

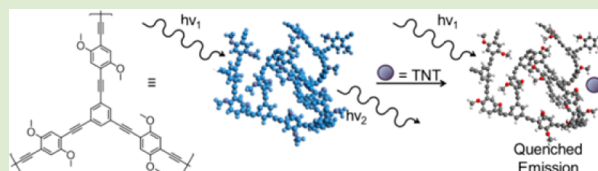
Conjugated Porous Polymers For TNT Vapor Detection

Jennifer L. Novotney and William R. Dichtel*

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

Supporting Information

ABSTRACT: A conjugated porous polymer (CPP) that exhibits fluorescence quenching when exposed to TNT vapor was synthesized via a Sonaogashira cross-coupling reaction. Two polymerization solvents, DMF and PhMe, and two activation procedures, evacuation and lyophilization, were evaluated to optimize the response of the CPP to TNT vapor. Key differences in surface area and absorption were seen as a function of polymerization solvent and activation procedure. The polymer synthesized in DMF and activated by lyophilization had the highest surface area and the strongest response to TNT vapor. This paper demonstrates the importance of growth and activation conditions in optimizing the porosity and sensing performance of CPPs.



Explosive compounds, such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrotriazinane (RDX), and pentaerythritol tetranitrate (PETN), pose a large threat to public safety and military security. Detecting explosive devices or individuals contaminated by these compounds, which have low vapor pressures, represents a significant and important challenge.^{1–4} Contemporary approaches include itemizers commonly used in aviation security, trained canines, colorimetric spot tests,^{5,6} and chemoresistive devices,^{7–9} many of which are equipment intensive, expensive, or do not allow for stand-off, remote detection. Fluorescence quenching of conjugated polymers offers an attractive alternative, as TNT and its common contaminant, 2,4-dinitrotoluene (DNT), provide a highly sensitive “turn-off” response by nonradiatively deactivating their mobile excitons.² The most sensitive conjugated polymers readily detect TNT vapors and have achieved commercial and military adoption.¹⁰

Introducing free volume into conjugated polymer films was identified as an important design strategy for ultrasensitive TNT detection more than a decade ago, which was first accomplished by introducing large, shape-persistent monomers within the polymer backbone.^{11,12} Several alternative strategies to impart permanent porosity and high-surface area to organic and organometallic materials have since emerged. These new materials classes include crystalline metal–organic and covalent organic frameworks (MOFs and COFs),^{13–17} amorphous polymers of intrinsic microporosity (PIMs)^{18–20} and conjugated porous polymers (CPPs),^{21,22} and porous molecular cages.^{23–25} The high surface areas and tunable structures of many of these material classes make them interesting candidates for detecting explosives, potentially enabling simultaneous concentration and detection of analytes of interest. Significant progress toward this goal was reported by Li and co-workers, who observed rapid and reversible fluorescence quenching of pillared Zn-paddlewheel MOFs by DNT and the explosive taggant 2,3-dimethyl-2,3-dinitrobutane.²⁶ Jiang and co-workers also reported a di-indolinocarba-

zole-based CPP capable of detecting vapors of DNT and other more volatile nitroaromatic compounds.²⁷ Zang and Moore described carbazole-containing macrocycles that assemble into porous fibers that respond to TNT vapor, which is nearly 20 times less volatile than DNT.^{28–30} Here we report a CPP that responds to TNT vapor and evaluate important synthetic and processing parameters that impact its sensing performance. These considerations are particularly important for inherently insoluble materials, such as MOFs and CPPs, in order to evaluate their performance relative to other fluorescent materials and incorporate them into relevant sensing devices.

