Cocrystals of 10-Methylphenthiazine and 1,3-Dinitrobenzene: Implications for the Optical Sensing of TNT-Based Explosives

S. Keith McNeil, Steven P. Kelley, Cameran Beg, Hamilton Cook, Robin D. Rogers, and David E. Nikles*

Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, United States

Ⓢ *Supporting Information*

ABSTRACT: The evaporation of an ethanol solution containing an equimolar mixture of 10-methylphenothiazine and 1,3-dinitrobenzene gave red-purple crystals. The diffuse reflection spectrum for the cocrystals showed a low reflectance from the UV through the visible spectrum until the reflectance increased at the red end of the visible spectrum. The crystal structure showed alternating π stacking of the electron-rich 10-methylphenothiazine and the electron-poor 1,3-dinitrobenzene. There were also hydrogen bonding interactions between the nitro groups from 1,3-dinitrobenzene and the aromatic hydrogen atoms from 10-methylphenothiazine. The infrared spectrum showed a shift to lower wavenumbers for the symmetric and antisymmetric stretching modes for the nitro groups. Thin films containing 10-methylphenothiazine in polystyrene were exposed to 1,3-dinitrobenzene vapor, and spectroscopic ellipsometry showed an average increase in the refractive index of 0.006 through the entire range of wavelengths from 1000 to 300 nm.

KEYWORDS: *10-methylphenothiazine, 1,3-dinitrobenzene, cocrystals, crystal structure, charge transfer complex, explosives detection*
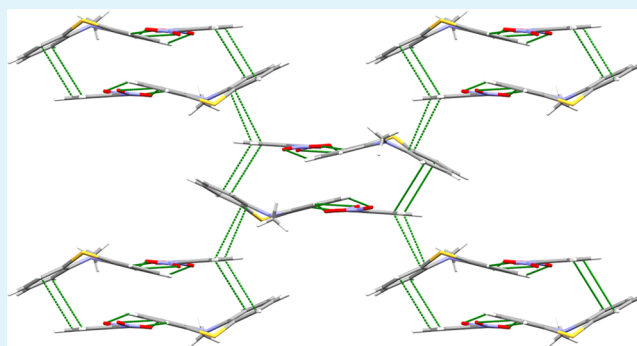
INTRODUCTION

Sensing the volatile nitro-aromatic compounds released by most common TNT-based explosives is the safest way to detect concealed explosives without disturbing them. The head space above TNT-filled land mines contains 0.35 to 9.7 pg/mL of 1,3-dinitrobenzene ($\sim 10^{-8}$ to 10^{-6} Torr), 0.28 to 1.4 pg/mL of 2,4-dinitrotoluene ($\sim 10^{-8}$ to 10^{-7} Torr), and 0.070 to 0.078 pg/mL of 2,4,6-trinitrotoluene ($\sim 10^{-9}$ Torr).[1] Although TNT was the main component in the explosive, it was a minor component in the equilibrium vapor above the mines. A sensor for landmines and other TNT-based explosives should sense for the presence of the more volatile components, such as 1,3-dinitrobenzene and 2,4-dinitrotoluene. We have chosen to begin our research by focusing on an optical sensor that would be sensitive to 1,3-dinitrobenzene vapor.

Ion-mobility spectrometers have been employed with great success[2] but are too expensive to be widely deployed outside specific high-risk areas such as airports. A simple and portable but highly sensitive chemosensor would be more suitable for large-scale deployment. Fluorescent or luminescent materials that undergo quenching in response to nitro-aromatics have been developed and used in the detection of trace nitro-aromatic vapors.[3−5] However, the structural requirements for making a material with strong fluorescence or luminescence as well as high affinity and selectivity for nitro-aromatics place serious restrictions on the other aspects of the sensor.

Mach−Zehnder interferometers have an extreme sensitivity to the optical phase and therefore can detect very small changes in refractive index. A sensor in the form of a Mach−Zehnder interferometer was capable of detecting optical-phase changes of less than 2.2π mrad and was sensitive to refractive-index changes of 10^{-6}.[6] This sensor could detect the difference in the refractive index between pure water and a solution containing 0.007% glucose ($\Delta n \sim 10^{-5}$). A waveguide Mach−Zehnder interferometer was designed to detect atrazine in an aqueous solution at concentrations as low as 100 ng/L.[7] A waveguide interferometer having a molecularly imprinted film was shown to be a highly sensitive and selective sensor for TNT vapor with the ability to detect gas-phase TNT in the parts per trillion concentration range.[8] The sensing mechanism was not understood but was presumed to arise from changes in the complex optical constants ($\tilde{n} = n − ik$, where n is the refractive index and k is the extinction coefficient) resulting from the formation of a charge-transfer complex with the electron-donating aromatic molecules in the film.

