# Conjugated Amplifying Polymers for Optical Sensing Applications

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ABSTRACT: Thanks to their unique optical and electrochemical properties, conjugated polymers have attracted considerable attention over the last two decades and resulted in numerous technological innovations. In particular, their implementation in sensing schemes and devices was widely investigated and produced a multitude of sensory systems and transduction mechanisms. Conjugated polymers possess numerous attractive features that make them particularly suitable for a broad variety of sensing tasks. They display sensory signal amplification (compared to their small-molecule counterparts) and their structures can easily be tailored to adjust solubility, absorption/emission wavelengths, energy offsets for excited state electron transfer, and/or for use in solution or in the solid state. This versatility has made conjugated polymers a fluorescence sensory platform of choice in the recent years. In this review, we highlight a variety of conjugated polymer-based sensory mechanisms together with selected examples from the recent literature.

KEYWORDS: conjugated polymers, fluorescence, chemical sensing, fluorescence quenching, explosive detection, biosensing
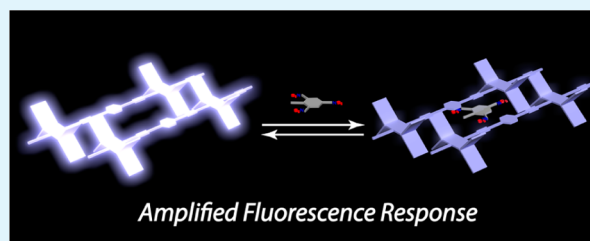
INTRODUCTION

The delocalized electronic structures of conjugated polymers confer on them attractive optical and electrochemical properties. In particular, the large extinction coefficients as well as the highly emissive properties provide great advantages for sensing applications. Indeed, the property that makes conjugated polymers a material of choice for chemical sensing is their ability to translate a binding (or unbinding) event into an easily measurable optical or electrochemical response. As a consequence of their conjugated nature, they display highly efficient intra- and interchain energy transfer. Specifically, when compared to small molecule sensors, conjugated polymers exhibit large signal amplification resulting from the collective response of many conjugated units. In optical transduction, the signal amplification is related to excited state (exciton) transport along a polymer backbone in solution, and to additional inter-polymer transport in aggregates or in thin films. The capture of the mobile (diffusing) exciton by the presence of an analyte is detected as changes in the fluorescence spectrum. The analyte can also promote color changes in the material; however, direct absorbance changes do not benefit from the signal gain provided by exciton transport. Some sensing schemes allow the naked-eye detection of analytes by observing the sensory materials in visible (color change) or black (UV) light (fluorescence change). The synthesis of conjugated materials has been extensively studied and established methods (e.g., Sonogashira, Stille, or Suzuki couplings, or Gilch polymerization) can reliably produce functionalized materials in sufficiently high purity and yields. The present state of the field allows for the design of a diversity of polymers that can be tailored for different applications. For example, water solubility can be achieved by appending ionic and/or poly(ethylene)glycol side-chains, and sterically demanding groups such as iptycenes can give rise to optimal emission in the solid state, as will be demonstrated later. Using established design principles, the electronic properties can also be varied to match specific applications. An illustration of this is that most conjugated polymers can be considered to have low electron affinities (electron-rich) and are highly effective for the detection of electron-deficient analytes such as nitro-aromatic explosives. However, it is possible to invert this axiom and produce electron-deficient polymers that display strong sensory responses to electron-rich bioanalytes. Likewise, complementary charges can play a role and polymer electrolytes that are highly positively charged are effective in the sensing of polyanionic bioanalytes such as DNA. In summary, tailor-made conjugated polymers are readily accessible, and the field is poised to functionalize them with more sophisticated receptors for the development of selective sensory schemes.

In the first part of this review, we describe the fundamentals of energy migration and a selection of seminal articles. Then, we cover a series of analytes that have been investigated by our laboratory, and by others. In particular, we mention sensory polymers for small, electron-deficient molecules, as well as compounds designed for the detection of electron-rich bioanalytes. We conclude by showing sensing assays for biomolecules such as DNA, or for monitoring the activity of enzymes such as proteases. In order to keep this article to a reasonable length and scope, we have mainly focused on selected key studies related to the various mentioned analytes

and sensing mechanisms, and on recent reports that have been published since a previous comprehensive review of the field.[1]

ENERGY MIGRATION AND AMPLIFICATION EFFECT

Excited state (or exciton) migration along conjugated polymer chains to well-defined emissive traps was initially investigated in photophysical studies of rigid-rod, soluble poly(p-phenyl-eneethynylene)s (PPEs).[2] Specifically, upon excitation of anthracene-end-capped poly(p-phenyleneethynylene) 1, the resulting light emission originated predominantly (>95%) from the anthracene end-groups. This observation was attributed to fast exciton (electron−hole pair) transfer to the decreased band gaps (trapping sites) at the polymer's extremities. This antenna effect afforded by exciton migration within and between conjugated polymers is of primary importance to all of the emission-based sensing applications reviewed herein, and to applications that have been abundantly reviewed elsewhere, such as polymer-based organic solar cells,[3−7] field-effect transistors,[3,8,9] and electroluminescent devices.[10,11]


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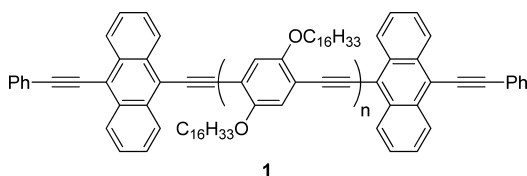
This energy migration facilitated by the π system of a conjugated polymer was subsequently shown to be the basis of signal amplification or superquenching phenomena, where a minority interaction between the polymer and another molecule (analyte) dominates the emission. This concept was demonstrated in poly(p-phenyleneethynylene)s adorned with cyclophane receptors (**2**) for paraquat (PQ^{2+}), a well-known electron transfer quenching agent (Figure 1).[12,13] These studies focused on single isolated polymers in solution and carefully deconvoluted the role of binding and exciton transport as a function of the length of the polymer chains. These studies revealed that the exciton could diffuse over 65 receptors (130 −Ph−CC− units) and thereby produced a 65-fold amplification in sensitivity as compared to an equivalent single-receptor fluorescent molecule. In other words, for polymers isolated in solution that are up to 130 phenylene ethynylene units long, the binding of a single PQ^{2+} is sufficient to quench the emission of an entire polymer chain. This measurement also stands as perhaps one of the most direct measurements of the exciton diffusion length in these polymers. The finite nature of this diffusion length is clearly revealed by the fact that increasing the molecular weight beyond 130 phenylene ethynylene units does not provide an additional increase in efficiency, and is attributed to the finite excited state lifetime (≈ 0.6 ns), the inefficient nature of one-dimensional diffusion processes and the conformational disorder in solution.

Although the solution studies with **2** stand out as the most precise quantification of amplification of fluorescence sensing in conjugated polymers, the level of signal gain is limited by the fact that exciton diffusion is constrained to a one-dimensional random walk process. In this process, the exciton effectively revisits the same sites many times because it is randomly diffusing along an isolated polymer chain. On the basis of simple random walk statistics, simply allowing the excitons more freedom to diffuse in three dimensions should allow for dramatic increases in signal gain. As a result, our laboratory hypothesized that higher-dimensionality polymer assemblies would afford further enhanced sensory properties, owing to interchain excitation transfer for the sampling of the largest possible number of repeating units.[14] These processes were thoroughly studied in thin films of polymer **2** precisely deposited a monolayer at a time by the Langmuir−Blodgett deposition (LB) technique. The power of this deposition method was critical, since not only are the films deposited a monolayer at a time, but the polymer chains are aligned as a
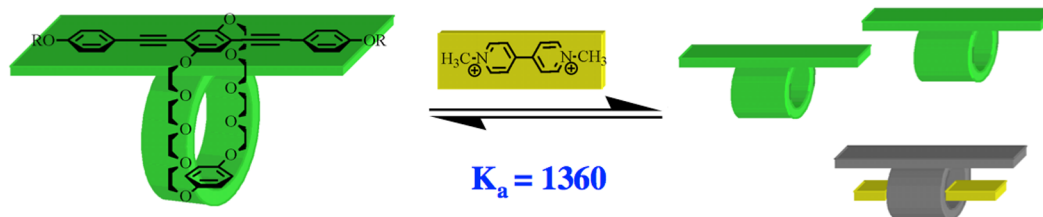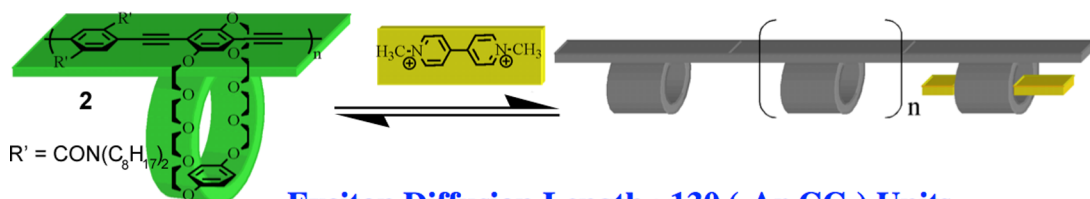
Figure 1. Schematic illustrating the comparative quenching of a monomer and of polymer **2** by PQ^{2+}.

consequence of the fact that the monolayers at the air–water interface are liquid crystalline, and the flow induced in the deposition to a glass slide creates bulk alignment. In contrast, deposition by spin coating affords disordered films. Systematic studies on monolayer assemblies with low energy dyes on the outer surface allowed for the rates of energy transfer to be deduced both within each monolayer and between monolayers. Although intralayer energy transfer is highest along the direction of the polymer chains, energy transfer between monolayers (perpendicular to the polymer chains) also occurs at an extremely high rate ($k > 1 \times 10^{11}$ s^{-1}), and through distances in excess of 10 nm. These results have been the foundation for the design of sensory polymer-based devices, because they prove that polymer films can be formed that possess superior amplification properties compared to the same polymers in solution.

