Progress in the Development of Molecularly Imprinted Polymer Sensors

Bradley R. Arnold, Alex C. Euler, Amanda L. Jenkins, O. Manuel Uy, and George M. Murray

Remote chemical sensors rely on a means of chemical recognition. Most of these sensors apply some previously discovered phenomenon as the basis for measurement. A means to produce sensors for any specific chemical that requires quantitation would be ideal. The technique of molecular imprinting provides chemical recognition based on need and not happenstance. One flexible and sensitive method for chemical sensing is luminescence spectroscopy using optical fibers. This article examines the combination of fiber-optic–based luminescence and molecular imprinting to create highly sensitive chemical sensors to systematically meet the demands of modern society. (Keywords: Chemical sensors, Luminescence, Molecularly imprinted polymer.)

INTRODUCTION

Remote chemical sensors must fulfill two goals: (1) the development of a specific chemical recognition element that allows a molecule, or class of molecule, to be identified, and (2) a means of signal transduction in which the presence of the molecule causes a measurable change in a physical property of the material. Although these goals are not always separable, the successful design of chemical sensors requires that both be satisfied.

Most transduction approaches are based on optical, resistive, surface acoustic wave, or capacitive measurements. These well-developed methods dominate largely because of their ease of operation, sensitivity, and cost. The chemical recognition elements in these detectors, however, lag far behind. Indeed, most reports

on chemical sensors suggest that many other devices could be fabricated if only suitable chemical recognition units were available. The missing element is a general approach to chemical recognition that allows the rational design and assembly of materials in a stable and reusable form. Our approach to solving this problem is based on the fabrication of molecularly imprinted polymers (MIPs).

An MIP is generally described as a plastic cast or mold of the molecule of interest, where recognition is based on shape, much like a lock and key. MIPs are made by adding the molecule of interest to a solution of binding molecules that can be chemically incorporated into a polymer[1] (see Fig. 1). These binders usually have an affinity for the target and form a complex.
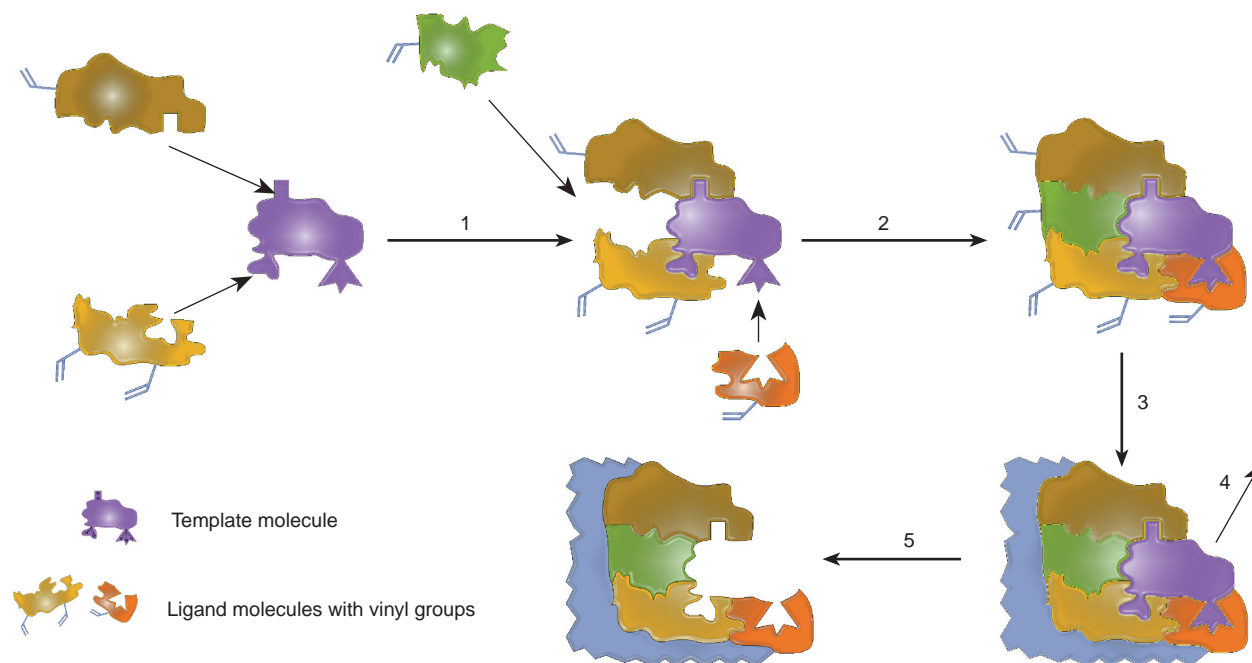
Figure 1. Synthesis of molecularly imprinted polymers: 1 and 2 = self-assembly of the templates and ligand molecules; 3 = incorporation of the ligand–template complex into the polymer matrix; 4 = removal of the template molecule; 5 = formation of the template cavity.

