How Does Amine Substitution Affect Nanoporous Material Selectivity for Nitroaromatic Compounds?

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Introduction

Terrorist activities involving explosives in the global transportation system have caused destruction, loss of life, and fear. New analytical methods to identify trace amounts of explosive compounds have the potential to provide rapid, on site detection before damage is done.[1] The purpose of the research described here is to develop selective sensors for explosives. The initial target was 2,4-dinitrotoluene (DNT), a model for 2,4,6-trinitrotoluene (TNT). The sensors are based on highly selective and versatile sol-gel materials synthesized from a mixture of organosilanes and an orthosilicate.[2,3] These materials polymerize around templates that have the same, or closely related structures to the target molecule. Sol-gel chemistry and an idealized nanocavity structure selective for a DNT template are shown in **Figures 1** and **2**, respectively. **Figure 3** illustrates the principle of templated nanocavities as vapor sensors.

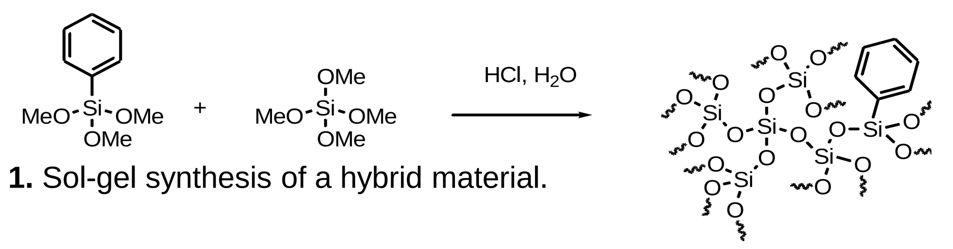


Figure 1. Sol-gel synthesis of a hybrid material.

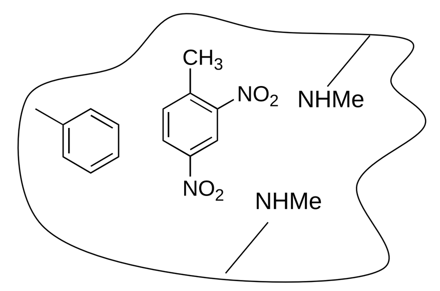


Figure 2. Nanocavity within a hybrid material that preferentially interacts with DNT. Nanocavities are white dots In Figure 3.

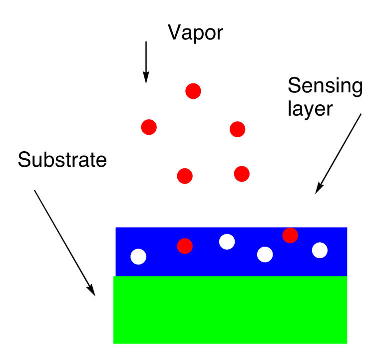


Figure 3. Thin film containing nano-cavities formed by template (DNT) exposed to template (DNT) vapor.

Sol-Gel & Film Synthesis

Sol Gel Synthesis. The sol-gel films were created in a 25 mL round bottom flask with the following modified general recipe:[2] tetraethoxyorthosilicate (TEOS, 3.0 mL), phenyl trimethoxysilane (**1**, PTMOS, 0.2 mL), HCl (170 μL), ethanol (3.0 mL); amine (0.83 mmol equivalents) and water (1.0 mL) were added dropwise and in order to the round bottom flask according to a. This solution was stirred at a constant rate for 20 h. Then, 1 mL of the clear solution was transferred to a sample vial and DNT added (7.2 mg). This sol-gel mixture was stirred for 4 h.

Film Formation. The films were created on glass cover slides and silicon wafers. The fused silica slides (1" x 1" x 1 mm- Dell Optics), or borosilicate cover slides (0.8" x 0.8" Fischer Scientific) were prepared by washing with ethanol and drying with nitrogen gas. Control slides with no DNT and slides with the DNT template solution were made by spin-coating 40 μL aliquots for 20 s at 2000 rpm on each chosen substrate. At least 3 replicates were made of each film. The films were dried overnight in a dessicator to prevent fast drying and stored in a laminar flow hood to protect from dust and contamination. The glass cover slides were thin and backs became contaminated by the spin-coater. To create clear films, the back of the sides were cleaned with acetone after spin-coating to remove contamination before baking.

Film Annealing. To ensure that the films were fully polymerized, they were heated slowly (1 °C / min to 80 °C and heated for 1 h) in a Lindberg furnace. This step was added for amine **3** films generated by GRA during Spring 2014.

