Sensors

DOI: 10.1002/anie.201003899

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. As one of the smallest plant hormones, ethylene 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 vegetables and fruits, such as bananas, exposure to ethylene gas results in a continuation of the ripening process after harvesting, thus the monitoring of ethylene gas in storage rooms is important to avoid the 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 a value of less than 1 ppm is required in storage facilities.[1] Traditionally, gas chromatography[2a] and photoacoustic spectroscopy[2b] 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[2c] or chemoresistive methods,[2d] magnetoelastic sensing,[2e] and photoluminescence quenching.[2f] 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.[3] These compounds readily transform a chemical signal into an easily measurable optical event and can achieve large signal amplification compared 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*. It has been found that copper(I) is an essential cofactor and responsible for the binding of ethylene, and it is assumed that a cysteine residue serves as ligand.[4] 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 partially quenched by the presence of copper(I) moieties that can coordinate to the polymer (Figure 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 fluorescence quenching can occur 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 can allow trace detection.

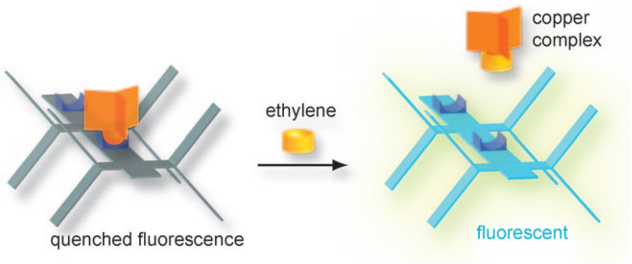


Figure 1. Design of a sensory system for the detection of ethylene gas.

Several requirements have to be met by the sensory system: 1) The copper complex must have the ability to quench the polymer fluorescence, but 2) the binding of the copper complex to ethylene must be stronger in order to provoke a large turn-on response. 3) For a practical application of the system in thin films, 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.[3b] Poly(*p*-phenylene ethynylene)s (PPEs) have shown impressive performance in sensing applications. The introduction of shape-persistent pentiptycenes, such as in polymer **P2** (Scheme 1), in thin films has led to improved photophysical properties compared to planar polymers[5,6] as the three-dimensional structures create interstitial space in thin films, thus resulting in higher luminescence efficiencies.

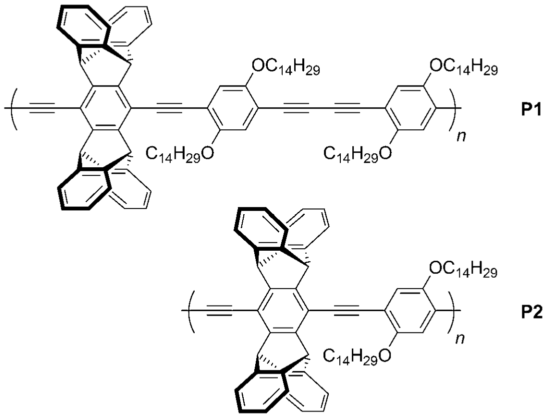
In our sensory system, the triple bonds in PPEs can serve as coordination sites for copper(I) to promote efficient fluorescence quenching. The complexation of triple bonds

---

[*] Dr. B. Esser, Prof. Dr. T. M. Swager
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, MA 02139 (USA)
Fax: (+1) 617-253-7929
E-mail: tswager@mit.edu

[**] B.E. is grateful to the German Academy of Sciences Leopoldina for a postdoctoral fellowship (LPDS 2009-8). This work was supported in part by the NSF. We thank Prof. S. Buchwald for the use of computational resources.

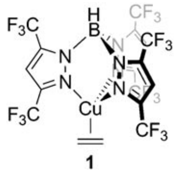
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003899.



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

in PPEs by transition metals has been shown to reduce their fluorescence intensity.[7] Copper(I) alkyne complexes are well-known and well-studied,[8] but, to the best of our knowledge, fluorescence quenching by copper(I) remains unreported to date.

