Electronic Supplementary Information

Detection of High-Energy Compounds Using Photoluminescent Silicon Nanocrystal Based Paper Sensors

Christina M. Gonzalez,[a] Muhammad Iqbal,[a] Mita Dasog,[a] Davin Piercey,[c] Ross Lockwood,[d] Thomas M. Klapötke,[c] and Jonathan G. C, Veinot [a,b*]

[a]*Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada*

[b]*NRC National Institute for Nanotechnology, Edmonton, Alberta, T6G 2M9, Canada*

[c]*Department of Chemistry, Energetic Materials Research, Ludwig-Maximilian University, Butenandtstr. 5–13 (D) 81377 München, Germany*

[d]*Department of Physics, University of Alberta, Edmonton, Alberta T6G 2G2, Canada*

E-mail: jveinot@ualberta.ca

Tel: +1-780-492-7206, *Fax: +1-780-492-8231*

Experimental

Chemicals/Reagents and Materials.

Hydrogen silsesquioxane (HSQ, trade name Fox-17, sold commercially as a solution in methyl isobutyl ketone) was purchased from Dow Corning Corporation (Midland, MI). Hydrofluoric acid (HF, 49% aqueous solution) was purchased from J.T. Baker. Reagent grade methanol, ethanol, toluene, 1-dodecene (95%), 2,4-dinitrotoluene (DNT), and mononitrotoluene (MNT) were purchased from Sigma Aldrich. Nitrobenzene (99%) was received from Alfa Aesar. 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and cyclotrimethyllenetrinitramine (RDX) were synthesized using established literature procedures.[1]

Preparation of hydride-terminated Si nanocrystals.

A composite consisting of Si-NCs embedded within a SiO_2-like matrix was prepared via thermal processing of HSQ as described previously.[2] Briefly, solid HSQ was placed in a quartz reaction boat and heated at 1100°C in a tube furnace for 1 hour under reducing conditions (*i.e.,* 95% Ar/5% H_2). This procedure yields Si-NCs (diameter *ca.* 3.7 nm) within a protective oxide. After cooling to room temperature, the composite was crushed using an agate mortar and pestle to form a fine brown powder. Additional grinding was performed upon shaking with high-purity silica beads with a Burrell Wrist Action Shaker for 12 hours. The resulting Si-NC/SiO_2 composite was chemically etched to liberate hydride-terminated Si-NCs. 0.4 g of ground composite powder was transferred into a polypropylene beaker with a stir bar. 5 mL of water and 5 mL of ethanol were added to the beaker with mechanical stirring. 5 mL of 49% HF solution (**Caution!** HF must be handled with extreme care) was then slowly added to the beaker and the mixture was stirred for 1 h. The hydride-terminated Si-NCs were extracted from the aqueous layer into *ca.* 30 mL (*i.e.,* 3x 10 ml) of toluene. The cloudy yellow Si-NC toluene suspension was transferred into test tubes and centrifuged at 3000 rpm to isolate the Si-NCs for immediate dodecyl functionalization (*vide infra*).

Synthesis of dodecyl functionalized silicon nanocrystals

The toluene supernatant was decanted and hydride-terminated Si-NCs were immediately dispersed in *ca.* 30 mL dodecene and transferred to a flame dried Schlenk flask that was equipped with a magnetic stir bar. The flask was attached to a Schlenk line and evacuated and backfilled with argon three times to remove air. The reaction mixture was heated to 190 °C and stirred for 12 h to yield a transparent orange-yellow solution. The resulting solution was cooled to room temperature and mixed with 105 mL of a 1:1 methanol:ethanol mixture and placed in a high-speed centrifuge at 14000 rpm for 0.5 h. The supernatant was decanted and 10 mL of toluene was added to redisperse the particles. 35 mL of 1:1 methanol:ethanol solution was then added and the centrifugation/decanting/redispersion procedure was repeated twice. The purified particles were finally redispersed in toluene (10 mL), filtered through a 0.45 µm PTFE syringe filter, and stored in vials under ambient conditions for future use.