The interactions that hold these complexes together include π–π interactions, hydrogen bonding, metal–ligand binding, and even covalent bond formation, but they must be reversible. The binder must also have a chemical functionality that allows it to be irreversibly bound to polymers. Vinyl groups are a common functional group used to prepare many polymers, e.g., polyethylene, polystyrene, polyvinylalcohol, and polyvinylchloride. The target–binder complex is dissolved in excess matrix monomer (for example, styrene) and possibly other additives such as a cross-linker and porogens (see the Glossary for the definition of selective terms used throughout this article).

Cross-linkers have two or more functional groups that bind with the polymer chain to form a rigid, three-dimensional structure. Polymers made with cross-linkers have increased structural integrity and will not dissolve in common solvents. Cross-linking ensures the rigidity necessary to hold the binder in place and maintain the correct cavity shape, even after the target molecule has been removed. Porogens, on the other hand, are inert components that get trapped in the growing polymer. After they are removed, the porogens leave gaps or pores in the three-dimensional structure and provide greater accessibility to the internal polymer bulk. This facilitates the removal and subsequent rebinding of the template molecule.

Once mixed, polymerization is initiated either photochemically or by using chemical initiators such as 2,2′-azobisisobutyronotrile or benzoyl peroxide. In

GLOSSARY

Analyte: The molecule being determined in a chemical analysis.

Charge transfer (CT): The process by which one molecule or ion transfers an electron to another molecule or ion. (In this article, the molecules are in contact and the energy to transfer the electron comes from light.)

Cross-linker: A single molecule having two or more chemical functional groups that link chains of polymers, thereby making them rigid and insoluble.

Extinction coefficient (ϵ): A term that describes how effective a material is at absorbing light of a certain wavelength.

Interferent: A molecule similar to an analyte that may bias a chemical measurement.

Ion exchange resin: A polymer that contains materials that allow the exchange of ions from solution with the ion that is loosely bound to the resin.

Ligand: A molecule that binds to another molecule or ion via some form of electrostatic attraction to form a complex. The ligating atom is the atom of the ligand at the point of contact.

Matrix monomer: The bulk constituent of a polymer that functions as the main structural component.

Monomer: A single molecule that has a chemical functional group that allows for polymerization.

Porogen: An inert solvent (e.g., alcohol) added to a mixture to be polymerized to create gaps or holes in the finished polymer.

Steric hindrance: A term used to describe restraints on chemical interactions due to the size and shape of the molecules that are interacting.

typical sensor fabrication, a solid plastic mass, consisting of the matrix and binder, is obtained which is chemically bound to the polymer/cross-linker matrix and the target molecule. Removal of the target is possible since it is reversibly bound to the binder. The cavity it leaves behind is permanently shaped like the target.

Slight variations in the preparation procedure allow suitable polymer samples to be obtained for a wide range of uses. For example, if surface-active sensors are required, polymers with minimal porosity are preferred. Such sensors will display higher binding rates, with a concomitant loss in capacity, resulting in a relatively fast response time. The ability to tailor the polymers to the specific needs of the sensor is one of the major advantages in the production of MIP-based sensors.

Pioneers in this area have developed the basics of template polymer technology that can now be used to develop sensors. The key feature is to use MIPs as standard chemical recognition devices that trap specific molecules, hold them in a prearranged orientation, and concentrate them within the template resin. Coupled with suitable signal transduction methods, the systematic development of sensors is possible.

SENSOR APPLICATIONS

Metal Ion Sensors

A previous report[2] described the use of molecular imprinting for specific ion exchange resins and for the fabrication of ion-selective electrodes. Existing ion exchange resins extract ions, but with little discrimination. Our goal was to make a resin that selectively complexed a single type of ion in solution, thus exceeding the selectivity criterion of currently available resins. The successful development of a resin that responds primarily to lead in solution resulted in the fabrication of an ion-selective electrode using MIP technology. This resin has been used to remove lead from drinking water. Since only the lead is removed, the remaining mineral content of the water is unchanged. The resin serves as an electrode, allowing the effluent of the resin to be continuously monitored to ensure that no lead passes through the filter. It also serves as an indicator of when the filter should be replaced.

Conventional ion exchange resins have an affinity for metals in a certain order due to the type of binding site employed. This site affinity is a function of the chemical nature of the binding group and is called thermodynamic affinity owing to the varying amounts of energy released by ion binding. The directional quality of specific metal ion bonding was used to acquire selectivity beyond simple thermodynamic affinity. Metal ion imprinting was used to produce ion exchange resins for lead and uranyl ions. The polymers were later

incorporated into ion-selective electrode sensors for these ions. The characterization of these materials has shown previously unrevealed trends in the behavior of imprinted polymers.

Our goal was to make a resin that selectively complexed a single type of ion in solution, thus exceeding the selectivity criterion of currently available resins.