The CPP **3** (Figure 1) was synthesized from dialkyne monomer **1** and 1,3,5-tribromobenzene **2** under typical

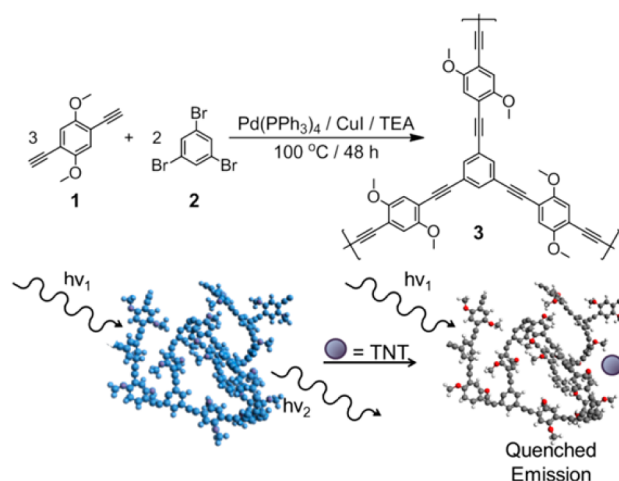


Figure 1. Synthesis of CPP **3** and schematic of its fluorescence response to nitroaromatic quenchers.

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Sonogashira cross-coupling conditions (0.02 equiv Pd(PPh₃)₄; 0.02 equiv CuI; excess NEt₃). The π -electron-rich monomer **1** was employed because of its electronic complementarity to TNT and the use of 1,4-dialkoxybenzene subunits in highly sensitive linear-conjugated polymers.^{11,31} These linear polymers commonly incorporate larger alkyl chains as solubilizing groups. Because CPP **3** is inherently insoluble, methoxy groups were used instead to maximize the free pore volumes of the CPP. A similar polymer network lacking methoxy groups (denoted CMP-4) was reported by Cooper and co-workers with a BET surface area of 744 m²/g.³² We prepared CPP-4 under similar conditions used to prepare **3** and obtained a BET surface area of 767 m²/g (Figure S26), which is approximately double that we obtained for a sample of **3** prepared in parallel (408 m²/g, see below). These differences may reflect a combination of the added size of monomer **1** and changes in the solubility and aggregation behavior of its growing polymer networks.

We prepared samples of **3** in two different solvents, DMF and PhMe, which provide polymers of similar chemical composition but significantly different porosity and TNT sensitivity (see below). For each solvent, **3** was isolated and characterized as an amorphous, insoluble powder. For optical characterization, we formed thin films of **3** by including a fused SiO₂ substrate in the growth solution. Powder samples of **3** were characterized by solid-state cross-polarization magic angle spinning (CP-MAS) ¹³C NMR spectroscopy, FT-IR, UV-vis absorption, fluorescence emission, thermal gravimetric analysis, and N₂ adsorption measurements. The solid-state CP-MAS ¹³C NMR spectra were virtually identical for all powder samples (Supporting Information, Figure S4), with resolved resonances at δ 148 and 53 ppm, corresponding to the aryloxy and methoxy carbons, respectively. The spectra also exhibit broad peaks from 100 to 140 ppm, corresponding to the other aromatic carbons, and the alkyne carbons resonate at 80–100 ppm. The FT-IR spectra of each powder sample were also identical (Supporting Information, Figures S5–S8), with absorbances at 1205 and 2210 cm⁻¹ that are characteristic of the methoxy and asymmetric alkyne stretches, respectively. Finally, all powders displayed high thermal stability associated with porous organic polymers and covalent organic frameworks (Supporting Information, Figures S18–S21). These complementary analyses indicate that the expected arylene-ethynylene linked network structure is formed in each growth solvent.

In spite of their similar chemical structures, the polymer samples show dramatic differences in accessible surface area, as measured by their N₂ adsorption behavior. Independent of their polymerization solvent, CPP powders that were activated by evacuation under high vacuum (DMF-E or PhMe-E) showed low N₂ uptake and were essentially nonporous (Figure 2). In contrast, we found that freezing the polymers in 1,4-dioxane and removing the solvent by lyophilization provided higher surface area materials that demonstrated type II isotherms associated with microporous materials. A lyophilized polymer synthesized in DMF (DMF-L) showed the highest N₂ uptake, with an average BET surface area of 259 m²/g obtained over five samples. A lyophilized polymer synthesized in PhMe (PhMe-L) exhibited reduced N₂ uptake and BET surface area of 53 m²/g. These data indicate that evacuation induces near-complete pore collapse independent of the growth solvent and that this process is at least partially prevented by lyophilization. In addition, DMF provides higher surface areas than PhMe, which is expected to influence their sensing performance. Although the choice of reaction solvent must be optimized

