

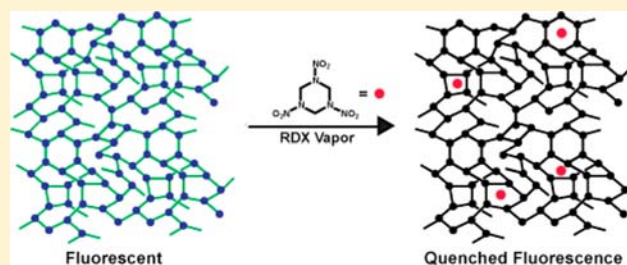
Direct Detection of RDX Vapor Using a Conjugated Polymer Network

Deepti Gopalakrishnan and William R. Dichtel*

Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301, United States

S Supporting Information

ABSTRACT: 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX) is a principal component of plastic explosives used in acts of terrorism and within improvised explosive devices, among others. Approaches to detect RDX compatible with remote, “stand-off” sampling that do not require preconcentration strategies, such as the swabs commonly employed in airports, will benefit military and civilian security. Such detection remains a significant challenge because RDX is 10^3 less volatile than 1,3,5-trinitrotoluene (TNT), corresponding to a parts-per-trillion vapor pressure under ambient conditions. Therefore, while fluorescence quenching of conjugated polymers is sufficiently sensitive to detect TNT vapors, RDX vapor detection is undemonstrated. Here we report a cross-linked phenylene vinylene polymer network whose fluorescence is quenched by trace amounts of RDX introduced from solution or the vapor phase. Fluorescence quenching is reduced, but remains significant, when partially degraded RDX is employed, suggesting that the polymer responds to RDX itself. The polymer network also responds to TNT and PETN similarly introduced from solution or the vapor phase. Pure solvents, volatile amines, and the outgassed vapors from lipstick or sunscreen do not quench polymer fluorescence. The established success of TNT sensors based on fluorescence quenching makes this a material of interest for real-world explosive sensors and will motivate further interest in cross-linked polymers and framework materials for sensing applications.



1. INTRODUCTION

Low-volatility explosives, such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), 1,3,5-trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN), pose major security risks and safety hazards throughout the world. RDX in particular is one of the most common components of plastic explosives. The detection of trace amounts of these compounds, ideally from the vapor phase, is essential for identifying explosive devices and individuals who have handled them recently. Vapor detection of 1,3-dinitrotoluene (DNT) and TNT has been studied extensively for the past two decades, resulting in several technologically relevant solutions.^{1,2} However, detecting RDX vapor remains an important and difficult challenge, as it is three orders of magnitude less volatile than TNT and is a weaker electron acceptor than nitroaromatic explosives.³

Analytical techniques that have been applied for trace RDX sensing include colorimetric immunoassays,^{4,5} surface enhanced Raman spectroscopy,^{6,7} ion mobility spectroscopy,⁸ and changes in the surface plasmon resonance of Au nanoparticles.^{9,10} Many of these techniques require specialized equipment and/or require preconcentration strategies.¹¹ Andrew and Swager recently reported that dihydroacridine derivatives show a “turn-on” fluorescence response to nitration induced by the photodegradation of RDX and PETN.^{12,13} This strategy demonstrated 100 pg sensitivity to RDX, similar to that of current swab-based transportation security systems.

Fluorescence quenching of conjugated polymers by appropriate analytes is a highly sensitive phenomenon that enables the direct detection of explosive vapors.^{1,14} In addition to its

high sensitivity, the simplicity of photoemission measurements facilitates the design of stand-off detection devices. Many conjugated polymers fluoresce intensely upon exposure to visible light. Following light absorption, excited states, or excitons, diffuse along and among polymer chains, where they may encounter the analyte of interest. The analyte non-radiatively deactivates the mobile excitons, interrupting the fluorescence of the material. Since excitons sample many polymer chains during their lifetimes, a small amount of the analyte can quench much of the fluorescence of a thin polymer film; this amplification strategy provides the high sensitivity necessary for vapor-phase detection.¹⁴ The most sensitive conjugated polymers sense TNT at parts per quadrillion levels,^{15,16} and these materials have been commercialized for military and security use. Recently developed material classes with high surface area to interact with analytes, including metal–organic frameworks (MOFs),^{17,18} conjugated microporous polymers,¹⁹ and self-assembled conjugated macrocycles,²⁰ have shown promise for detecting energetic compounds. However, most of these materials respond to TNT or more volatile nitroaromatics; none has demonstrated a response to RDX. Lei and co-workers observed unexpectedly high fluorescence quenching sensitivity from electrospun pyrene/polystyrene nanofibers for many nitro-containing explosives,²¹ although their sensitivity to RDX vapor was slow and demonstrated qualitatively. Here we describe a