Most MIPs have been designed as sequestering agents. The design criteria were therefore chosen to maximize the capacity of the resins. Since our goal has been the production of sensors, polymers that had higher selectivity at the expense of binding capacity were preferred. The path we followed diverged from conventional wisdom in two key areas. First, we reasoned that the large degree of cross-linking normally employed in the polymer preparation would cause strain in the polymer matrix and, upon the removal of the template ion, the ligating atoms would move to relieve that strain. This would result in decreased specificity of the binding sites. Second, we expected that if large amounts of complex were used to make the resins, an increase in site–site interactions would occur, which would also reduce selectivity. To obtain fast binding kinetics, we prepared the electrode materials with MIPs that were designed to be surface active. The key features of a surface-active polymer include the comparatively low content of the metal ion complex relative to the matrix monomer (typically styrene) and the absence of a porogen.

MIPs prepared with less cross-linking and lower complex loading exhibit higher selectivity than polymers fabricated conventionally. The Nernst equation describes the response of an electrode to ions in solution.[3] Ion-selective electrodes prepared from these materials give the theoretical, or Nernstian, response to the imprint ion and a much smaller response to other ions in solution, providing good selectivity. However, we encountered a problem in the region of low ion concentration with some of the electrodes. When the potential of solutions with no imprint ion and only a small amount of interferent ion was measured, it was higher than expected. If the interferent concentration was increased to greater than 1×10^{-5} M or if a small amount of imprint ion was introduced, "normal" behavior was restored. Apparently, some imprinted sites have very high affinity for the imprint ion and do not release the bound ion unless other ions are available for exchange in solution. Such sites are called tight-binding sites. Because of these sites, the sensor reads too high a potential when measuring solutions that do not

contain an analyte ion. This problem can be addressed by performing measurements with the method of standard additions. That is, the concentration of the analyte is inferred from the potential change due to one or more additions of a small amount of a standard sample of analyte ion extrapolated to zero added standard. Although this is an established analytical technique, it is preferable to solve this problem in another way.

The problem of anomalously high potential readings was greatest in electrodes prepared with polymers of relatively high weight percent content of metal ion complex. Although the phenomenon of tight-binding sites is impossible to eliminate, their numbers can be reduced by reducing the amount of imprint complex in the polymer. The number of binding sites is reduced sufficiently to change the concentration regime for electrode response to lower values. This approach was not only successful but also produced sensors with an enhanced low-concentration response. The application of the resins to flow injection analysis systems is being explored.[4]

Nerve Agent Sensors

The idea of using a metal ion to direct the binding of an analyte molecule was applied to the detection of nerve agents via a commercially available hydrolysis product of Soman, pinocolylmethylphosphonate (PMP).[5] PMP has nearly the same structure as Soman with an OH group substituted for the fluorine atom. This substitution reaction of Soman in water renders the chemical safe to handle. Since the nerve agent Sarin has the same working end as Soman, the sensor should respond to it as it would Soman. To construct the prototype sensor, we used Eu^{3+}, the europium ion in the +3 oxidation state. Eu^{3+} exhibits a large affinity for phosphonate and, when properly coordinated, displays intense luminescence. This approach allows the indirect detection of Soman since the agents will rapidly hydrolyze in water. The use of PMP eliminated the hazards and difficulties associated with working with nerve agents during the design and testing of the sensor.

The laboratory prototype for this fiber-optic sensor consisted of a polymer-coated optical fiber. The fibers were prepared by terminating one end of a 400-μm multimode optical fiber with a standard screw-type fiber-optic connector (SMA connector) and removing the cladding from the distal end. The distal end was then tapered using a standard glass-blowing torch. The tapered ends were dip-coated with a partially polymerized viscous polymer solution, leaving a uniform coating on the fiber approximately 200 μm thick. The coating was subsequently cured under ultraviolet light for about 12 h. After curing, the imprint ion PMP was removed by swelling the polymer coating in a water/methanol solution and rinsing with 1 M nitric acid. The composition of the polymer currently in use is 3 mole percent of the imprinted complex and 1 mole percent of the cross-linking agent divinylbenzene (DVB), with the bulk of the matrix being the monomer styrene.

Luminescence is excited using the 465.8-nm line from an argon ion laser that is resonant with the $^5D_2$ electronic level of Eu^{3+}. The optical configuration of the fiber sensor is shown in Fig. 2. This benchtop device has a limit of detection of 660 parts per quadrillion (ppq) PMP in 0.1 M sodium hydroxide with a linear dynamic range from 750 ppq to 10 ppm. Basic conditions decrease the response time and catalyze the hydrolysis of nerve agents. The sensor's 80% response time (the time it takes for the sensor to exhibit 80% of its long-term response) is less than 8 min; however, a positive response is detected within 1 min. The response time is inversely related to the polymer thickness. Thus, thicker coatings respond slower but allow more active sites and permit measurements in regions of higher concentration.

