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Conjugated-polymer grafting on inorganic and organic substrates: A new trend in organic electronic materials

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ABSTRACT

This review highlights recent developments in the grafting of conjugated polymers onto various substrates for organic electronic devices. The rapid development of multi-layer architectures demands the preparation of well-defined interfaces between both compatible and incompatible materials. It is promising therefore that interface-engineering is now known to help passivate charge trap states, control energy level alignments, enhance charge extraction, guide active-layer morphologies, and improve material compatibility, adhesion and device stability. In organic electronic devices, conjugated polymers are in contact with a wide range of constituents, such as metals, metal oxides, organic materials, and inorganic particles. Covalent bonds between these materials and macromolecules are desired to yield intimate contacts and well-defined interfaces. Following an overview of the various synthetic methodologies of conjugated polymers, the chemistry of tethering macromolecular chains onto nanoparticles and flat surfaces is described. The creation of functional hybrid materials offers the potential to deliver efficient and low-cost devices.

Abbreviations: AFM, atomic force microscopy; Ar, aromatic; Bipy, 2,2′-bipyridil; CdSe, cadmium selenium; CdTe, cadmium tellurium; CNM, carbon nanomaterial; CNT, carbon nanorube; COD, 1,5-cyclooctadiene; CP, conjugated polymer; CTP, chain transfer polycondensation; CV, cyclic voltammetry; Đ, dispersity; DA, Diels–Alder; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,2-bis(diphenylphosphino)propane; DSSC, dye synthesized solar cell; GO, graphene oxide; HOMO, highest occupied molecular orbital; IR, infra-red; ITO, indium tin oxide; LUMO, lowest unoccupied molecular orbital; MALDI-TOF, matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry; MEH-PPV, poly[1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylene vinylene]; M_n, average number molar mass; M_m, average mass molar mass; MW, multi-wall; NC, nanocrystals; NMR, nuclear magnetic resonance; NP, nanoparticle; NR, nanorod; OLED, organic light-emitting diodes; OPV, organic photovoltaics; P3AT, poly(3-alkylthiophene); P3HT, poly(3-hexylthiophene); P3MT, poly(3-methylthiophene); P3OT, poly(3-octylthiophene); P4VP, poly(4-vinylpyridine); PA, polyacetylene; PCE, power conversion efficiency; PEDOT:PSS, poly(3,4-ethylenedioxythiophene)-*compl*-poly(vinylbenzenesulfonic acid); PF, polyfluorene; PFCF, poly-[4,4′-(9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylbenzenamine)(4-(9*H*-carbazol-9-yl)benzaldehyde(9,9-dihexyl-9*H*-fluorene)]; PFTPA, poly{4,4′-[4-(9-phenyl-9*H*-fluoren-9-yl)phenylazanediyl]dibenzaldehyde}-[4,4′-(9*H*-fluorene-9,9-diyl)bis(*NN*-diphenylbenzenamine)]-(9,9-dihexyl-9*H*-fluorene); PMMA, poly(methyl methacrylate); PNIPAM, poly(*N*-isopropyl acrylamide); PTM, poly(thiophene-maleimide); PP, polyphenylene; PPE, poly(phenylene ethynylene); PPh_3, triphenylphosphine; PPV, poly(phenylene vinylene); PSBr, poly(4-bromostyrene); PSI, poly(4-iodostyrene); QD, quantum dots; SAM, self-assembled monolayer; GPC, gel permeation chromatography; SEM, scanning electronic microscopy; SI-KCTP, surface-initiated Kumada catalyst transfer polycondensation; SiO_2, silicon dioxide; SW, single wall; TEM, transmission electron microscopy; TGA, thermo-gravimetric analysis; THF, tetrahydrofuran; TiO_2, titanium dioxide; TNT, trinitrotoluene; UV, ultra-violet; XPS, X-ray photoelectron induced spectroscopy; ZnO, zinc oxide.

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1. Introduction

The field of conjugated polymers for electronic organic applications was opened in 1977 with the discovery of conducting polymers and their ability to be doped to cover a full range of conductivity, from insulator to metal [1]. These materials have since been developed for numerous applications, such as sensors and heating systems. In parallel, non-doped polymers in their semi-conducting form are under rapid development and production for several applications: organic light-emitting diodes (OLEDs) for flat panel displays and lighting; field-effect transistors for display backplanes and disposable electronics; photodetectors; and last but not least organic photovoltaics (OPVs). Organic-based devices promise low costs, and properties based on their low density, conformability, flexibility and versatility due to the wide potential of chemical structures. Initial work was to conceive new materials with improved control over electrical and optical properties, along with improved processibilities; a particular target was to create soluble conjugated polymers. Another challenge was to understand the charge carrier transport mechanisms in molecular and macromolecular organic materials. More recently, several research groups have turned their attention toward the possibility of creating hybrid materials containing both conjugated polymers (CPs) and inorganic, metal or carbon-based materials, through covalently binding components. This report reviews various synthetic strategies that have been followed to graft semi-conducting macromolecules onto various substrates.

The first question that arises is why consider this field? It is all about interface. Organic electronic devices consist of superposed layers of different chemical natures, be they organic, inorganic, or metallic (Fig. 1). The performances and lifetimes of organic electronic devices are critically dependent on the properties of both the active materials and, importantly, their interfaces. Two examples of interface improvement via polymer grafting are given below.

Firstly, interfaces between electrodes and the organic semiconductor layers play a decisive role in optimizing charge-injection, -transport and -recombination. For example in OLED applications, device efficiency is dependent on the balanced injection of charge carriers. This requires the anode and the cathode work function to be matched with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the hole transporting layer and the light emitting layer, respectively. In response to this concern, interface engineering with small molecules and polymers has been developed and recently reviewed in several papers [2,3]. Similarly for OPVs, contact resistance between

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