The generalization of these concepts is illustrated in Figure 2 for two different modes of signal transduction. The quenching
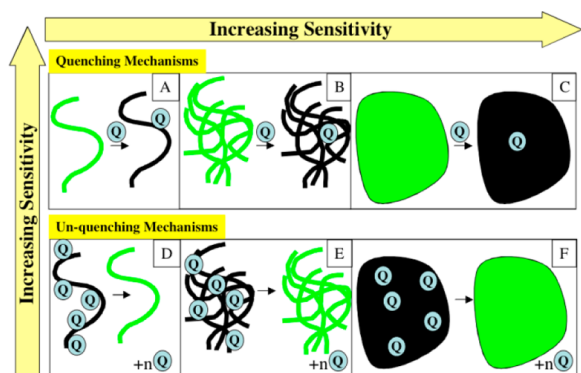

Figure 2. Effect of dimensionality on (un)quenching mechanisms. Quenching mechanisms are by nature more sensitive than unquenching mechanisms (a single quencher can affect the properties of a larger fluorophore), whereas higher-dimension materials display higher sensitivity relative to one-dimensional, or isolated, polymer wires. Reprinted with permission from ref 1. Copyright 2007 American Chemical Society.

mechanism involves the addition of an analyte that quenches the excited state of the polymer through electron transfer or energy transfer. The gain in this process is dependent on the exciton diffusion length and the form of the material, with continuous films displaying the optimal amplification. The unquenching process, although a turn-on mechanism, tends to suffer from lower sensitivity because to obtain a highly quenched state, some of the quenching groups will inevitably be located within the exciton diffusion length. A sensing process that removes these groups will therefore have reduced sensitivity because the removal of a quencher that resides within the exciton diffusion length of another quencher will not restore all of potential fluorescence. We emphasize this point because we have found that it is a common misperception to equate all turn-on mechanisms to higher sensitivity. Clearly, chemiluminescence sensing is extraordinarily sensitive because there is no background fluorescence and single photon counting can be utilized in the signal detection.

An alternative approach to the use of solid-phase polymers for signal amplification is represented by analyte-induced aggregation of polymers in solution. As an example, the anionic conjugated polymer **3** is highly responsive to polycationic

biogenic amines (spermine, spermidine, putrescine, and the antibiotic neomycin) in ethanol/water solutions (Figure 3).[15] The signaling mechanism in this scheme utilizes the tight aggregation that is induced between the anionic polymer chains by the presence of polycationic analytes. This analyte-induced aggregation dramatically increases the efficiency of exciton transfer to minority low-energy anthracene-based traps in the polymer chain, thereby giving a blue to green change in the emission color. The degree of aggregation is critically dependent on the number of charges on the analytes, and for example, analytes with three or more ammonium ions were required to induce aggregation. It is also noteworthy that **3** contains perfluorinated side-chains which appear to assist the polymer to undergo organization in the aggregate that enhances energy migration. Similar aggregation-induced sensory schemes have been developed for polyanionic molecules, as will be detailed later.

It is desirable to have detection assays that can be performed in solutions wherein mixing can allow for rapid diffusion of the analyte to the sensory polymer. However, as mentioned earlier, relying only on intrapolymer energy transfer restricts exciton diffusion and limits the degree of amplification observed in sensing schemes. To achieve higher sensitivity in a solution scheme, we can deposit polymer layers onto silica- or polystyrene-based microspheres.[16,17] Care is needed to minimize polymer aggregation and self-quenching, and pentiptycene groups were incorporated in the anionic PPEs (**4**) in order to prevent π-stacking. The microspheres were coated by layer-by-layer deposition with the polycationic polymer poly(diallyldimethyl-ammonium) chloride (PDAC),[16] as well as by direct adsorption.[17] The emission properties of the polymer-coated microspheres were very similar to that of polymers in solutions (because of the absence of π-stacking). In sensing applications, these polymer-coated microspheres displayed optical properties similar to that of solutions of the same polymers, but with an enhanced sensitivity (up to 200-fold) to electron-deficient nitro-aromatics or to PQ^{2+}-based quenchers. As a result of the amphiphilic character of the polymers, hydrophobic interactions with the quenchers were also found to play a significant role in the interaction mechanism.
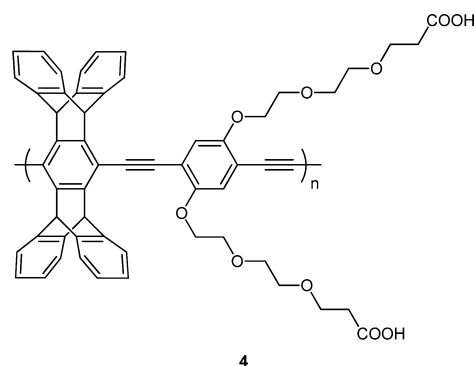
SENSING APPLICATIONS: SELECTED EXAMPLES

Detection of Explosives. Perhaps the most successful application of conjugated polymer sensors is in the detection of nitro-aromatic explosives.[18,19] This work represented an early example of thin film sensors and a series of poly(p-phenyleneethynylene)s were developed (**5a–5c**) that first introduced rigid iptycene moieties into a conjugated polymer backbone.

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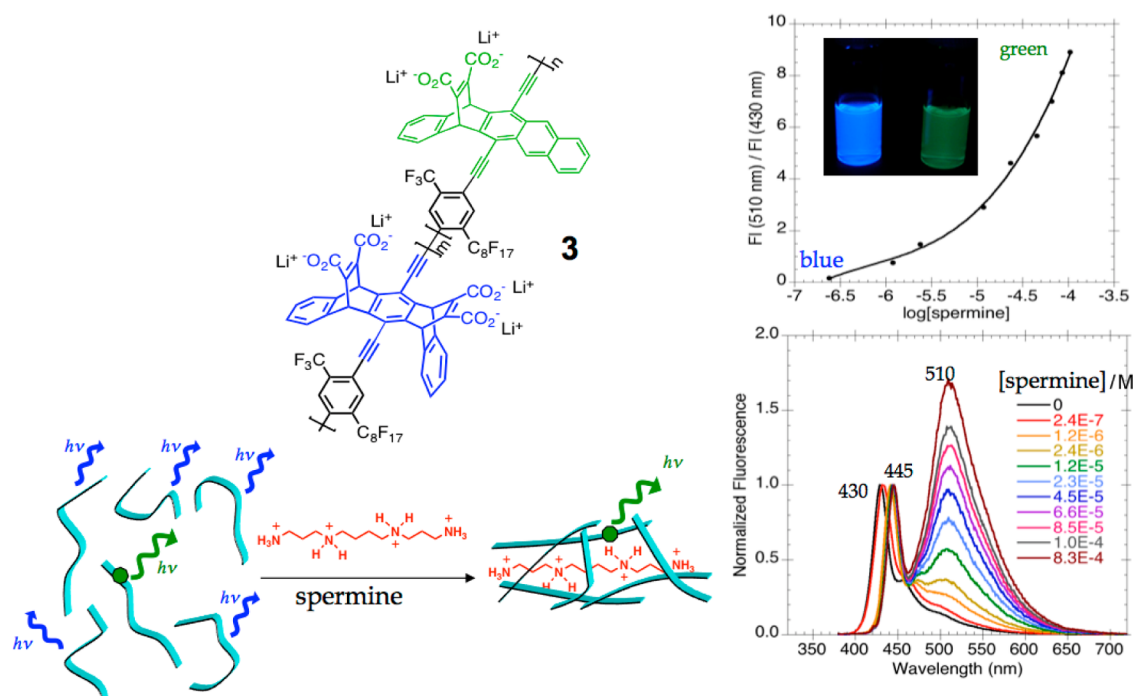
Figure 3. Schematic showing how spermine-induced aggregation of anionic polymer **3** triggers enhanced energy transfer to the minority anthracene emitter. As shown in the associated spectra and plots, submicromolar detection was established.

These designs create materials that display solution-like (non-π-aggregated) optical properties in thin films by preventing quenching interactions that can limit exciton migration. The structures also produce free volume in the films that facilitates diffusion of small molecules into the film, but also give rise to size exclusion properties and insensitivity to larger analytes.[19] The decreased interchain interactions were also found to impart enhanced solubility compared to other poly(p-phenyleneethynylene)s, whereas thin films displayed high fluorescence quantum yields and stabilities. Taken together, these properties allowed the development of powerful sensory devices responsive to electron-deficient small nitro-compounds such as 2,4,6-trinitrotoluene (TNT). The high electron affinity of TNT results in highly efficient electron transfer quenching reactions with the excited state of the polymers. A detailed study[18] identified the influence of polymer properties (electronic structure, film thickness, and morphology) as well as of analyte characteristics (vapor pressure, quenching ability, binding strength with the polymer, and diffusion rate through the film) on the sensitivity and selectivity of several polymers toward small organic molecules. In particular, thin film of polymer **5a** was found to be able to detect TNT at a 10 ppb concentration after a few seconds exposure (passive diffusion), underlying the extraordinarily high sensitivity imparted by energy migration through polymer films. When placed in designed sensory devices, these materials enabled for the real-time vapor detection of trace explosives and commercial sensors based on this technology have been used in the detection of buried landmines, roadside bombs, detection of suspected bomb makers, and a variety of other homeland security-related tasks.[20] An interesting expansion of this work was reported in 2008,[21] wherein multiphoton irradiation was used to excite polymer **6**. Specifically, compound **6** was found to have a large two-photon cross-section, and its response in solution to the presence of low millimolar amounts of TNT was found to be in qualitative agreement with that reported
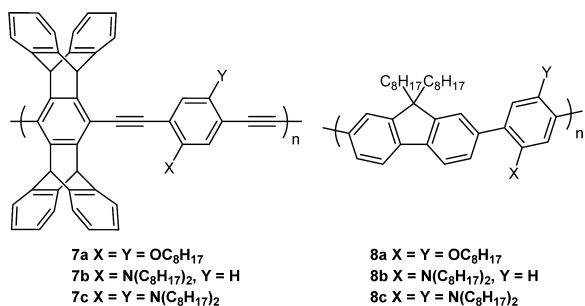
under single-photon excitation conditions for similar polymers. Using multiphoton excitation allows for the use of infrared irradiation, which is advantageous from a safety point of view, but also to reduce scattering and absorbance by the medium and improve penetration depth for stand-off (remote) sensing.