Received: March 15, 2013

Published: May 3, 2013

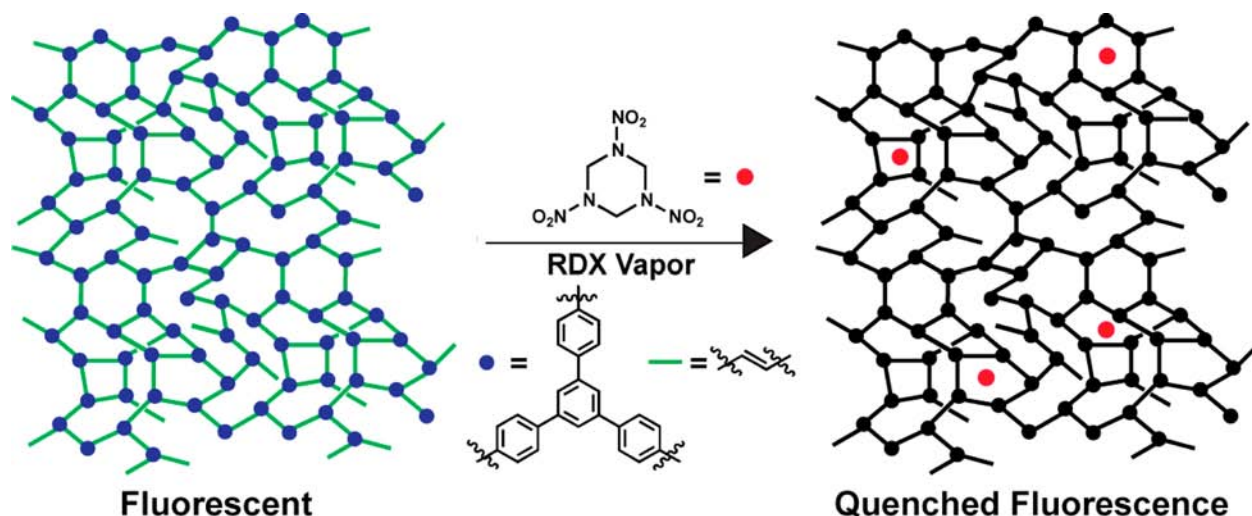


Figure 1. Schematic of RDX vapor detection by the TPV conjugated polymer network.

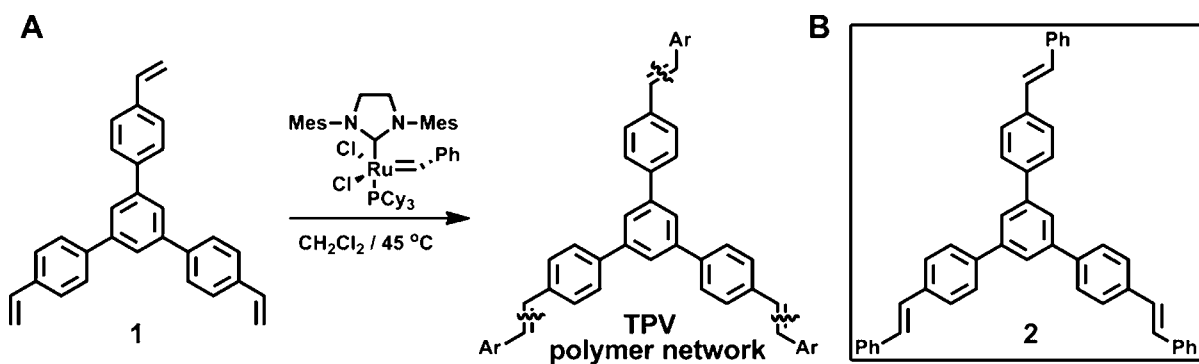


Figure 2. (A) Synthesis of the TPV network under ADMET reaction conditions. (B) Structure of soluble model compound 2.

conjugated polymer network prepared using olefin metathesis. Its films exhibit fluorescence quenching when exposed to RDX, TNT, and PETN delivered from either solution or vapor phase (Figure 1). This quenching response is not observed for solvent vapors, various amines, or volatile compounds outgassed from common household items. These results are relevant for practical RDX sensors, and we expect them to inspire further investigations of polymer networks and framework materials for sensing applications.