Organophosphorus pesticides and herbicides are the compounds most chemically similar to nerve agents and were tested as possible interferents. The sensor was exposed to 1000 ppm of each pesticide, a concentration much higher than that typically found in water systems—even with runoff from nearby agriculture. A sodium phosphate solution was also screened. The influence of these chemicals was apparent from the changing intensity of the major 617-nm europium luminescence band. However, none of the pesticides produced a luminescence peak in the region of the PMP peak, and therefore did not interfere with detection.
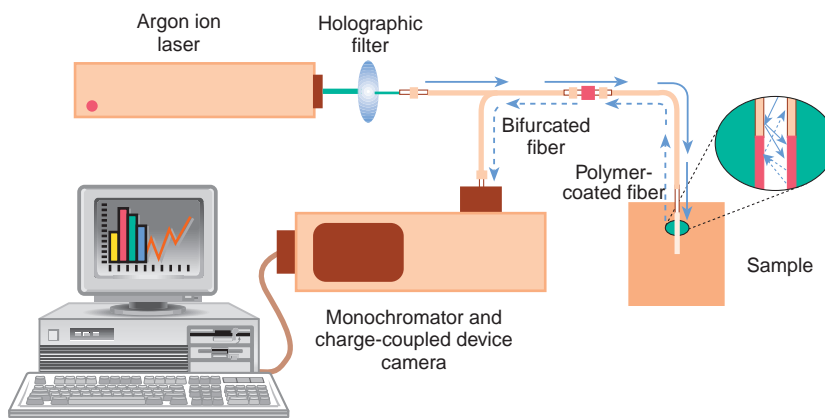

Figure 2. Schematic of the fiber-optic sensor's instrumental support.

The spectra resulting from the exposure of the sensor to selected pesticides (concentration at 1000 ppm) appear in Fig. 3, together with the response of the sensor to 100 ppm PMP for comparison. The pesticides were demonstrated to bind to the sensor reversibly, so loss of function or "poisoning" of the sensor was not a concern.

A smaller version of the device based on an Ocean Optics S2000 spectrometer shows promise for both sensitivity and selectivity in detecting the agents on a smaller scale. The entire instrument fits on a board $\approx 1.07 \times 0.76$ m. The limit of detection for this device is 7 ppt, with a linear dynamic range from 10 ppt to 10 ppm using a 200-μm polymer-coated fiber. This response should be sufficient to detect air concentrations that are orders of magnitude lower than the lethal dose. The response time for this smaller sensor is the same as that for the benchtop sensor. The main size-limiting factor for the device is the blue light-emitting argon laser and its power supply. Recent advances in blue light-emitting diodes and the use of other alternate excitation sources may eliminate the need for the "large" laser and allow miniaturization.

Explosives Detectors

Methods for the detection of explosives and explosive residues require complex analytical instruments such as liquid or gas chromatographs coupled with mass spectroscopic or chemiluminescent detection. The associated instrumentation is usually large, expensive, and difficult to maintain and requires skilled operators. If laboratory analysis is necessary, extensive documentation is needed for sample transport, increasing the possibility of sample contamination. Immunoassay tests are available for some explosives, but these are cumbersome and have short shelf lives. Conversely, sensors using optical fibers or self-contained optical devices could be small, simple, and portable. To incorporate optical transduction into a sensor design requires chemically specific recognition elements that have been unavailable until the development of MIPs. The phenomenon used to create the spectral signatures required for sensing is the formation of a specific discrete or charge-transfer (CT) complex.

All explosives used today are powerful oxidants. As such, they are good electron acceptors and will complex electron donor molecules in the ground state:

$$A + D \xrightleftharpoons{K_{CT}} AD + D \xrightleftharpoons{K_{CT_2}} AD_2 ,$$
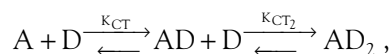
where A is an electron acceptor (the explosive), D is an electron donor (as part of the binder), and K is the equilibrium constant. AD represents the formation of a CT complex. These complexes have unique photophysical properties that are not present in either of the individual acceptors or donors. The theory behind CT absorption is well established[6] and is pictured in Fig. 4. The interaction between the donor highest-occupied molecular orbital (HOMO) with the acceptor lowest-unoccupied molecular orbital (LUMO) results in a net stabilization. This stabilization is directly related to the binding energy of the complex when compared with the individual components. In addition, this mixing of HOMO and LUMO results in the appearance of a new electronic transition for the complex, the CT absorption.

Of particular interest in this approach is the ability of CT complexes to absorb light at wavelengths that are relatively long, much longer than potential interferences. Such absorbances are specific to the combination of acceptor and donor, which allows a tuning of the absorption characteristics through judicious choice of donor. CT complex formation has been used for decades to help identify many classes of compounds, including explosives.[6,7]