5a R = OC$_{14}$H$_{29}$
5b   CON(C$_8$H$_{17}$)$_2$
6   OC$_{10}$H$_{21}$

5c
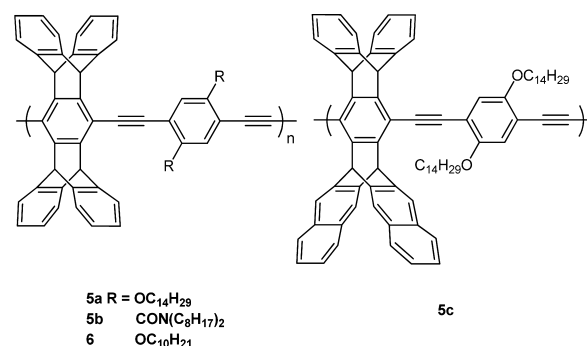
In addition to the direct detection of explosive materials, it is desirable to detect taggants, which are higher-volatility materials added to explosives to facilitate detection. The most widely used taggant is 2,3-dimethyl-2,3-dinitrobutane (DMNB), which is a required additive in all legally manufactured plastic explosives. Rigid poly(p-phenyleneethynylene)s similar to those presented above (**7a**–**7c**) were found to be relatively inefficient for the vapor detection of DMNB. This fact is the result of the lower electron affinity of DMNB (relative to nitroaromatics), and the band energies of the polymers lacked the necessary thermodynamic potentials to display photoinduced electron transfer quenching. Indeed, the LUMO levels of PPEs were found to be too low, even after attempted optimizations, to allow efficient electron transfer to the LUMO of DMNB and result in a quenching of the emission of the PPEs. As a consequence, a series of poly(phenylene)s (PPs), which display larger band gap, and as a consequence, higher-energy LUMO orbitals, were prepared (**8a**–**8c**). This rationale allowed for the
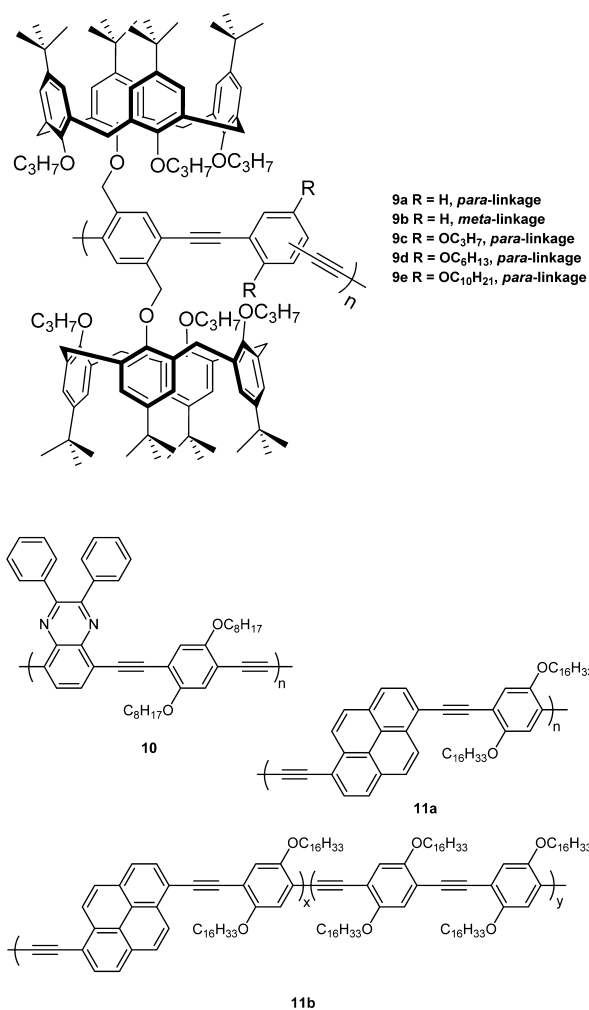
elaboration of polymers that were able to detect DMNB at subppm levels.[22] The detection limits for DMNB are higher than those previously observed for TNT as a result of its physical properties. Indeed, the strong π-associations between TNT and surfaces lead to its intrinsically low vapor pressure, which causes it to preconcentrate in the films. As a result, with long exposure times most materials will be able to detect ppb levels of TNT, and the sensitivity must take into account the response time. Alternatively, DMNB was chosen as a taggant because of its higher vapor pressure that is related to its lack of planarity. As a result, DMNB does not tend to preconcentrate in polymer films and displays fast absorption/desorption kinetics. A combination of electronic structure and photochemical stability results in **8a** being a superior DMNB sensory material with subppm detection limits.

7a X = Y = OC$_8$H$_{17}$
7b X = N(C$_8$H$_{17}$)$_2$, Y = H
7c X = Y = N(C$_8$H$_{17}$)$_2$

8a X = Y = OC$_8$H$_{17}$
8b X = N(C$_8$H$_{17}$)$_2$, Y = H
8c X = Y = N(C$_8$H$_{17}$)$_2$

Considering the interest for the detection of explosives, it comes as no surprise that several research groups have been continuing investigations in this field, and there have been recent reviews of this area.[23−25] Recent examples of PPE-based sensory materials for electron-poor nitro-aromatics involve calixarene-functionalized polymers (**9a−9e**), as well as quinoxaline- and pyrene-incorporating PPE skeletons (**10** and **11a-b**, respectively). The calixarene substituents of polymers **9a−9e** prevent π-stacking in the solid state, thus preserving the optical properties of the material.[26] Further, the bulky, bowl-shaped building block helped form porous materials, and allowed to create films that were highly sensitive to explosives such as TNT or DNT: in the presence of 10 ppb TNT, a 50% emission quenching was recorded in 10 s. In comparison, PPE films not carrying calixarene receptors displayed very limited sensing capacities. The optical properties of films of polymer **10** were indicative of strong interchain interactions (both absorbance and emission were substantially red-shifted going from solution to solid state).[27] Nevertheless, **10** was able to interact with TNT in both solution and the solid state, resulting in a nearly complete quenching of the fluorescence. The relatively limited sensitivity of this system (in the low ppm range) is likely a consequence of strong π-stacking of polymer chains that results in shortened excited state lifetimes and trapping. Thin films of the pyrene-containing polymers[28] (**11a** and **11b**) were found to be responsive when immersed in aqueous solutions containing low micromolar amounts of TNT. The pronounced emission quenching was attributed to the formation of nonfluorescent complexes between the polymer and TNT, which is promoted by matching the polymer's orbital energies with those of the analyte. The presence of pyrene units was found to be essential, and provided selectivity for TNT over the usual interferent analytes such as DNT (dinitrotoluene), nitrobenzene, and trinitrophenol.

In addition to PPEs, numerous classes of conjugated polymers have been investigated for the sensing of explosives.

9a R = H, *para*-linkage
9b R = H, *meta*-linkage
9c R = OC$_3$H$_7$, *para*-linkage
9d R = OC$_6$H$_{13}$, *para*-linkage
9e R = OC$_{10}$H$_{21}$, *para*-linkage

10

11a

11b

Poly(*p*-phenylene)vinylenes (PPVs) have been reported as being efficiently quenched by viologen-type fluorophores and to act as amplifying polymers,[29] and hence they similarly function in the detection of electron-poor nitrated aromatics. PPV derivative **12** was found to be responsive to TNT, both in solution and in the solid state.[30] In solution, fluorescence quenching by TNT is observed together with a slight to moderate red-shift of the emission maximum, suggesting that TNT changes the polymer's conformation. Interestingly, compound **12** was found to be responsive enough to allow detection of TNT on surfaces, and the authors report a color change when the polymer is sprayed on traces of TNT. Similarly to polymer **6**, PPV compound **13** was found to have a large two-photon cross-section, and could be employed for the multiphoton detection of TNT.[21] As was described for the above-mentioned PPE polymers, large triptycene moieties prevent interchain interactions and dense packing in the solid state. Nevertheless, PPV **13** was found to be less responsive to TNT than the PPE reported in the same study (**6**), which was attributed to the advantageous rigidity displayed by PPEs, that results in enhanced exciton transport as compared to that of more flexible PPVs. Other recent uses of PPVs for the detection of explosives have focused on systems where the sensory polymer was deposited onto porous materials or nanoparticles. The adsorption of the commercially available MEH-PPV (**14**) on porous silica creates a composite material responsive to vapor traces of TNT, as evidenced by fluorescence and reflectance measurements.[31] The benefit of using a porous substrate was reflected in the wavelength-dependence

of the fluorescence quenching, which was modulated by the resonance of the microcavities.