Template Removal. DNT was partially removed from films using Soxhlet extraction in methanol at different times from 24 h up to 100 h. Different recipes extract different percentage of DNT at different time ranges.

UV Spectroscopy. The sol-gel coated slides were analyzed by UV spectroscopy before baking, after baking, and after extraction to establish the presence of DNT (λ_{max} ~ 250 nm). The control films were used as background spectra.

Hypotheses

***Hypothesis 1**.* An annealing (heating) step was added to the procedure for a film containing amine **3** before extraction with methanol should improve reproducibility of films by ensuring complete polymerization of the sol-gel before extraction of the template.

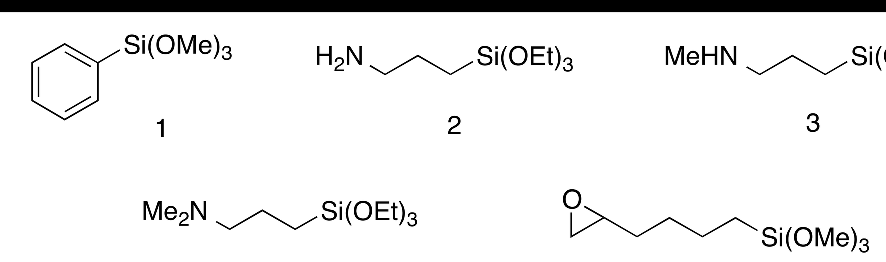
***Hypothesis 2**.* Secondary amine **3** will be the best amine component to add to the sol-gel because it can hydrogen bond to nitro groups strongly enough to bind (sense) DNT, yet not bind as strongly as primary amine **2**. Tertiary amine **4** is polar, but will not bind as well due to lack of a proton.

Sensing Methods

Materials. The film components are shown in **Table 1** and film properties are shown in **Table 2**.

DNT Absorption and Removal. The films were tested for efficiency in reabsorption of DNT vapor by exposure of template-free films to DNT vapor in screw-cap Teflon jars containing 7.2 mg DNT. The success of DNT reabsorption over 24-72 h was detected and confirmed by UV spectroscopy data. Removal of DNT was accomplished by methanol extraction over 24-72 h.

Film Synthesis



1 2 3 4 5

Table 1. Sol-Gel Synthesis Components and Conditions

Recipe [a]	TMOS (mL)	TEOS (mL)	PTMOS (mL)	HCl (mL)	Silane (#) (mL)	H_2O (mL)	Ethanol (mL)	Time (h)
A	-	3.00	0.20	0.1	**2,** 0.2	1.0	3.00	24
B	-	3.00	0.20	0.17	**3,** 0.17	1.0	3.00	24
C	-	3.00	0.20	0.17	**4,** 0.18	1.0	3.00	24
E	2.00	-	0.5	0.66 [b]	**5**	0.66	2.00	2
D[c]	-	3.00	-	0.1	**-**	2.0	2.4	2

[a] All reagents in mL; [b] 0.1M HCl; [c] Inorganic.

Film Properties

Film Thickness and Hydrophobicity. A Veeco profilometer and Woollam M-2000 Spectrometric Ellipsometer were used to measure thickness. A Rame-Hart 100 Goniometer was used to measure water contact angle.

Table 2. Film Thickness and Contact Angles

Film	Ellipsometric thickness (nm)	Profilometry (nm)	Water Contact angle ϴ (° adv/rec)
E	767 ± 1	775 ± 1	68 ± 2 / 64 ± 1
A	651 ± 4	711 ± 1	66 ± 2 / 64 ± 1
A	749 ± 11	774 ± 8	62 ± 1 / 61 ± 2
B	690 ± 2	707 ±1	72 ± 2 / 60 ± 3
C	623 ± 1	608 ± 1	73 ± 1 /52 ± 2
B*	674 ± 3	950 ± 79	

** Spring 2014 results*

Sensor Performance

UV Spectroscopy of **DNT films.** UV of films on fused silica was used to quantify the amount of template and phenyl groups within the films. **Figure 8** shows films characteristic of Film A.

