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METAL-CONTAINING CONJUGATED POLYMERS AS FLUORESCENT CHEMOSENSORS IN THE DETECTION OF TOXICANTS

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Abstract

Fluorescent conjugated polymers have received a great deal of recent interest due to their ability to act as chemosensors to detect various chemical species in both environmental and biological systems with sensitivity and selectivity. Examples from the literature include polymer chemosensors that operate on either fluorescence “turn-on” or “turn-off” as mechanisms of sensor response. These responses can be related to either photoinduced electron transfer or electronic energy transfer mechanisms. Recently, a series of metal-containing polymers or metallopolymers have been explored by various research groups for their use as chemosensors. In many cases, these metallopolymers have been shown to be more sensitive and selective for specific chemical species. This review focuses on fluorescent conjugated polymers as chemosensors, with a specific concentration on recent advances in metallopolymer chemosensors.

Keywords

metallopolymer; conjugated polymer; chemosensors; fluorescent enhancement and quenching

1. Introduction

1.1 Fluorescent Chemosensors

The development of sensitive and selective sensors has been a primary focus for many scientists in recent years. 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 sensor generally contains three components: a receptor, a signal transducer and a read-out mechanism (see Figure 1) [1]. The recognition element is known as the receptor which is the key component of the sensor device that interacts directly with the analyte. The receptor should be selective in having the ability to discriminate the stimulus of interest, avoiding interferences from the environment. The transducer component converts the input from the stimulus interaction with the receptor to another form, suitable for readout. The read-out

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domain is the part responsible for reporting the recognition event and processing the signal from the transducer.

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. Chemical sensors have been developed for cations, anions, neutral molecules, acids, vapors, volatile organics and many more [2–4]. A wide variety of transduction mechanisms exist including electrochemical (such as potentiometric, voltammetric), optical (such as fluorescent or chromophoric), thermal and so on. The ideal performance of a sensor device for real application is determined by the following factors [5]: selectivity, sensitivity, detection limit, reversibility, response and recovery time and lifetime.

Chemosensors based on fluorescence signal changes are commonly referred to as fluorescent chemosensors [6]. Fluorescent chemosensors are gaining increased attention due to their high sensitivity and ease of measurement [7–15]. Fluorescent chemosensors are usually made up of three components: a receptor, a fluorophore and a spacer moiety that links them together. These three components are not exactly the same as the three components shown in Figure 1. The read-out of a fluorescent sensor can be either a change in the fluorescence intensity, a shift in the emission wavelength, or a change in the fluorescence lifetime.

1.2 Mechanism of analyte detection

There are several mechanisms of fluorescence sensing, among them, photoinduced electron transfer (PET) and electronic energy transfer (EET) have been extensively studied and widely used in the design of small molecule sensors with fluorescence intensity changes as the signal read-out [7–9].

1.2.1 Photoinduced electron transfer - turn-on vs turn-off chemosensors—In a fluorescent conjugated polymer chemosensor system, the PET process can be classified into two categories, fluorescence “turn-off” or fluorescence “turn-on”. In these two categories, the receptors take part in the photophysical process either directly or indirectly, a role facilitated by the flexibility and conjugation between the polymer backbone and the receptor. In a fluorescence “turn-off” sensor, the fluorescence intensity decreases when the analyte becomes bound to the receptor and in this case the receptor plays an indirect role in the PET process. For indirect quenching to occur, the only known role of the receptor is to recognize the analytes and hold it close to the fluorophore. When this happens, the LUMO energy level of the receptor/analyte pair is between the HOMO and LUMO energy levels of the fluorophore, creating a non-radiative PET quenching pathway (Figure 2) which leads to dissipation of the excitation energy and the quenching of the fluorescence of the fluorophore [16].

For fluorescence “turn-on” chemosensors, the receptors usually contain a relatively high energy non-bonding electron pair [17]. In the absence of analytes, this electron pair quenches the fluorescence of the chemosensor by rapid intra-molecular electron transfer from the receptor to the excited polymer backbone, as shown in Figure 3. When this electron pair coordinates to electron deficient analytes in solution, the energy of the HOMO of the receptor is lowered creating a direct fluorescence emission pathway to the ground state. This decreases the driving force for the PET process an0d can turn on the fluorescence of the chromophore. We are able to deduce this because the changes in absorption of the bound and unbound chemosensor are minor, suggesting that the energy gap of the chemosensor is unaffected by the binding event. The binding of the cation however, is usually accompanied by a large increase in fluorescence suggesting that the binding event created a new radiative pathway that was absent prior to binding[18].

As demonstrated, there is a fundamental difference between the “turn-on” and “turn-off” mechanisms of the PET process. In the first case, the PET process occurs before binding the analyte, which consequently “turns-off” or stops the process. In the latter case, PET is created by the binding event. In both cases, the relative electronic potential of the HOMO and LUMO gap are critical in the design of a selective system.

1.2.2 Electronic Energy Transfer—Electronic energy transfer (EET) is another mechanism that can be involved in fluorescence quenching. While all current examples of EET chemosensors are turn-off in nature, there are two kinds of EET mechanisms that should be considered: the through bond exchange (Dexter) energy transfer or the dipole-dipole coupling (Förster) energy transfer [19, 20]. In organic fluorophore systems, usually the Dexter energy transfer dominates as shown in Figure 4. In this case, the fluorophore returns to the ground state through a nonradiative decay. Dexter energy transfer requires close contact between the donor and the acceptor. This would involve direct orbital overlap. This type of fluorescence quenching requires matching in energy levels between the donor and acceptor orbitals.

The Förster energy transfer mechanism involves the long range coupling of dipoles, allowing for an exchange of excitation energy through space, i.e. without a path of direct orbital overlap [19,20]. In this case, overlap of the emission and absorption spectrum is the key factor and there is no dependence on conjugation.