The formation of a charge-transfer complex between TNT and dicyclohexylamine and the subsequent color change in polymer films was the basis for spectroscopic assays of the TNT concentration in contaminated soils. Acetone−water (1:1) solutions containing 2,4,6-trinitrotoluene and dicyclohexylamine had a red-violet color with a peak at 531 nm ($\varepsilon = 1.16 \times 10^4$ M^{-1} cm^{-1}) in the electronic absorption spectrum.[9]

TNT and dicyclohexylamine formed a charge-transfer complex, giving rise to the absorption band. TNT was extracted from contaminated soil using organic solvents, the charge-transfer complex was formed, and the amount of TNT was determined spectrophometrically. The limit of detection was 0.38 μM. Other nitroaromatic compounds, including dinitrophenol picric acid, 2,4-dinitrotoluene, dinitroaniline, RDX, and PETN, did not interfere with the assay. However, tetryl (2,4,6-trinitrophenylmethylnitramine) did interfere with the assay. This concept was further developed to make optically clear, colorless polymer test strips made from poly(vinyl chloride) containing dicyclohexylamine and plasticized with dioctylphthalate.[10] When exposed to 30% aqueous acetone solutions containing TNT, the strips developed a violet color with an absorption at 530 nm resulting from the formation of the charge-transfer complex between TNT and dicyclohexylamine. These TNT-sensitive test strips could be used for a colorimetric assay of TNT extracted from contaminated soil with a lower limit of detection of 3 mg/L. Only tetryl interfered with this assay, whereas RDX, PETN, dinitrobenzene, and picric acid did not interfere with this assay. The selective formation of a charge-transfer complex either in solution or in the solid state (polymer film) is of interest for the detection of TNT. However, there were no reports on the use of this as a sensor for TNT in the vapor phase.

It has been known for more than a century that nitro aromatic molecules will form molecular complexes with electron-rich aromatic molecules, producing intense color changes. 1,3-Dinitrobenzene and 2,4-dinitrotoluene both formed jet-black molecular complexes with benzidine (4,4′-diaminobiphenyl).[11] Chloroform solutions containing aniline and either 1,3-dinitrobenzene, 1,4-dinitrobenzene, or 1,3,5-trinitrobenzene exhibited new absorptions extending from the UV region into the visible region with extinction coefficients of 10^2 to 10^3 M^{-1} cm^{-1}.[12] Mixtures of picryl chloride and hexamethylbenzene or picric acid and naphthalene formed highly colored solutions in chloroform.[13,14]

The crystal-structure packing observed in complexes between an electron-rich donor molecule and an electron-poor nitro-aromatic molecule exhibits a general trend with alternating stacking in charge-transfer complexes. The crystal structure of a 1:1 molecular complex between 1,4-dinitrobenzene and phenazine showed alternating stacks of phenazine and 1,4-dinitrobenzene molecules with a 361 pm distance between the center of the phenazine molecule and the center of the 1,4-dinitrobenzene molecule.[15] A 1:1 molecular complex of 2-aminobenzimidazole and 1,3,5-trinitrobenzene also showed alternating stacks.[16] In each case, the electron-poor nitro aromatic ring and the electron-rich aromatic rings were stacked face-to-face. This pattern of alternating stacking of the donor and acceptor molecules was also observed in the molecular complex of tetrathiafulvalene and 1,3-dinitrobenzene as well as in the molecular complex of 4-iodotetrathiafulvalene and 1,4-nitrobenzene.[17,18]

Our objective is to develop an interferometer-based sensor for the real-time detection of explosives such as TNT. The intense color changes observed when an electron donor formed a molecular complex with various nitro-aromatics suggest that nitro-aromatic molecules could be detected by forming a molecular complex with an electron-rich molecule. Our research is focused on developing electron-rich polymers with an affinity for nitro-aromatics that can be used in optical waveguides to detect nitro-aromatic molecules by changes in

the optical properties (i.e., the complex refractive index) of the polymer thin films. Here, we report the formation of a crystalline, highly colored charge-transfer complex between 10-methylphenothiazine and 1,3-dinitrobenzene. We also demonstrate the preparation and use of a polystyrene film loaded with 10-methylphenothiazine that showed a measurable change in its refractive index when exposed to vapor containing 1,3-dinitrobenzene.

■ EXPERIMENTAL SECTION

10-Methylphenothiazine (98%) and 1,3-dinitrobenzene (97%) were purchased from Sigma-Aldrich and used as received. Reagent grade ethanol was used as received. Technical grade acetonitrile was purchased from BDH Prolabo Chemicals and used as received.

Preparation of the Cocrystals. Two solutions were prepared: 10-methylphenothiazine (0.213 g, 1 mmol) in 15 mL of ethanol and 1,3-dinitrobenzene (0.168 g, 1 mmol) in 15 mL of ethanol. The solutions were mixed in a crystallization dish where the mixture turned a dark-red color. The ethanol was allowed to evaporate over the course of 2 days to deposit red-purple crystals. An ethanol solution of 10-methylphenothiazine was evaporated to produce colorless needles, whereas an ethanol solution of 1,3-dinitrobenzene was evaporated to deposit pale-yellow needles.

The melting point of 10-methylphenothiazine, 1,3-dinitrobenzene, and the cocrystals were measured using an Electrothermal model IA9100 digital melting-point apparatus. The crystals were ground into a fine powder and transferred to a capillary tube, filling less than 1 cm of the capillary tube. The instrument was allowed to equilibrate at 30 °C for 24 h. After the instrument was equilibrated, three samples were placed in a capillary tube holder and heated at a ramp rate of 1 °C/min. The melting point was determined as the temperature at which liquid formation appeared until the solid completely melted to form a meniscus. KBr pellets containing the crystals were used to obtain FTIR spectra at room temperature using a JASCO FT/IR-4100 FT infrared spectrometer. Diffuse reflectance spectra were recorded using a Shimadzu model UV-3600 spectrophotometer. A 200 mg sample was ground to a fine powder and placed in the sample holder. Spectra were recorded with 0.5 nm steps from 200 to 900 nm. X-ray crystallography was performed using a Siemens CCD SMART (Area Detector). The crystallographic information file is in the Supporting Information.