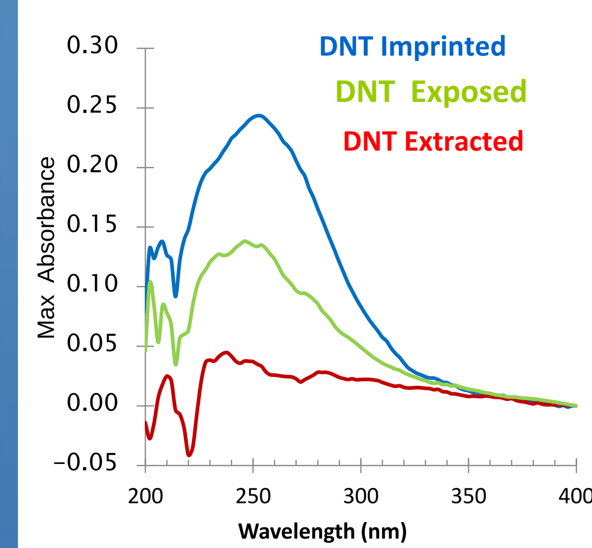


Figure 8. UV spectra for ormosil film imprinted with DNT (blue line), after Soxhlet extraction with methanol (red line), and after exposure to DNT vapor (green line).

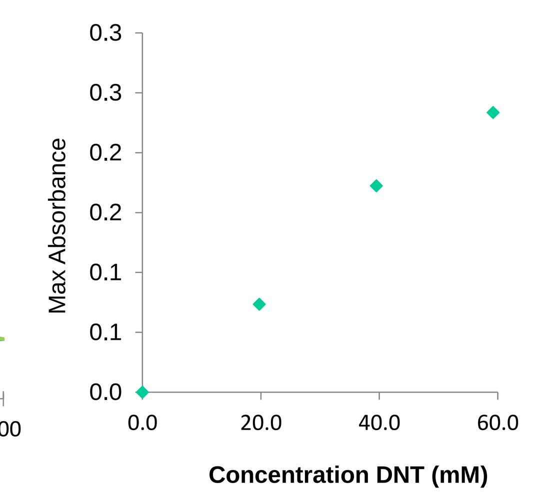


Figure 9. Calibration curve for DNT concentration in Film A (amine **2**).

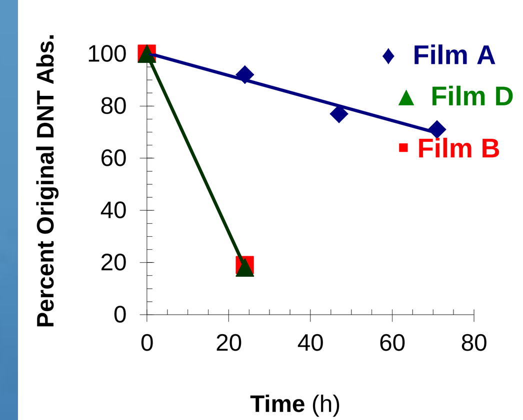


Figure 10. Percentage of DNT in each film type after extraction relative to the original absorbance value of the DNT template.

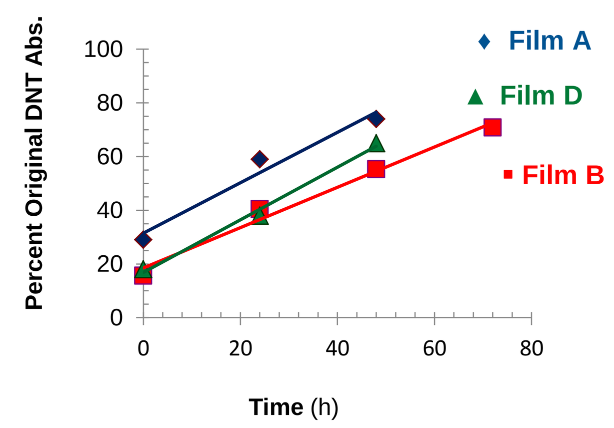
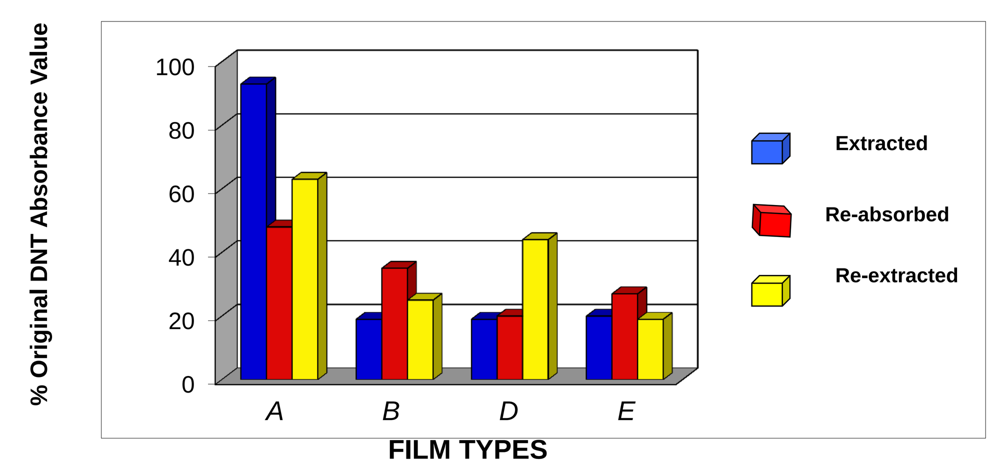
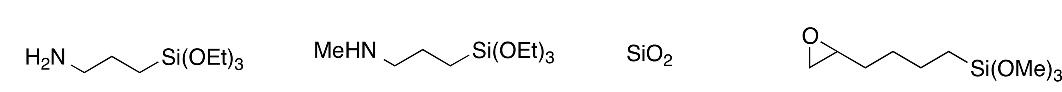