Building on the demonstration that under certain conditions, PPVs can efficiently act as lasing materials and therefore act as superior sensory substrates,[32] the sensing abilities of polymer **15** were evaluated after deposition onto titania nanoparticles.[33] Compound **15** displayed lasing emission that was 20 times more sensitive to explosive vapors than spontaneous emission. As a result, TNT vapor was detected at 10 ppb concentrations by observing the induced cessation of the lasing emission. An alternative, PPV-based scheme involves the formation of unsubstituted PPV inside mesoporous silica nanoparticles, which were functionalized with amines.[34] When dispersed in ethanol these particles display the expected PPV emission. Upon addition of TNT, Meisenheimer complexes are formed between TNT and the amines inside the pores. These charge-transfer complexes are highly absorbing, and therefore able to quench the PPV emission via a FRET process, as opposed to the electron-transfer quenching mechanism. DNT displays a much lower response because of its decreased electron accepting properties and lower propensity toward Meisenheimer complex formation.

12   **13**   R = OC$_8$H$_{17}$


14   **15**
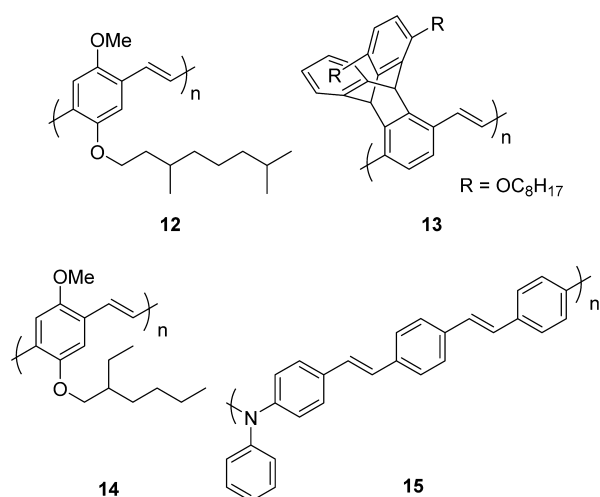
Oligo(*p*-phenylenevinylene) **16** is a fluorescent organogelator that forms fibrous structures when coated onto glass or paper substrates. Solution-based experiments showed a weak quenching of the fluorescence in the presence of sub- and low millimolar concentrations of TNT. However, exposure of fluorescent xerogels of **16** to vapors of nitro-aromatic compounds resulted in a very efficient emission quenching. X-ray diffraction studies revealed that the presence of absorbed nitro-aromatics in the interstitial space of **16** has a negligible impact on the packing, and the fluorescence quenching was attributed to excited-state phenomena and fast exciton migration within the self-assembled structures.[35] Exploiting the solid-state behavior, a simple filter paper-based assay was developed that was able to detect attograms of TNT by simple contact with a contaminated surface. Alternatively, the same paper strips were demonstrated to respond to aqueous solutions containing ppq concentrations of TNT.

Polymers incorporating silicon-based units have been widely investigated for their sensory properties. Polysiloles are effective in the detection of nitro-aromatic explosives[36] thanks to characteristic low-lying LUMO orbitals that result from mixing of the π^* and σ^* orbitals to give delocalized excited states that

R = C$_{16}$H$_{33}$ **16**
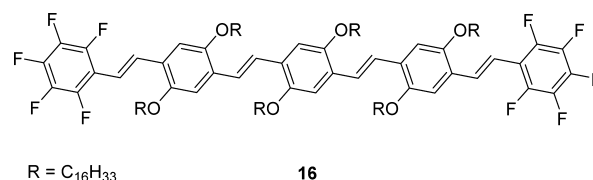
promote exciton diffusion.[24,37] A series of poly(silole)vinylenes (**17**−**19**) was prepared, and vinylene linkers were found to promote additional ground-state σ^*−π or excited-state σ^*−π^* mixing to give delocalized electronic states.[38] The solid-state fluorescence of polymers **17** and **18** was quenched in the presence of nitro-aromatic explosives, and the open structure of polymer **19** allowed for a less selective response to a wide array of explosive molecules and a detection limit of 200 pg cm^{-2} for Tetryl (i.e., 2,4,6-trinitrophenylmethylnitramine). Lewis acid−base interactions between the silicon centers and the nitro groups of the analytes were proposed as the driving force for this sensing scheme.


17   **18**   **19**
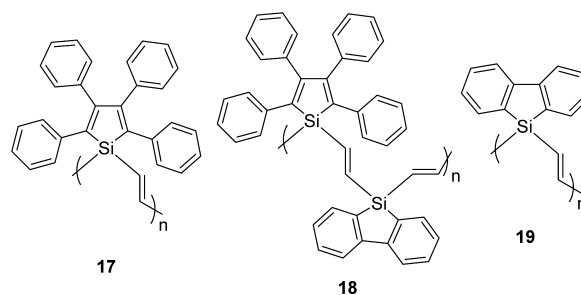
Polymers **20a**−**20c** contain fluorenyl building blocks that are conjugated to the silicon centers through vinylene bridges.[39] Both fluorene and silafluorene proved necessary to confer improved processability and optical properties on the polymers, and efficient fluorescence quenching of thin films of polymers **20a**−**20c** was observed in the presence of trace explosives. This response was attributed to excited-state electron transfer from the polymers to the LUMO of nitrated aromatics captured at the silacycle rings. The same type of polymers linked to silica gel plates display more efficient quenching, thereby allowing lower visual detection limits (down to 4.5 pg mm^{-2} for the detection of TNT with **20c**).[40]

20a: R, R' = H, H
**20b**: R, R' = CH$_3$, CH$_3$
20c: R, R' =
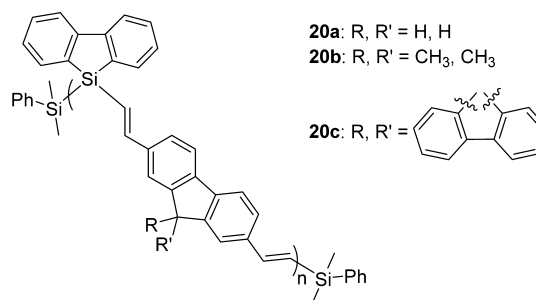
Polymer **20b** was also integrated into silica nanoparticles[41] that were suspended in aqueous solutions and displayed a pronounced quenching of the emission when treated with dissolved explosives TNT or RDX (cyclotrimethylenetrinitramine). These water-dispersible **20b**-coated nanoparticles possess a 35-fold increase in sensitivity for the detection of TNT (200 ppb), as compared to solutions of **20b** in toluene. Under the same conditions, an 800 ppb detection limit was determined for RDX, an explosive compound rarely targeted by conjugated polymer-based

sensing schemes. These enhanced sensing abilities were attributed to the close proximity between explosive analytes and polymers induced by the strong affinity of the analytes for the silica nanoparticles.

Hyperbranched conjugated polysiloles[42] and poly(silylene)-phenylenes[43] have limited fluorescence in solution as a result of fast nonradiative transitions mediated by intramolecular rotation of the phenyl rings. Their fluorescence is enhanced by addition of a "poor" solvent (e.g., water) which produces aggregation-induced emission (AIE).[44] The aggregates of these hyperbranched polymers, **21** and **22**, responded to picric acid (PA) with a 1 ppm limit in solution through emission quenching.[42,43] The authors point to the combined roles of the aggregates, the expanded conjugation with Si-containing fragments, and Lewis acid−base interactions as producing the necessary recognition process.