Material Characterization and Instrumentation

Fourier Transform Infrared Spectroscopy (FT-IR) of functionalized Si-NCs was performed using a Nicolet Magna 750 IR spectrophotometer by drop coating a toluene dispersion of Si-NCs. Transmission Electron Microscopy (TEM) analysis was performed using a JEOL-2010 (LaB_6 filament) electron microscope with an accelerating voltage of 200 keV. TEM samples were prepared by drop casting a toluene solution of Si-NCs onto a 200 µm mesh carbon coated copper grid and allowing the solvent to evaporate under vacuum prior to imaging. Size information was obtained by counting no fewer than 200 particles using Image J program. Photoluminescence (PL) spectra were acquired using a Cary Eclipse spectrophotometer (λ_{ex}= 350 nm). All solution-based quenching studies were performed using toluene solutions of functionalized Si-NCs (1 mg/mL).

Solution phase PL quenching studies

Stock solutions of NB, MNT, and DNT were prepared in toluene at appropriate concentrations. The working solutions were then stirred thoroughly prior to fluorescent measurements for a minimum of 5 min each. The solution samples were then transferred to a spectrophotometer quartz cuvette and fluorescent measurements were then taken at room temperature.

Solution phase PL lifetime studies

Photoluminescence lifetimes were acquired by shining a modulated argon ion laser (476 nm, ~30mW) into the quartz cuvette containing the as prepared solutions and then coupled to a fiber optic system. The laser was modulated by an acousto-optic modulator operating at 500 Hz. Light from the SiNCs was channeled into a photomultiplier (Hamamatsu H7422P-50) connected to a photon counting card (PMS-400A). Lifetime decay data was fit to a stretched exponential function in Mathematica given by $I(t) = I_o [\exp(-(t/\tau)^{\beta})] + C$, where I_o is the initial photon intensity, τ is the effective lifetime, and β is a stretching parameter that can vary between 0 and 1 (smaller values indicate broader lifetime distributions).[3]

As the concentration of nitroaromatic compounds (*i.e.* NB, MNT, DNT) increased, the values of τ decreased, indicating that the SiNCs were quenched by fast, non-radiative, processes. Additionally, β decreased indicating that the lifetime distribution grew due to the presence of non-radiative relaxation pathways with NB, MNT, and DNT.[4]

Si-NCs paper sensor for visual detection of nitroaromatic compounds

A piece of filter paper (Fisherbrand, qualitative P4) was cut into small rectangles and dipped into a beaker containing a 5 mg/mL solution of dodecyl functionalized Si-NCs for 10 min. The filter paper was then removed and dried under N_2 for 2 min. This indicator paper displayed red-orange luminescence when exposed to a hand held UV lamp (λ=365 nm). To display the potential application as a fluorescent paper sensor, solutions of nitroaromatic compounds were spotted onto the paper directly by pipette, "fingerprinted" with solid nitroaromatic compounds onto the paper, or exposed to nitrobenzene vapor. Finally, the paper was imaged under the UV lamp (λ=365 nm) and photos were taken by a digital camera.

For cotton swab residue studies, 2 μL of varying concentrations (0.0125, 0.05, 0.25 mM) of DNT were drop coated onto cotton swab tips. These swabs were then left to dry and should result in residues of 4.5, 18.2, 91.1 ng of DNT present on the swab. A blank swab was prepared by drop coating 2 μL of toluene onto the cotton swab tips and left to dry. All of the prepared swabs were then pressed onto the filter paper to observe if quenching of luminescence would occur.

For solid reside testing, 0.5 mg of DNT was weighed in a plastic tray, and then a gloved finger tapped onto the solid DNT sample. The excess solid was brushed off until there was no visible solid present on the glove. The gloved finger was then pressed four times successively on the filter paper. The paper was then viewed under the UV lamp to determine if quenching was achieved. Further solid residue testing was performed by swiping a gloved finger into the empty plastic tray where the DNT was once present. The gloved finger was then pressed onto the filter paper 4 times, and observed under a UV lamp. A similar procedure was followed to test if the filter paper could detect DNT solid residue that was present on cotton fabric. 0.5 mg of DNT was applied to cotton fabric, brushed off, and then the filter paper was rubbed onto the fabric, and finally observed under a UV lamp.

