Coordination Chemistry Reviews 253 (2009) 410–422

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Fluorescent conjugated polymer molecular wire chemosensors for transition metal ion recognition and signaling

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Contents

ARTICLE INFO

Article history:
Received 20 April 2007
Accepted 13 March 2008
Available online 21 March 2008

Keywords:
Fluorescent chemosensor
Conjugated polymer
Molecular wire
Electron transfer
Energy transfer
Fluorescent enhancement and quenching

ABSTRACT

Conjugated polymer molecular wires have advantages over small molecules for sensing applications due to enhancements associated with electronic communication along the polymer backbone. The majority of examples from the literature focus on fluorescence "turn-off" as the mechanism of sensor response. The energy transfer mechanism involved in these polymers focuses on energy transfer quenching and can be related to either a Dexter or Förster based mechanism. More recently, a series of chemosensors have been designed and synthesized which exhibit fluorescence "turn-on" behavior upon binding specific cations. The general assembly of both the turn-on and turn-off chemosensor structures involves assembling different organic receptor ligands onto the conjugated polymer backbones. Careful spectroscopic analysis of the energy and electron transfer mechanisms in these systems creates a myriad of opportunities for the design of new sensor materials.

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doi:10.1016/j.ccr.2008.03.008

1. Introduction

1.1. Fluorescent chemosensors

Great effort has recently been devoted to the design and construction of molecular sensory systems for a broad range of environmental and biological analyses [1–12]. A sensor is defined by the Oxford English Dictionary as "a device that detects or measures a physical property and records, indicates or otherwise responds to it". A sensor achieves this goal by responding to an external stimulus and converting it into a signal which can be measured or recorded. A chemical sensor is a device that qualitatively or quantitatively detects the presence of specific chemical substances, a class of chemicals or a specific chemical reaction.

Generally, a sensor device contains three elements: a receptor, a signal transducer and a read-out (Fig. 1). The receptor should have the ability to discriminate and bind a specific target substance known as the analyte. Successful, selective receptor–analyte complex formation depends on the size, shape and binding energy of the receptor and analyte molecules. Signal transduction is the process through which an interaction of receptor with analyte yields a measurable form of energy change and is converted to a signal change that can be read and quantified. The read-out domain is the part responsible for reporting the binding event. Some parameters that define a sensor's performance are selectivity, sensitivity, stability, reproducibility and cost.

A chemosensor is a chemical sensor based on one molecule if we view one individual molecule as one engineered molecular device. It has been defined as a molecule of abiotic origin that signals the presence of a target chemical substance [7]. The three elements of a sensor device are not necessarily independent and physically separated into the three components. Sometimes, one part of the molecule can act as a combination of two or more elements.

Fluorescence is the emission of photons following relaxation from an excited electronic state to the ground state [13]. Chemosensors based on fluorescence signal changes are commonly referred to as fluorescent chemosensors [7]. Fluorescent chemosensors are gaining increased attention due to their high sensitivity and ease of measurement [5–12]. Fluorescent chemosensors are usually made up of three components: a receptor, a fluorophore and a spacer to link them together. These three parts do not exactly correspond to the three components shown in Fig. 1. In most cases, the spacer is not responsible for signal transduction. The read-out of a fluorescent chemosensor usually is measured as a change in fluorescence intensity, intensity decay lifetime, or a shift of the emission wavelength. An important feature of the fluorescent chemosensors is that signal transduction of the analytes binding event into the readout can happen in a very short time and without any other assistance. This makes real-time and real-space detection of the analyte possible as well as imaging associated with analyte distribution. In this review, we will restrict our discussion to those sensors based on a change in fluorescence emission intensity.

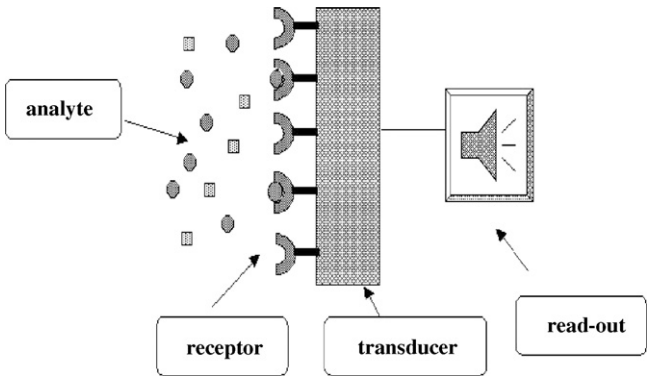

Fig. 1. Schematic illustration of a sensor device (especially a chemical sensor device).

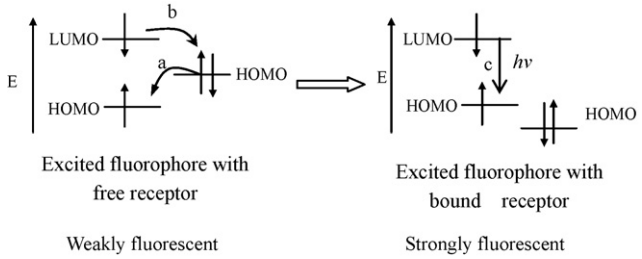

Fig. 2. Orbital energy diagrams for fluorescence "turn-on" PET sensors before and after binding cation and (a) forward electron transfer; (b) backward electron transfer; (c) fluorescence emission processes.

1.2. Mechanism of analyte detection

There are several mechanisms of fluorescence sensing. Photoinduced electron transfer (PET) and electronic energy transfer (EET) are mechanisms that have been extensively studied and widely used in the design of the chemosensors. Both mechanisms result in changes in fluorescence intensity. This review will be focused on the detection of cations by either mechanism. These sensing mechanisms are applicable to a broad array of analytes as has been reviewed previously [8–10].

1.2.1. Photoinduced electron transfer

Photoinduced electron transfer sensors can be classified into two categories: fluorescence "turn-on" or fluorescence "turn-off" upon binding cations. For fluorescence "turn-on" sensors, the receptors usually contain a relatively high-energy non-bonding electron pair. In the absence of analytes, this electron pair quenches the emission by rapid intramolecular electron transfer from the receptor to the excited fluorophore, as shown in Fig. 2. When this electron pair coordinates to Lewis acid cations in solution, the HOMO of the receptor is lowered. This decreases the driving force for the PET process effectively stopping the quenching event and turning on the fluorescence of the chromophore.

In some cases, the receptor takes part only indirectly in the photophysical process. If the energy level of the cation LUMO is between the energy levels of the fluorophore HOMO and LUMO, the binding of the cations by the receptor provides a non-radiative path to dissipate the excitation energy, resulting in a quenching of the fluorescence of the chemosensor (Fig. 3).

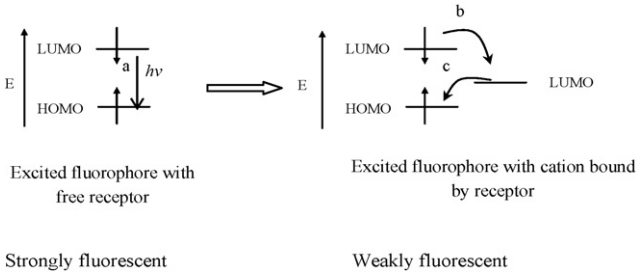

Fig. 3. Orbital energy diagrams for fluorescent "turn-off" PET sensors before and after binding cation and (a) fluorescence emission; (b) forward electron transfer; (c) backward electron transfer processes.