Real-time, Ultrasensitive Detection of RDX Vapors Using Conjugated Network Polymer Thin Films

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Supplementary Information

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A. Materials

Unless otherwise stated, all reagents were purchased from commercial sources and used without purification. Grubbs 2nd generation catalyst was purchased from Sigma-Aldrich. THF, CH_2Cl_2, toluene and ethanol were purchased from commercial sources and purified using a custom-built activated alumina-based solvent purification system. Other solvents were purchased from commercial sources and used without purification. The commercial RDX and HMX standard solutions were purchased from Cerriliant (1 mg/mL CH_3CN). TrueScent™ non-explosive RDX, K-9 training aid (Signature Science LLC, Austin, TX) were used for vapor sensing experiments. TrueScent™ non-explosive RDX was also used for isolating pure RDX. Hermes Brin De Réglisse perfume was used for control experiments.

B. Instrumentation and Methods

NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using a ^{1}H/X Z-PFG probe with a 20 Hz sample spin rate. Gas chromatography/electron impact mass spectrometry was performed on an Agilent 6890N Network GC System with a JEOL JMS-GCmate II Mass Spectrometer (magnetic sector) using a gradient oven temperature from 60 °C to 270 °C over 30 min. $CDCl_3$ was used as a NMR solvent (^{1}H NMR δ= 7.26 ppm, ^{13}C NMR δ= 77.2 ppm (3))

UV/Vis/NIR absorbance spectroscopy of films was performed on a Cary 5000 spectrophotometer using a praying mantis diffuse reflectance accessory Transmission mode spectra were recorded of films grown on SiO_2 substrates (~1.5 cm^2). The background was recorded using a similar SiO_2 substrate without the film.

Photoemission and excitation experiments were performed on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrophotometer equipped with a 450 W Xe lamp, double excitation and double emission monochromators, a digital photon-counting photomultiplier, and a secondary InGaAs detector for the NIR range. Correction for variations in lamp intensity over time and wavelength was achieved with a solid-state silicon photodiode as the reference. The spectra were further corrected for variations in photomultiplier response over wavelength and for the path difference between the sample and the reference by multiplication with emission correction curves generated on the instrument. Emission from films on SiO_2 was observed using a front face detection accessory.

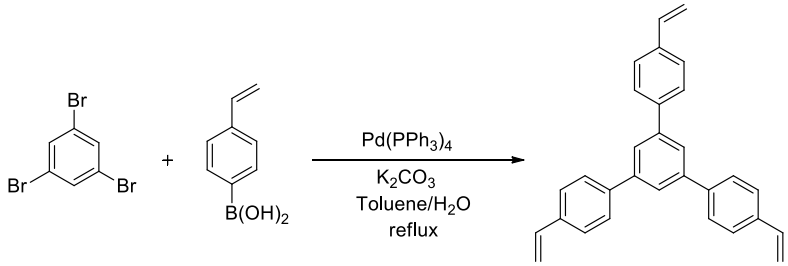
Fluorescence quenching experiments using RDX introduced from solution were performed by recording the initial fluorescence of the **TPV** film. Next, a known quantity of an RDX standard solution was added to the film. The film was evacuated for 6 min under high vacuum to remove the

solvents. The fluorescence intensity of **TPV** film was then recorded. This procedure was repeated for incremental amounts of RDX ranging from attograms to femtograms.

Real time fluorescence quenching data was recorded on a custom made fluorometer fitted with cage-compatible dichroic filter mount, fixed cage cube platform, epoxy-encased LED (375 nm, 2.5 mW, T-1 3/4), 409 nm bright line dichroic beamsplitter (25.2 x 35.6 mm) neutral density filter (350-700 nm, OD: 0.3). RDX placed in a vial was attached to the sample holder to diffuse vapor to the fused SiO_2 film.