Polystyrene Films. Polystryene (3 and 1 wt %) stock solutions were prepared by dissolving polystyrene in toluene. The polymer solutions were then placed in a wrist-action shaker until the polymer completely dissolved. After the polymer dissolved, the polymer solutions were filtered once to remove any particles present in the solutions. Thin polymer films were prepared by spin coating using a Laurell (Model WS-400B-6NPP/LITE) spin coater. A silicon wafer (1 in. × 1 in.) surface was flooded with a polymer solution. The rotation speeds and times were varied to control the film thickness. After spin coating was complete, the films were dried at room temperature for 24−48 h, allowing the residual solvent to evaporate.

The thickness and the wavelength dependence of the optical constants (n and k) for the films were determined using a J.A. Woollam Co. variable-angle spectroscopic ellipsometer. Values of ψ and Δ were determined from 300 to 1000 nm at angles of 60, 65, 70, 75, and 80°. The data were fit to a model consisting of a thin polymer film of unknown optical constants and thickness on an infinitely thick silicon wafer having a 20 Å thick SiO_2 native oxide film. The thickness of the polymer film was estimated using surface profilometry (Dektak IIa) on a scratch made through the film. The real part of the refractive index for the polymer film was constrained to a Cauchy model.[19] Curves for the refractive index (n) and extinction coefficient (k) as a function of the wavelength for the polymer films were recorded before and after exposure to a saturated vapor of either 1,3-dinitrobenzene or 4-nitrotoluene.

■ RESULTS AND DISCUSSION

The slow evaporation of an ethanol solution containing 1 mmol of 10-methylphenothiazine and 1 mmol of 1,3-dinitrobenzene deposited dark-red−purple cocrystals, Figure 1a. A portion of the crystals were dissolved in CDCl$_3$, and ^{1}H NMR (Supporting Information) determined that the stoichiometry of the cocrystal was 1:1 (10-methylphenothiazine to 1,3-dinitrobenzene). The slow evaporation of an ethanol solution containing only 10-methylphenothiazine gave colorless needles, Figure 1b. The melting point of the cocrystals was compared with the melting points of the pure compounds. 10-Methylphenothiazine melted at 101.7−104.1 °C (lit. 99−100 °C[20]). The melting point of 1,3-dintrobenzene was 90.3−91.9 °C (lit. 90 °C[21]). The cocrystals melted at 61.7−63.4 °C, which was much lower than either of the pure compounds, to give a dark-red melt.

(A)

(B)
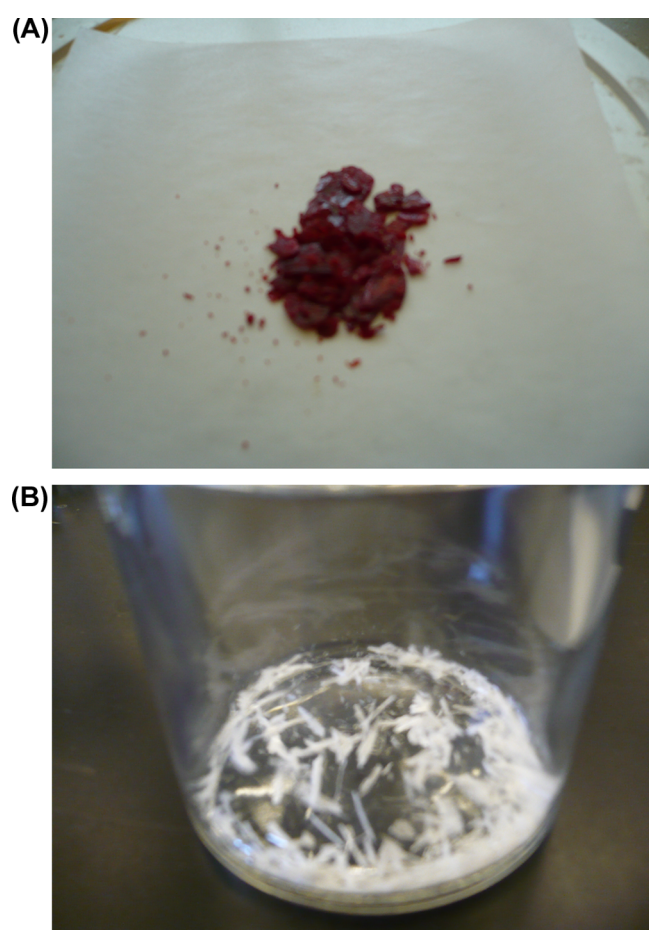
Figure 1. Images of the cocrystals containing 10-methylphenothiazine and 1,3-dinitrobenzene (a) and crystals of pure 10-methylphenothiazine (b).