Another important photophysical aspect of these complexes is that they also emit light, allowing relatively sensitive luminescence techniques to be used in their detection. An advantage of CT emissions is that they exhibit significant Stokes shift, emitting light of wavelengths that are much longer than the light they absorb. These two features make CT complexes unique in
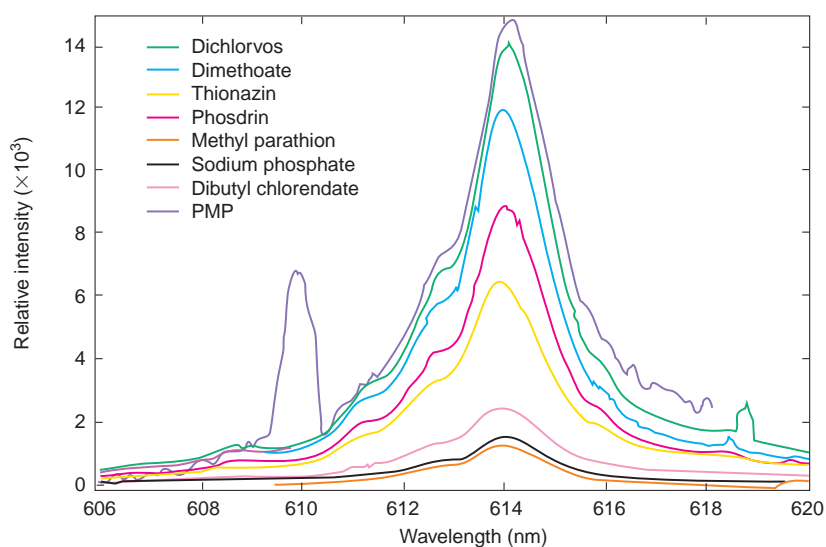
Figure 3. Sensor response to PMP (100 ppm) and likely interferents (all at 1000 ppm).
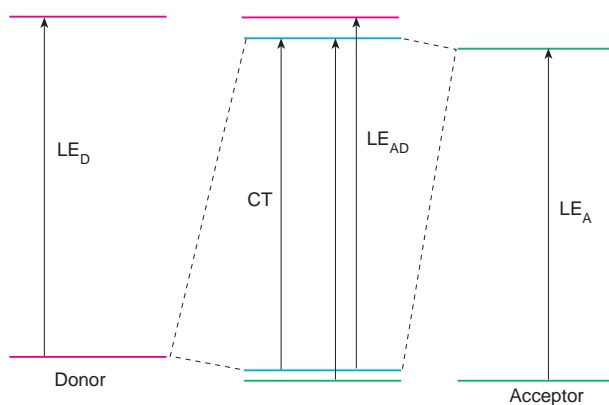
Figure 4. Diagram depicting the stabilizing interaction between the electron acceptor and electron donor, which results in the allowed charge-transfer (CT) transition. LE_A and LE_D are the acceptor and donor localized absorption, respectively.

their ability to absorb and emit light of a characteristic frequency, thus minimizing false positives.

A third feature of CT complex formation is that the forces that bind the acceptor and donor are extremely sensitive to steric interactions.[8,9] Template polymer techniques can be used to ensure that only the target molecules have access to the donor binding sight; molecules of different shape, even if they have similar electronic requirements, will not form CT complexes because they do not fit into the cavity. Potential interferences are greatly reduced because of this sensitivity. These interferences, including perfumes and deodorants, do not absorb (or emit) light in the range proposed for this sensor. Structurally related herbicides and pesticides such as 4,6-dinitro-o-cresol (detal, sinox, dinitrol), dinoseb, dicloran, or nitrolin will not form CT complexes with the same spectral characteristics as the target explosive, and therefore will not be falsely detected.

One must have an understanding of the solution photophysics of the CT complex before developing a working device. The first steps on this course are currently in progress using the 2,4,6-trinitrotoluene (TNT) model compound 1,3,5-trinitrobenzene (TNB). The latter is similar in shape and of comparable reduction potential to TNT, but does not pose as significant a safety hazard.

Three criteria were used to judge possible donor candidates:

1. The CT complex between the model acceptor and donors should have significant absorption at 630 nm or greater.

2. The extinction coefficient (ϵ_{CT}) at these wavelengths should be as large as possible.
3. The equilibrium constant K for formation of the complex must be relatively high.

These criteria are based on several factors. First, long-wavelength excitation will avoid significant interferences from most common volatile sources. Very few aromatic compounds absorb beyond 630 nm and therefore will not pose a significant problem in the detection of target molecules. In addition, the availability of low-cost, low-weight, low power consumption diode lasers that emit at 630 nm and beyond makes this an excellent target wavelength for compact device designs. The highest possible extinction coefficients at 630 nm are desired since the higher the extinction coefficients the lower the detection limits. Finally, high equilibrium constants for complex formation are necessary if vapor phase detection is to be successful. The target explosives have low vapor pressures and must be trapped and concentrated before detection will be possible.