The labile nature of the copper–ethylene interaction has resulted in only a small number of air-stable copper(I) ethylene complexes being reported.[9] Compound **1** (Scheme 2), which features a fluorinated tris(pyrazolyl)borate ligand, demonstrates several of the requisite properties with regard to stability and synthesis.[10] The copper–ethylene bond in **1** is sufficiently strong to make the complex stable under both ambient conditions and 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 nonexpensive starting materials.[11]



Scheme 2. Complex of copper(I), a fluorinated tris(pyrazolyl)borate ligand, and ethylene employed in the sensory system.

To investigate the coordination of alkynes by copper(I) scorpionate **1**, ^{1}H NMR and ^{19}F NMR experiments and quantum chemical calculations were performed on complexes of diphenylacetylene **2**, diphenylbutadiyne **3**, and bis(2,5-dimethoxyphenyl)butadiyne, which represent subunits of polymers **P1** and **P2**. The coordination of the copper complex is evident by the changes observed in the ^{1}H NMR and ^{19}F NMR spectra. In the ^{19}F NMR spectra, a downfield shift of approximately $\delta = 1$ 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 $\delta = 0.04$ ppm (see the Supporting Information).

The phenyl rings in the optimized structure of **2** are twisted by 68° because of the steric demand of the scorpionate ligand (Figure 2).[12] The phenyl rings in the diphenylbutadiyne complex **3** 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 coordination sites for copper scorpionate **1**, and thus we chose polymer **P1** as a modified version of **P2** (Scheme 1) for the sensory system.

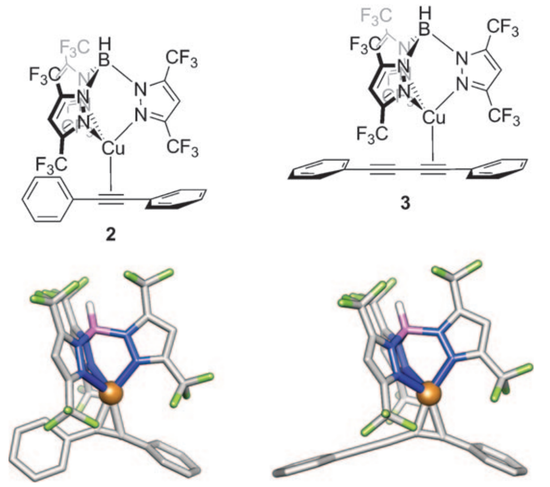
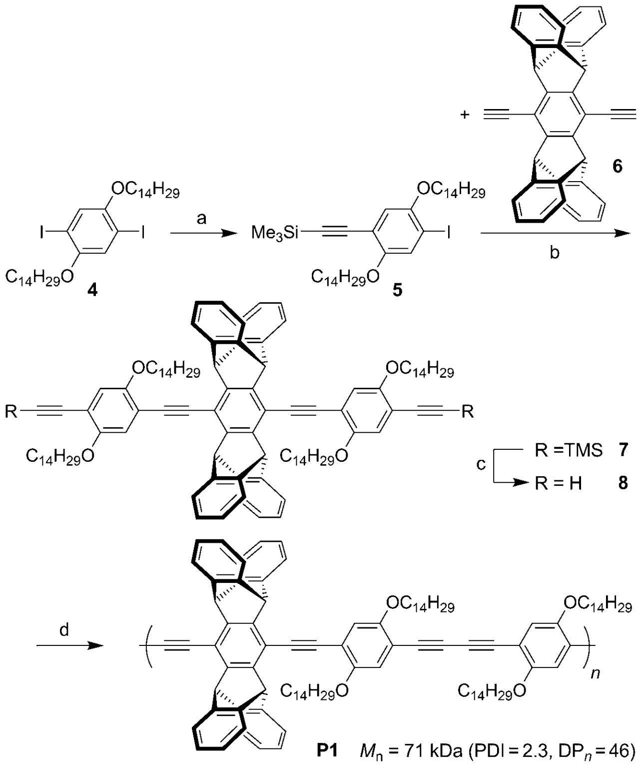


Figure 2. Optimized structures (B3LYP/6-31G*, SDD for Cu) of copper(I) alkyne complexes **2** and **3** (hydrogen atoms are omitted for clarity except for on the boron atoms).