Vapor testing of nitrobenzene was performed by placing the prepared sensor paper over the mouth of a bottle containing concentrated NB and leaving for 3 min. The resulting paper was then removed and imaged under UV lamp. To check if the filter paper sensor was reusable, it was then placed under a N_2 airstream for 2 min to evaporate off NB, then removed and imaged under UV lamp.

References

1 J. Ledgard *The Preparatory Manual of Explosives*, 3rd ed.; USA, 2007

2 C. M. Hessel, E. J. Henderson, J. G. C. Veinot, *Chem. Mater.,* 2006, **18**, 6139.

3 M. N. Berberan-Santos, E. N. Bodunov, B. Valeur, *Chemical Physics*, 2005, **315**, 171.

4 J. H. Song and M. J. Sailor, *J. Am. Chem. Soc.*, **1997**, *119*, 7381.

Table S1. Concentration of nitro compounds (*i.e.* NB, MNT and DNT) used for PL and lifetimes measurements

PL measurements (mM)	PL lifetime measurements (mM)
0	0
0.05	0.05
0.075	0.075
0.25	0.25
0.5	0.5
0.75	0.75
1	1
1.5	1.5
2.5	2.5
5	5
7.5	-
10	-
25	-

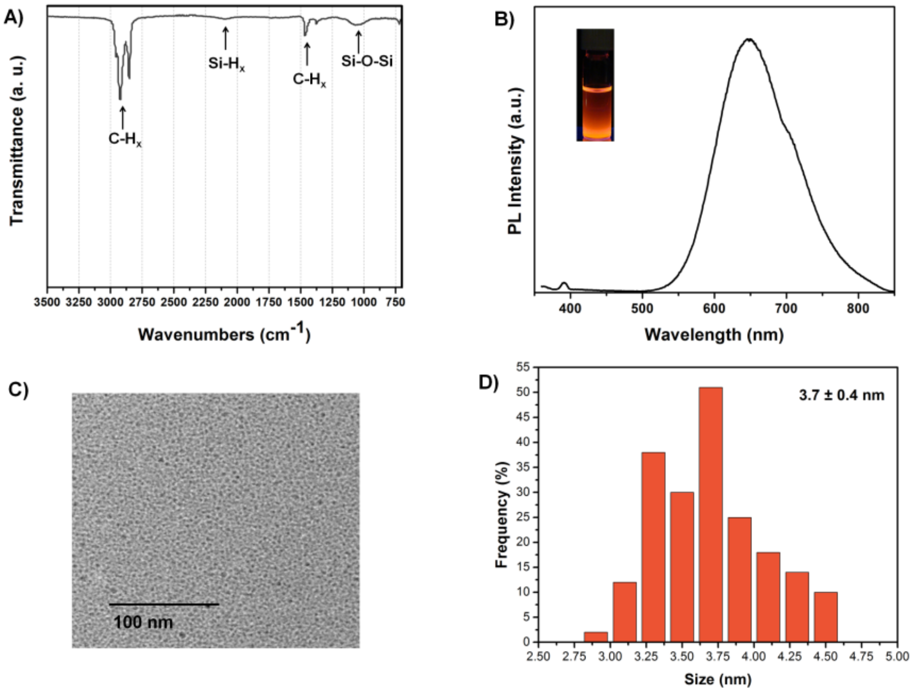

Fig. S1 Characterization of dodecyl functionalized Si-NCs. (A) FTIR spectrum of Si-NCs. (B) Fluorescence spectrum of Si-NCs with an inset of the nanocrystals displaying the red-orange luminescence atop UV benchtop. (C) TEM image of resulting nanocrystals and (D) the particle size distribution analysis of the Si-NCs.