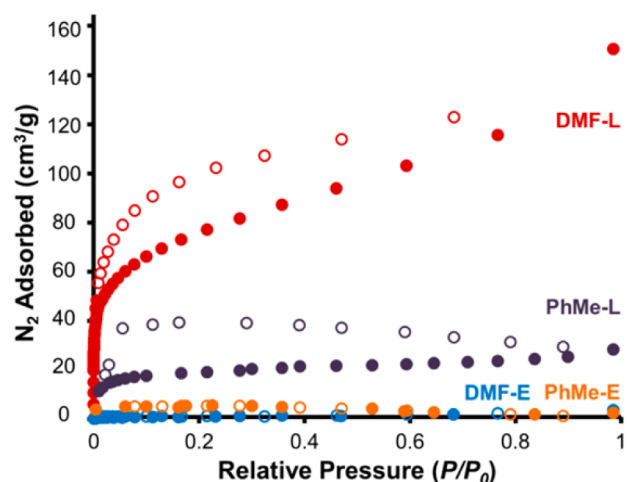


Figure 2. Representative N₂ adsorption isotherms for the CPP powder samples as a function of growth solvent and activation method.

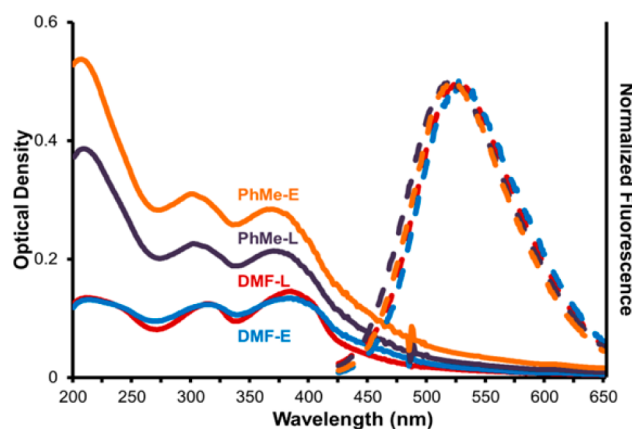


Figure 3. Absorption and normalized emission curves ($\lambda_{\text{ex}} = 396$ nm) of polymer thin films.

Table 1. Relative Fluorescence Quantum Yields of **3 as a Function of Growth Solvent and Activation Method**

polymer	relative fluorescence quantum yield (Φ_{rel})
DMF-L	1.00
DMF-E	0.13
PhMe-L	0.45
PhMe-E	0.41

empirically for each new CPP, Cooper et al. also noted superior surface areas for similar CPPs synthesized in DMF.³³

The absorbance properties of the CPP films show subtle but reproducible differences as a function of the polymerization solvent (Figure 3). Each film absorbs strongly out to ~450 nm, as expected for a *m*-polyphenyleneethynylene network. Local λ_{max} are observed at 325 and 380 nm for DMF growths and 300 and 370 nm for PhMe growths, which could indicate an increased degree of conjugation in the DMF polymers consistent with their increased TNT sensitivity (see below). Although the normalized fluorescence spectra of polymers activated through each method are similar, their fluorescence quantum yields differ significantly. DMF-L films are the most emissive ($\Phi_{\text{rel}} = 1$), while the other activation methods provide less emissive films (see Table 1 and Figure S17). These differences in emission efficiency may arise from variable

