Detection of Ethylene Gas by Fluorescence Turn-On of a Conjugated Polymer

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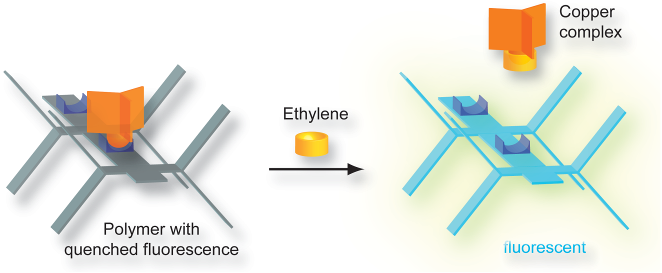
Detection of Ethylene Gas by Fluorescence Turn-On of a Conjugated Polymer

*Birgit Esser and Timothy M. Swager**

The detection and monitoring of ethylene is of great interest and importance in the food and agricultural industries. Ethylene as one of the smallest plant hormones is responsible for the ripening of fruit and plays an important role in many more developmental plant processes such as seed germination, fruit ripening, senescence and abscission. As fruits and vegetables start ripening, ethylene is produced and emitted, and the internal ethylene concentration in some fruits is used as a maturity index to determine the time of harvest. In some fruits and vegetables, such as bananas, the ripening process is continued after harvesting by exposure to ethylene gas, and the monitoring of ethylene gas in storage rooms is important to avoid deterioration of ethylene-sensitive produce. The ethylene concentration in ripening rooms is held between 10 and 200 ppm depending on the type of fruit or vegetable, while in storage facilities a value of less than 1 ppm is required.[i] Traditionally, gas chromatography[iia] and photoacoustic spectroscopy[iib] have been used to measure ethylene concentrations. Both techniques suffer from the disadvantage of being operationally impractical and do not allow for real-time measurements. Other sensing systems that have been suggested use electrochemical[iic] or chemoresistive methods,[iid] magnetoelastic sensing,[iie] and photoluminescence quenching.[iif] However, all of these systems have drawbacks such as high cost, impracticability, or insufficient sensitivity towards ethylene.

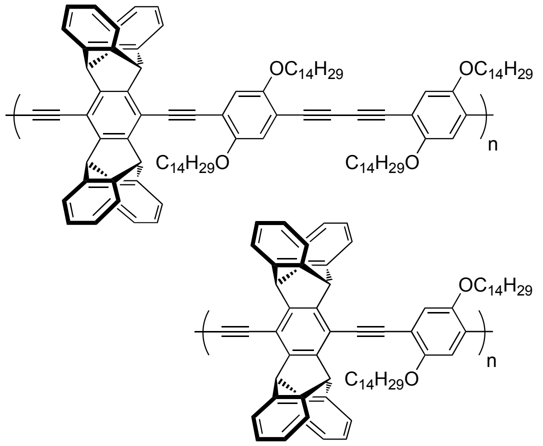
We have designed a sensory system that makes use of the advantages of fluorescent conjugated polymers as sensory materials.[iii] They readily transform a chemical signal into an easily measured optical event and can achieve large signal amplification relative to small molecule chemosensors. For the recognition of ethylene we were inspired by the mechanism of ethylene binding in plants. The reception of ethylene occurs through the receptor ETR1, which is studied in *Arabidopsis thaliana*. Through these studies it has been found that copper (I) is an essential cofactor and responsible for the binding of ethylene, and it is assumed that a cystein residue serves as ligand.[iv] The sensing scheme we have designed for the detection of ethylene is based on a fluorescence turn-on mechanism and mimics nature by using a copper (I) complex to bind to ethylene. The fluorescence of the conjugated polymer is partly quenched by the presence of copper (I) moieties that can coordinate to the polymer (***Scheme 1***). Upon exposure to ethylene gas, the copper complexes bind to the ethylene molecules and no longer quench the polymer fluorescence. The advantage of this fluorescence turn-on over a turn-off mechanism is that it requires a specific binding event to the copper to create a new signal whereas a fluorescence quench can take place in multiple ways. Furthermore, if a completely dark background (completely quenched) state can be achieved, even a weak turn-on signal can be readily measured and thereby allow trace detection.



Scheme 1. Design of a sensory system for the detection of ethylene gas.