2. RESULTS AND DISCUSSION

2.1. Polymer Synthesis and Characterization. Conjugated networks were synthesized through an acyclic diene metathesis (ADMET) polymerization of a trifunctional styrene derivative **1** (Figure 2). Olefin metathesis was chosen for its high functional group tolerance, mild reaction conditions, benign stoichiometric byproducts (ethylene), and synthetically convenient monomers. **1** was polymerized under solvothermal conditions in CH_2Cl_2 at 45°C in the presence of 6 mol % of the Grubbs second-generation olefin metathesis catalyst, which provided tris(phenylene)vinylene (TPV) as an insoluble amorphous powder. FT-IR spectra of the TPV powders are consistent with the formation of a network linked by stilbene moieties and feature $\text{C}=\text{C}$ stretches at 1593 cm^{-1} and vinyl $\text{C}-\text{H}$ out-of-plane bends at 963 cm^{-1} (Figure 3A). We prepared tris(1,3,5-stilbenyl)benzene **2** as a model of the TPV network, which exhibits similar vibrations at 1594 and 959 cm^{-1} , respectively. Very weak peaks at 1627 and 987 cm^{-1} are

also observed in the TPV FT-IR spectrum, which correspond to unreacted styrene moieties that remain within the polymer network. These peaks are prominent in the FT-IR spectrum of monomer **1**. TPV powders were also characterized by solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR, which was also consistent with the expected stilbene-linked structure. The spectrum indicates two broad aromatic resonances centered at 141 and 137 ppm , as well as a peak corresponding to the vinylic carbons at 128 ppm (Figure S3). Despite the known reversibility of olefin metathesis, which might give rise to a crystalline network, all samples of TPV prepared under these conditions are amorphous and non-porous, as indicated by their low N_2 uptake (Figures S13 and S14). They may be heated to 600°C before decomposing to volatile products, as determined by thermogravimetric analysis (Figure S12).

Although characterizing the powder form of **1** provides important confirmation of the network structure, these powders strongly scatter light and are not ideal for detecting explosives via fluorescence quenching. Linear conjugated polymers are readily processed into films using solution-based methods, such as spin-coating or drop-casting.²² In contrast, cross-linked conjugated networks are inherently insoluble. We prepared thin films of TPV instead by including a fused SiO_2 substrate in the reaction vessel during its synthesis. The resulting films were washed extensively with CH_2Cl_2 to remove soluble byproducts and then activated by solvent evaporation under ambient conditions. The films show similar FT-IR spectra (Figure S9) as

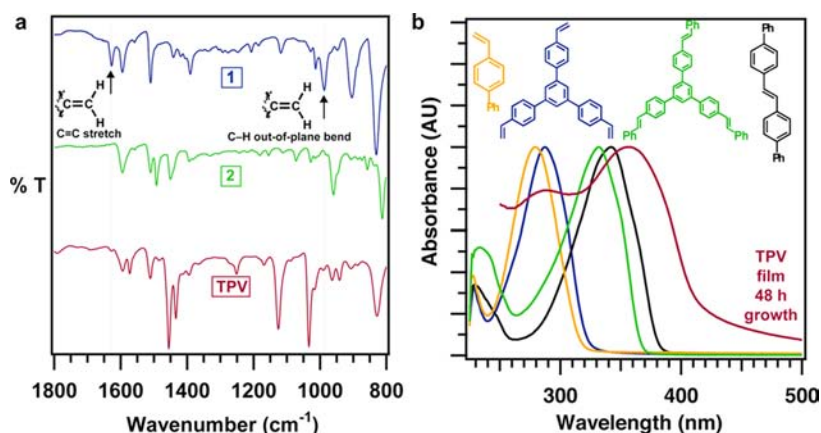


Figure 3. (A) Infrared spectra of **1**, **2**, and TPV powder. (B) Normalized UV/vis spectra (each in CH₂Cl₂) of 4-phenylstyrene (yellow), **1** (blue), 4,4'-biphenylstilbene (black), **2** (green), and TPV film grown on fused SiO₂ (red).

the TPV powders and are also amorphous, as determined by grazing incidence X-ray diffraction at the Cornell High Energy Synchrotron Source (CHESS). X-ray photoelectron spectroscopy indicated a narrow carbon signal centered at 284 eV, corresponding to the sp²-hybridized carbons within the TPV network. Strong Si and O peaks were also observed that originate from the fused SiO₂ substrate. Peaks corresponding to Ru were not observed, and only trace N was detected, indicating low amounts of catalyst decomposition products in the films (Figures S63–S65).