The 1:1 cocrystal of 1,3-dinitrobenzene and 10-methylphenothiazine crystallized in the chiral, orthorhombic space group $P2_12_12_1$ with two symmetry-independent formula units ($Z = 8$) (Figure 2). The molecules had geometries similar to those of the pure compounds. The 1,3-dinitrobenzene molecules were planar except for the nitro groups, which were twisted slightly out of plane, and the 10-methylphenothiazine molecules had the typical geometry of phenothiazine and its derivatives, with both phenyl rings joining at an acute angle. The corresponding

bond distances and N- and S-centered bond angles of both of the 10-methylphenothiazine molecules were statistically equivalent to each other and were very similar to those in the reported crystal structure of 10-methylphenothiazine.[22]
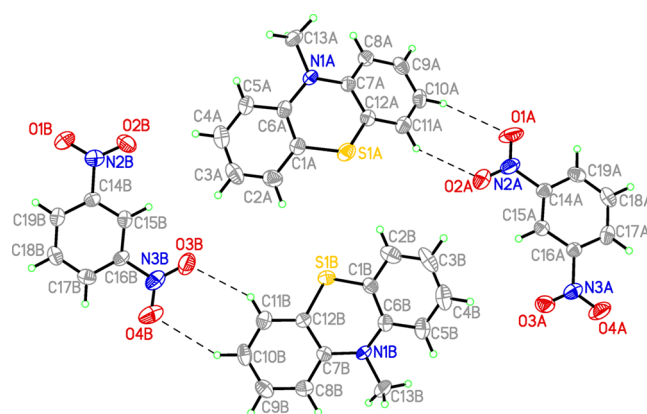

Figure 2. Fifty percent probability ellipsoid plot of the asymmetric unit of the cocrystal.

The symmetry-independent molecules had different short contact environments (Figure 3). Both of the 1,3-dinitrobenzene molecules made short contacts to five 10-methylphenothiazine molecules but not to the 1,3-dinitrobenzene molecules. Both accepted hydrogen bonds through either nitrate group. The major difference was that one of the 1,3-dinitrobenzene molecules, molecule A, formed π···π contacts with the end of a 10-methylphenothiazine molecule, whereas molecule B formed those contacts with the center.

(A) **(B)**
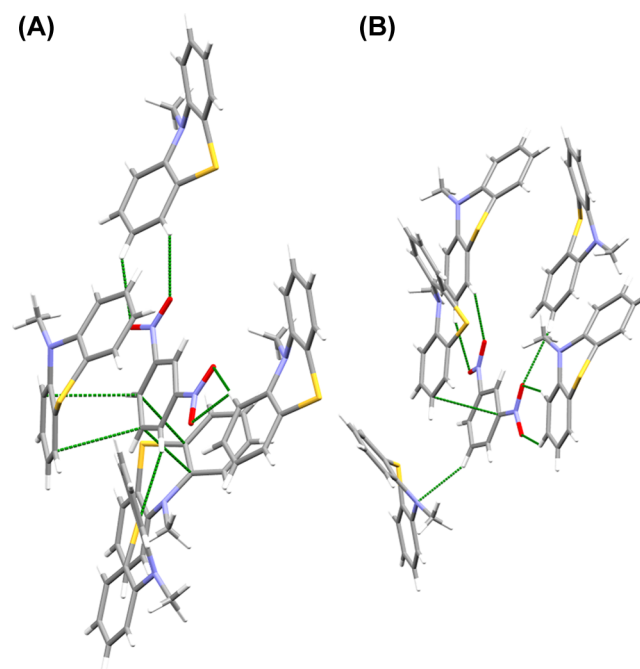
Figure 3. Short contact environments around 1,3-dinitrobenzene molecule A (left) and molecule B (right). The green lines indicate the contacts where the distance is less than the sum of the van der Waals radii.

The short contact environments of the 10-methylphenothiazine molecules also differed (Figure 4). 10-Methylphenothiazine molecule A interacted only with 1,3-dinitrobenzene molecules through hydrogen bonding to the nitro groups or through inter-ring $\pi\cdots\pi$ stacking. The nitrogen and sulfur atoms of 10-methylphenothiazine molecule A were not involved in short contacts. Molecule B made short contacts to two 10-methylphenothiazine molecules as well as four 1,3-dinitrobenzene molecules. The 10-methylphenothiazine B molecules interacted with each other through herringbone-type C−H$\cdots\pi$ interactions between the phenyl rings. 10-Methylphenothiazine molecule B did not π-stack with any 1,3-dinitrobenzene molecules; instead, it donated hydrogen bonds to nitro groups on two 1,3-dinitrobenzene molecules and accepted hydrogen bonds from 1,3-dinitrobenzene molecules at the N and S atoms.
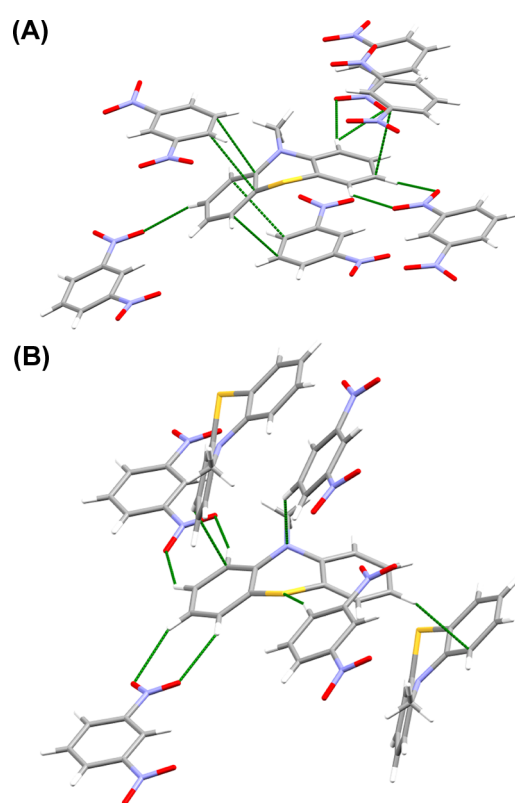
Figure 4. Short contact environment around 10-methylphenothiazine molecules A (top) and B (bottom). The green lines indicate the contacts where the distance is less than the sum of the van der Waals radii.