Several requirements have to be met by the sensory system: a) The copper complex must have the ability to quench the polymer fluorescence, but b) the binding of the copper complex to ethylene must be stronger in order to provoke a large turn-on response. For a practical application of the system in thin film c) the polymer matrix must be porous enough to accommodate the copper moieties.

Conjugated polymers have emerged as an important class of sensory materials. The signal is amplified through the migration of excitons throughout the polymer chains or between different chains in films.[iiib] Poly(*p*-phenylene ethynylene)s (PPEs) have shown great performance in sensing applications, and for usage in thin film the introduction of shape-persistent pentiptycenes, such as in polymer **P2** (***Figure 1***), has brought about an improvement.[v,vi]



P1

P2

Figure 1. Poly(*p*-phenylene butadiynylene) (PPB) **P1** and poly(*p*-phenylene ethynylene) (PPE) **P2** with pentiptycene units.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

These three-dimensional structures create interstitial space in thin films resulting in higher luminescence efficiencies. In our sensory system, the triple bonds in PPEs can serve as coordination sites for copper (I) to promote efficient fluorescence quenching. A complexation of triple bonds in PPEs by transition metals has been shown to reduce their fluorescence intensity.[vii] Cu^{I} alkyne complexes are well known and studied,[viii] but we found no reference for a quenching of fluorescence by Cu^{I}.

Due to the labile nature of the copper-ethylene interaction only a small number of air stable copper (I) ethylene complexes have been reported.[ix] With regard to stability and synthesis compound **1** (***Figure 2***) featuring a fluorinated tris(pyrazolyl)borate ligand demonstrates several of the requisite properties.[x] The copper-ethylene bond in **1** is sufficiently strong to make the complex stable under ambient conditions and in high vacuum, and its electron poor nature prevents facile oxidation of the copper center. Furthermore, the fluorinated tris(pyrazolyl)borate ligand is easily accessible in two steps from non-expensive starting materials.[xi]

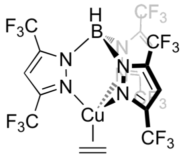

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Figure 2. Copper (I) ethylene complex employed in the sensory system with a fluorinated tris(pyrazolyl)borate ligand.

To investigate the coordination of alkynes through Cu^{I} scorpionate **1** NMR experiments and quantum chemical calculations were performed on complexes of diphenylacetylene (**2**), diphenylbutadiyne (**3**), and bis(2,5-dimethoxyphenyl)butadiyne representing subunits of polymers **P1** and **P2**. The coordination of the copper complex is evident by the changes observed in the NMR spectra. In the ^{19}F NMR spectra a downfield shift of approximately 1 ppm is observed for the CF$_3$ groups adjacent to the copper center upon addition of the alkyne. The proton signals for the pyrazol protons are shifted downfield by 0.04 ppm (see Supporting Information).

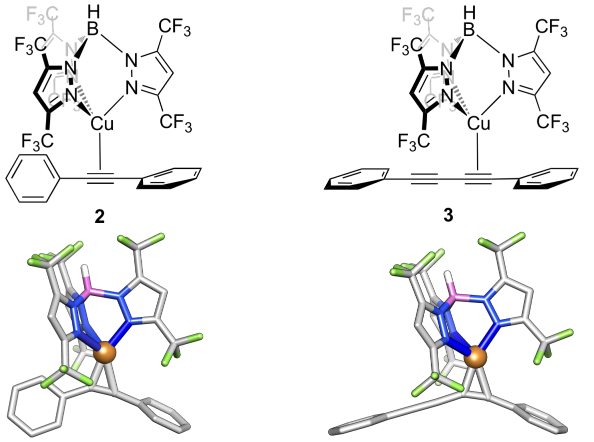
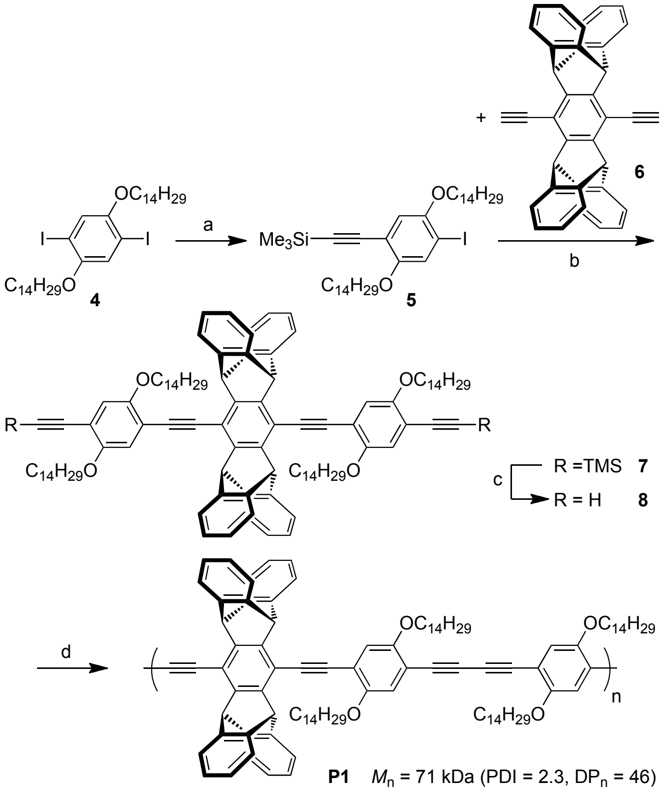