2. Fluorescent conjugated polymers as chemosensors

Small molecules have been extensively studied as fluorescence sensors in the past several decades [7–15]. The most commonly used fluorophores are aromatic compounds, especially anthracene [21]. Recently, conjugated polymer chemosensors have been used with great success in the past decade as fluorophores for detection of a range of analytes from biomolecules to explosives [22–27]. Swager and co-workers [22] first demonstrated that polyreceptor, conjugated polymer sensors, with their receptors connected in conjugation with each other, as molecular wires, have several advantages over small molecules for sensing applications. They were determined to be more sensitive which was linked to the efficient mobility of excitation energy between the receptors along the polymer backbone [22]. The polymer structure also provided for facile structural modification and good processibility.

Numerous studies have been made on the properties and applications of conjugated polymers such as poly(*p*-phenylenevinylene) (PPV) [28–31], poly(*p*-phenyleneethylene) (PPE) [32–37] and polythiophene (PT) [38–40] (Figure 5). Several research groups, including our own, have investigated the structure-property relationships of poly [*p*-(phenyleneethynylene)-alt-(thienyleneethynylene) (PPETE) [12,41–43]. The PPETEs were found to be highly luminescent with good processibility as a material. They differ slightly from the PPE rigid-rod structure due to the inclusion of the five member thiophene ring, but still have a relatively high degree of π electron delocalization.

The combination of the sensitivity of fluorescence and the unique electron and energy transfer properties of conjugated polymers provides new opportunities for sensory system development. One type of fluorescent conjugated polymer sensor is based on the conformational change of the conjugated backbone driven by interaction with the analyte. For instance, the fluorescence of poly[3-oligo(oxyethylene)-4-methythiophene] (Figure 6a) is either enhanced or quenched in the presence of alkali metals, as the polymer changes conformation. In this case, both the intensity of fluorescence and the emission wavelength changed as a function of the concentration of alkali metal cations [44].

Another early type of conjugated polymer sensor involved the introduction of molecular recognition units directly into the conjugation of the polymer backbone. An early example of this was the polymer synthesized by Wang and Wasielewski [45]. (Figure 6b) A bipyridyl group with a dihedral angle of 20° between two pyridine planes in the 2,2′-bipyridine system was introduced into the polymer backbone. It was forced into a planar configuration after chelation to certain transition metals such as Mn^{2+}, Zn^{2+} and Pd^{2+}. The result was an increased conjugation length. The conformational change was monitored by changes in both the UV-Vis and fluorescence spectroscopy.

Polymer synthetic strategies offer many more options for sensor application. Another excellent approach is to assemble the receptor pendants onto the conjugated polymer backbone [22,23]. This concept was first advanced and demonstrated by Swager's group [22,23]. They assembled cyclophane-based receptors onto a *para*-poly(phenyleneethynylene) backbone (Figure 6c). This fluorescent conjugated polymer showed a 65-fold fluorescence enhancement in sensitivity to paraquat, compared to a similar small molecule fluorescent chemosensor having one receptor. The enhancement in this polymer system was attributed to facile energy migration, along the fluorescent conjugated backbone, where the excitation energy gets quenched upon encountering the lower energy receptor bound site. In poly-receptor polymer systems, as illustrated in Figure 7, a single binding event affects the energy of the entire polymer producing a greater overall quenching effect or response relative to small molecule sensors [22,23].

3. Metallopolymers as chemosensors

Many recent reviews are available which discuss fluorescent conjugated polymers as chemosensors [14,46–47]. Metallopolymers are an exciting class of compounds which can be used in a variety of electronic and photonic applications [48]. This review specifically targets recent research that has been conducted on fluorescent metallopolymers for their applications as chemosensors for various chemical species [49–56].

3.1 Copper(II)metallopolymer chemosensors for iron cations

Inorganic/organic hybrid polymer chemosensors have been developed to selectively target key transition metal toxicants through a fluorescence "turn-on" response. Orginally, the polymer tmeda-PPETE, N,N,N'-trimethylethylene-diamino receptors loaded on the thiophenes of the PPETE backbone has been studied in our group [50,51]. (Figure 8a) The tmeda-PPETE polymer showed small fluorescence "turn-on" responses when most metal cations were added, but a significant quenching upon addition of Cu^{2+}. Based on the Cu^{2+} quenching, an inorganic/organic hybrid system, polymer preloaded with Cu^{2+}, was created in order to improve sensitivity by completely quenching the initial background fluorescence. Thus a fluorescence "turn-on" chemosensory system for cations was created based on a tmeda-PPETE/Cu^{2+} hybrid system. This hybrid system was shown to be highly selective for iron cations with fluorescence enhancements of 150-fold.

Recently, the role of conjugation in the polymer backbone has been explored. This work has involved increasing the conjugation of the backbone through replacement of the diethynylphenylene units of the PPETE system with diethynylnaphthalene units to create a poly [*p*-(naphthaleneethynylene)-alt-(thienyleneethynylene)] (PNETE) system [52]. Increasing π conjugation modifies the energy gap of the polymer backbone and could maximize the chemosensor's sensitivity and selectivity. Like tmeda-PPETE, the newly synthesized tmeda-PNETE polymer (Figure 8b) was shown to have a "turn-on" response to most metals except Cu^{2+}, which showed significant quenching upon addition.

As a comparison study, polymer/Cu^{2+} hybrid sensory systems were created for both polymers. The hybrid systems were prepared from THF solutions of each polymer with a repeat unit concentration of 5μM. $CuCl_2$ was added from an aqueous stock solution to reach a final concentration of 5μM and to achieve a 1:1 mole ratio of Cu^{2+} receptor. Each hybrid system was titrated with 13 different metal cations. During the titration, the emission maximum did not shift and the UV-vis spectra showed negligible changes, suggesting no significant change in the overall electronic structure of the polymer upon addition of metal cations. All cations were shown to increase fluorescence upon addition and both systems showed high selectivity for iron cations. (Figure 9) Interestingly, the tmeda-PNETE/Cu^{2+} hybrid sensor showed a greater response to Fe^{2+}. These polymer systems may provide the basis to distinguish Fe^{2+} from Fe^{3+} in biological environments.