The electronic absorption and fluorescence of the films show subtle but reproducible differences as a function of the reaction time, which also proved to strongly impact their RDX response (see below). UV/vis spectra of the TPV films yield local maxima at 287 and 358 nm. The 358 nm peak increases in intensity relative to that of 287 nm as a function of reaction time. Films grown for 1 h showed an I_{358}/I_{287} ratio of 0.87, which increased to ~1.2 at 24 and 48 h reaction times. The 287 nm peak of films grown for 72 h typically appeared only as a shoulder of the 358 nm peak (Table S1). We attribute these spectral changes to increased conversion of styrene to stilbene moieties in the films. This conclusion was further supported by the solution absorption spectra of relevant model compounds. The λ_{max} of 4-phenylstyrene (279 nm) and monomer **1** (287 nm) correspond to the 287 nm absorption observed in the TPV film. The spectra of model compound **2** (332 nm) and 4,4'-biphenylstilbene (342 nm) are indicative of extended conjugation (Figure 3B). These peaks correspond well to the 358 nm absorption of the TPV film, which is red-shifted further due to its greater conjugation and/or aggregated thin-film structure. In summary, UV/vis spectroscopy provides a qualitative indication of the extent of the olefin metathesis reaction in the TPV films and suggests increased conversion of the metathesis reaction over reaction times up to 72 h.

2.2. Fluorescence Response to Explosives Introduced from Solution. We first evaluated the fluorescence response of TPV films polymerized for 24, 48, and 72 h to RDX introduced from solution. RDX was extracted from commercial samples of the compound adsorbed onto sand that are used to train bomb-detecting canines. RDX was crystallized twice, stored at low temperature, and protected from light prior to performing quenching experiments (see SI for experimental details and safety considerations). ¹H NMR of the twice-crystallized material indicated the expected resonance for RDX, along with a trace amount of octahydro-1,3,5,7-tetranitro-1,3,5,7-

tetrazocine (HMX) (see Figure 5B). HMX is a cyclic tetranitramine explosive related to RDX and has an even lower vapor pressure. A RDX stock solution (1 mg/mL dissolved in 1:1 v/v CH₃CN:MeOH) was prepared and diluted further to deliver picogram quantities of RDX to the films. After the film's initial fluorescence was recorded, the RDX solution was introduced and the solvent evaporated under high vacuum. The film's fluorescence was again recorded. This procedure was repeated to introduce cumulative RDX dosages between 0 and 18 765 pg and reproduced in triplicate for films grown for 24, 48, and 72 h. Each TPV film showed reduced emission intensity when exposed to even 1 pg of RDX, and this response saturated at cumulative doses of ~1800 pg. The films exhibited increased quenching response as a function of their reaction time. The 72 h films showed 51 ± 15% quenching when exposed to 25 pg of RDX and saturated at 71 ± 9% at larger doses. In contrast, the 48 h films showed 24 ± 6% when exposed to 25 pg of RDX and saturated at 53 ± 10%, while the 24 h films showed only 9 ± 4% when exposed to 25 pg of RDX and saturated at 14 ± 9% (Figure 4A–D). Although each film responded to low picogram quantities of RDX, this response is nonlinear at this dosage. Nonlinear, reproducible quenching responses were also observed for 72 h films exposed to lower dosages of 0–2900 fg (Figure S24) and 0–1700 ag of RDX (Figure S25). Upon still further reduction of the RDX dosage, 72 h films exhibited an approximately linear quenching response over the 1–30 ag range (Figure 4E), a promising level of sensitivity for detecting RDX from the vapor phase. We also performed an important control experiment, in which the fluorescence responses of TPV films grown for 72 h were measured after sequential introduction and evaporation of the same 1:1 v/v CH₃CN:MeOH mixture used to prepare the dilute RDX solutions. We noted that residual amounts of these solvents induce an increase in TPV fluorescence intensity if they are not evaporated completely (Figure 4F). Therefore, quenching observed in response to the RDX-containing solution cannot be attributed to residual solvent or the presence of trace impurities found in these solvents. Similar responses were observed for 72 h films exposed to picogram amounts of TNT and PETN under the same conditions (Figure S37). We hypothesize that the increased response of the 72 h films compared to those grown for shorter times derives from longer exciton diffusion lengths that arise from the increased degree of polymerization of the network.