Figure 11. Percentage of DNT in each film after exposure to DNT vapor relative to the original absorbance value of DNT template before extraction.

Table 3. DNT Extraction, Re-absorption and Re-extraction





A B D E

Selectivity Tests

The films were exposed to four size and polarity probes to qualitatively determine selectivity of the M film environment for DNT. Density potential models (B3LYP optimized geometry in PC Spartan) for DNT, dimethoxytoluene (DMT), 3-nitro-biphenyl (NB), and 2,2'-dinitrobenzene (DNB) are shown below. DMT is the only probe that enters the film (Figure 12), perhaps because it is a similar in size to DNT. Although DNB similar polarity, biphenyls have low vapor pressure.

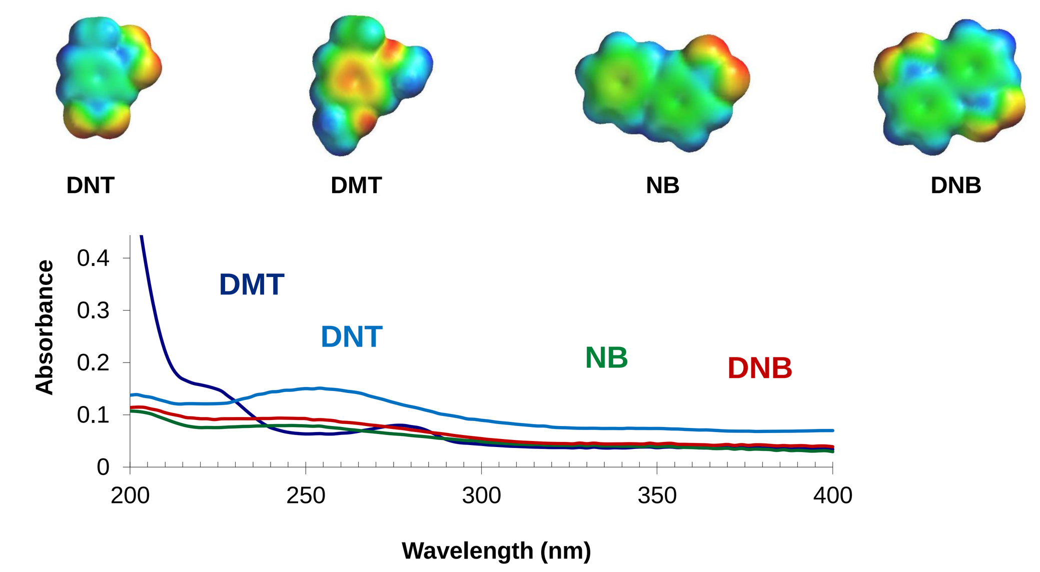


Figure 12. UV spectra for ormosil film exposed to DMT (navy line), DNT (blue line) for 24 h; NB (green line), and DNB vapor (red line) for 48 h.

Conclusions

- Sol-gels with four environments having different polarities were synthesized and spin-coated on slides to make smooth, transparent, reproducible films of 0.6-1.1 μm.
- Annealing did not affect the amount of DNT template but did improve the stability of the the film to methanol extraction.
- UV spectroscopy indicated that DNT vapor was incorporated into the films.
- Extraction of the DNT using methanol was fastest for I (In-organic films SiO_2) and M (methyl), slowest for film A (primary amines).
- Re-absorption of DNT vapors into extracted films depended on film environment and was fastest for film I, followed by film M.
- Anomolous result occurred for inorganic film because extraction rates are different before and after exposure to vapor. This will be repeated.
- Qualitative selectivity testing using shape and polarity probes DMT, NB, and DNB was inclusive so far.

References

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