph_2PCH_2CH_2PPh_2$) are in the upfield area (δ, around 2.66 ppm). The sharp signal of C≡C-H of every ligand is located at around 3.50 ppm, which disappeared in the spectra of those of ruthenium(II) complexes, revealing that the metal center ruthenium was capped by the two ligands. These ruthenium(II) complexes were also characterized by ^{31}P NMR spectroscopy. The signals for phosphorus atoms of the starting material *cis*-[$RuCl_2(dppe)_2$] resonate at 37.8 and 45.1 ppm [23], which disappeared in **D1**–**D4**. The presence of new signals at 52.82, 52.64, 53.73 and 52.63 ppm, respectively, for **D1**–**D4** indicates the equivalence of the four phosphorus atoms and therefore a *trans* arrangement of the alkynyl ligands around the metallic center [24]. The FTIR spectra showing the stretching vibrations of the terminal



x = 1 (R = H), y = 1, z = 0 **L1**
x = 1 (R = C_6H_{13}), y = 0, z = 1 **L2**
x = 0, y = 1, z = 1 **L3**
x = 1 (R = C_6H_{13}), y = 1, z = 1 **L4**

x = 1 (R = H), y = 1, z = 0 **1**
x = 1 (R = C_6H_{13}), y = 0, z = 1 **2**
x = 0, y = 1, z = 1 **3**
x = 1 (R = C_6H_{13}), y = 1, z = 1 **4**

Scheme 1. The synthetic procedures for complexes **D1**–**D4**.