Considerable spectroscopic data concerning complexes of TNT and various classes of donors are available.[10,11] The CT absorption spectra of a series of potential donors are shown in Fig. 5. The study of simple, substituted amine systems is likely to yield successful candidates for further studies for the following reasons. First, the target amines are readily available with an array of possible substitution, which allows tuning of the HOMO energies and oxidation potentials of the donor molecules. Thus, tuning of the absorption and emission characteristics of the complexes will be possible. Second, the parent compounds do not absorb at 630 nm, but the CT complexes absorb relatively strongly, as seen in Fig. 5. These systems are highly polarizable, which results in large extinction coefficients for the CT absorption and therefore lower
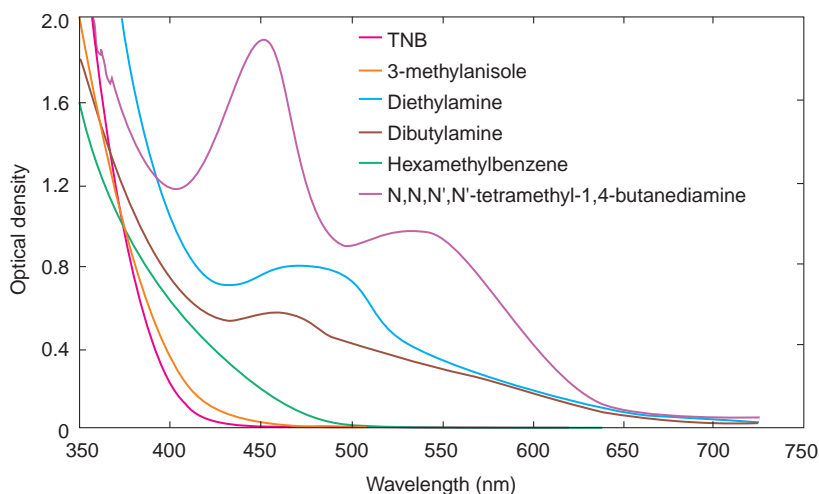
Figure 5. Absorption spectra obtained by the addition of donors to solutions of 1,3,5-trinitrobenzene (TNB) in dichloroethane.

detection limits. In addition, these compounds are easily copolymerized into malleable polymers that are generally thermally and photochemically stable as well as nontoxic.

There are several reports of equilibrium constants and extinction coefficients for TNT/donor and TNB/donor complexes in the literature.[10,11] Unfortunately, in many cases, errors have been made and unreliable values reported. A new method, which was developed in our laboratory, allows extinction coefficients and binding equilibrium constants for CT complexes to be correctly measured for the first time.[12,13]

A series of absorption spectra of the complex between TNB with diethylamine is shown in Fig. 6. The complex absorption spectrum has a maximum at 480 nm, with a second peak at 585 nm, although absorption does extend out past 630 nm. The concentration dependence of the spectral features indicates that the maximum at 480 nm has significant contributions from a 2:1 donor/acceptor complex (AD_2). Although the presence of AD_2 does complicate the determination of K_{CT} and ϵ_{CT}, it may, in fact, have an added benefit, i.e., a second "binding" site may make these systems more selective. Furthermore, the 2:1 complexes generally have much higher extinction coefficients than the related 1:1 complex.

The insert in Fig. 6 shows the dependence of the observed optical density at 585 nm (AD complex) on the relative dilution of the sample. The fact that a linear plot is obtained is evidence that, for this complex, binding is reversible. The determination of the equilibrium constant and extinction coefficient for this complex is in progress but, as we will show, the situation is much more complex than that depicted in the expression previously given.
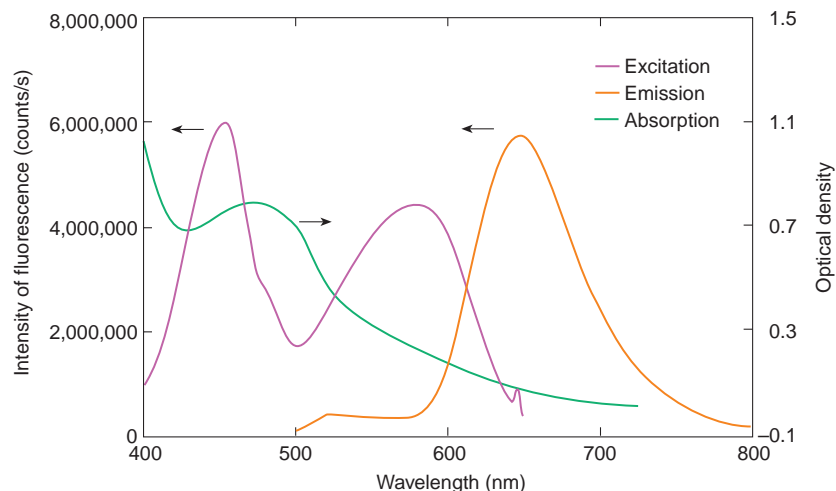
The emission and excitation spectra for the diethylamine/TNB complex are shown in Fig. 7 along with the absorption spectrum. The fact that the excitation and absorption spectra do not share the same features indicates that another nonemitting species must be present in these samples. Furthermore, based on the spectral evidence and the concentration dependence of these spectra, this nonemitting species
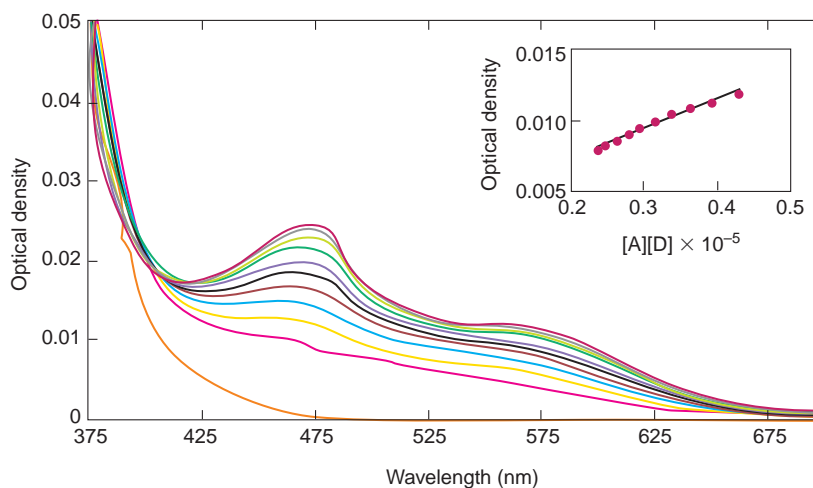
Figure 6. Spectral changes associated with the formation of a CT complex between TNB (concentration = 5×10^{-4} *M*) and diethylamine in 1,2-dichloroethane (0 to 2×10^{-2} *M*). The insert shows the dependence of the observed optical density at 585 nm on the relative dilution of the sample.