A major structural feature was the infinite hydrogen-bonded chains along the *b* axis formed by one of the 10-methylphenothiazine phenyl rings donating hydrogen bonds to 1,3-dinitrobenzene molecules on either side of it (Figure 5). Each of these chains only involved hydrogen bonds between 1,3-dinitrobenzene molecule A and 10-methylphenothiazine molecule A or 1,3-dinitrobenzene molecule B and 10-methylphenothiazine molecule B. The A and B chains were interdigitated with each other, which allowed for extra hydrogen bonding between the chains, as shown in Figure 5. The molecular recognition that allows cocrystallization may stem from this hydrogen bonding because neither 1,3-

dinitrobenzene or 10-methylphenothiazine can form these chains without the other.
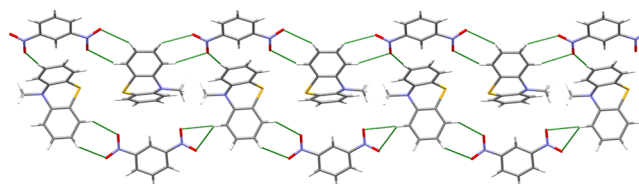
Figure 5. Hydrogen-bonded chains of 1,3-dinitrobenzene and 10-methylphenothiazine along the *b* axis. The green lines indicate the contacts where the distance is less than the sum of the van der Walls radii.

Other supramolecular structures can be described in terms of how the A and B chains, the hydrogen-bonded chains formed between 1,3-dinitrobenzene and 10-methylphenothiazine A, respectively, interacted with each other. Two adjacent A chains formed a dimer through $\pi\cdots\pi$ stacking. These chain dimers interacted with each other through $\pi\cdots\pi$ stacking as well forming a 3D network (Figure 6). The B chains were
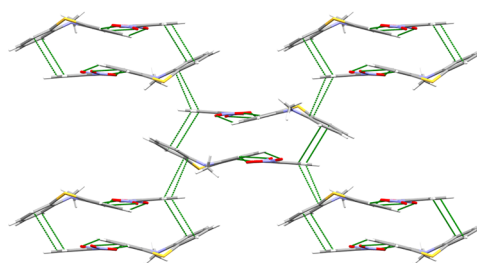

Figure 6. View along the *b* axis of the $\pi\cdots\pi$ stacking interactions between the A chains. The green lines indicate the contacts where the distance is less than the sum of the van der Waals radii.

interwoven into the A chain network through $\pi\cdots\pi$ stacking between 1,3-dinitrobenzene B molecules and 10-methylphenothiazine A molecules as well as through the hydrogen bonding of 1,3-dinitrobenzene A molecules to the S atom of the 10-methylphenothaizine B molecules. The B chains also formed a network with each other through the 10-methylphenothiazine-10-methylphenothiazine C−H$\cdots\pi$ contact as well as through hydrogen bonding between 1,3-dinitrobenzene B molecules and the N atom of 10-methylphenothiazine. Figure 7 shows the network of A chain dimers and the packing down the *b* axis.

The infrared spectrum in Figure 8 for the cocrystals containing 1,3-dinitrobenzene and 10-methylphenothiazine showed a shift to lower wavenumbers for the symmetric and antisymmetric stretching modes for the nitro groups (Table 1). This was consistent with the observations in the crystal structure that the nitro groups on 1,3-dinitrobenzene were hydrogen-bond acceptors. Serving as a hydrogen-bond acceptor will weaken the nitrogen−oxygen bond and thereby lead to a decrease in the stretching frequencies. There were no other obvious shifts in the peaks of the cocrystals relative to the spectra for 1,3-dinitrobenzene and 10-methylphenothiazine.