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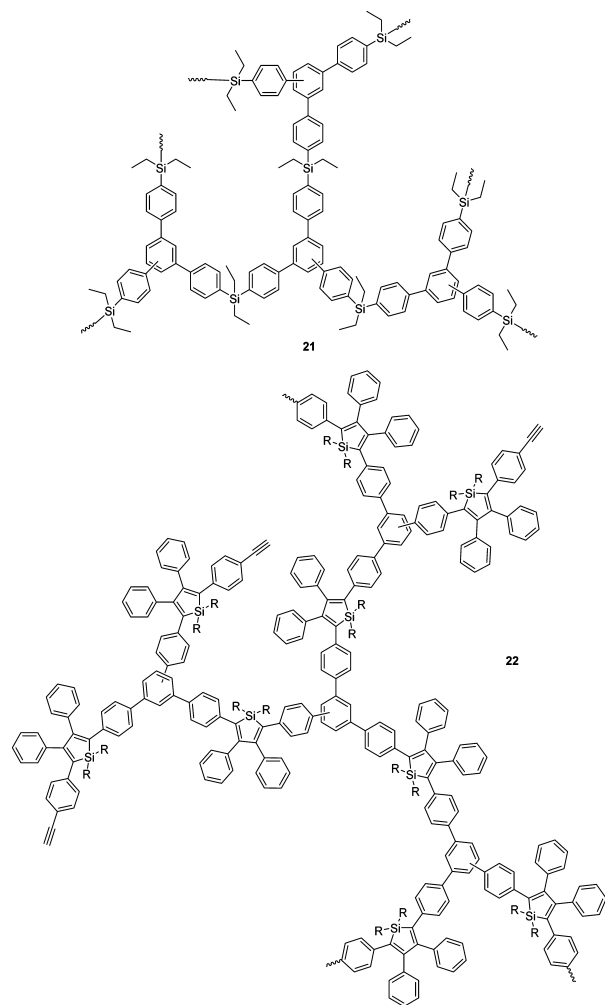
Recently, poly(arylene)ethynylene silols have also been reported for the solution-based detection of electron-deficient explosive compounds. The aggregation-induced emission of compounds **23**[45] and **24**[46] was quenched in the presence of nitrated aromatics (PA, TNT, DNT) in organic solvents, allowing detection of such compounds in the low parts per million concentration range. As in formerly described silicon-containing polymer sensors, the recognition relies on Lewis acid/base interactions between the nitro groups of the explosives and the silacycle cores, whereas the emission quenching results from excited-state electron transfer.
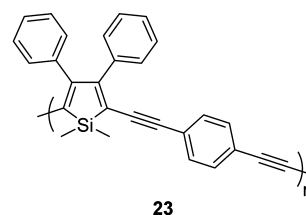
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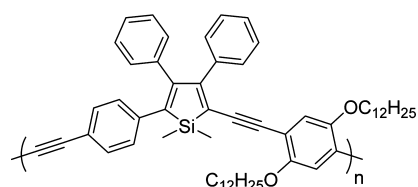
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Polythiophenes have been relatively rarely investigated in the context of small molecule fluorescence sensing applications. It was demonstrated that polymer **25** with long alkyl side-chains did not display aggregation-induced emission quenching in the solid state.[47] When exposed to vapors of TNT or DNT, thin films of polymer **25** displayed a strong, fast and reversible response. The very polar triazole groups were proposed as the basis of a strong interaction between the polymer and nitro-aromatic compounds, resulting in an efficient fluorescence quenching. The intensity and kinetics of the response were slightly below those that were determined for PPE **5a**.
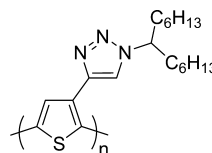
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In addition to poly(phenylene)s **8a−8c**, which were mentioned earlier for their ability to interact with taggant DMNB,[22] other poly(phenylene)s have been investigated in the context of nitro-aromatic sensing. In particular, it was reported that polymer **26**, with bulky groups (alkyl chains and, interestingly, cholesteryl moieties) along a poly(fluorene)phenylene backbone,[48] displayed limited interchain interactions in thin films that were porous to allow DNT vapor molecules to penetrate them. As a result, the emission of the polymer was rapidly quenched, and at sufficiently long exposure times, the emission was completely extinguished. Polymer **26** was further incorporated in an optic-fiber probe, allowing remote detection of explosive compounds.
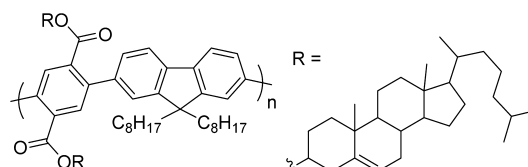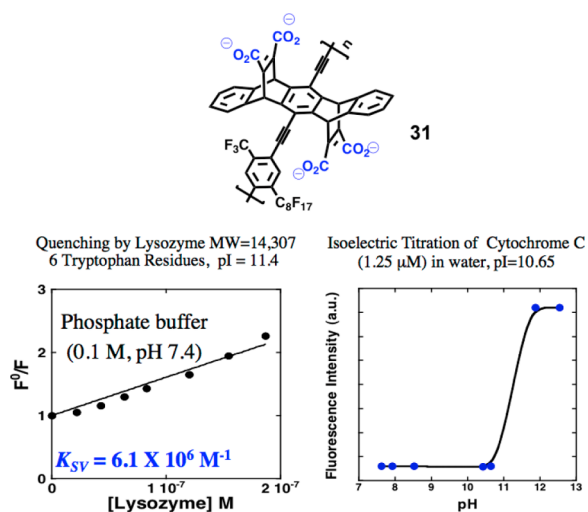

26

Detection of Hydrazine. Contrary to the "turn-off" response of conjugated polymers **5−8** to vapors of electron-deficient small molecules (TNT, DNT, DMNB), hydrazine's reducing power was found to create increases in the emission intensity in thin films of polymer **6**, **7b**, or **7c**.[49] These polymers are electron-rich and are readily photo-oxidized to give a few quenching sites that dramatically lower their emission.

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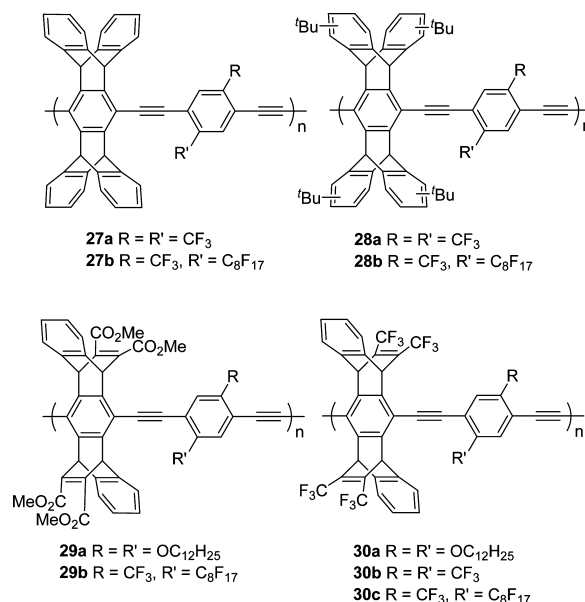
Trace vapors of hydrazine are able to reduce these oxidized defects, resulting in an "unquenching" mechanism. It was found that the polymer that is the most readily oxidized (7c) gives a larger on–off ratio upon exposure to hydrazine. Hence, this unique, alternative mechanism makes it possible to detect a very toxic compound such as hydrazine at a 100 ppb concentration (10% of its permissible exposure limit).

Detection of Electron-Rich Small Molecules. As a complement to the common electron-rich conjugated polymers, electron-poor (high electron affinity) polymers 27–31[50,51] were developed for the detection of electron-rich analytes. These PPEs contain [2.2.2] bicyclic ring systems structurally related to iptycene-based fragments in order to prevent π-stacking, increase solubility and enhance emission intensity in the solid state. The electron-withdrawing substituents increase the ionization potential (lower the HOMO level) of the polymers, such that they have sufficient excited state oxidation power to undergo electron transfer quenching with electron-rich species. A unique effect in these types of materials is the homoconjugation between the bridging electron-poor alkene in the [2.2.2] ring system and the polymer backbone that allows an additional mechanism for the tailoring of the electronic energy levels. In accord with these designs, the emission of thin films of polymer 30c are quenched by indole vapor, whereas no change was observed in the presence of the electron-poor DNT, which broadly quenches most conjugated polymers' emission. The electron-poor nature of polymers 29b and 30c resulted in the formation of excited-state charge-complexes (exciplexes) with electron-donating analytes such as indole, dimethylaniline, 1,4-dimethoxybenzene, and N,N-dimethyl-p-toluidine. The new long wavelength emission from these exciplex species suggests new modes for the selective detection of electron-rich aromatic analytes.
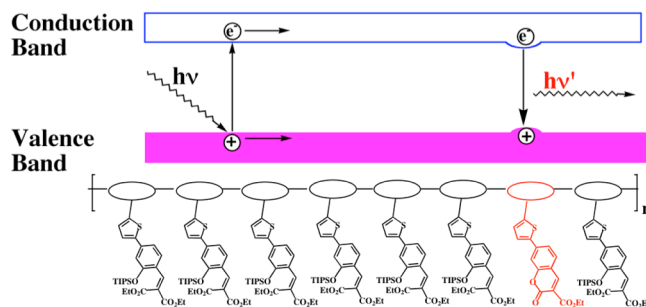
The utility of these electron-deficient polymers for biological sensing was demonstrated with the water-soluble polymer 31, and electron-donating bioanalytes (amino acids, proteins, or neurotransmitters) could be detected at trace concentrations through amplified quenching of the polymer's fluorescence (Figure 4).[50]

27a R = R' = CF_3
27b R = CF_3, R' = C_8H_{17}

28a R = R' = CF_3
28b R = CF_3, R' = C_8H_{17}

29a R = R' = $OC_{12}H_{25}$
29b R = CF_3, R' = C_8H_{17}

30a R = R' = $OC_{12}H_{25}$
30b R = R' = CF_3
30c R = CF_3, R' = C_8H_{17}

Detection of Fluoride Anion. Selective detection of fluoride anion by compound 32a was achieved by exploiting the unique reactivity of fluoride with silicon.[52] Specifically, a fluoride-triggered removal of the silyl protecting group resulted in the formation of a highly emissive coumarin fluorophore (32b), that was integrated into a polymeric structure (Figure 5).
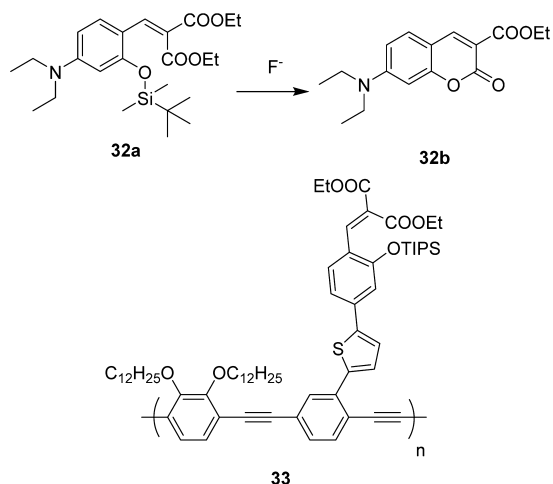

Figure 5. Schematic band diagram showing how an exciton migrates along polymer 33 until it reaches a trap created by the presence of a coumarin unit produced by the fluoride-triggered lactonization reaction. As a result, a new, amplified emission is observed. Reproduced with permission from ref 52. Copyright 2003 Wiley–VCH.