Figure 3. Optimized structures (B3LYP/6-31G*, SDD for Cu) of copper (I) alkyne complexes **2** and **3** (apart from on the boron atoms hydrogen atoms are omitted for clarity).

In the optimized structure of **2** the phenyl rings are twisted by 68° due to the steric demand of the scorpionate ligand (***Figure 3***).[xii] In the diphenylbutadiyne complex **3** the phenyl rings show only a small twist of 31°, the coplanarity of the phenyl rings is better maintained. As a result butadiyne units seem more suited to act as a coordination sites for copper scorpionate **1**, and thus we chose polymer **P1** (***Figure 1***) for the sensory system as a modified version of **P2**.

Calculations using isodesmic equations were performed to estimate the energy differences between the coordination of ethylene or an alkyne to copper scorpionate **1**.[xii] The coordination of ethylene is preferred by 13.8 kcal/mol relative to diphenylacetylene, and by 14.8 kcal/mol over diphenylbutadiyne. Considering entropy factors the equilibrium constants strongly favour ethylene (2×10^{12} for diphenylacetylene and 4×10^{12} for diphenylbutadiyne). Acetonitrile forms a stable complex with **1**, [xiii] and we used acetonitrile as a ligand in quantitative fluorescence experiments in solution as a substitute for ethylene due to the ease of quantitative addition. The energy difference between coordination of ethylene or acetonitrile to the Cu^{I} center was calculated to be small compared to the alkynes **2** and **3** (-0.6 kcal/mol or $K_{eq} = 10^{-3}$).

P1 was synthesized by oxidative polymerization of the terminal diyne **8** (***Scheme 2***). The synthesis of **8** started from the diiodo-, dialkoxy substituted benzene derivative **4**[xiv] with a single-fold Pd-catalyzed cross-coupling with TMSA yielding **5**. Coupling with the pentiptycene dialkyne **6**[vb] followed by basic deprotection of **7** led to **8** in excellent yield. The polymerization was conducted under Pd catalysis with *p*-benzoquinone as oxidant.[xv] To maintain complete solubility molecular weights no more than 10^4 were required for **P1**, and to achieve this the oxidative polymerization was performed at 0 °C under careful monitoring by GPC analysis.



Scheme 2. Synthesis of polymer **P1** by oxidative polymerization of **8**. a) TMSA, PdCl$_2$(PPh$_3$)$_2$, CuI, Et$_3$N, rt, 33%; b) Pd(PPh$_3$)$_4$, CuI, *i*-Pr$_2$NH, toluene, 65 °C, 16 h, 83%; c) K$_2$CO$_3$, MeOH, THF, rt, 4 h, 92%; d) *p*-Benzoquinone, Pd(PPh$_3$)$_4$, CuI, *i*-Pr$_2$NH, toluene, 0 °C, 4 h, 73%.

Polymer **P1** shows a main absorption at 434 nm and emits with a maximum at 462 nm. The quenching of its fluorescence by copper scorpionate **1** and a turn-on by ethylene was investigated in a preliminary visual experiment (***Figure** 4*). A toluene solution of in situ prepared "naked" copper scorpionate **9** was employed in all quenching experiments. The fluorescence of **P1** in solution (left picture) was quenched by the addition of **9** (middle). When the resulting solution of **P1** and **9** was purged with ethylene gas, a complete turn-on of polymer fluorescence was observed (right picture).

