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Review

Conjugated polyelectrolytes as fluorescent sensors

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ABSTRACT

Conjugated polyelectrolytes (CPEs) have become one of the most utilized materials in chemo- and bio-sensory systems. Useful properties of CPEs, such as amplified quenching effects and aggregation behavior, are illustrated in detail in order to provide guidelines for underlying concepts of CPE-based sensors. Well established sensing mechanisms, such as conformational changes and fluorescence resonance energy transfer, are reviewed with representative examples. Target species include small ions, small biomolecules, proteins, enzymatic activities, and DNA. New and unique mechanisms for CPE-based sensing are also described.

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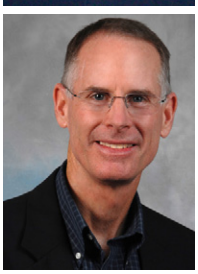
Katsu Ogawa received BS in Chemistry from Minnesota State University Mankato. He pursued his career in Materials Chemistry and received the PhD degree from North Dakota State University under the direction of Professor Seth. C. Rasmussen. He continued his study as a postdoctoral fellow under the supervision of Professor Kirk S. Schanze at the University of Florida. He was appointed as an Assistant Professor of Chemistry at California State University Northridge in July 2009.



Kirk S. Schanze was born in Florida and he received his BS degree in Chemistry at the Florida State University. His interest in photochemistry began during his undergraduate career, when he worked under the direction of Prof. Jack Saltiel. He then received his PhD at the University of North Carolina, where he worked with Prof. David G. Whitten. After a brief postdoctoral period with Prof. Thomas J. Meyer at UNC, Schanze was a Miller Postdoctoral Fellow at the University of California at Berkeley. He has served as a faculty member at the University of Florida since 1986, and his research interests are in the area of photoactive materials, conjugated polymers, sensors, solar cells, and organometallic photochemistry.

1. Introduction

Over the past several decades, advances in the design of molecular fluorescent probes coupled with significant advances in the ability to detect and process optical signals have led to a dramatic increase in the availability of versatile fluorescence-based systems for the detection and analysis of chemical and biological analytes [1–3]. Highly sensitive, real-time fluorescent sensors have been developed for a variety of biologically significant targets including small molecules, peptides, proteins, nucleic acids and microorganisms [4]. High-throughput assays have been devised that allow application of fluorescent sensors to rapidly screen candidates for drug development [5]. Fluorescent sensors have also been developed for metal ions and small organic molecules which are significant in the environment, are toxic hazards or security threats.

In the past two decades, advances have been made in the area of conjugated polymers (CP) which have opened up new applications for these materials as fluorescent sensors [6]. While there have been a variety of different approaches used to implement CPs in fluorescent signaling schemes, there has been particular recent interest in the use of water-soluble conjugated polymers that contain ionic solubilizing groups (conjugated polyelectrolytes, CPE). The objective of the current review is to provide an overview of recent activity in the area of CPE-based fluorescent sensors. This account is not meant to be exhaustive; rather, it is intended to provide a background of the area of CPE-based sensors along with examples of specific systems that illustrate the utility of CPEs in fluorescent sensor assays. The reader is also directed to several other authoritative recent reviews which give other perspectives in this area [7–13].

2. Conjugated polymers

Conjugated polymers have become an important class of materials in a wide variety of applications, including light-emitting diodes (LEDs) [14,15], light-emitting electrochemical cells (LECs) [16], plastic lasers [17], solar cells [18], and field-effect transistors (FETs) [19,20]. One recent area of interest in CPs is their use in chemical or biological sensor applications [8,12]. In particular, the chemical structures of CPs offer several advantages in sensor applications, especially increased sensitivity. The delocalized electronic structure of CPs enables them to exhibit strong absorption and emission. Rapid exciton transport along the conjugated backbone contributes to the increased sensitivity [12,21,22]. CP-based sensors have been fabricated in a variety of forms depending on the types of signals, such as conductometric (electrical conductivity) [23], potentiometric (chemical potential) [24], colorimetric (absorption) [25], and fluorometric (fluorescence) [12]. As shown in Fig. 1, CPs can be obtained with a variety of backbone structures, including poly(*para*-phenylene) (PPP) [26], poly(*para*-phenylene vinylene) (PPV) [14], poly(*para*-phenylene ethynylene) (PPE) [27], polythiophene (PT) [28], polypyrrole (PPy) [29], polyaniline (PANI) [30] and polyfluorene (PF) [31]. Some CPs are prepared *via* a palladium-catalyzed cross-coupling polymerization which offers the benefits of mild reaction conditions and functional group compatibility while others are prepared via electrochemical oxidation [9].

3. Conjugated polyelectrolytes

Solubility in aqueous media is essential for the sensing ability of CPs in a biological environment. Incorporation of ionic functionality as pendant groups on the conjugated backbone results in polymers known as conjugated polyelectrolytes (CPEs). Commonly used ionic side groups include sulfonate (SO_3^-), carboxylate (CO_2^-), phosphonate (PO_3^{2-}) and quarternary ammonium (NR_3^+) groups (Fig. 2) [9]. CPEs combine the intrinsic electronic and optical properties of the organic π-conjugated backbone and the charge interaction ability of polyelectrolytes. Such unique characteristics provide excellent platforms for the development of chemo- and biosensors. In addition to their water solubility, the charged nature of CPEs facilitates their interaction with ionic species. For example, most CPE-based sensor approaches utilize the electrostatic interaction between the probes and the target species, such as metal ions, fluoride ions, polyelectrolytes, proteins, and oligo and polynucleic acids [12].

The unique structural properties of CPEs provide additional advantages. For example, CPEs can be processed into films from water or other polar solvents (e.g., methanol), which are considered as being superior to organic solvents in terms of "green" chemistry. Because of their amphiphilic nature, some CPEs are capable of self-assembly into supramolecular structures, such as colloids and polyelectrolyte layer-by-layer films [32].

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