Calculations using isodesmic equations were performed to estimate the energy differences between the coordination of ethylene and an alkyne to copper scorpionate **1**.[12] The coordination of ethylene is more favorable by 13.8 kcal mol^{-1} relative to diphenylacetylene, and by 14.8 kcal mol^{-1} relative to diphenylbutadiyne. Considering entropic factors, the equilibrium constants strongly favor ethylene (2×10^{12} for diphenylacetylene and 4×10^{12} for diphenylbutadiyne). Acetonitrile forms a stable complex with **1**,[13] thus we used acetonitrile as a ligand in quantitative fluorescence experiments in solution as a substitute for ethylene because of the ease of quantitative addition. The energy difference between the coordination of ethylene or acetonitrile to the copper(I) center was calculated to be small compared to the alkynes **2** and **3** (-0.6 kcal mol^{-1} or $K_{eq} = 10^{-3}$).

P1 was synthesized by oxidative polymerization of the terminal diyne **8** (Scheme 3). The synthesis of **8** started with a single Pd-catalyzed cross-coupling between the diiodo-, dialkoxy-substituted benzene derivative **4**[14] and trimethylsilylacetylene (TMSA) to give **5**. Coupling with the pentiptycene dialkyne **6**[5b] followed by basic deprotection of **7** led to **8** in excellent yield. The polymerization was catalyzed by Pd with *p*-benzoquinone as oxidant.[15] To maintain complete solubility, molecular weights of 10^4 were required for **P1**, and thus the oxidative polymerization was performed at 0 °C with careful monitoring by gel permeation chromatography (GPC).

In toluene solution, polymer **P1** shows an absorption maximum at 434 nm and an emission maximum at 462 nm.



Scheme 3. Synthesis of polymer **P1** by oxidative polymerization of **8**. a) TMSA, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, RT, 33 %; b) $[Pd(PPh_3)_4]$, CuI, iPr_2NH, toluene, 65 °C, 16 h, 83 %; c) K_2CO_3, MeOH, THF, RT, 4 h, 92 %; d) *p*-benzoquinone, $[Pd(PPh_3)_4]$, CuI, iPr_2NH, toluene, 0 °C, 4 h, 73 %; PDI = polydispersity index.

The fluorescence quenching of **P1** by copper scorpionate **1** and a fluorescence turn-on by ethylene was investigated in a preliminary visual experiment (Figure 3). A solution of the in situ prepared "naked" copper scorpionate **9** in toluene was employed in all quenching experiments. The fluorescence of **P1** in solution (Figure 3, left) was quenched by the addition of **9** (center). When the resulting solution of **P1** and **9** was purged with ethylene gas, a complete turn-on of polymer fluorescence was observed (Figure 3, right).

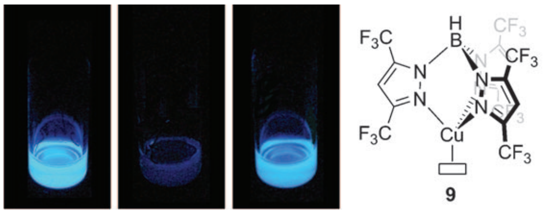


Figure 3. Photographs of a solution of **P1** in toluene (left), after quenching with **9** (center), and after purging with ethylene (right) illuminated at 365 nm; empty rectangle represents a vacant coordination site.

Fluorescence spectra recorded during the quenching of **P1** by **9** are shown in Figure 4. A quantitative assessment that employs the Stern–Volmer equation[16] $F_0/F = 1 + K_{SV}[Q]$ (F_0 is the (original) fluorescence intensity at the emission maximum, K_{SV} is the Stern–Volmer constant, and [Q] the concentration of quencher) leads to a quenching constant of $K_{SV} = (2.0 \pm 0.3) \times 10^3\,\mathrm{M}^{-1}$. When the solution is purged with ethylene gas, the polymer fluorescence is restored to 95 % of its original intensity (Figure 4, dashed line). Titration of a solution of **P1** and **9** with micromolar concentrations of acetonitrile (as a substitute for ethylene) led to a measurable turn-on of fluorescence (see the Supporting Information).