does not correspond to the 2:1 complex. At least one addition intermediate (perhaps more) is required to explain the observed behavior. The proposed reaction scheme is depicted in Fig. 8.

Formation of the 1:1 complex can lead to the 2:1 complex, although this can be avoided at low concentrations of donor. In addition, the 1:1 CT complex may rearrange to give the σ complex. This latter complex, which apparently does not emit, must also be formed reversibly, as proven in Fig. 6 (insert). In addition, the σ complex may rearrange to yield a substitution product. Although the formation of a permanent substitution product will complicate the fabrication of sensors using amines as donors, the rate of product formation in solution is slow and may not occur at all in polymer samples, depending on the dielectric constant of the polymer matrix. Conversely, the formation of an

Figure 7. Absorption, excitation, and emission spectra of the diethylamine/TNB CT complex.
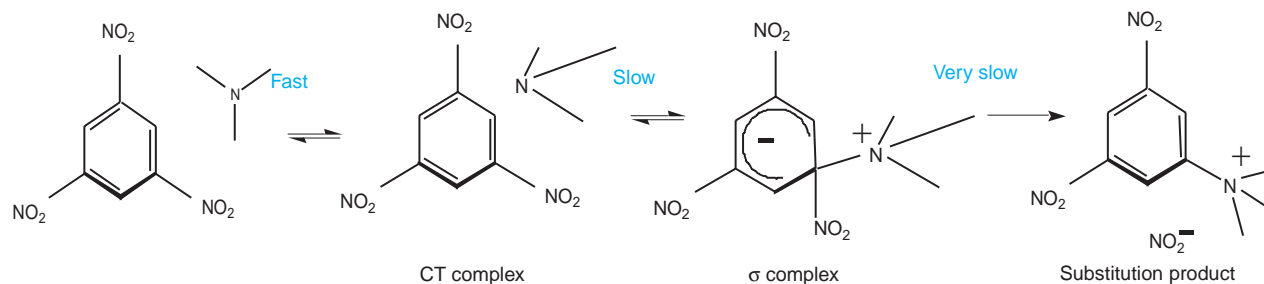
Figure 8. Reaction scheme for TNB and amines in solution.

amine substitution product will render the explosives inert, a potentially useful application in itself.

On the basis of the solution studies, it appears that tertiary amines substituted with vinyl groups show considerable promise as binders to produce template resins. The photophysics of these complexes allows luminescence detection to be used for signal transduction with excitation wavelengths in the 600-nm range and emission monitoring at 650 nm. MIPs to be used in explosive detectors are currently being fabricated based on these findings. Further studies using other donor systems are also under way.

CONCLUSIONS

Following the successful application of molecular imprinting to the sensing of metal ions and nerve agents, a new strategy has been found to extend the method to the detection of common explosives. This strategy relies on the nature of explosive molecules in that they are strong oxidizers and can accept electrons from donors to form complexes with useful spectral properties. The production of MIPs designed to facilitate the formation of CT complexes is expected to produce sensors with both selectivity and sensitivity. As new approaches are realized, molecular imprinting is rapidly becoming a solution to many sensing needs.[14]