Results for both polymers showed there was no significant difference in fluorescence enhancement among any of these cations for the pure chemosensor polymers. In all cases, the fluorescence enhancement was significantly smaller for the pure polymer model compared to the polymer/Cu^{2+} systems. From these results, it was concluded that the high sensitivity and selectivity requires the polymer/Cu^{2+} hybrids. Both polymer/Cu^{2+} systems were highly selective toward iron cations in solution. Since this selectivity is not present for the parent tmeda-PPETE solutions, it must not be based simply on the association constant between the receptor ligand and the cation. This would typically be expected for a simple host–guest interaction, in this case between the Lewis acid metal ion and the Lewis base receptor. It is likely that the selectivity is related to the relative ability of the cations to replace the Cu^{2+} already in coordination with the receptor. Competitive binding has previously been observed in small molecule sensors and other host–guest interactions [57,58]. The relative coordination of metal cations can often be related to their Lewis acid–base properties. However, Fe^{2+} and other cations do not follow a consistent trend so more work is necessary to specifically identify the mode of action for the selectivity.

3.2 Metallopolymers for nitric oxide detection

3.2.1 Copper(II) metallopolymer for nitric oxide and nitrosyl detection—Lippard and co-workers explored a strategy whereby a nitric oxide (NO) analyte was used to reduce Cu (II) ion-based metallocomplexes of π-conjugated polymer (CP) fluorophores [53]. When reduction occurs in this system the fluorescence intensity of the complex is enhanced, as illustrated in Scheme 1 below. One particular fluorophore used in this sensing study consists of poly(p-phenyleneethynylene) building blocks with bipyridyl ligands embedded within the π-conjugated backbone. The function of the bipyridyl ligands is to act as the binding units for the copper (II) ions in the formation of the metallopolymer.

In another example, Lippard and co-workers showed that both nitric oxide (NO) and nitrosyl (HNO) were able to reduce the cupric-based metallopolymer [54]. The polymer used in this study differs from the first, in that, bithiophene replaces the bipyridyl units. Emission response studies of metallopolymer to similar concentrations of NO and HNO, in MeCN/H_2O, resulted in an increase in integrated emission of the polymer. The sensitivity of the metallopolymer to HNO is however greater.

3.2.2 Cobalt(II) metallopolymer for nitric oxide detection—Holliday and co-workers synthesized solid-state based cobalt containing conducting metallopolymers sensors that responded to parts per million levels of NO in the gaseous phase [55]. This specific example uses the conducting property of conjugated polymers versus fluorescence for its sensing abilities. The metallopolymers are based on a 3,4-(ethylenedioxy)thiophene monomer unit. The authors prepared two identical metallopolymer films that were conditioned at different voltages. Their response against gaseous analytes such as O_2, NO,

NO_2, CO and CO_2 was measured and compared to a poly-EDOT film for control and comparison purposes. Tremendous selectivity of the metallopolymers towards nitric oxides was reported, the films showed only a response to NO and NO_2. NO_2 displayed an irreversible resistance change to the initial resistance that was large in magnitude. The authors attributed the magnitude and the irreversibility as a one-electron electron transfer between the NO_2 analyte and the cobalt conducting metallopolymer leading to the formation of a Co^{3+}/nitrite complex. Overall, the films displayed very good detection limits of NO and NO_2 below 1 ppm.

3.3 Copper(II) metallopolymer for cyanide anion detection

Li and co-workers developed a sensitive and selective chemosensor for cyanide (CN^-) that was based on the formation of a stable cyanide complex [56]. In this study, various metal cations, Mn^{2+}, Fe^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, Ag^+, Zn^{2+}, Fe^{3+}, Ni^{2+}, and Co^{2+}, were found to quench the fluorescence of a imidazole-functionalized polyfluorene. However, addition of Cu^{2+} showed the most efficient quenching ability and completely quenched the initial fluorescence of the polymer. When cyanide anion was then added to the resulting polymer/ Cu^{2+} hybrid, the fluorescence intensity was enhanced, and allowed for sensitive detection of cyanide down to 0.31 ppm. Overall, this polymer sensor system uses a “turn-off” approach for the detection of Cu^{2+} followed by an indirect “turn-on” approach utilizing the polymer/ Cu^{2+} hybrid to detect cyanide with both sensitivity and selectivity, as shown in Figure 9.

4. Conclusion

Several new chemosensory systems based on metallopolymers have been explored by various research groups, including our own. These metallopolymers have been shown to be sensitive and selective for different chemical species including metal cations and inorganic anions present in biological and environmental systems. Specifically, most of these sensors are based on the successful combination of coordination between the receptor and transition metal and the molecular wire concept for conjugated polymers which has shown improved sensitivity and selectivity when compared to their pure organic polymer counterparts. The metallopolymer chemosensor examples described in this review were shown to be selective sensors for either iron cations, nitric oxide or cyanide anions. Further research in this field is essential in order to design the next generation of fluorescent conjugated polymer and metallopolymer sensors with the purpose of altering and improving the sensitivity and selectivity of chemosensors towards key toxicants.

Research Highlights

- Conjugated fluorescent polymers can be used as sensors for transition metal ions in solution.
- Metallopolymers can be prepared which provide for better selectivity in chemosensor response.
- Both “turn-on” and “turn-off” fluorescent chemosensors can be prepared by these methods.