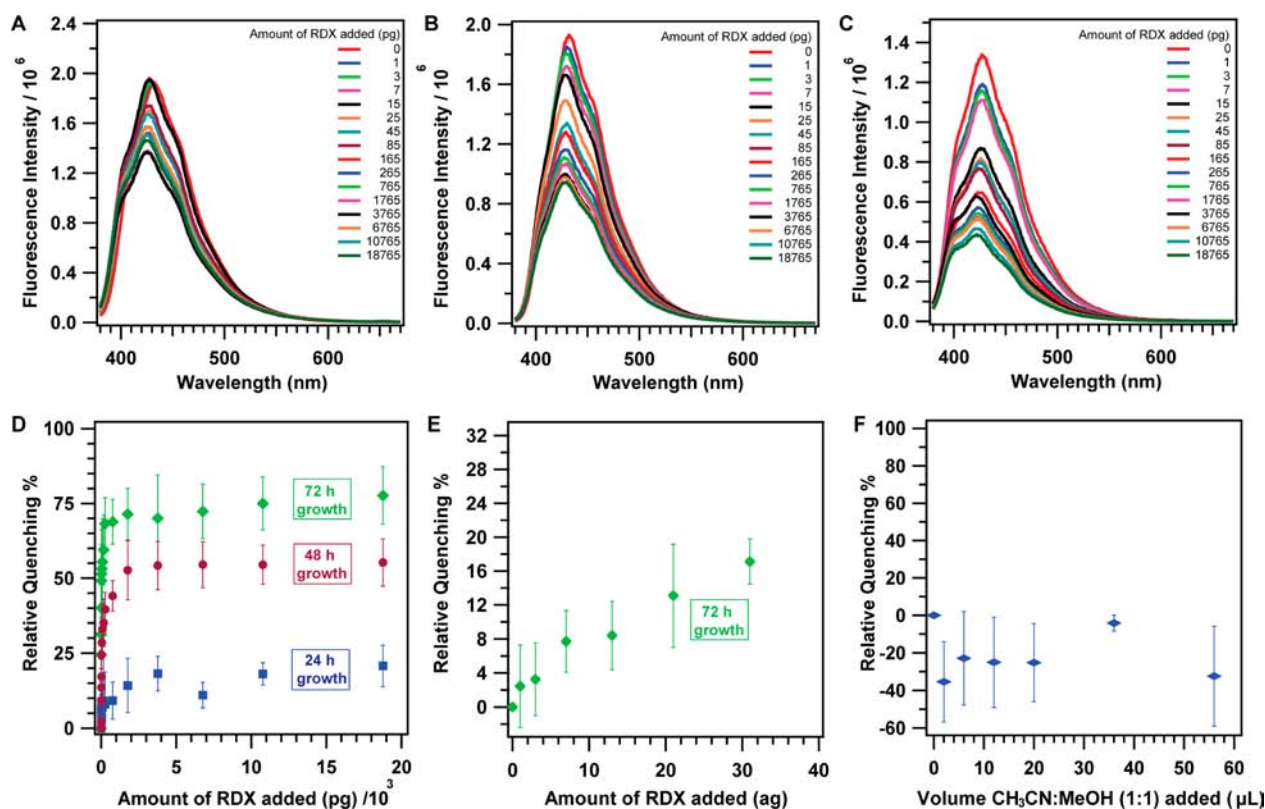


Figure 4. (A) Quenching of fluorescence of TPV film grown for 24 h. (B) Quenching of fluorescence of TPV film grown for 48 h. (C) Quenching of fluorescence of TPV film grown for 72 h. (D) Relative quenching % of TPV films on exposure to RDX in solution with varying time of reaction. Each data point indicates the average response of three different films. The error bars show one standard deviation from the average. (E) Fluorescence quenching % of TPV films grown for 72 h in response to attogram (ag) quantities of RDX. (F) Response of 72 h TPV films to 1:1 v/v $\text{CH}_3\text{CN}:\text{MeOH}$ solution in the absence of RDX.