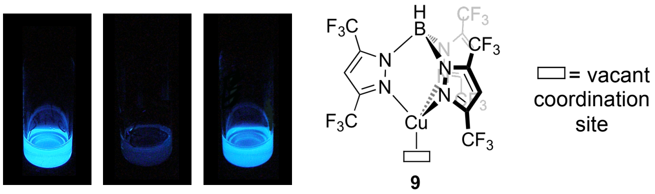


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Figure 4. Solution of **P1** in toluene (left), after quenching with **9** (middle) and after purging with ethylene (right) illuminated at 365 nm.

Fluorescence spectra during the quenching of **P1** by **9** are shown in ***Figure** 5*. A quantitative assessment employing the Stern-Volmer equation[xvi] $F_0/F = 1 + K_{SV}[Q]$ ($F_{(0)}$ is the (original) fluorescence intensity at the emission maximum, K_{SV} the Stern-Volmer constant and $[Q]$ the concentration of quencher) yields a quenching constant of $K_{SV} = (2.0 \pm 0.3) \times 10^3$ M^{-1}. When the solution is purged with ethylene gas the polymer fluorescence is restored to 95% of its original intensity (see dashed line). When titrating a solution of **P1** and **9** with acetonitrile as substitute for ethylene micro molar concentrations lead to a measurable turn-on of fluorescence (see Supporting Information).

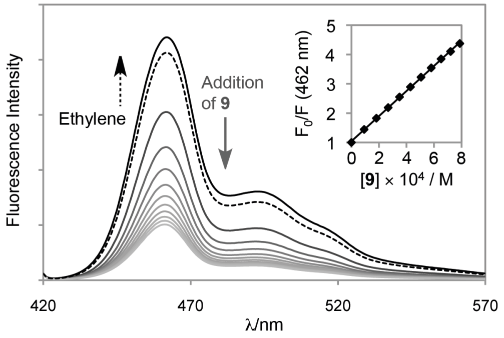

Figure 5. Fluorescence spectra of **P1** in toluene during addition of **9** and after purging with ethylene (dashed line; the inset shows the Stern-Volmer plot; conc. of **9** (top to bottom in 10^{-5} M): 0, 7.2, 14.1, 20.9, 27.4, 33.7, 39.9).

The fluorescence of PPE polymer **P2** is also partly quenched by the addition of **9**, the Stern-Volmer constant, however, is much lower than for **P1** with $K_S = 3.8 \times 10^2$ M^{-1}. This finding is in agreement with our assumption that due to steric reasons the quenching of **P1** by **9** is much more effective than that of **P2**.

In a practical application other fruit metabolites might interfere with the measurement. The effect of ethanol, acetaldehyde, and water on the fluorescence of solutions of **P1** and **9** were tested and the results are shown in ***Figure 6*** (left). Small increases in fluorescence could be observed in all three cases; however, those are very small compared to the turn-on observed with acetonitrile.

For many applications the sensory system needs to function in thin films. We prepared thin films of **P1**/**9** mixtures by spin-casting toluene solutions onto glass slides. As shown in ***Figure 6*** (right) the polymer fluorescence in thin film is effectively quenched when **9** is present. The degree of quenching is about ten times larger than in solution.

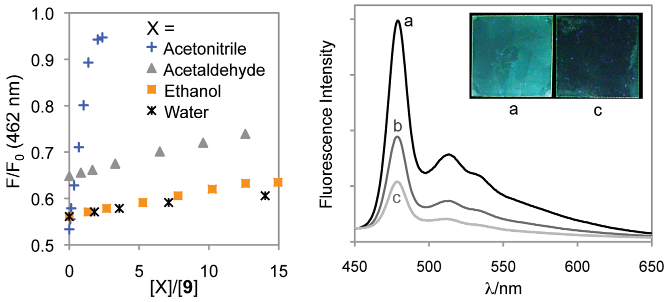

Figure 6. Left: Relative fluorescence of solutions of **P1** and **9** during titration with acetonitrile, acetaldehyde, ethanol, and water (concentrations of **9** (in 10^{-4} M) for X = CH_3CN: 3.7, acetaldehyde: 2.9, EtOH: 3.4, H_2O: 4.0). Right: Fluorescence spectra of thin films of **P1** (a) and **P1**/**9** mixtures (b, c) spin-cast from toluene solutions containing 0.64 mg/mL **P1** and 0, 2, or 6 × 10^{-5} M **9** (top to bottom); and photographs of films a and c, illuminated at 365 nm.