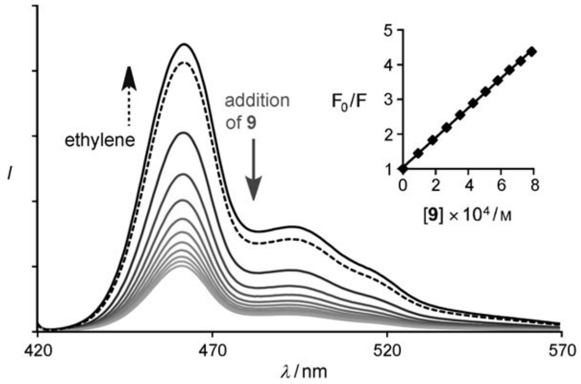


Figure 4. Fluorescence spectra of **P1** in toluene during addition of **9** and after purging with ethylene (dashed line; the inset shows the Stern–Volmer plot (462 nm); concentration of **9** (top to bottom in $10^{-5}\,\mathrm{M}$): 0, 7.2, 14.1, 20.9, 27.4, 33.7, 39.9.

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

In a practical application, other fruit metabolites might interfere with the measurement. The effects of ethanol, acetaldehyde, and water on the fluorescence of solutions of **P1** and **9** were tested (Figure 5, left). Small increases in fluorescence could be observed in all three cases; however, the increases are very small compared to the turn-on observed with acetonitrile.

The sensory system needs to function in thin films for many applications. We prepared thin films of mixtures of **P1** and **9** by spin-casting solutions in toluene onto glass slides. As

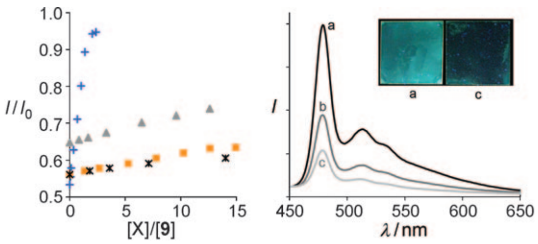


Figure 5. Left: Relative fluorescence of solutions of **P1** and **9** at 462 nm during titration with acetonitrile (blue cross), acetaldehyde (gray triangle), ethanol (yellow square), and water (black asterisk); concentrations of **9** (in $10^{-4}\,\mathrm{M}$) for acetonitrile: 3.7, acetaldehyde: 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^{-1} **P1** and 0, 2, or $6 \times 10^{-5}\,\mathrm{M}$ **9** (top to bottom); insets: photographs of films a and c, illuminated at 365 nm.

shown in Figure 5 (right) the polymer fluorescence in thin films is effectively quenched in the presence of **9**. The degree of quenching is about ten times larger than in solution.

The fluorescence response of the copper(I)/polymer films to diluted ethylene gas was tested in real-time fluorescence response studies using a Fido sensor.[17] 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 recorded at the end of the capillary. Figure 6a shows the response of a **P1/9** film during repeated exposures to 0.6% and 0.1% ethylene (diluted with dinitrogen). The response to pure dinitrogen is shown as a control experiment (gray line). Repeated exposures to ethylene gas mixtures lead to a strong, stepwise increase in absolute polymer fluorescence (Figure 6a, black and dashed line), whereas with pure dinitrogen no absolute increase in fluorescence is observed. Using air instead of dinitrogen gives the same result (see the Supporting Information). A film of polymer **P1** itself shows no difference in behavior when exposed to ethylene/dinitrogen mixtures or to pure dinitrogen, and no increase in absolute fluorescence is observed (Figure 6b).

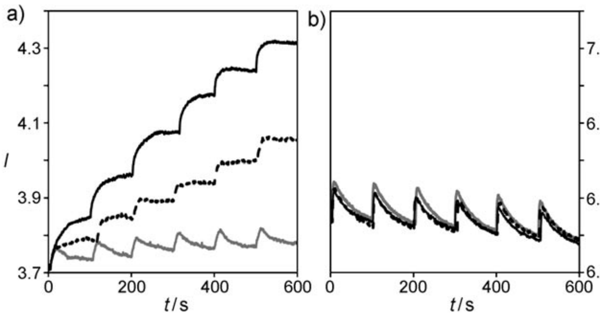


Figure 6. Real-time fluorescence responses measured in a Fido sensor[17] to ethylene/N_2 mixtures and to N_2 of a) a **P1/9** mixed film and b) a film of **P1** (the gas mixture was applied in 100 s intervals for 3 s each; black line: ethylene/N_2 (0.6%), dashed line: ethylene/N_2 (0.1%), gray line: N_2).