Given RDX's poor photostability, which was utilized in the detection strategy of Andrew and Swager,^{12,13} we evaluated the response of the 72 h TPV film to partially degraded samples of RDX to determine whether the polymer responds to RDX itself or its degradation products. RDX photolysis produces a complex mixture of products: hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), 1,3-dinitro-1,2,3,4-tetrahydro-1,3,5-triazine (MUX), 1,3,5-triazine (TUX), and perhaps others, any of which might quench the fluorescence of the TPV network (Figure 5A).²³ To assess this possibility, we photolyzed a solution of recrystallized RDX (10 mg/mL in 1:1 v/v $\text{CD}_3\text{CN}:\text{CD}_3\text{OD}$) for 88 h using a hand-held UV lamp. ^1H NMR analysis of the solution clearly indicated significant degradation, along with $\sim 42\%$ residual RDX (Figure 5B). This solution was diluted with 1:1 v/v $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ to a $10 \mu\text{g}/\text{mL}$ concentration based on the initial concentration of crystallized RDX. A 72 h film exposed to 25 pg of RDX from this solution showed 26% quenching and saturated at 46% (Figure 5C). The reduced saturated quenching response, despite the photolyzed solution containing significant amounts of RDX, indicates that the photo-degradation products do not quench the fluorescence of the TPV network. A similar reduction in quenching efficiency was observed when commercial RDX standard solutions, which had been stored for prolonged periods, were employed. The films showed $27 \pm 13\%$ quenching on exposure to 25 pg and saturated at $53 \pm 14\%$ (Figure 5C). These observations suggest that TPV films respond to RDX itself and not its degradation products.

2.3. Fluorescence Response to Explosive Vapors.

Military and civilian security applications will greatly benefit from directly detecting RDX vapor at equilibrium or subequilibrium vapor pressures without the need for preconcentration strategies. We evaluated each of the TPV films in this context by storing the film in the headspace of a closed glass vessel containing a sample of crystallized RDX at ambient temperature and pressure. Prior to the quenching experiments, the vessel containing the RDX was placed under high vacuum for 6 h at 25°C while protected from light exposure to minimize the presence of other volatile compounds. The fluorescence of 24, 48, and 72 h films was recorded in triplicate as a function of exposure time. As before, the 72 h film showed both the fastest and largest response, with $22 \pm 11\%$ quenching within 30 s, which saturated at $50 \pm 11\%$ at longer exposure times. The 48 and 24 h films showed qualitatively similar quenching behavior, but with a reduced response (Figure 6A). We also evaluated the response of the films directly to the canine training aids, which contain RDX, presumably alongside its degradation products. Similar, albeit reduced responses were observed (Figure S36), which are consistent with our solution RDX degradation study. The 72 h TPV films also responded to vapors of canine training samples of TNT and PETN vapors (Figure S40). We also subjected films grown for 72 h to vapors of compounds or household items typically encountered in airport security environments: EtOH, lipstick, and sunscreen (Figure 6B). None of these compound mixtures quenched the fluorescence of the TPV films, which instead showed increased fluorescence intensity in