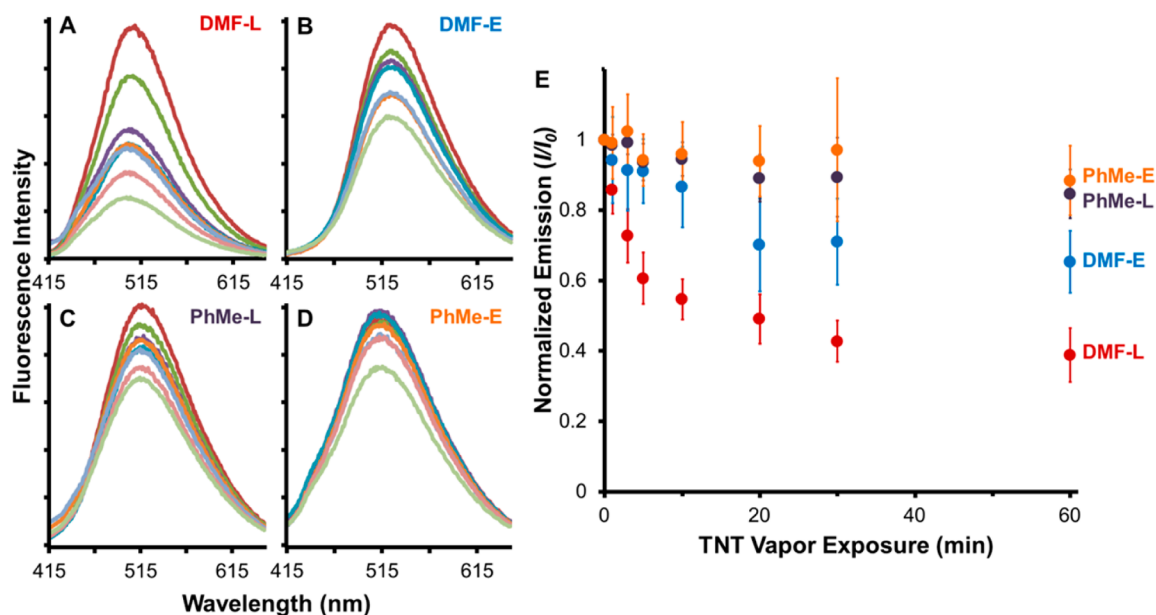


Figure 4. (A–D) Fluorescence emission ($\lambda_{\text{ex}} = 396$ nm) of polymer films exposed to TNT vapor for times ranging from 0 to 60 min. (E) Combined quenching curves of polymer films (7–12 films of each type) with exposure to TNT vapor.

degrees of chromophore aggregation obtained from the growth and activation protocols.

The sensitivity of polymer fluorescence to TNT vapor (~ 5 ppb equilibrium concentration) was evaluated using films of each growth and processing method. The initial fluorescence of a film was measured, after which it was stored in a sealed desiccator containing an open sample of TNT adsorbed onto sand, which are commonly used to train bomb-sniffing dogs. The film was removed from the desiccator at various time intervals and its fluorescence spectrum was recorded. The DMF-L, PhMe-L, DMF-E, and PhMe-E films each showed decreased emission in response to TNT vapor over the course of 1 h (Figure 4A–D). The magnitude of this effect depended strongly on the synthesis and processing methods. Figure 4E indicates the average relative fluorescence quenching for 7–12 samples of each type of film as a function of TNT exposure time. Independent of activation method, polymer films synthesized in DMF show increased TNT response as compared to films synthesized in PhMe. We attribute this difference to longer excitation diffusion lengths in the DMF films, as suggested by the differences in their absorbance spectra. These differences might arise from increased conversion of the Sonogashira polymerization or from differences in chromophore aggregation. Furthermore, DMF-L films show both faster and more complete quenching than those activated through evacuation. This trend is consistent with the surface area analysis of the corresponding powder samples, in which DMF-L samples showed the highest porosity. Interestingly, PhMe-L and PhMe-E films showed similar quenching responses, indicating either that they are inherently insensitive to TNT or that the only modest surface areas of the PhMe-L samples do not confer additional sensitivity. These results indicate the importance of optimizing sensing performance of conjugated porous polymers by varying both the growth solvent and activation protocols.

In conclusion, we report a CPP that detects TNT vapor. Through this study we have shown how growth and activation procedures strongly influence analyte response and introduce lyophilization as a gentle and convenient activation method that

requires no specialized equipment. With this preliminary study, we have demonstrated that this class of polymers shows promise for detecting low-volatility explosives, but further work is required to achieve the rapid and reversible response seen in other electron-rich polymer systems. Future work will involve optimizing the CPP chemical structure and synthetic and processing conditions to address this challenge. Controlled methods for forming CPP films and characterizing their structure will be of great future value.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and additional supporting figures and schemes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wrd33@cornell.edu.

Notes

The authors declare no competing financial interest.

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