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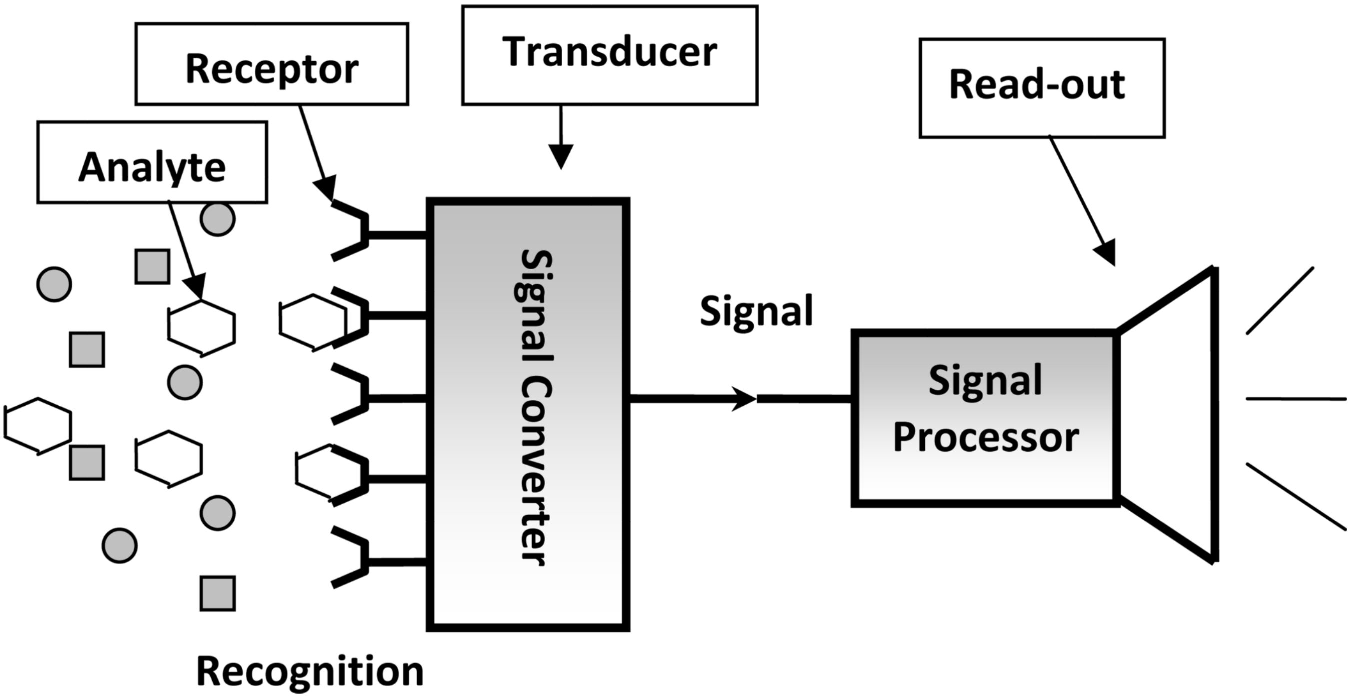


Figure 1.
Schematic illustration of a sensor

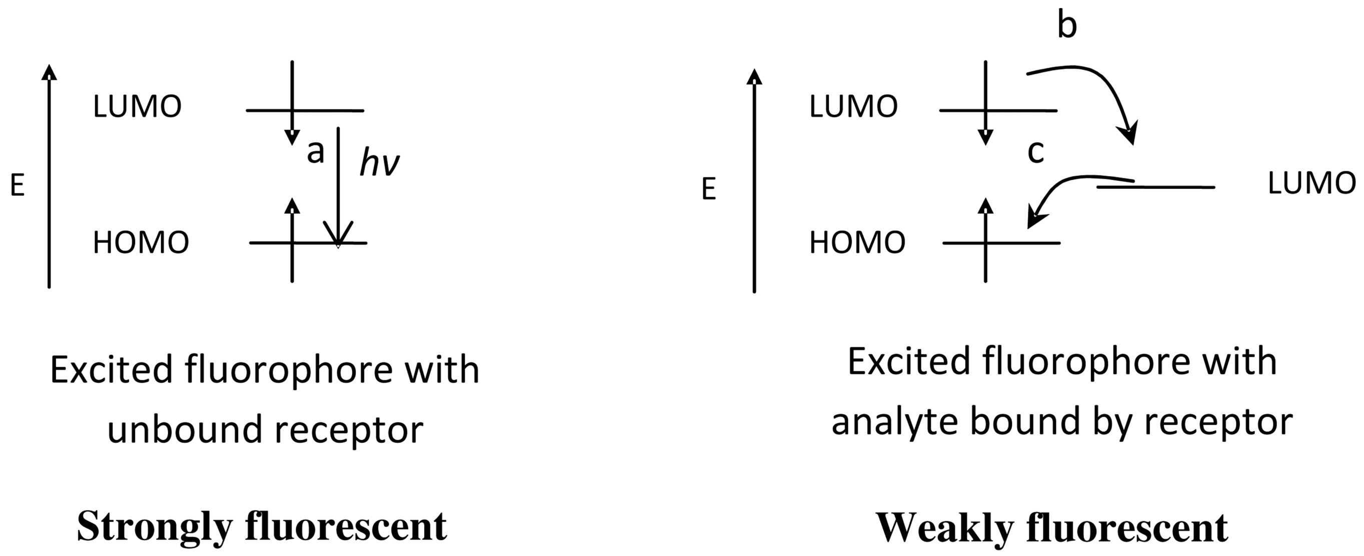


Figure 2.

Orbital energy diagrams for fluorescent “turn-off” PET sensors before and after binding analyte: (a) fluorescence emission; (b) forward electron transfer; (c) backward electron transfer processes.