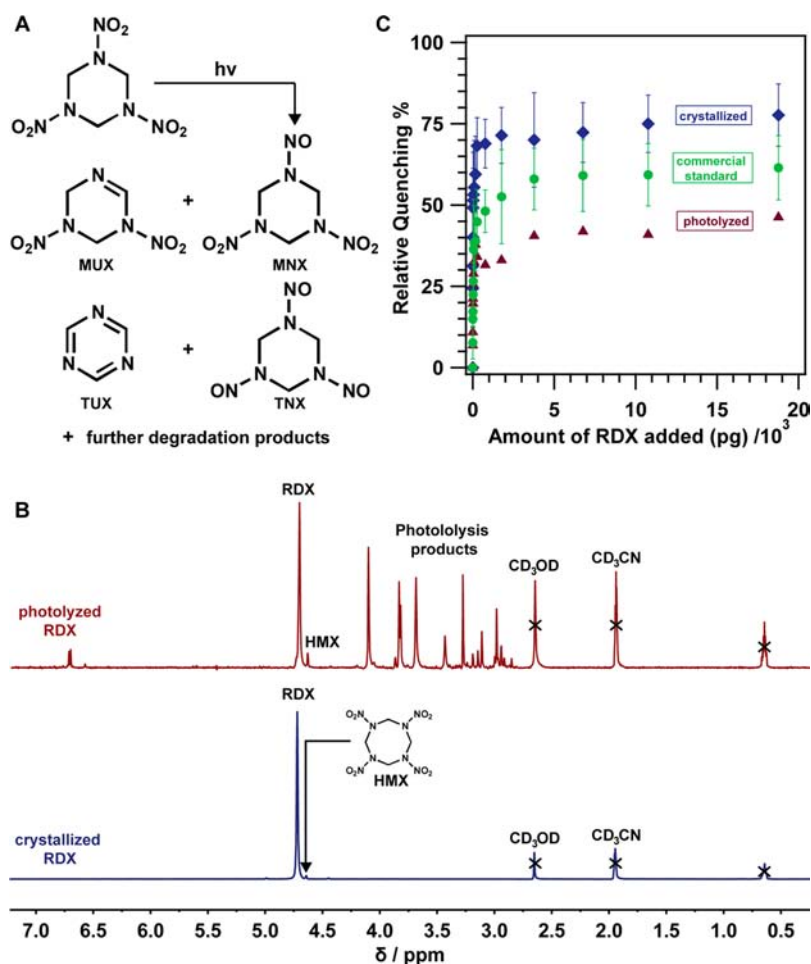


Figure 5. (A) Schematic of several possible RDX photolysis products (see refs 12, 13, and 23). (B) Partial ¹H NMR spectra (300 MHz 1:1 CD₃CN:CD₃OD, 298 K) of crystallized RDX before (blue) and after irradiation (red) with UV light. The photolyzed spectrum shows clear evidence of RDX degradation. (C) Fluorescence quenching curves of 72 h TPV films exposed to solutions of crystallized (blue) and photolyzed (red) and a RDX commercial standard (green). Each data point indicates the average response of three different films. The error bars show one standard deviation from the average.

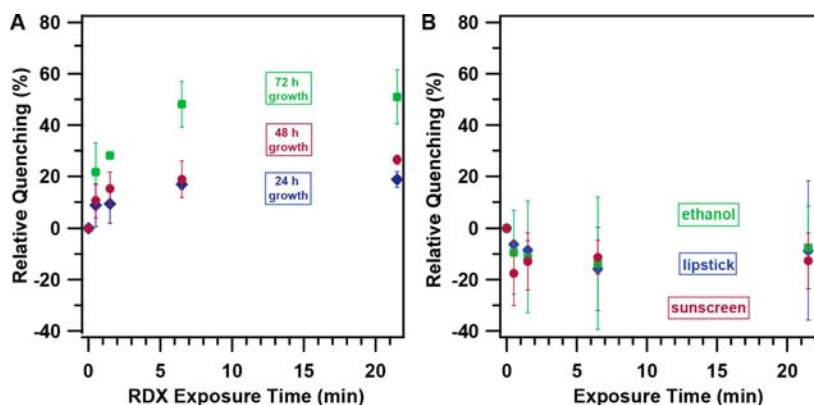


Figure 6. (A) Response of TPV films to RDX vapor exposure. (B) Response of 72 h TPV films to outgassed vapors from EtOH, and household items, lipstick and sunscreen. Each data point indicates the average response of three different films. The error bars show one standard deviation from the average.

each case. This response is similar to that observed when residual volatile solvents remain in the films. Electron-rich aromatics have also been shown to increase the fluorescence intensity of conjugated microporous polymers capable of sensing DNT.^{19,24} Vapors of several volatile amines, including NEt₃, pyridine, aniline, and *N*-methylpiperidine, also induce

increases in emission intensity (Figure S56), also indicating that quenching occurs only in the presence of the electron deficient explosives. The reduced potential for false positives and high sensitivity to RDX make TPV polymers a potential material for commercial sensing technology. These findings represent a

promising demonstration of RDX vapor detection through a fluorescence quenching mechanism.

3. CONCLUSIONS

We synthesized a conjugated polymer network whose fluorescence is quenched by explosive vapors. Analysis of the insoluble powder form of the polymer confirmed that the olefin metathesis reactions employed in its synthesis provided the anticipated chemical linkages. Thin films of these polymers were grown on fused SiO₂ substrates, and UV/vis absorption spectroscopy of these films suggested increased conversion of their reactive groups over 72 h. The fluorescence of these films decreased upon exposure to RDX, introduced either from solution or from the vapor phase, and depended strongly on the film's growth time. Degradation studies also suggest that the films respond to RDX itself and retain most of their sensitivity to partially degraded samples. These promising findings warrant future inquiry into conjugated polymer networks, as their performance might be improved by achieving long-range order, high surface area, and improved control over film thickness. While it remains challenging to characterize and control the mesoscopic structure of amorphous, cross-linked polymer films, we will continue to study these materials and will elucidate structure–property relationships of additional functional aromatic monomers. The high RDX and PETN sensitivity of the conjugated network demonstrated herein justifies investment in these efforts.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data for all new compounds and materials and fluorescence response of TPV films to explosives. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