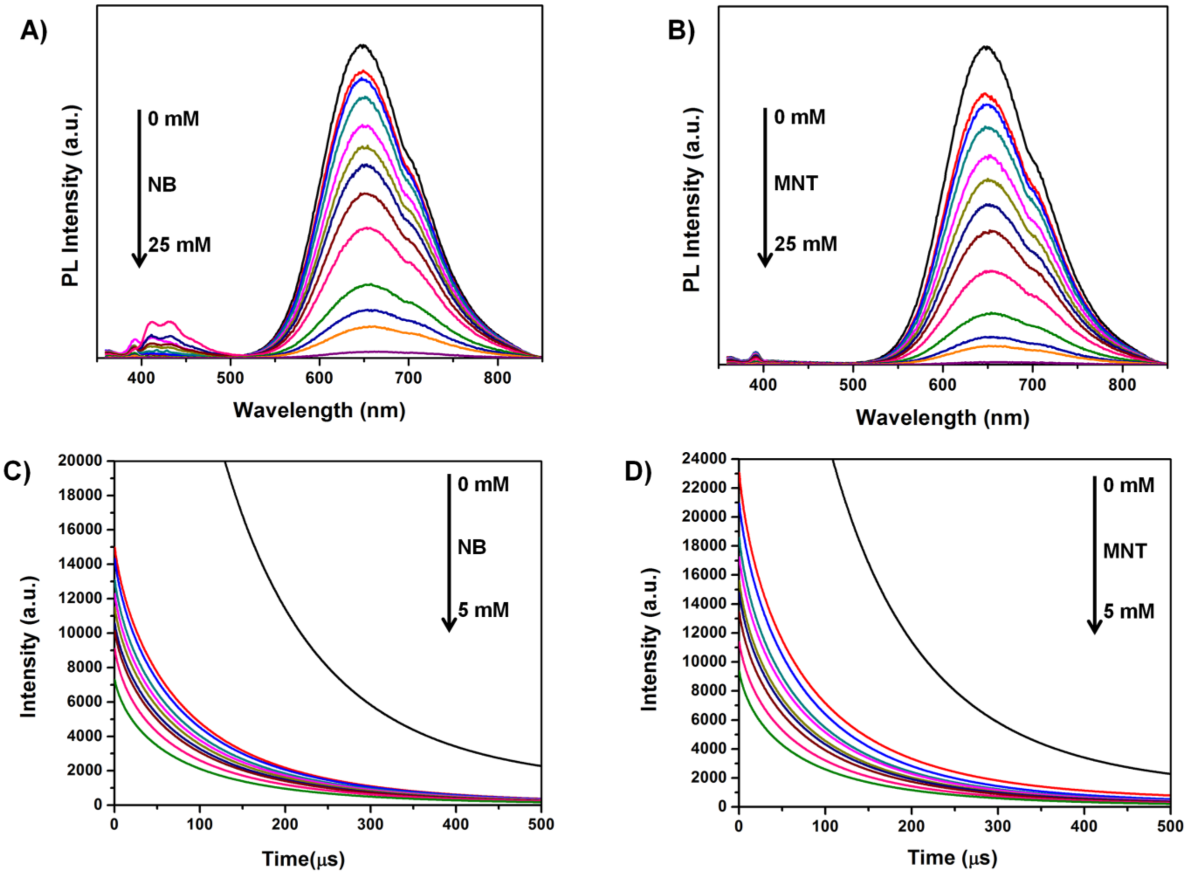

Fig. S2 The fluorescence quenching spectrum of Si-NCs at different concentrations of (A) NB and (B) MNT in solution. The PL lifetimes of Si-NCs with varying concentrations of (C) NB and (D) MNT in solution. The quencher concentrations for all studies can be found in Table S1.

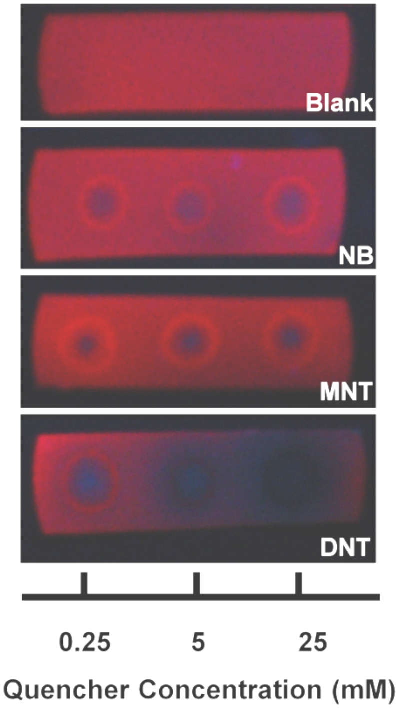

Fig. S3 Solution spot tests of nitroaromatics NB, MNT, and DNT (at concentrations of 0.25, 5 and 25 mM).