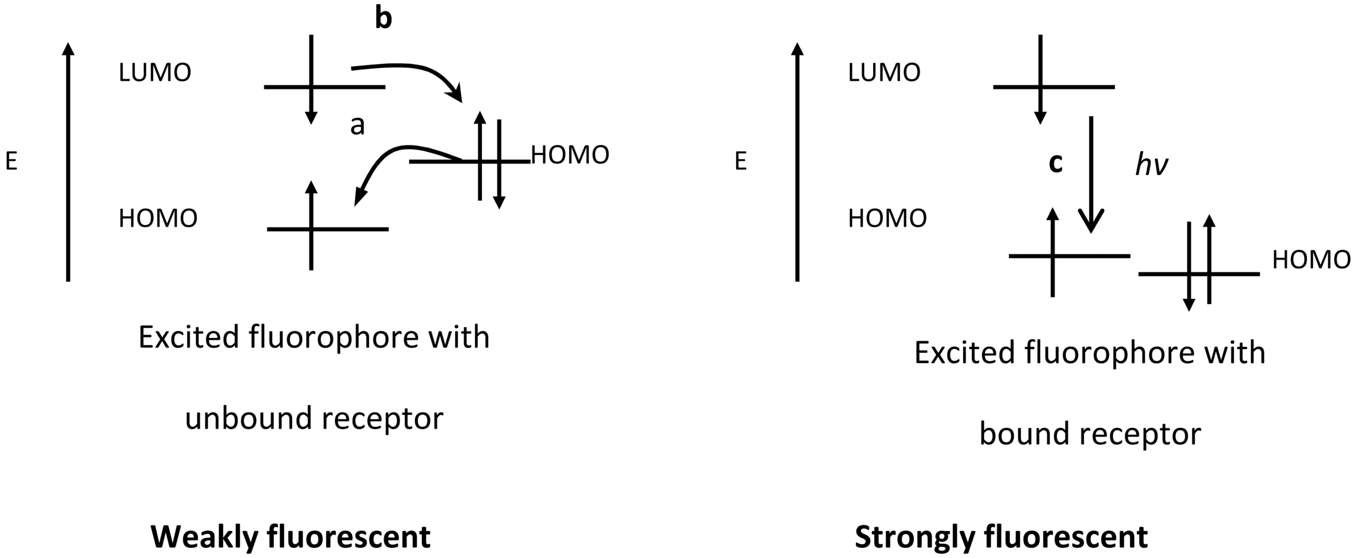


Figure 3.

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

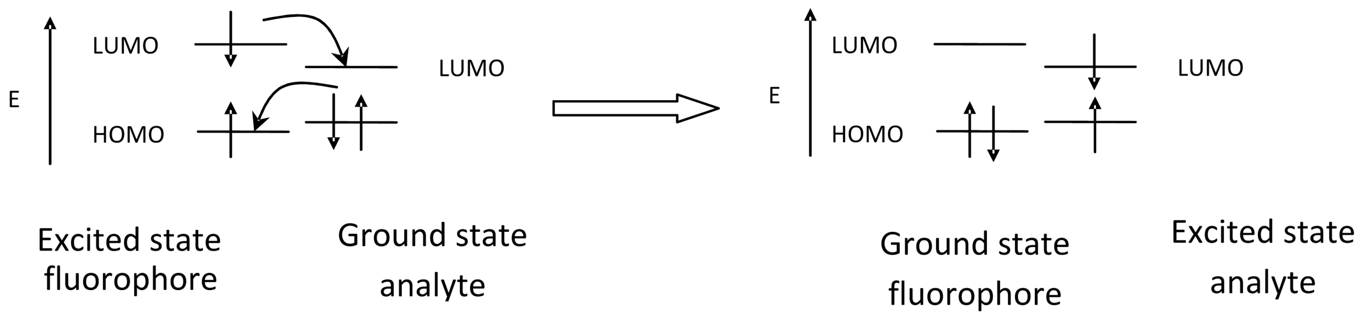
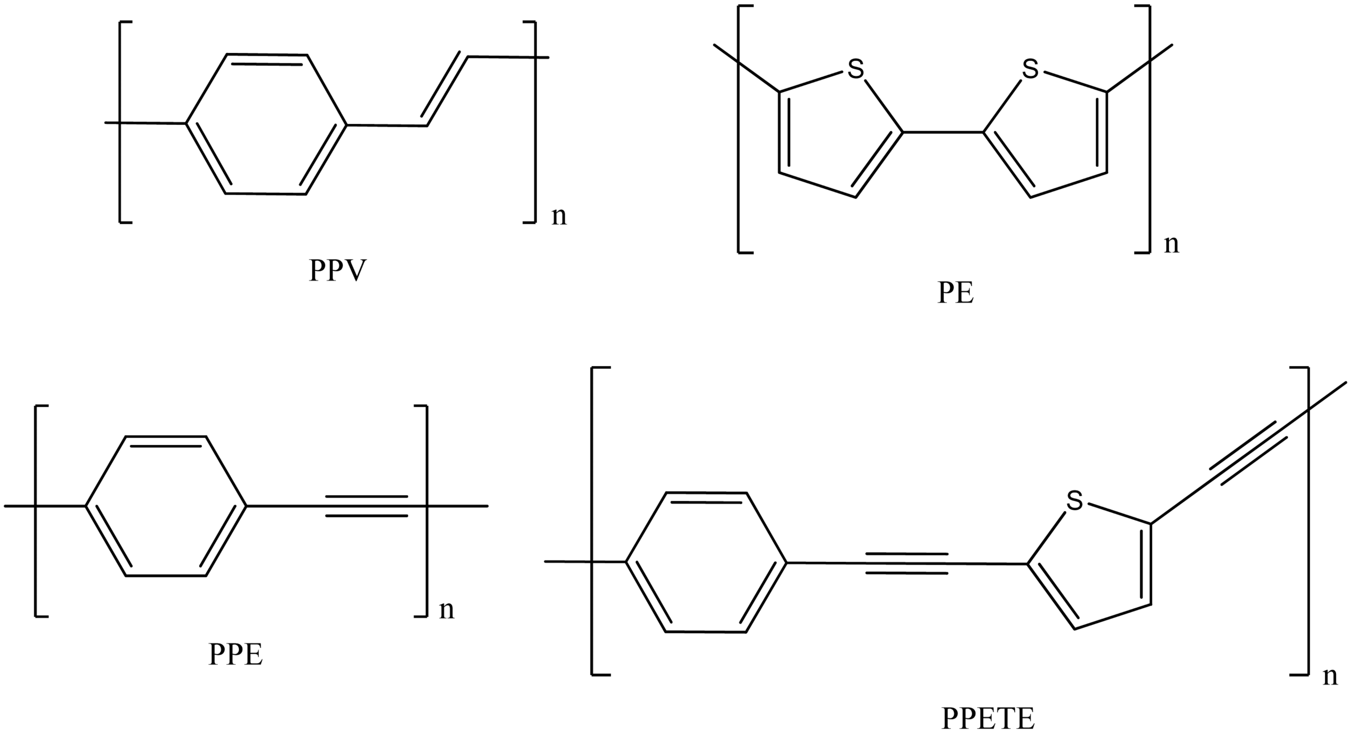