REFERENCES

[1]Wulff, G., and Sarhan, A., "Use of Polymers with Enzyme-Analogous Structures for the Resolution of Racemates," *Angew. Chem. Int. Ed.* **11**(2) 341–346 (1972).
[2]Murray, G. M., Jenkins, A. L., Bzhelyansky, A., and Uy, O. M., "Molecularly Imprinted Polymers for the Selective Sequestering and Sensing of Ions," *Johns Hopkins APL Tech. Dig.* **18**(4), 464–472 (1997).
[3]Skoog, D. A., and Leary, J. J., *Principles of Instrumental Analysis*, Saunders College Publishing, Houston, TX (1992).
[4]Bae, S. Y., Zeng, X., and Murray, G. M., "A Photometric Method for the Determination of Pb2+ Following Separation and Preconcentration Using a Templated Ion Exchange Resin," *JAAS* **10**(10), 1177–1181 (1998).
[5]Jenkins, A. L., Uy, O. M., and Murray, G. M., "Polymer Based Lanthanide Luminescent Sensors for the Detection of Nerve Agents," *Anal. Comm.* **34**(8), 221–224 (1997).
[6]Mulliken, R. S., *Molecular Complexes*, Wiley-Interscience, New York (1969).
[7]Foster, R., *Organic Charge-Transfer Complexes*, Academic Press, New York (1969).
[8]Rathore, R., Lindeman, S. V., and Kochi, J. K., "Charge-Transfer Probes for Molecular Recognition via Steric Hindrance in Donor-Acceptor Pair," *J. Am. Chem. Soc.* **119**(40), 9393–9404 (1997).
[9]Frey, J. E., Aiello, T., Fu, S.-L., and Hutson, H., "Charge-Transfer Complexes of Tetracyanoethylene with Alkyl and Aryl Derivatives of the Halogens," *J. Org. Chem.* **61**(1), 295–300 (1996).
[10]Jurinski, N. B., and deMaine, P. A. D., "Charge-Transfer Complexes in Solution. I. Spectroscopic Studies of Aromatic Hydrocarbon-Aromatic Nitro Compounds Dissolved in Carbon Tetrachloride," *J. Amer. Chem. Soc.* **86**(16), 3217–3222 (1964).
[11]Thompson, Jr., C. C., and deMaine, P. A. D., "Solvent Effects on Charge-Transfer Complexes. II. Complexes of 1,3,5-Trinitrobenzene with Benzene, Mesitylene, Durene, Pentamethylbenenzene, or Hexamethylbenzene," *J. Phys. Chem.* **69**(8), 2766–2771 (1965).
[12]Ewald, A. H., "Effect of Pressure on Charge-Transfer Complexes in Solution," *Trans. Faraday Soc.* **64**(4), 733–738 (1968).
[13]Zaini, R., Orcutt, A. C., and Arnold, B. R., "Determination of Equilibrium Constants for Weakly Bound Charge Transfer Complexes," *IAPS Newsletter* **21**(1), 18–26 (1998).
[14]Murray, G. M., and Fish, R. H., "Chemical Slippers," *New Scientist* **155**(2099), 35–38 (1997).

THE AUTHORS

BRADLEY R. ARNOLD is Assistant Professor of chemistry at the University of Maryland, Baltimore County. He received his Ph.D. in chemistry from the University of Utah in 1991 and performed postdoctoral research at the National Research Council of Canada, Ottawa, and the Center for Photo-Induced Charge Transfer, University of Rochester. Dr. Arnold's research interests include the photochemistry of charge-transfer complexes and the investigation of photo-induced linear dichroism. He is a member of the American Chemical Society and the Inter-American Photochemical Society. He serves on the editorial board of *Spectroscopy Letters*. Dr. Arnold's e-mail address is barnold@umbc.edu.

ALEX C. EULER is a masters student at the University of Maryland, Baltimore County, where he received his B.S. in biochemistry in 1998. His current research interests include the determination of the thermodynamic binding parameters of charge-transfer complexes and the elucidation of the structure and electronic criteria that most strongly influence these weakly bound complexes. His e-mail address is aeuler1@umbc.edu.

AMANDA L. JENKINS is a postdoctoral researcher in the Chemical Analysis Laboratory of APL's Mechanical Services Group. Her research involves the design of polymer-based fiber-optic sensors and electrodes for environmental and counterterrorism applications. She obtained her M.S. degree (1996) and Ph.D. (1998) from the University of Maryland, Baltimore County, where she specialized in analytical chemistry. Dr. Jenkins has published many peer-reviewed articles in her field. She is a member of the American Chemical Society and the Society for Applied Spectroscopy. Her e-mail address is amanda.jenkins@jhuapl.edu.

O. MANUEL UY is a Principal Professional Staff chemist in APL's Technical Services Department. He earned a Ph.D. in physical chemistry from Case-Western Reserve University and was a postdoctoral fellow at Rice University and the Free University of Brussels. Before joining APL in 1981, he worked at Space Sciences, Inc., and General Electric as a research chemist. Dr. Uy has been engaged in research in space environmental effects and instrumentation, reliability, failure analysis, and advanced sensors for environmental and threat agent monitoring. He has published more than 100 papers. Dr. Uy is a member of Sigma Xi, the American Chemical Society, the Royal Chemistry Society, SPIE, and AIAA. His e-mail address is manny.uy@jhuapl.edu.

GEORGE M. MURRAY is a Senior Professional Staff chemist in APL's Technical Services Department and Adjunct Associate Professor of chemistry at the University of Maryland, Baltimore County. He received a B.A. in chemistry in 1982 and a Ph.D. in chemistry in 1988, both from the University of Tennessee, Knoxville. He performed his postdoctoral research at the Transuranium Research Laboratory located at the Oak Ridge National Laboratory. Dr. Murray's research interests focus on developing methods of analysis for the ultratrace determination of toxic substances in real samples. His laboratory specializes in the production of imprinted polymers and spectrochemical analysis. He is a member of the American Chemical Society and the Society for Applied Spectroscopy. Dr. Murray's e-mail address is george.murray@jhuapl.edu.