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Conjugated poly-ynes and poly(metalla-ynes) incorporating thiophene-based spacers for solar cell (SC) applications☆

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ABSTRACT

Solar cells (SCs) are of considerable current research interest because of their potential as a clean alternative to fossil fuels. Researchers across the globe are developing novel polymeric materials with enhanced power conversion efficiency (PCE). Conjugated poly-ynes and poly(metalla-ynes) incorporating late transition metals and thiophene-based spacers have played a very important role in this strategic area of materials research. The performance of the SCs can be optimized by varying the conjugated spacers and/or the metal ions along the polymer backbone. Therefore, an analysis of structure-photovoltaic property relationships in poly-ynes and poly(metalla-ynes) is desirable as a guide for the development of new functional materials for use in SCs. Keeping the importance of this strategic topic in mind, herein we present a brief review on conjugated poly-ynes and poly(metalla-ynes) incorporating thiophene-based spacers that have potential SC applications. Attempts have been made to correlate the photovoltaic performance of the SCs to the chemical structure of thiophene-incorporated poly-ynes and poly(metalla-ynes). The performance of SCs is also strongly influenced by other factors such as morphology and device structure.

1. Introduction

Rising global demand for clean and sustainable energy sources has put considerable pressure on the scientific community for the development of efficient and low-cost renewable energy sources [1]. Solar energy has emerged as a potential non-contaminating alternative energy source to meet the increasing demand [2]. In fact, the planet Earth receives more energy from the sun each second than is required to meet the needs of mankind for one year [3]. However, the conversion of solar energy into electrical energy is a daunting task in the context of industrial and practical applications. The conversion is achieved by using specially designed devices embedded within cells called solar cells (SCs). SC devices are comprised of different components which govern the overall performance of the cells. These include electrodes, interfacial layers, and active materials composed of donor (D) and acceptor (A) components [4]. All of these components contribute to the overall efficiency of a SC. However, most of the research has been dedicated to the development of novel donor materials. In the past two or three decades there has been a large volume of research relating to the development of donor materials [5], particularly conjugated poly-ynes and poly(metalla-ynes) incorporating a variety of spacer groups because of their good absorption profile, energy conversion ability, processability and low-cost [4b,4c,6]. Poly-ynes incorporating several carbocyclic and heterocylic spacers [7], for example, benzene [8], anthracene [9], 2,1,3-benzothiadiazole (BTD) [10], cyclopentathiophene [11], thienopyrazine [12], dithienothiophene [13], bithiazole [14] and dithienopyrrole [15], etc. have been synthesized and assessed for SC applications. Heterocyclic spacers are considered more efficient compared to their purely carbocyclic counterparts in producing efficient SCs. Among the heterocyclic spacers, thiophene-based materials have been extensively studied and used for making low band-gap (E_g) conjugated polymers [16], which is one

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☆ Dedicated to the memory of late Professor the Lord Lewis of Newnham for his pioneering contribution in the field of transition metal clusters, coordination chemistry and organometallic polymer chemistry.

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of the prime requirements for efficient SCs. Thiophene-based spacers are also known to lower the polarity and enhance the solubility of the polymer materials [17]. It is a well-established fact now that the incorporation of heavy transitional metals along polymer backbone induces large spin–orbit coupling and imparts novel opto-electronic (OE) properties to the materials [7c,18]. Researchers have exploited the novel photo-physical properties and discovered the photovoltaic (PV) effect of organometallic poly-ynes and successfully demonstrated the utility of heavy metal incorporation into the poly-yne framework. Historically, the work on metal-based SC started around two decades ago when Köhler et al. [8a] reported a Pt(II) poly-yne-based SC with a PCE of ~0.6%. The efficiency was too low for commercial application, but this finding added a new dimension to the research and the development of conjugated poly(metalla-ynes) for SC applications. Many organic and organometallic (metal-based) donor materials have been reported as active layers for SC applications [7d,14,16b,19], a few with remarkably high efficiencies. For example, Zhan et al. [20] achieved 3.8% PCE for the organic oligo-yne incorporating cyclopentadithiophene (CDT) as a central spacer unit. Likewise, Kumar et al. [16b] reported A-π-D-π-A based oligo-yne, with extended absorption in the NIR region giving PCE of 3.65% and 5.24%, depending on solvents THF and pyridine-THF respectively. Baek et al. [4b] reported a poly(platina-yne) incorporating thienothiophene, having enhanced interaction between D and A units in the polymer backbone and obtained a PCE of 4.13% with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$). Wong et al. [17f] reported poly(platina-yne) incorporating a thiadiazole spacer with oligothiophene units at the two ends. A PCE of 2.50% was achieved for a material with three thiophene rings at each end. For further details of other recently reported SCs, the interested readers are referred to refs [7d,14,16b,19], [17e,17f,21]. The device performance of polymer SCs is greatly affected by various parameters including the chemical structures [22], the optical band gap (E_g) [23], the charge mobilities [22a], the absorption co-efficients [10], the accessibility of triplet excitons (a bound electron-hole pair) [24], the molecular weights [25], the blend film morphologies [4b,26] and the connectivity order of the ligands in co-polymers. Hence, the PV performance of the SCs can be modified by changing all these parameters, which are associated with the materials. Many poly-ynes with narrow E_g (<1.9–2.0 eV), absorptions in the longer wavelength region (extended IR region) and good to moderate PCEs have been reported [17e,17f,21]. In most of the cases, researchers focused on developing novel donor materials and optimizing their properties by incorporating late transition metals in a way that resulted in efficient SCs. Considering these facts, herein we present a brief review on thiophene-based poly-yne and poly(metalla-yne) materials for SC application. Attempts have been made to forge a link between the PV performance and the structure of poly-ynes and poly(metalla-ynes) incorporating thiophene spacers. This will give a broad overview to researchers for the design and development of novel donor materials for applications in SCs.