Figure 4.

Orbital energy diagrams for double exchange transfer between the excited fluorophore to the analyte bound by receptor followed by analyte return to the ground state by nonradiative decay.



PPV

PE

PPE

PPETE

Figure 5.
Basic structures of several fluorescent conjugated polymers

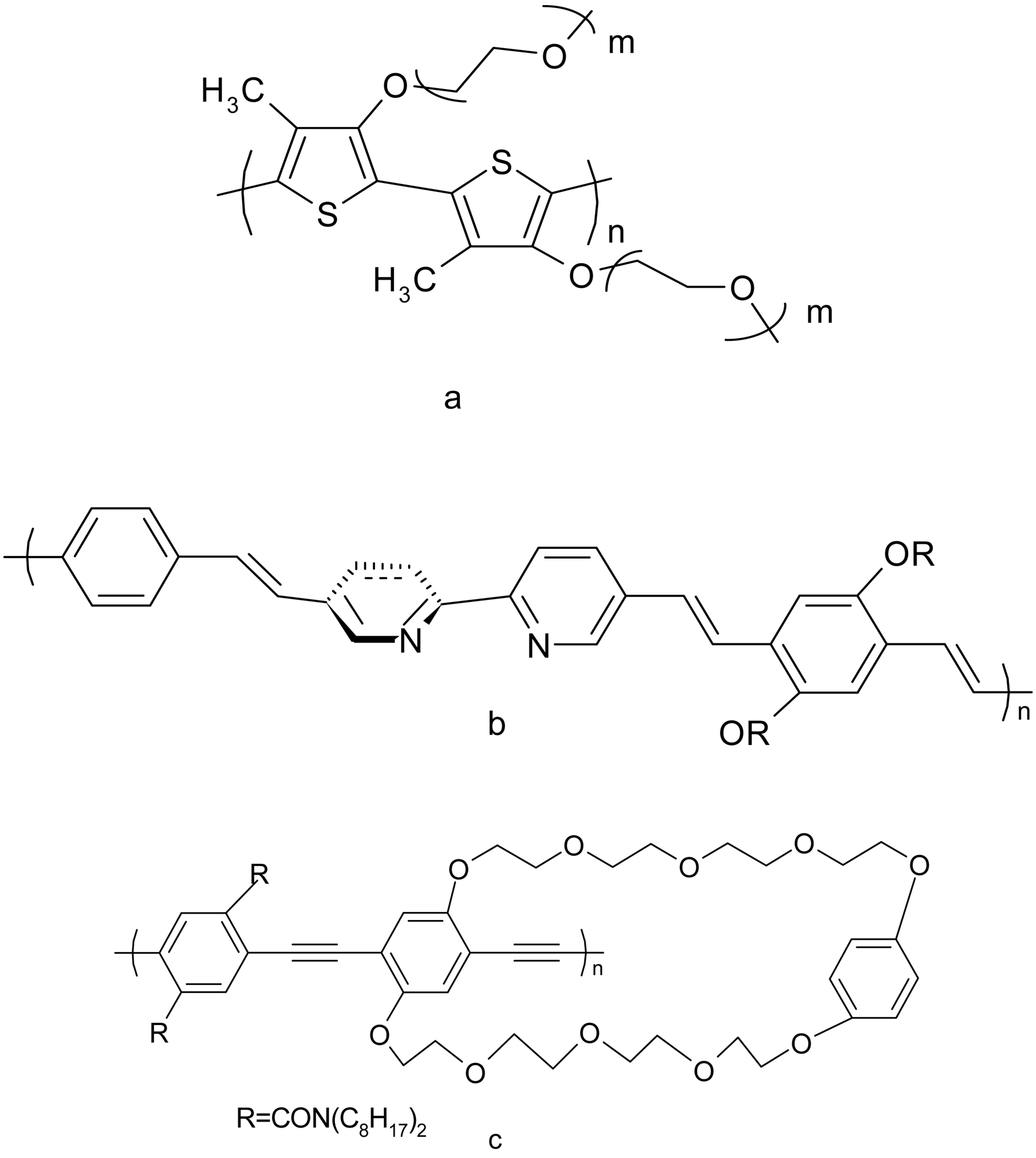


Figure 6.