Figure 4. Polymer 31 is a powerful photo-oxidant that is quenched by tryptophan units in cationic (high pI) proteins. Note that the electrostatic assembly allows for the direct measurement of the pI of the analyte.
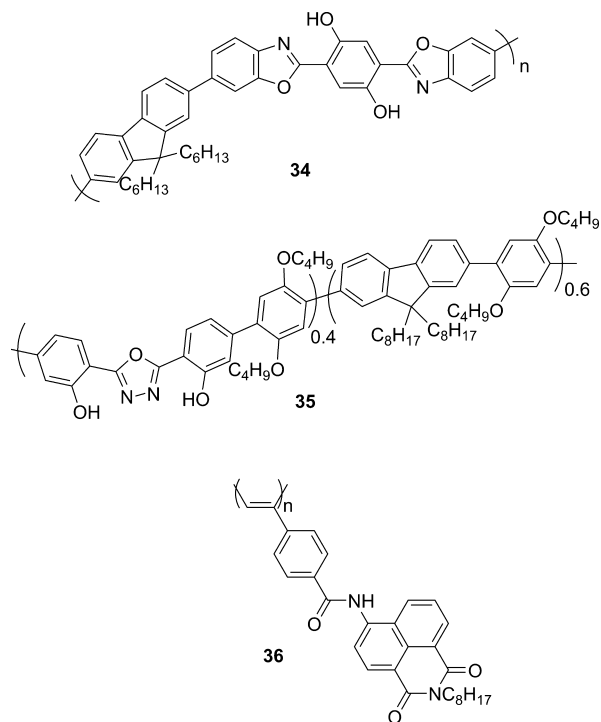
To optimally implement this polymer-based amplifying scheme, polymer 33 was prepared with the goal of creating a strongly electronically coupled coumarin unit. As expected, fluoride-induced formation of coumarin residues along the PPE polymer chain acts as local band gap traps for the mobile excitons and gives an amplified signal. As a result, the presence of submicromolar amounts of fluoride translates into a highly enhanced emission (up to 100-fold) compared to single molecule-based detection. In addition to increased fluorescence quantum yield, the fluoride-induced cyclization translates into red-shifted absorbance and emission bands compared to those of original polymer 33.

Recent conjugated polymer-based fluoride sensing schemes have relied on alternate mechanisms. The polymer 34 exhibits a low fluorescence quantum yield as a result of the presence of bis(hydroxyphenylbenzoxazole) groups. However, in the presence of anions (such as fluoride, acetate or hydroxide), the fluorescence is enhanced by as much as a factor of 20, and
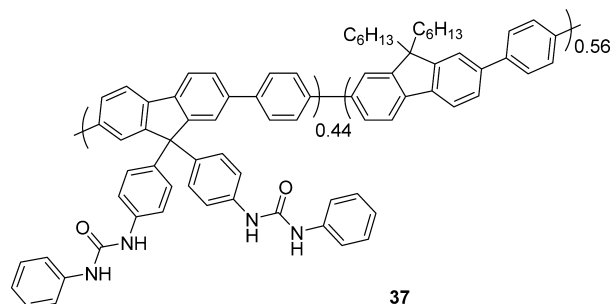
32a → **32b**

33

naphthalimide groups. Submillimolar concentrations of F^- are detected by polymer **36**, which displays a transition from blue to orange in its emission color.[55] Fluorescence quenching of random copolymer **37** in the presence of fluoride, acetate, or dihydrogen phosphate was reported,[56] and was attributed to an enhanced photoinduced electron transfer (PET) process when anions were complexed by urea protons through H-bonding, thus increasing the electron density on the polymer side-chains.

37

undergoes a slight red shift. This behavior is attributed to deprotonation of bis(hydroxyphenylbenzoxazole) by the basic anions.[53] The resultant anionic chromophore is then unable to undergo the efficient nonradiative processes that quenched the fluorescence. Polymer **35** also contains acidic OH groups and responds to fluoride in a selective fashion (only dihydrogen phosphate also showed a minor response). Contrary to the response of polymer **34**, a 380-fold reduction of the emission of polymer **35** is observed in the presence of fluoride. H-bonding between fluoride anions and the highly acidic phenolic protons are proposed as the basis of this selective sensing scheme. The polymer also displayed greater sensitivity as compared to small molecules for the detection of fluoride, and the proportion of oxadiazole units in the structure proved critical in order to achieve optimal performance.[54]
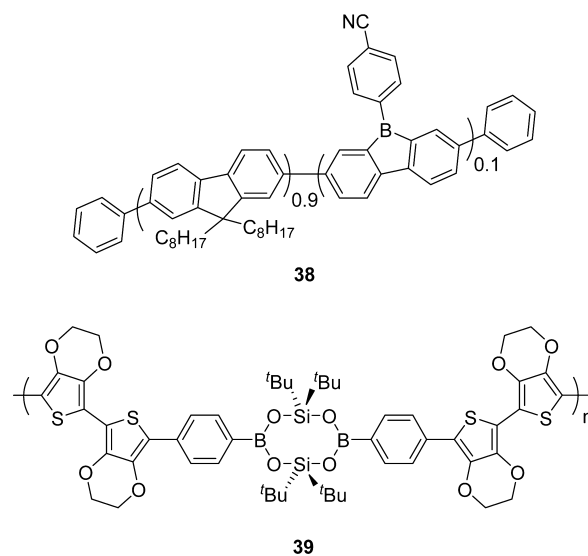
Approaches based on Lewis acid−base interactions have also been devised. For example, random copolymer **38** bearing acidic borane groups was reported and its response to fluoride, iodide and cyanide was studied.[57] Although it lacked selectivity, **38** could detect F^- in the submillimolar concentration range in THF by a fluorescence quenching mechanism induced by notoriously strong boron-fluoride interactions. Fluoride and cyanide were found to quench the fluorescence via static quenching mechanisms, whereas iodide induced collisional quenching. Organoboron polymer **39** displays a through-space electronic coupling between polythiophene fragments with a UV−vis spectrum that is noticeably red-shifted compared to that of monomeric fragments.[58] In the presence of fluoride, a reversible quenching of the fluorescence was observed that was attributed to the formation of B−F bonds. Upon reaction with fluoride, the p_z orbital of the boron center is removed from the conjugated system, which results in an increased band gap and a blue-shifted absorbance band that can be visually detected when a thin film of polymer **39** is exposed to F^-.

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In polyacetylene **36**, the naphthalimide side-chains are isolated from the polymer backbone. In the presence of fluoride, the amide is deprotonated, which results in extended conjugation connecting the polymer's π-system with that of the

Sensing of Cyclic Ketones. The detection of simple alkyl carbonyl compounds is challenging as a result of their low basicity and high band gaps. Cyclohexanone is an analyte of interest because it is used to recrystallize the highly explosive

compound RDX and can be a vapor signature of explosive compositions. The detection of cyclic ketones was accomplished by the noncovalent association of a light-collecting polymer and a receptor containing a fluorescent dye.[59] The green emitting PPE **5a** possessing pentiptycene units has the molecular porosity that allows the diffusion of cyclic ketones into the bulk, and the associated free space allows for some mobility of the embedded red-emitting squaraine-based sensing units **40**. Dye **40** also has an integrated urea unit for hydrogen-bonding interactions with cyclic ketones. A unique aspect of these sensors is that the squaraine dye's absorption has negligible overlap with the emission of the polymer and therefore, the Förster energy transfer to the low energy dye is minimal. Nevertheless, only a few percent of the low energy squaraine dye is required to dominate the emission, and efficient energy transfer is mediated by an electron exchange mechanism. Hence, in contrast to Förster energy transfer that can occur over long distances, the dominating energy transfer to the squaraine dye is highly dependent on very short-range orbital overlap. This mechanism allows for large fluorescence changes to be induced by small changes in the interactions of the dyes with the polymer backbone. Consequently, exposure of the dye/polymer composite to cyclic ketone vapors (cyclopentanone, -hexanone and -heptanone) produced ratiometric emission responses with the emission of the squaraine dye decreasing and the polymer's emission increasing. Studies of a number of different ketones as well as parallel quartz crystal microbalance studies unraveled several effects that contributed to the unique sensitivity to cyclic ketones. In particular, the steric hindrance around the ketone functionality could limit the binding with the urea-containing dyes, larger ketones partition more effectively into the sensory films, and there can be commensurate swelling of the film which can reduce self-quenching of the polymer. Remarkably, this scheme allows sensitive detection of analytes possessing no electronic states capable of interacting with the electronic properties of either the polymer or of the dye. These sensors are particularly effective for cyclohexanone and a vapor phase detection limit of 4.76 ppm was determined.


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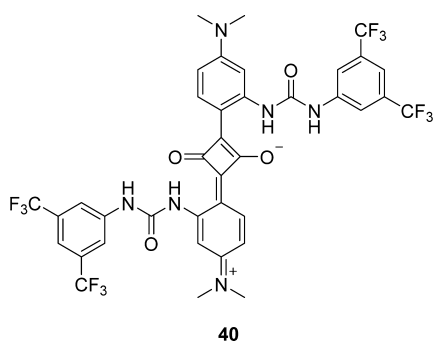
Detection of Ethylene. As a turn-on fluorescence sensing scheme for the plant hormone ethylene, a conjugated polymer was developed that could bind to a copper(I) scorpionate complex (**41**), which displays strong albeit labile interactions with ethylene.[60] Reversible copper(I) coordination to the polymer is observed and results in the emission being quenched. However, a small concentration of ethylene shifts the equilibrium to the ethylene−copper(I) complex and thereby restores the polymer's emission.[61] Quantum calculations revealed that the planarity and conjugation of the Ar−CC−Ar linkages in a PPE would be strongly disturbed by

the steric demand imposed by complexation of the alkynes with **41**. Therefore, polymer **42** (poly(*p*-phenylene butadiynylene) was prepared in order to allow sterically more accessible dialkyne linkages to interact with copper complex **41** and thereby minimize the disruption of the π system. This scheme also provides some molecular level porosity as a result of the shape-persistent pentiptycenes for rapid gas diffusion in the film. As a result, this system works both in solution and in thin films and was able to detect ethylene in the micromolar range (solution-based measurements) and at 1000 ppm concentration (vapor-phase measurements).