The diffuse reflectance spectrum in Figure 9 showed a high reflectance throughout the visible region for crystals of 10-methylphenothiazine, which was consistent with the off-white color. The reflectance spectrum for the dark-red cocrystals showed very low reflectance throughout the visible region that
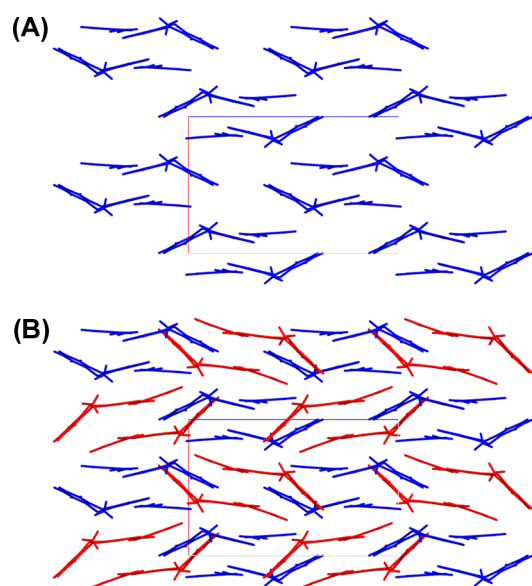
Figure 7. Packing down the *b* axis showing only A chains (top) and all atoms (bottom). The A chains are colored blue in both pictures. The B chains are colored red. Crystallographic axes are color coded as *a* = red, *b* = green, and *c* = blue.
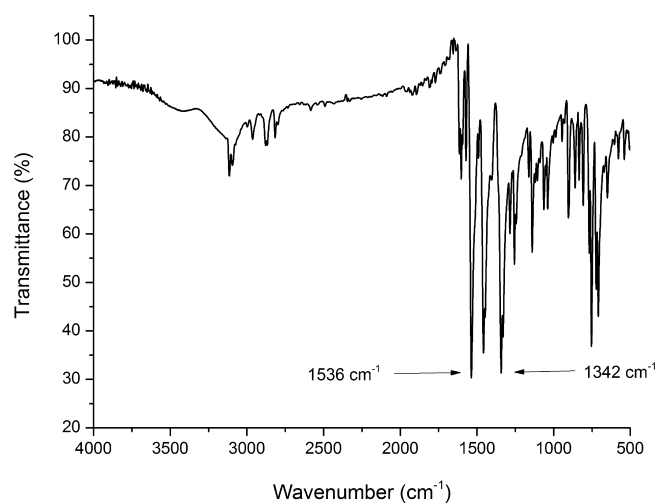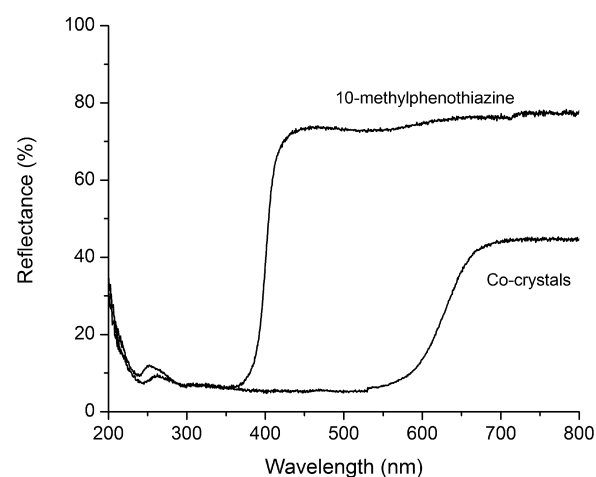

Figure 8. FTIR spectra of the cocrystal containing 10-methylphenothiazine and 1,3-dinitrobenzene recorded in a KBr pellet at room temperature.

Table 1. Stretching Vibrations Assignments for the NO$_2$ Asymmetric (ν_{as}) and Symmetric (ν_s) Stretching Frequencies

crystal	color	NO$_2$ ν_{as} (cm^{-1})	NO$_2$ ν_s (cm^{-1})
1,3-dinitrobenzene	white−yellow	1540	1347
10-methylphenothiazine	white		
cocrystal	red−purple	1536	1342

increased at the red end of the spectrum and continued to increase into the near-infrared. The increasing reflectance in the red end of the visible spectrum explained the red-purple color.

Implications for the Optical Sensing of TNT-Based Explosives. The intense color changes resulting from the interaction of electron-poor 1,3-dinitrobenzene with electron-rich 10-methylphenothiazine led to the expectation that this could form the basis of a new polymer waveguide


Figure 9. Diffuse reflectance spectra of the crystals of 10-methylphenothiazine and the cocrystals containing 1:1 10-methyl-phenothiazine and 1,3-dinitrobenzene.

interferometric sensor for the volatile components of TNT-based explosives, namely, 1,3-dinitrobenzene. This would not be a colorimetric sensor but rather a sensor for changes in the index of refraction (Δn) when the sensor is in the presence of 1,3-dinitrobenzene vapor. We envision a lab on a chip device consisting of a laser emitter, a waveguide sensor, and a detector. The sensor would be in the form of two parallel polymer waveguides with the polymer containing 10-methylphenothiazine. A laser beam would be split such that half the beam travels through one waveguide and the other half travels through the other waveguide. As long as the refractive index and the path length of each waveguide are the same, when the two beams leave the waveguide they will be in phase and interfere constructively. When 1,3-dinitrobenzene enters one of the waveguides (the sample path) and interacts with the 10-methylphenothiazine there will be a color change, leading to a peak in the spectrum for the extinction coefficient (k). Associated with this peak for k will be an anomalous dispersion for n, with an increase in the value of n in the spectroscopic region on the long wavelength side of the peak in k. The laser beam will have a wavelength chosen so that it is in the spectroscopic region on the long-wavelength side of the peak in k. As the laser beam travels through the sample path, it will not be attenuated. Instead, it will suffer a phase lag resulting from the increased value of the refractive index relative to the beam traveling through the other waveguide (the reference path). When the two beams leave the waveguides and recombine, they will not be in phase and will destructively interfere. This will be the basis for a waveguide sensor for vapor phase 1,3-dinitrobenzene, a volatile component of TNT-based explosives. Accordingly, we sought to determine whether films containing 10-methylphenothiazine could show an adequate change in their refractive index after exposure to 1,3-dinitrobenzene.