Structures of several conjugated polymers as fluorescent sensors (a) poly[3-oligo(oxyethylene)-4-methythiophene] [44] (b)poly(bipyridyl-phenylenevinylene) [45] (c) para poly(phenyleneethynylene) [24]

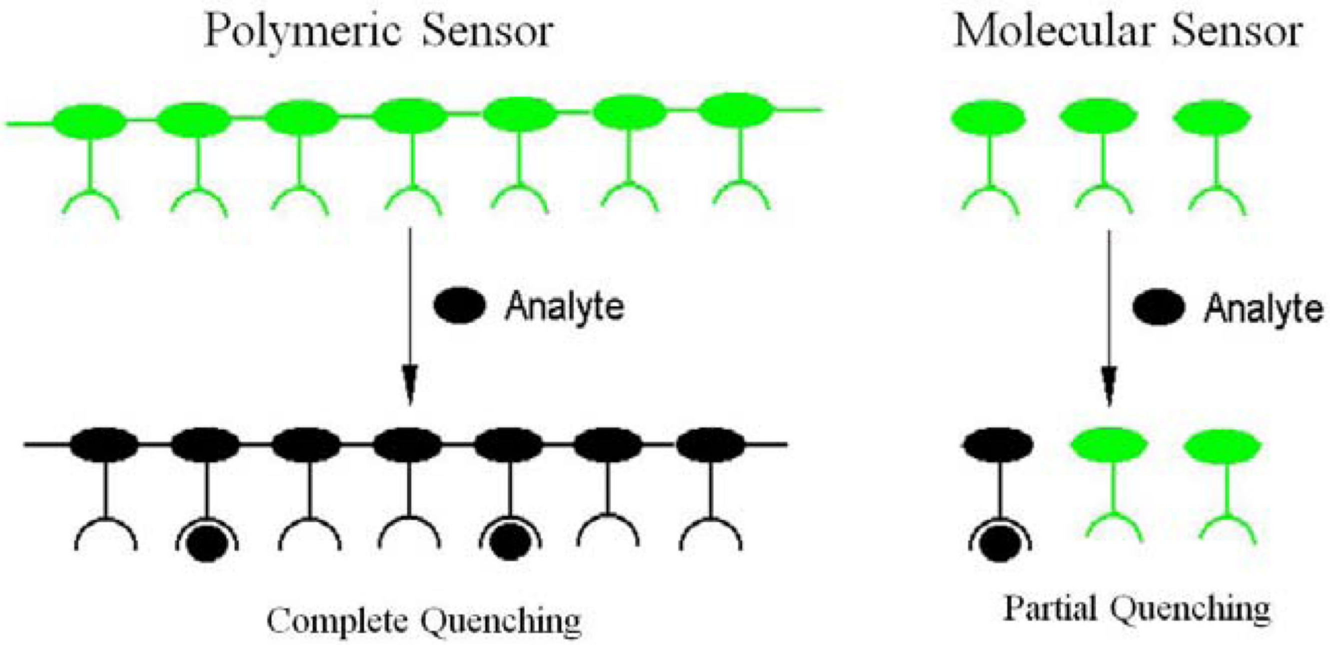


Figure 7.

Schematic representation of sensory signals amplification in fluorescent conjugated polymers/ “molecular wires” a concept advanced by Swager *et al* [22-24].

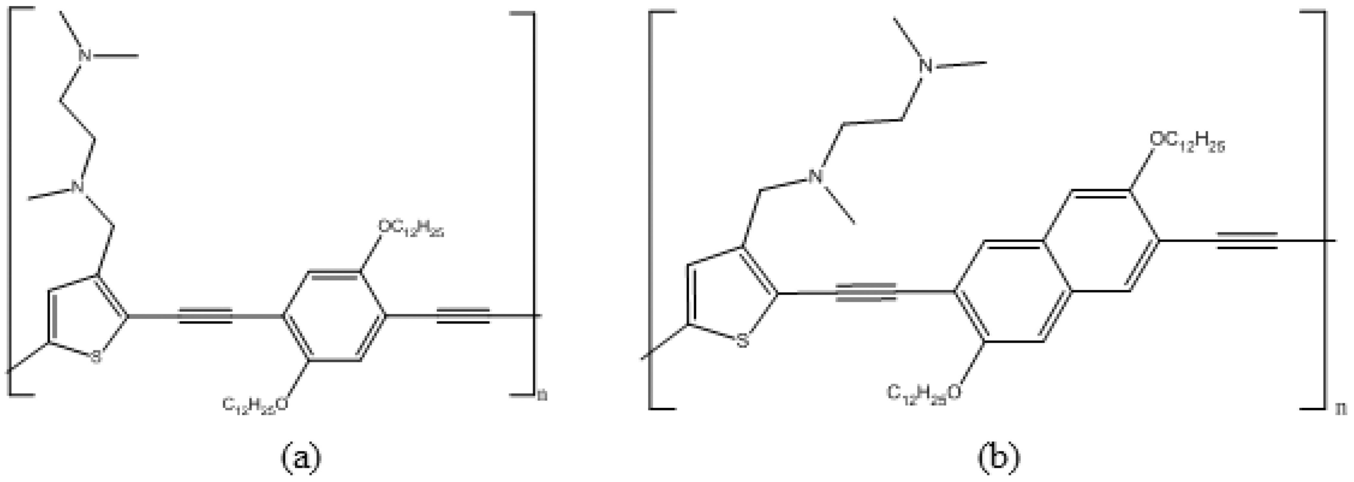


Figure 8.
Structures of (a) tmeda-PPETE and (b) tmeda-PNETE.

