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Review

Strategies to design conjugated polymer based materials for biological sensing and imaging

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A B S T R A C T

In recent years, conjugated polymers (CPs) characterized with excellent optical properties and versatile chemical structures have become popular species for biological sensing and imaging. Many creative strategies have been proposed to furnish CPs with distinguished properties or integrate CPs with other functional moieties to form multifunctional materials, which have been widely applied in different biological conditions, ranging from *in vitro* to *in vivo* experiments. This review provides a brief introduction to recent strategies for constructing these CP-based materials for biological sensing and imaging applications, where the design strategies of the two basic components (backbones and side chains) of CPs are firstly highlighted, followed by the construction of CP-based composites including nanoparticle strategies and hybridization strategies. The challenges and opportunities in this field are also discussed in this review.

Contents

Abbreviations: Ach, acetylcholine; ACQ, aggregation-caused quenching; AIE, aggregation-induced emission; ATP, adenosine 5′-triphosphate; AuNPs, gold nanoparticles; BT, benzothiazole; BTE, 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene; CaM, calmodulin; CB[7], cucurbit[7]uril; CD, cyclo-dextrin; CL, chemiluminescent; CP, conjugated polymer; CPNs, conjugated polymer nanoparticles; CRET, chemiluminescence resonance energy transfer; CTAB, cetyltrimethylammonium bromide; DB24C8, dibenzo[24]crown-8; DBT, 1,4-dithienylbenzothiadiazole; DE, dithienylethene; DHP, dihydropyridine; DPP, diketopyrrolopyrrole; FA, fluoresceinamine; Fl-ssDNA, fluorescein-labeled single-stranded DNA; FRET, fluorescence resonance energy transfer; GO, graphene oxide; HA, hyaluronan; HAase, hyaluronidase; MEF, metal-enhanced fluorescence; MIP, molecularly imprinted polymer; NIR, near-infrared; PAA, poly-(acrylic acid); PDA, polydiacetylene; PEI, polyethyleneimine; PKA, cAMP-dependent protein kinase; PM α-CD, permethylated α-cyclodextrin; PNx, the nanoparticles of Px, x refers to number of conjugated polymer; QDs, quantum dots; SA, streptavidin; scGFP, supercharged green fluorescent protein; TAT, trans-activating transcriptional activator; TPE, two-photon excitation; UV, ultraviolet; β-CD, β-cyclodextrin.

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1. Introduction

To elucidate the complex biological processes and get a better understanding of the very secrets of life, many sensing and imaging technologies have been invented [1], accompanied with the prosperity of optical probes, such as fluorescent proteins [2], small-molecular organic dyes [3], quantum dots (QDs) [4] and aggregation-induced emission (AIE) molecules [5]. These probes emerged with unique properties have greatly enriched the toolkit that directed to sensing and imaging. Conjugated polymers (CPs, also termed as semiconducting polymers) originally for its electrical properties, found to have distinguished optical properties, have drawn more and more attention as sensing and imaging probes. CPs combining both the narrow bandgap character of inorganic semiconductors and the physicochemical properties of organic polymers reveal their superiorities in biological sensing and imaging. Firstly, delocalized π-conjugated backbones endow CPs with many intrinsic optical performances, such as light-harvesting ability and high energy transfer efficiency [6–10]. Secondly, the organic nature of CPs make it possible to tune the constitution and conformations of backbones, and at the same time, to tag functional moieties to the side chains, which greatly enrich the constitutions of CPs [11–13]. What's more, hydrophobic backbones make CPs tend to form conjugated polymer nanoparticles (CPNs) in water, hence more surprising characters can be obtained through core modifications and surface modifications of the nanoparticles. And for CPs containing ionic side chains, they can interact with a variety of oppositely charged materials through electrostatic interactions.

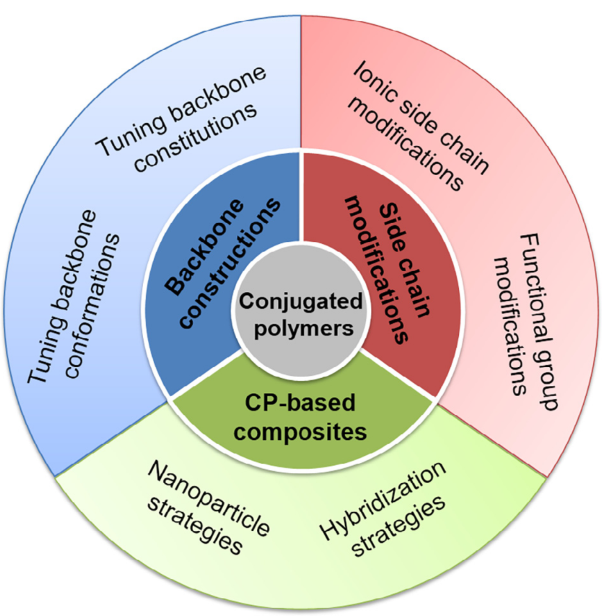

Fig. 1. Overview of the strategies to design CP-based materials for biological sensing and imaging.

In the last few years, we have witnessed the prosperous development of CP-based materials in biological sensing and imaging. Many reviews have emerged to introduce these progresses, which have covered specific application cases or sensing methods of water soluble CPs [11,14–17], and the preparation, function and application of CPNs [18–24]. While it should be noticed that, all the progresses may contain many creative strategies to furnish CPs with functions that make them competent in definite applications. These modifications mainly focused on the modulation of the properties of CPs, such as regulation of optical properties, enhancement of the aqueous dispensability, addition of recognitive, reactive or responsive elements. Considering the fact that modification strategies act as the linkages between structures of CPs and their desired properties, it is necessary to systematically introduce these creative ideas and concepts. Here in this tutorial review, we firstly introduce the modification strategies of two primary components of CPs, the backbones that decide the basic optical performances of CPs (Section 2), and the side chains that synergistically function with the backbones to affect the properties of the entire CPs (Section 3). Subsequently, regarding CPs as an entirety, we highlight the construction of CP-based composites, which include the prevalent nanoparticle strategies and the burgeoning hybridization strategies (Section 4). As we focus on the progress in recent four years, many classical strategies may be not comprehensively included, still we wish to provide readers a reference to rationally choose modification strategies to construct efficient tools for their interests Fig. 1.

2. Backbone constructions

The backbone structures play a dominant role in the outstanding optical and physicochemical properties of CPs. Similar to the operation mechanism of proteins, both the constitution of monomers and the conformation of the backbones can affect the performances of CPs. On the one hand, through the modulation of the monomer constitutions, CPs can be regulated to exhibit varied absorption and emission spectra, or be furnished with additional functions. On the other hand, the structure or arrangement of monomers may result in diverse conformations of the backbones, which can also be utilized to fabricate CPs or CP-based composites for biological sensing or imaging.

2.1. Composing of backbones with diversified monomers

Benefiting from the C—C coupling techniques on aromatic groups (such as the Suzuki coupling, Heck coupling, Sonogashira