Films of 10-methylphenothiazine in a polystyrene matrix were cast onto silicon wafers by spin coating from a toluene solution. The amount of 10-methylphenothiazine that could be loaded into the polystyrene and give homogeneous films was limited to 0.1 wt %. Attempts to increase the 10-methylphenothiazine loading gave heterogeneous films with a phase separation of some of the 10-methylphenothiazine from the polystyrene matrix. This was unacceptable because this would lead to the scattering of the laser beam as it traveled

through the waveguide. Figure 10 shows the refractive index (n) as a function of the wavelength for a polystyrene film
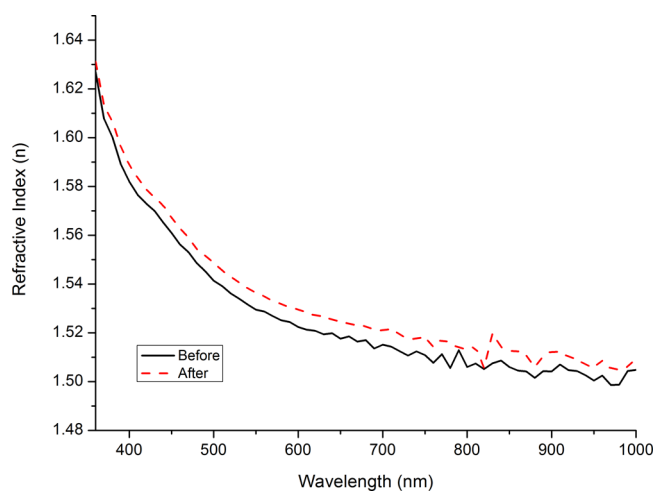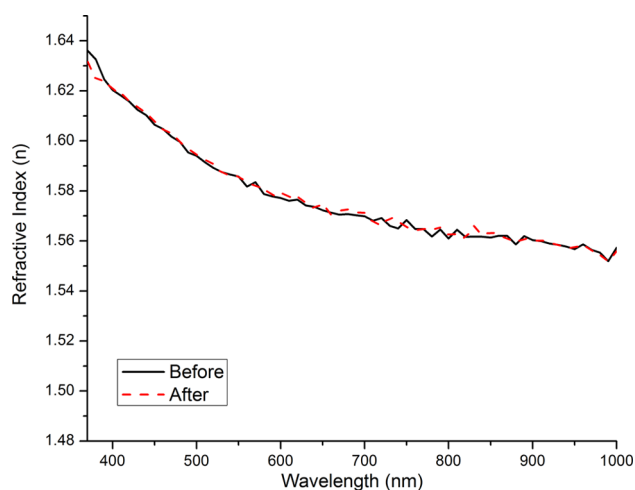

Figure 10. Plot of the refractive index as a function of the wavelength for a polystyrene film containing 0.1 wt % 10-methylphenothiazine before (black solid curve) and after (red dashed curve) a 10 s exposure to a saturated vapor of 1,3-dinitrobenzene.

containing 0.1% 10-methylphenothiazine before and after exposure to 1,3-dinitrobenzene. The refractive index of the 10-methylphenothiazine-loaded polystyrene film increased with decreasing wavelength, as expected for pure polystyrene. The presence of a small amount of 10-methylphenothiazine has no discernible effect on the refractive index of polystyrene. After 10 seconds of exposure to a saturated vapor of 1,3-dinitrobenzene, the refractive index of the film increased at all wavelengths. The average increase (Δn) was 6×10^{-3}, which was two to three orders of magnitude higher than that needed for use in a Mach−Zehnder optical sensor. The extinction coefficient (k) was found to be very low ($k > 0.01$), which was expected considering the very small amount of 10-methylphenothiazine. This result suggested that much lower detection limits could be achieved if more 10-methylphenothiazine was incorporated into the polymer.

4-Nitrotoluene has also been identified as one of the volatile components of TNT-based explosives.[23] Repeated attempts to grow cocrystals of 10-methylphenothiazine and 4-nitrotoulene resulted in a mixture of 10-methylphenothiazine crystals and 4-nitrotoluene crystals, as indicated by SCXRD analysis on multiple crystals selected from these reactions. Clearly, these two molecules did not form cocrystals. Spin-coated films containing 0.1 wt % 10-methylpheothiazine in a polystyrene matrix were exposed to a saturated vapor of 4-nitrotoluene. In Figure 11, plots of the refractive index as a function of the wavelength for the film before and after exposure are shown. There was no change in the refractive index (average Δn = 0.000). 10-Methylphenothiazine had very little affinity for 4-nitrotoluene, whereas it has a high affinity for 1,3-dinitrobenzene. This suggested the possibility of selectively sensing different nitro-aromatic molecules. This will be the subject of future research.