C. Synthetic Procedures

Scheme 1: Synthesis of 1,3,5-tri(4-vinylphenyl)-benzene **1**



1,3,5-tribromobenzene (2.00 g, 6.35 mmol), 4-vinyl boronic acid (5.62 g, 38.1 mmol), and K_2CO_3 (5.27 g, 38.1 mmol) were added to a dry 250 mL 3-neck round-bottom flask, under a N_2 atmosphere. Toluene (24 mL) and H_2O (4 mL) were added to the flask. The reaction mixture was degassed through freeze-pump-thaw cycles. $Pd(PPh_3)_4$ (0.35g, 0.381 mmol) was added to the frozen solution and the reaction mixture was degassed through freeze-pump-thaw cycles. The reaction mixture is heated to reflux for 12 h, and was monitored by TLC (10% EtOAc / Hexanes). Once complete the reaction mixture was filtered through celite and the solvent was removed under vacuum. The crude orange solid obtained was dissolved in $CHCl_3$ (10 mL) and triturated with MeOH (50 mL), and recovered by filtration. (2.21 g, 91%) was obtained as a grey solid. NMR and IR spectra matched previously reported data.

General procedure for silanization of fused SiO_2. Allytrimethoxysilane (0.286 g, 1.763 mmol) was added to a bottle containing five fused SiO_2 films. Toluene (2.8 mL) and H_2O (0.2 mL) were added to the bottle and the bottle was sealed. The solution was refluxed for 24 h. Then the fused SiO_2 substrates were washed with H_2O, soaked in CH_2Cl_2 for 10 min, sonicated, then washed with fresh CH_2Cl_2 and finally air dried.

General procedure for preparation of TPV films. Monomer **1** (0.08 mg, 0.208 mmol), Grubbs 2nd Generation catalyst (0.011g, 0.013 mmol) were added to a 15 mL cylindrical pressure vessel and dissolved in CH_2Cl_2 (1.56 mL), after which the allyl silanized fused SiO_2 substrate was added to the vessel. The sealed vessel was heated in a sand bath at 45 ^oC for 't' hours. The vessel was cooled to room temperature and the resulting grayish black powder was recovered by filtration and dried under vacuum. The fused SiO_2 substrate was submerged in CH_2Cl_2 for 10 min, stirred occasionally, and then washed with fresh CH_2Cl_2 and finally air dried.

Extraction of RDX from K-9 training aid

The training aid simple (5.2 g) was suspended in CH_3CN (8 mL) for 20 min, after which the sand was removed by filtration through qualitative filter paper. The filtrate was concentrated to 1 mL, on a rotary evaporator, during which time RDX partially precipitated from the solution [CAUTION: RDX poses an explosión hazard, and the solution was not allowed to fully evaporate.]. Additional CH_3CN (1 mL) was added to redissolve the solid, after which $CHCl_3$ (4 mL) was added dropwise. $CHCl_3$ addition caused RDX to crystallize from the solution. These crystals were isolated by filtration, redissolved in CH_3CN (2 mL), and crystallized again by adding $CHCl_3$ dropwise. RDX was isolated as a white crystalline solid (0.037 g, 0.167 mmoles), which was divided into ~10 mg portions and stored at -4 ^oC protected from light. ^1H NMR analysis of the RDX indicated its identity and purity. A ~2% impurity of the related nitramine explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was also observed in the spectrum. NMR matched previously reported data.