The fluorescence response of the copper/polymer films to diluted ethylene gas was tested in real-time fluorescence response studies using a Fido™ sensor.[xvii] In the Fido™ platform thin films are spin-cast on the inside of a glass capillary through which the gas flow is directed. The polymer is excited at 410 nm and its fluorescence above 460 nm is measured at the end of the capillary. ***Figure** 7*a shows the response of a **P1**/**9** film during repeated exposures to 0.6% and 0.1% ethylene (diluted with dinitrogen). As a control experiment, the response to pure dinitrogen is shown (gray line). Repeated exposures to ethylene gas mixtures lead to a strong, stepwise increase in absolute polymer fluorescence (black and dashed line). With pure dinitrogen no absolute increase in fluorescence in observed. Using air instead of dinitrogen gives the same result (see Supporting Information). A film of polymer **P1** itself shows no difference when exposed to ethylene/dinitrogen mixtures or to pure dinitrogen, and no increase in absolute fluorescence is observed (***Figure** 7*b).

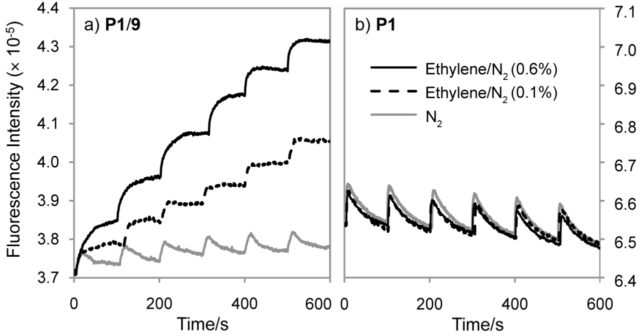

Figure 7. Real-time fluorescence responses measured in a Fido™ sensor[xvii] to ethylene/N_2 mixtures and to N_2 of (a) a **P1**/**9** mixed film and (b) a film of **P1** (the gas mixture was applied in 100 s intervals for 3 s each).

In conclusion we have developed a new sensory concept for the detection of ethylene gas that is based on the fluorescence turn-on of a conjugated polymer. The system can be used in solution and in thin film, achieving sensitivities in the micro molar range in solution and of 1000 ppm in film. For a practical application the sensitivity of the system has to be improved, and we are currently investigating the use of different polymers and small molecule fluorophores.

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[xvii] Fido^{TM} is a commercial sensory device available from ICx Technologies.

Entry for the Table of Contents (Please choose one layout)

Layout 2:

Ethylene Detection

Birgit Esser, Timothy M. Swager
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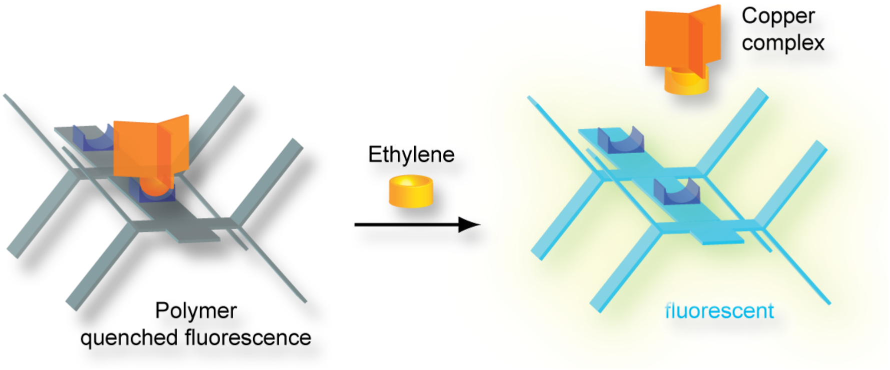

A new ethylene sensor was created from a conjugated polymer-copper (I) composite. The fluorescence of the conjugated polymer is quenched by the presence of copper (I) moieties. Upon exposure to ethylene gas the copper complexes bind to ethylene and no longer quench the polymer fluorescence. This new sensory concept can be used in solution and in thin film.