It was unfortunate that the amount of 10-methylphenothiazine that could be loaded into the polystyrene films was limited to 0.1 wt %. It was anticipated that when 1,3-dinitrobenzene entered the polystyrene films and interacted with the 10-methylphenothiazine the color will change as a charge-transfer

Figure 11. Plot of the refractive index as a function of the wavelength for a polystyrene film containing 0.1 wt % 10-methylphenothiazine before (black solid curve) and after (red dashed curve) a 10 s exposure to a saturated vapor of 4-nitrotoluene.

complex forms. This would allow the observation of the absorption spectrum for the films and an attempt to interpret the peaks in the spectrum of k as a function of the wavelength. However, because the amount of 10-methylphenothiazine was very low, the values for k were very low. In future work, we will seek to prepare polymer films with high 10-methylphenothiazine content. The approach will be to include the 10-alkylphenothiazine functional group as part of the polymer. An example would be the homopolymer of 3-vinyl-10-methylphenothiazine.[24]

■ CONCLUSIONS

10-Methylphenothiazine formed a strongly colored charge-transfer complex with 1,3-dinitrobenzene, a signature molecule for explosives such as TNT, both in solution and in the 1:1 cocrystal of the two compounds. Although the crystal structure showed that hydrogen bonding between 10-methylphenothiazine and 1,3-dinitrobenzene played a dominant role in the packing, the characteristic alternating $\pi−\pi$ stacking of a molecular charge-transfer complex was observed as well. Additionally, 10-methylphenothiazine incorporated into a polystyrene film underwent a measurable change in its refractive index when exposed to vapor containing 1,3-dinitrobenzene. This very exciting result underscores the potential of interferometry as a trace sensing method and encourages us to pursue new methods for increasing the sensitivity, such as increasing the concentration of the sensor molecule by covalently bonding it to the polymer chain.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
^{1}H NMR spectra for the cocrystals containing 10-methyl-phenothiazine and 1,3-dinitrobenzene and the crystallographic information file for the crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: dnikles@mint.ua.edu.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Jenkins, T. F.; Leggett, D. C.; Miyares, P. H.; Walsh, M. E.; Ranney, T. A.; Cragin, J. H.; George, V. *Talanta* **2001**, *54*, 501−513.
(2) Mäkinen, M.; Nousiainen, M.; Sillanpää, M. *Mass Spectrom. Rev.* **2011**, *30*, 940−973.
(3) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321−5322.
(4) Meaney, M. S.; McGuffin, V. L. *Anal. Bioanal. Chem.* **2008**, *391*, 2557−2276.
(5) Thomas, S. W., III.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339−1386.
(6) Lenferink, A. T. M.; Schipper, E. F.; Kooyman, R. P. H. *Rev. Sci. Instrum.* **1997**, *68*, 1582−1586.
(7) Schipper, E. F.; Rauchalles, S.; Kooyman, R. P. H.; Greve, J. *Anal. Chem.* **1998**, *70*, 1192−1197.
(8) Edmiston, P. L.; Campbell, D. P.; Gottfried, D. S.; Baughman, J.; Timmers, M. M. *Sens. Actuators, B* **2010**, *143*, 574−582.
(9) Üzer, A.; Erçağ, E.; Apak, R. *Anal. Chim. Acta* **2005**, *534*, 307−317.
(10) Erçağ, E.; Üzer, A.; Apak, R. *Talanta* **2009**, *78*, 772−780.
(11) Buehler, C. A.; Heap, A. G. J. *J. Am. Chem. Soc.* **1926**, *48*, 3168−3172.
(12) Landauer, J.; McConnell, H. *J. Am. Chem. Soc.* **1952**, *74*, 1221−1224.
(13) Ross, S. D.; Bassin, M.; Finkelstein, M.; Leach, W. A. *J. Am. Chem. Soc.* **1954**, *76*, 68−74.
(14) Ross, S. D.; Kuntz, I. *J. Am. Chem. Soc.* **1954**, *76*, 74−76.
(15) Sharma, C. V. K.; Rogers, R. D. *Cryst. Eng.* **1998**, *1*, 139−145.
(16) El-Medani, S.; Youssef, T. A.; Ramadan, R. M. *J. Mol. Struct.* **2003**, *644*, 77−87.
(17) Bryce, M. R.; Davies, S. R. *Synth. Met.* **1988**, *25*, 25−28.
(18) Batsanov, A. S.; Lyubchik, S. B. *Acta Crystallogr., Sect. E* **2003**, *59*, o326−o327.
(19) Cauchy, L. *Bull. Sci. Math.* **1830**, *14*, 9.
(20) Schmaltz, A. C.; Burger, A. *J. Am. Chem. Soc.* **1954**, *76*, 5455−5459.
(21) *CRC Handbook of Chemistry and Physics*, 76th ed.; Linde, D. R., Ed.; CRC Press: Boca Raton, FL, 1995−1996; pp 3−43.
(22) Chu, S. S. C.; Van der Helm, D. *Acta Crystallogr., Sect. B* **1974**, *30*, 2489.
(23) Harper, R. J.; Almirall, J. R.; Furton, K. G. *Talanta* **2005**, *67*, 313−327.
(24) Gipstein, E.; Hewett, W. A.; Need, O. U. *J. Polym. Sci., Part A-1* **1970**, *8*, 3285−3294.