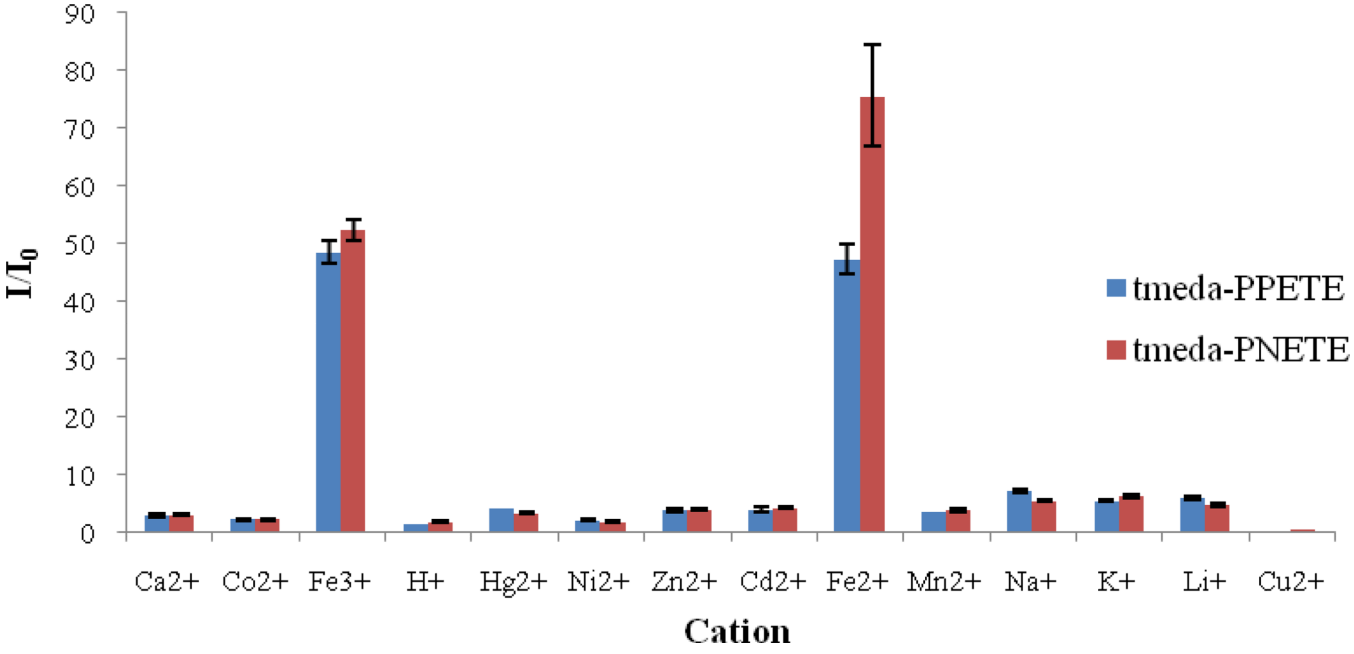


Figure 9.

Fluorescence response of tmeda-PPETE/Cu^{2+} or tmeda-PNETE to various 5μM cation concentrations. Concentration of polymer (with respect to the repeat unit) and Cu^{2+} were 5μM.

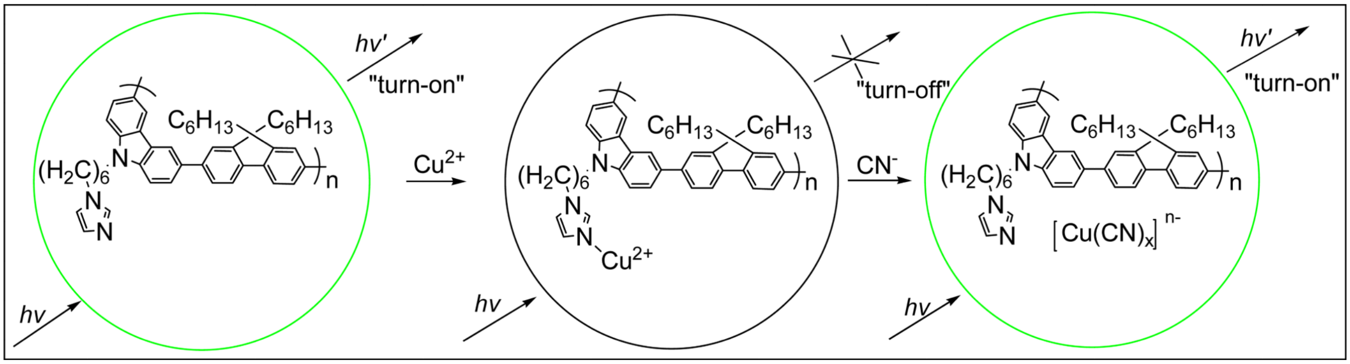
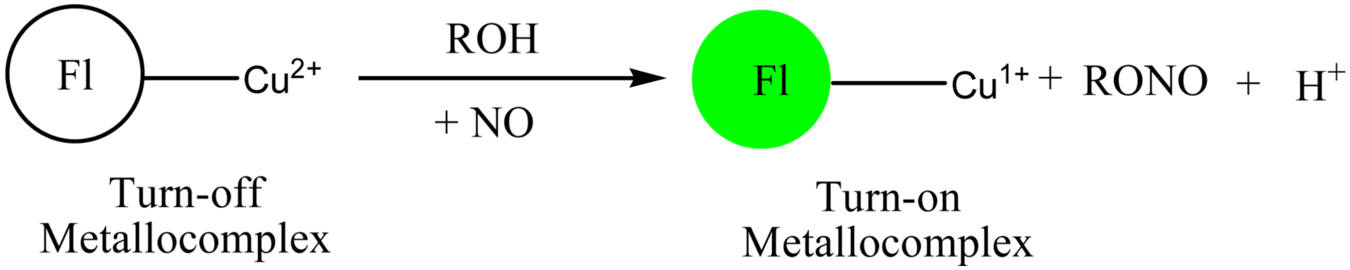


Figure 10.

Polyfluorene chemosensor system for the detection of Cu^{2+} and CN^{-} based on a fluorescence “turn-on” and “turn-off” response. [55]



Scheme 1.

Strategy for Transition Metal-Based Fluorescent Detection of Nitric Oxide by Reductive Nitrosylation [53]