41

42
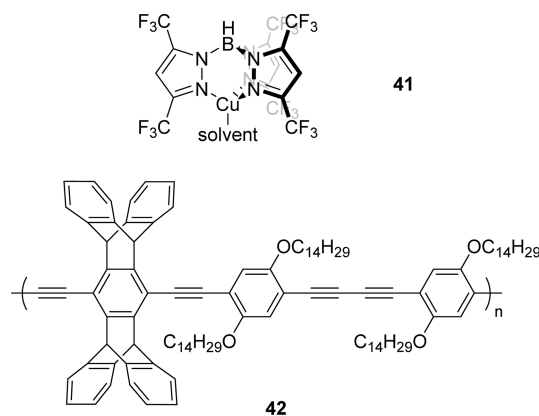
Ag(I) salts embedded in polymeric or oligomeric matrices have also been found to function as sensory systems for ethylene.[62] Ethylene, ammonia and propylene induced fluorescence quenching, and a system made of oligomeric 1,4-bis(methylstyryl)benzene (BMSB, **43**) impregnated with AgBF$_4$ was responsive to ethylene vapor at a pressure of 50 Torr. The presence of silver ions is essential in this mechanism, as they serve as recognition units for ethylene, and transduce the binding event to the fluorescent oligomers.


43
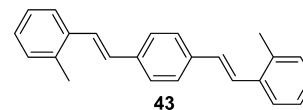
Sensing of DNA. Considerable efforts have been devoted to the use of conjugated polymers for biosensing purposes, and we restrict our overview to only a few significant contributions. Cationic conjugated polyelectrolytes were first utilized over a decade ago for the detection of polyanionic bioanalytes.[63,64] A diverse array of detection schemes has since been developed, and we focus here on label-free techniques (i.e., where the target analyte is label-free). FRET-based schemes have proved to be very effective for the detection of DNA single strands (ssDNA). In such a scheme, a polycationic poly(fluorene)-phenylene (**44**) is paired with a probe peptide nucleic acid (PNA) that is labeled with a fluorescent indicator (fluorescein). The high spectral overlap of the fluorescein and cationic polymer **44** (Figure 6a) is critical. In the absence of complementary DNA, the PNA strand, which is electrically neutral, does not interact electrostatically with **44** and no FRET is detected. However, upon hybridization of the PNA strand with a complementary ssDNA (the target analyte), the resultant duplex is negatively charged and binding of the cationic polyelectrolyte **44** produces a FRET signal.[65] Detection limits of 10 pM were determined, and exciting the polymer resulted in a 25-fold amplification of fluorescein emission, compared to a direct excitation of the fluorophore. Interestingly, a fluorescein-labeled,
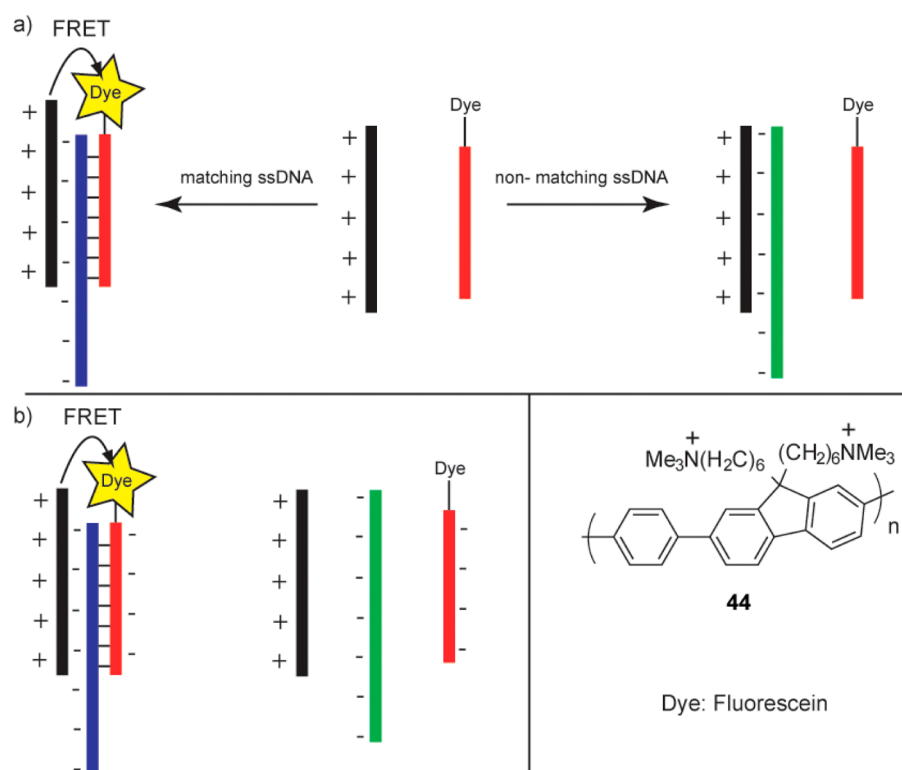
Figure 6. Schematic description of the use of water-soluble cationic conjugated polymer (black, **44**) with specific (a) fluorescein-labeled PNA reporter (red), or (b) fluorescein-labeled ssDNA reporter (red), to detect a complementary ssDNA sequence (blue). The green strand represents a noncomplementary ssDNA strand.

negatively charged, ssDNA could also be used as a probe instead of a PNA strand. In this case, the detection mechanism relies on a stronger binding of **44** to the larger negative charge of the hybridized dsDNA (Figure 6b).[66]

A variety of sensing schemes have been elaborated based on the electrostatic assembly scheme, and using conjugated cationic polymers with minority low band gap emitters in their structures eliminated the need of a fluorescent label (**45**). The approach in this case is similar to what was previously described for anionic polymer **3**, and has allowed for the detection of dsDNA in pM concentrations with a dynamic range spanning nearly 7 orders of magnitude.[67] Polymer **45** contains a fraction of 2,1,3-benzothiadiazole (10−20%), and in the presence of negatively charged DNA strands, higher emission is observed from the benzothiadiazole fragments.

R = -(CH_2)_3NMe_3Br
45   R' = -(O(CH_2)_2)_3NMe_3Br
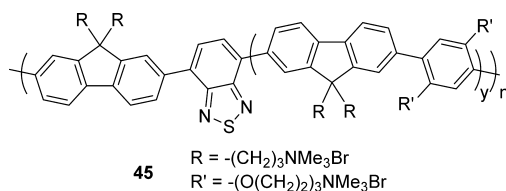
Other efforts enabled the naked-eye detection of dsDNA in the low nM range with the covalent incorporation of DNA intercalators in the side chains of **44**.[68] The DNA intercalator approach allows a strong selectivity for dsDNA against ssDNA, and the FRET mechanism from the conjugated polymer to the dye is strongly enhanced in the presence of dsDNA. Further, a two-step FRET scheme between cationic polymer **44** and a dye appended to a probe ssDNA strand and a DNA intercalator was reported.[69] In the presence of the target ssDNA, the intercalator can insert into the newly formed dsDNA.

A subsequent cascade of FRET events from the polymer to the labeled probe and finally to the intercalator indicates hybridization. The molecular-beacon nature of this sensing scheme improves the selectivity for the desired ssDNA target against targets possessing mismatches (Figure 7).
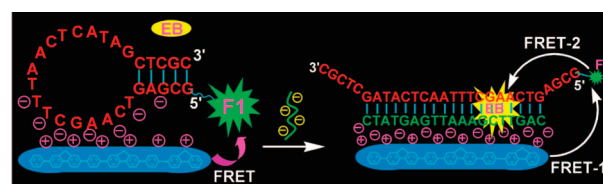

Figure 7. Schematic representation of a double-FRET, molecular-beacon mechanism for the detection of ssDNA. The conjugated polymer is compound **44**; Fl and EB indicate fluorescein and ethidium bromide dyes, respectively. Reproduced with permission from ref 69. Copyright 2008 American Chemical Society.