wdichtel@cornell.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the NSF CAREER award (CHE-1056657). We also made use of the Cornell Center for Materials Research Shared Facilities, which are supported through the NSF MRSEC program (DMR-1120296). CHESS is supported by the NSF and NIH/NIGMS via NSF award DMR-0936384. The authors thank J. W. Colson for acquiring grazing incidence X-ray diffraction at CHESS. D.G. acknowledges the award of a Faculty for the Future fellowship from the Schlumberger Foundation.

■ REFERENCES

- (1) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.
- (2) Toal, S. J.; Trogler, W. C. *J. Mater. Chem.* **2006**, *16*, 2871.
- (3) Pon Saravanan, N.; Venugopalan, S.; Senthilkumar, N.; Santhosh, P.; Kavita, B.; Gurumalles Prabu, H. *Talanta* **2006**, *69*, 656.
- (4) Charles, P. T.; Kusterbeck, A. W. *Biosens. Bioelectron.* **1999**, *14*, 387.
- (5) Desmet, C.; Blum, L. J.; Marquette, C. A. *Anal. Chem.* **2012**, *84*, 10267.
- (6) Moros, J.; Laserna, J. J. *Anal. Chem.* **2011**, *83*, 6275.

- (7) Farrell, M. E.; Holthoff, E. L.; Pellegrino, P. M. *Proc. SPIE* **2012**, *8358*, 835816/1.
- (8) Tabrizchi, M.; Ilbeigi, V. *J. Hazard. Mater.* **2010**, *176*, 692.
- (9) Riskin, M.; Tel-Vered, R.; Willner, I. *Adv. Mater.* **2010**, *22*, 1387.
- (10) Ja, S.-J. *Proc. SPIE* **2012**, *8358*, 83580S/1.
- (11) Xiong, R.; Odbadrakh, K.; Michalkova, A.; Luna, J. P.; Petrova, T.; Keffer, D. J.; Nicholson, D. M.; Fuentes-Cabrera, M. A.; Lewis, J. P.; Leszczynski, J. *Sens. Actuators, B* **2010**, *B148*, 459.
- (12) Andrew, T. L.; Swager, T. M. *J. Am. Chem. Soc.* **2007**, *129*, 7254.
- (13) Andrew, T. L.; Swager, T. M. *J. Org. Chem.* **2011**, *76*, 2976.
- (14) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.
- (15) Rose, A.; Zhu, Z.; Madigan, C. F.; Swager, T. M.; Bulovic, V. *Nature* **2005**, *434*, 876.
- (16) Anzenbacher, P.; Mosca, L.; Palacios, M. A.; Zyryanov, G. V.; Koutnik, P. *Chem.—Eur. J.* **2012**, *18*, 12712.
- (17) Lan, A.; Li, K.; Wu, H.; Kong, L.; Nijem, N.; Olson, D. H.; Emge, T. J.; Chabal, Y. J.; Langreth, D. C.; Hong, M. *Inorg. Chem.* **2009**, *48*, 7165.
- (18) Lan, A.; Li, K.; Wu, H.; Olson, D. H.; Emge, T. J.; Ki, W.; Hong, M.; Li, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2334.
- (19) Liu, X.; Xu, Y.; Jiang, D. *J. Am. Chem. Soc.* **2012**, *134*, 8738.
- (20) Che, Y.; Gross, D. E.; Huang, H.; Yang, D.; Yang, X.; Discekici, E.; Xue, Z.; Zhao, H.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2012**, *134*, 4978.
- (21) Wang, Y.; La, A.; Ding, Y.; Liu, Y.; Lei, Y. *Adv. Funct. Mater.* **2012**, *22*, 3547.
- (22) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.
- (23) Peyton, G. R.; LeFaivre, M. H.; Maloney, S. W. *Verification of RDX Photolysis Mechanism*; Defense Technical Information Center, Nov 1999; Accession No. ADA371755.
- (24) Pramanik, S.; Zheng, C.; Zhang, X.; Emge, T. J.; Li, J. *J. Am. Chem. Soc.* **2011**, *133*, 4153.