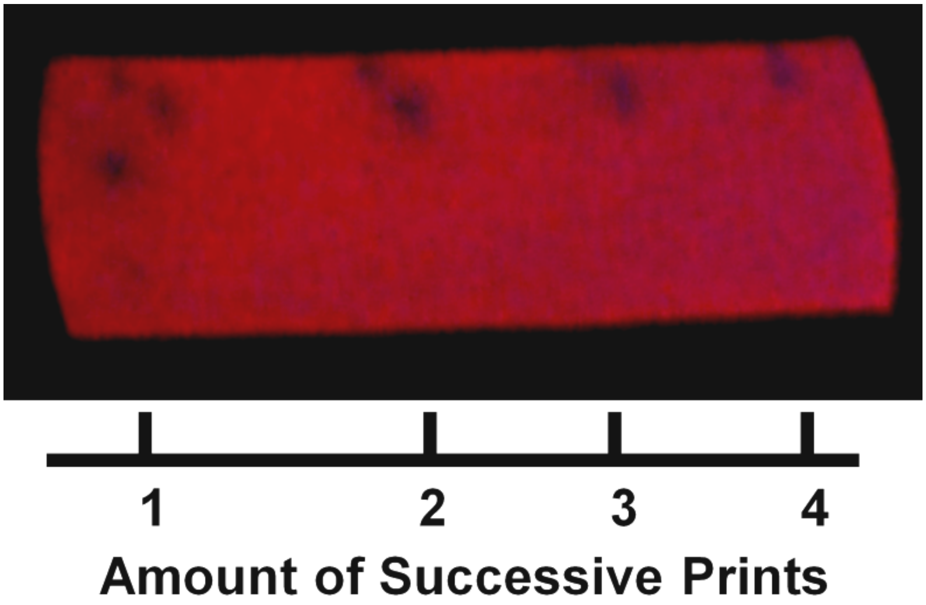

Fig. S4 Solid DNT residue testing on glove. The gloved finger was "finger-printed" successively onto the luminescent filter paper up to four times.

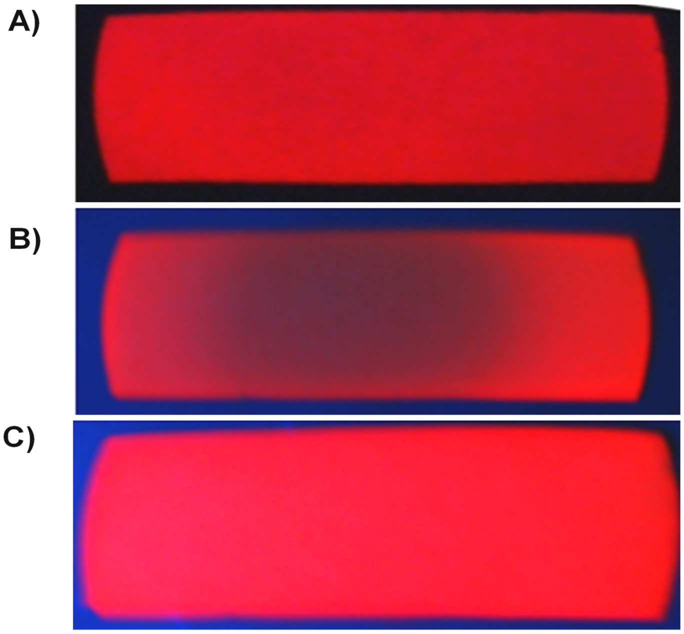

Fig. S5 Images of Si-NCs impregnanted filter paper under a handheld UV-lamp (A) without the presence of nitrobenzene vapor (B) after quenching with nitrobenzene vapor, and (C) the quenched filter paper after 2 min in N_2 airstream.