Cationic polythiophenes are able to detect ssDNA without the need of any external signaling unit.[70,71] When polymer **46** is mixed with an ssDNA probe, the initially yellow solution turns red, indicating the formation of electrostatically bound duplex wherein the polymer is in a more planar conformation that promotes extended electronic delocalization. The addition of complementary DNA target produces dsDNA, and a triplex structure forms with a change in color from red back to yellow. These processes are modulated by the charge density, by the rigidity of the assembly, and by hydrophobicity, and are best monitored through the emission of the polythiophene, which is sensitive to the conformation. This approach made it possible to detect ssDNA at an attomole concentration (1×10^{-18} M) and with excellent selectivity utilizing polymer **47**.[71]

Approaches where the ssDNA probe is labeled with a fluorescent dye have also been developed, and the FRET intensity was weak when the labeled ssDNA probe and the cationic polythiophene **47** were mixed in solution. However, upon addition of target ssDNA, the formation of dsDNA resulted in the formation of triplex structures (dsDNA-polymer) that display an enhanced FRET emission intensity.[72]

The use of conjugated polythiophenes for the sensing of DNA has also been reported making use of interactions between DNA and a zwitterionic polythiophene (**48**).[73] The structural changes experienced by the polymer in the presence of a probe ssDNA and upon hybridization of the probe ssDNA with a target ssDNA translated into emission changes. Interestingly, these responses persist in the solid state, allowing the fabrication of microchips for sequence-selective DNA sensing.
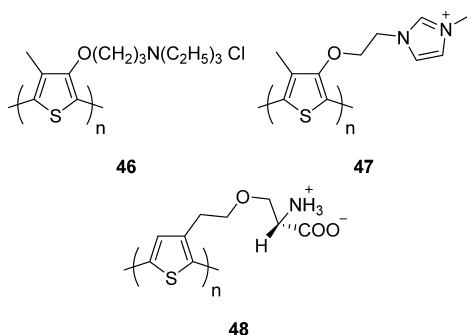
Detection of Proteases. Protease activity can be correlated with several diseases and cancers and as a result, there is considerable interest in the monitoring of their presence/activity. Schemes for the detection of protease activity often include molecular constructs that are substrates for the enzyme, and these activity assays have been implemented with fluorescent conjugated polymers. Initial examples[74,75] take advantage of this mechanism by employing the activity of an enzyme to modify the assembly with quenchers of water-soluble PPE polymers. Covalent attachment of the enzymatic substrate has advantages for immobilization on surfaces, and was accomplished using PPEs containing long oligo-(ethyleneglycol) side-chains,[76] some of which were terminated
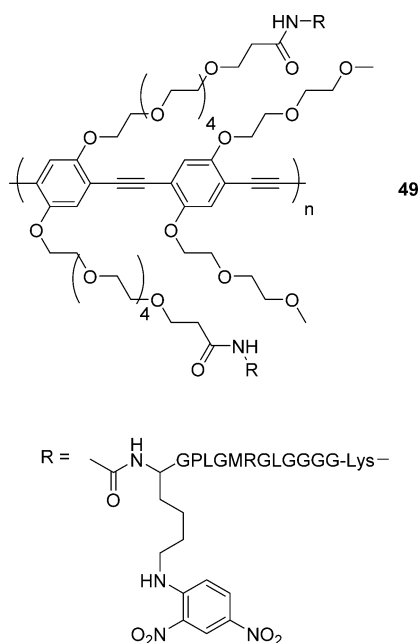
by carboxylic acid functionalities. The carboxylic acid groups afford conjugation to polypeptide substrates that were terminated by dinitrophenylamino quencher groups (**49**). This system functions in molecular beacon mode wherein the dinitrophenylamino groups efficiently quench the fluorescence, and protease cleavage of the polypeptide unquenches the polymers. This system can be made to work in buffered solution that can often compromise electrostatic assembly processes, and strong responses were obtained for trypsin (3 μg mL^{-1}).

Polythiophene **48** together with bovine serum albumin (BSA) and Cu(II) also provides a simple assay for the detection of trypsin.[77] Copper(II) efficiently coordinates to the serine residues of polymer **48**, thus quenching its fluorescence. However, when trypsin is added to the solution that also contains BSA as enzyme substrate, the latter is cleaved into small amino acids fragments, which efficiently coordinate to Cu(II) ions, thus removing them from the polymer. As a result,
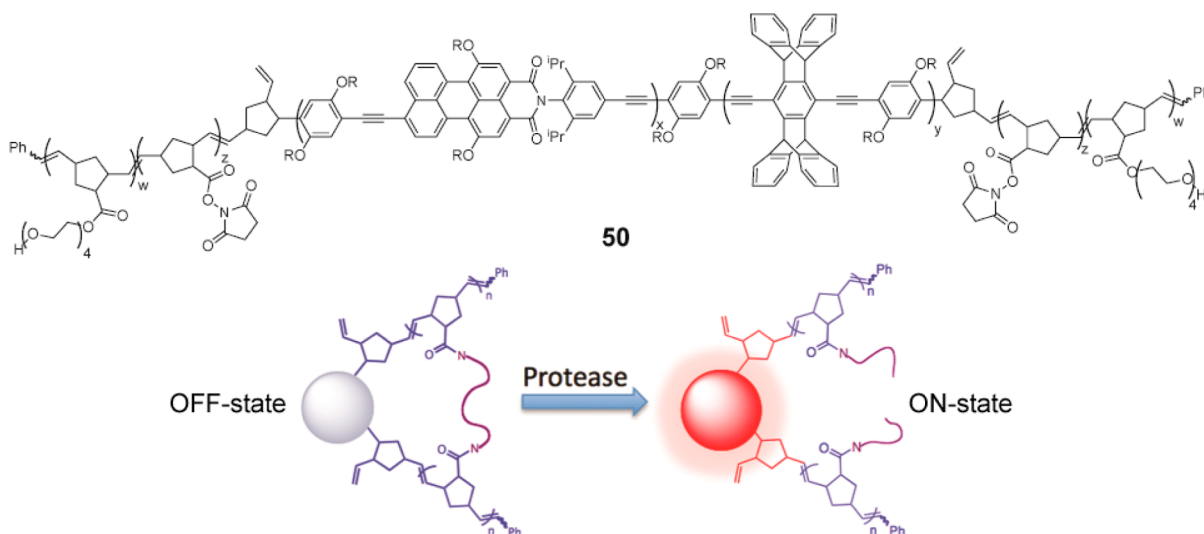
Figure 8. Top: copolymer **50** used for the protease assay; bottom: protease-induced emission turn-on scheme.

4499

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the fluorescence of the polythiophene is restored and can be used to monitor the enzyme activity.

An alternative approach to protease detection has recently been reported that makes use of changes in the physical properties of polymers as a function of peptide cross-linking.[78] This method also represented a dramatic expansion in the polymer architectures used in sensing by employing pentablock "ABCBA" copolymers to produce structured nanoparticles. The cores of the particles are based on PPEs with rigid pentiptycenes as well as a small fraction of a highly emissive low band gap perylene fluorophore (**50**). The conjugated backbone is an efficient antenna that captures and transfers energy to the perylene dyes. Hence, direct irradiation at the absorbance maximum produced dual emission from the majority PPE and the minority perylene groups for ratiometric sensing. The sensing nanoparticles are produced when THF solutions of the ABCBA pentablock polymer **50** are added to water. The core (C block) of the nanoparticles contains the PPE bearing the red-emitting chromophores (perylenes), whereas the outer shells were made of two blocks, one containing functional groups (succinimidyl ester groups, Figure 8), and the other based on a hydrogel. The succinimidyl ester containing blocks are then cross-linked by oligopeptides that are substrates for proteases. Cross-linking compresses the particles, and the emission intensity of the nanoparticles was reduced, owing to a tighter packing of the fluorescent core. The fluorescence is then recovered in the presence of proteases. The mechanism is described as a strain-release process, because the nanoparticles are effectively being squeezed by the cross-linking peptides, and cleavage of these linkages by a protease under physiological conditions allows for an observable expansion in the size of the nanoparticles and a 15-fold increase in emission intensity.

CONCLUSION AND FUTURE PERSPECTIVES

In this review, we emphasized some fundamentals of conjugated polymers for sensing applications, and demonstrated how they have been implemented in a large variety of detection schemes. Since the initial reports dating from the mid-1990s, which featured PPEs for the sensing of electron-deficient aromatic analytes, much progress has been made in order to tune the polymers' properties to the analytes to be detected, and to the conditions under which the sensing events have to happen. Hence, detection can now be achieved in the liquid or in the solid state, in aqueous or in organic environments, and even in a complex matrix such as blood serum. Analytes as varied as nitro-aromatic explosives, cyclic ketones, plant hormones, short peptides, DNA strands, or enzymes have been successfully detected by schemes relying on the properties of conjugated polymers. New insights in detection mechanisms have led to improvements in sensitivity, selectivity, and transduction of sensing events, that in some cases led to systems where naked-eye detection of desired analytes could be performed in extremely diluted conditions.

We identify two main avenues for future progress in the field of sensory conjugated polymers. First, one of the most attractive features of these systems relies on their simplicity: the polymers are in principle easily accessible (some of them are even commercially available), and their colorimetric or fluorescence behaviors can be monitored with simple instrumentation, when not just with the naked eye. A challenge is therefore to keep improving the sensitivity and selectivity of these assays, such as to decrease detection limits and increase response intensity, while maintaining their ease of preparation and use. It appears clear that a fundamental understanding of the mechanisms and interactions that are at the origin of the sensory behaviors is necessary in order to be able to improve the polymers involved in these detection schemes. A second research avenue that is being pursued (albeit not covered in this review) is the incorporation of sensory polymers in more sophisticated devices and on surfaces. Developments along these lines lead to more practical applications of such materials. For example, sensory materials can be incorporated into microfluidic devices or adsorbed on responsive surfaces (such as microcantilevers or quartz crystal microbalances). Although the sophistication level is higher in these cases and applications probably require more highly trained users, important improvements in sensitivity and reliability are at stake. Further, the need for high-throughput screening assays, in particular for the detection of bioanalytes, emphasizes the need for economically viable detection schemes, leading to multiple-use or recyclable sensory devices, which are generally easier to build upon solid-state-based technologies, as opposed to solution-based detection schemes. Finally, progress still has to be made in order to implement polymer-based sensing schemes working in "real-world" conditions (humid and/or polluted air, biological fluids or "as-collected" water samples), and that can operate in the presence of potentially interfering species and with minimal sample pretreatment.

In summary, the field of conjugated polymers for sensing applications has been flourishing in the last decades, but we believe it still has to reach its full potential. Research efforts are still needed in order to broaden the scope of analytes that can be detected, as well as the sensitivity, selectivity, and practicality of the detection schemes.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): Timothy Swager has patented some of the methods described and may receive royalty income.

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