2. Basics of SCs

2.1. Structure of SCs

Several leading articles and monographs are available describing the structure of SCs and the mechanism by which they work [27]. However, for the sake of general readers and new researchers in this area, we present a brief view of the basic structure of SCs, their performance parameters and working mechanism. Fig. 1a depicts a basic SC architecture consisting of a transparent anode made of indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), followed by an interfacial layer [28]. The interfacial layer plays a very important role in the device performance and is known to enhance V_{oc} and FF by optimizing solar absorption and suppressing charge carrier recombination [29]. Poly(3,4-ethylenedioxy thiophene) poly(styrenesulfonate) (PEDOT:PSS) is the most widely used interfacial layer. It acts as an efficient hole transport layer (HTL)/electron-blocking layer [30], due to its good conductivity, easy processability, transparency (>80%), insolubility in common organic solvents and matching work function (~-5.1 eV) with the fermi level of a wide E_g polymer in making good Ohmic contact at the anode/BHJ interface [31]. Then comes a more vital active layer, which absorbs light and supplies excitons. This is the layer where most of the modifications have been made so far. Generally, the active layer includes a p-type (D) and an n-type (A) material, which functions as a hole transporting material and an electron accepting material, respectively. It should be noted that the surface morphology of the active layer of SC can be modified by using different solvents, additives and by the application of thermal annealing. Hence, the parameters like the open-circuit potential (V_{oc}) and short-circuit current density (J_{sc}) (*discussed in next section*), which determine the PV efficiency, can be modified. Similarly, the concentration of acceptor material in the active layer also plays a crucial role [16b]. Finally, there is a cathode made up of a metal such as aluminium and is separated by a second interfacial layer (electron transport layer, ETL). Numerous n-type materials like LiF, cesium carbonate (Cs_2CO_3) [32], TiO_x [33], doped TiO_2 [34], ZnO [35], ZnO as a self-assembled monolayer [36], graphene [37] and CrO_x [38] have been employed as ETL in SC. Combination of LiF with C_{60} [39] and other metal oxides e.g. CuO_x [40] have also been used as ETLs in SC. These wide E_g ETL materials provide a barrier for excitons [41].

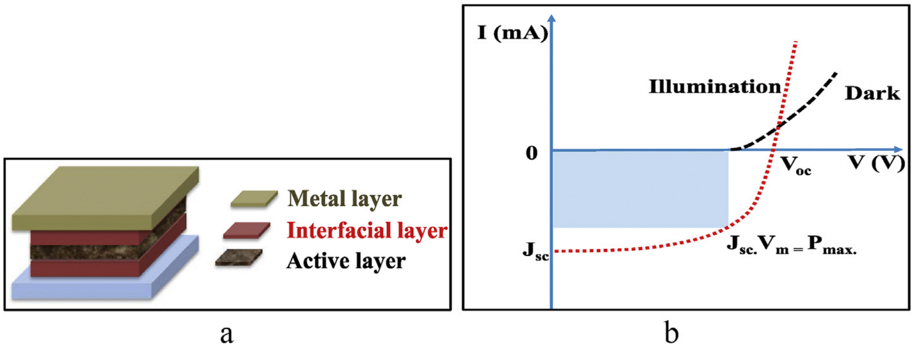

Fig. 1. (a) Schematic diagram of SC architecture and (b) A typical J-V characteristics curve (Reproduced with permission from Ref. [42]).

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