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 films, thus achieving sensitivities in the micromolar range in solution and of 1000 ppm in thin films. 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.

Received: June 27, 2010
Revised: August 27, 2010

Keywords: alkenes · copper · fluorescence · polymers · sensors

---

[1] A. A. Kader, M. S. Reid, J. F. Thompson in *Postharvest Technology of Horticultural Crops* (Ed.: A. A. Kader), University of California, Agricultural and Natural Resources, Publication 3311, **2002**, p. 39, 55, 113, 149.

[2] a) H. Pham-Tuan, J. Vercammen, C. Devos, P. Sandra, *J. Chromatogr. A* **2000**, *868*, 249–259; b) M. Scotoni, A. Rossi, D. Bassi, R. Buffa, S. Iannotta, A. Boschetti, *Appl. Phys. B* **2006**, *82*, 495–500; c) L. R. Jordan, P. C. Hauser, G. A. Dawson, *Analyst* **1997**, *122*, 811–814; d) Y. Pimtong-Ngam, S. Jiemsirilers, S. Supothina, *Sens. Actuators A* **2007**, *139*, 7–11; e) R. Zhang, M. I. Tejedor, M. A. Anderson, M. Paulose, C. A. Grimes, *Sensors* **2002**, *2*, 331–338; f) O. Green, N. A. Smith, A. B. Ellis, J. N. Burstyn, *J. Am. Chem. Soc.* **2004**, *126*, 5952–5953.

[3] a) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537–2574; b) S. W. Thomas III, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339–1386.

[4] a) F. I. Rodríguez, J. J. Esch, A. E. Hall, B. M. Binder, G. E. Schaller, A. B. Bleecker, *Science* **1999**, *283*, 996–998; b) B. M. Binder, *Plant Sci.* **2008**, *175*, 8–17.

[5] a) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322; b) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873.

[6] T. M. Swager, *Acc. Chem. Res.* **2008**, *41*, 1181–1189.

[7] a) C. Huber, F. Bangerter, W. R. Caseri, C. Weder, *J. Am. Chem. Soc.* **2001**, *123*, 3857–3863; b) S. Scholz, P. J. Leech, B. C. Englert, W. Sommer, M. Weck, U. H. F. Bunz, *Adv. Mater.* **2005**, *17*, 1052–1055.

[8] H. Lang, K. Köhler, S. Blau, *Coord. Chem. Rev.* **1995**, *143*, 113–168.

[9] H. V. R. Dias, J. Wu, *Eur. J. Inorg. Chem.* **2008**, 509–522.

[10] H. V. R. Dias, H.-L. Lu, H.-J. Kim, S. A. Polach, T. K. H. H. Goh, R. G. Browing, C. J. Lovely, *Organometallics* **2002**, *21*, 1466–1473.

[11] O. Renn, L. M. Venanzi, A. Marteletti, V. Gramlich, *Helv. Chim. Acta* **1995**, *78*, 993–1000.

[12] Calculations were performed using Gaussian 03 (Gaussian 03, Revision E.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2004; see the Supporting Information for complete citation), the B3LYP functional and as basis sets 6-31G* for C, H, B, F, N, and SDD for Cu. Energetic and structural data for all optimized compounds can be found in the Supporting Information.

[13] a) H. V. R. Dias, H.-J. Kim, H.-L. Lu, K. Rajeshwar, N. R. de Tacconi, A. Derecskei-Kovacs, D. S. Marynick, *Organometallics* **1996**, *15*, 2994–3003; b) M. N. C. Balili, T. Pintauer, *Acta Crystallogr. Sect. E* **2007**, *63*, m988–m990.

[14] T. M. Swager, C. J. Gil, M. S. Wrighton, *J. Phys. Chem.* **1995**, *99*, 4886–4893.

[15] V. E. Williams, T. M. Swager, *J. Polym. Sci. Part A* **2000**, *38*, 4669–4676.

[16] J. R. Lakowicz in *Principles of Fluorescence Spectroscopy*, 3rd ed., Springer, Berlin, **2006**, pp. 278.

[17] Fido is a commercial sensory device available from ICx Technologies.