D. UV/Vis Absorption

Figure S1 : UV of films grown at 5 mM concentration for 35 min

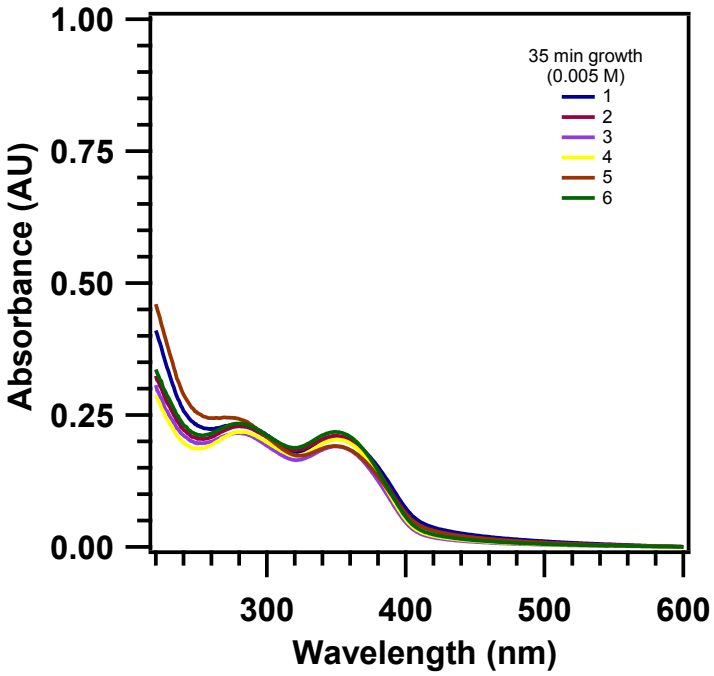


Figure S2 : Dependence of UV-Vis absorbance on concentration of reaction mixture

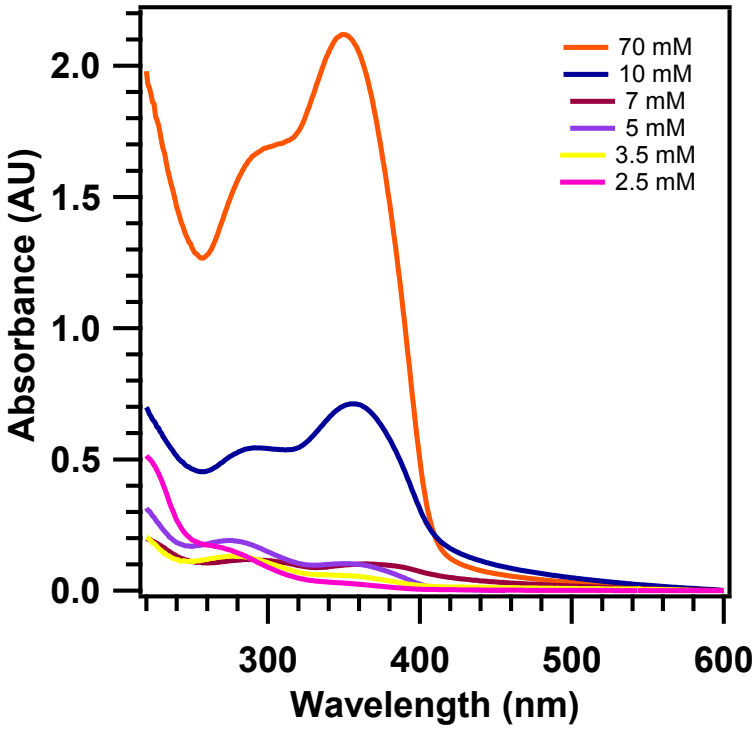
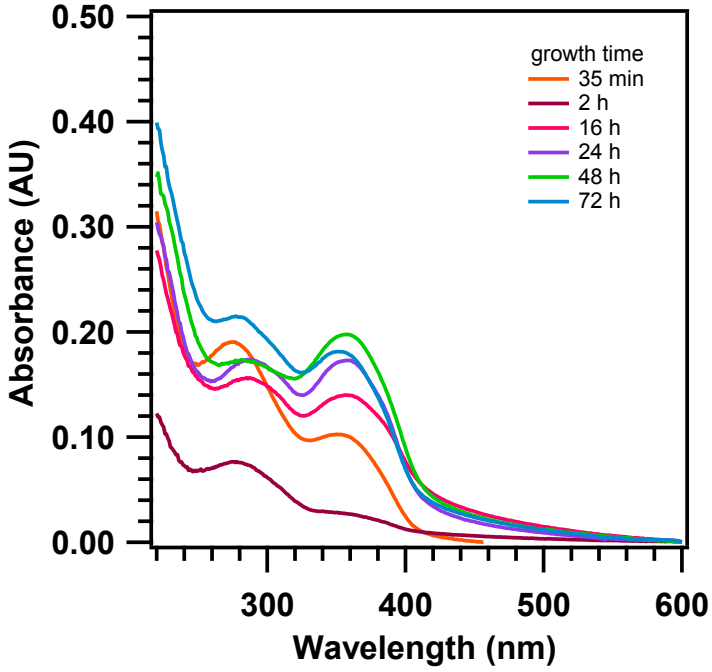


Figure S3 : Dependence of UV-Vis absorbance on growth time at 5 mM concentration



E. Real Time Fluorescence of TPV films

Figure S4 : Time dependent relative quenching % of TPV films grown at 70 mM concentration

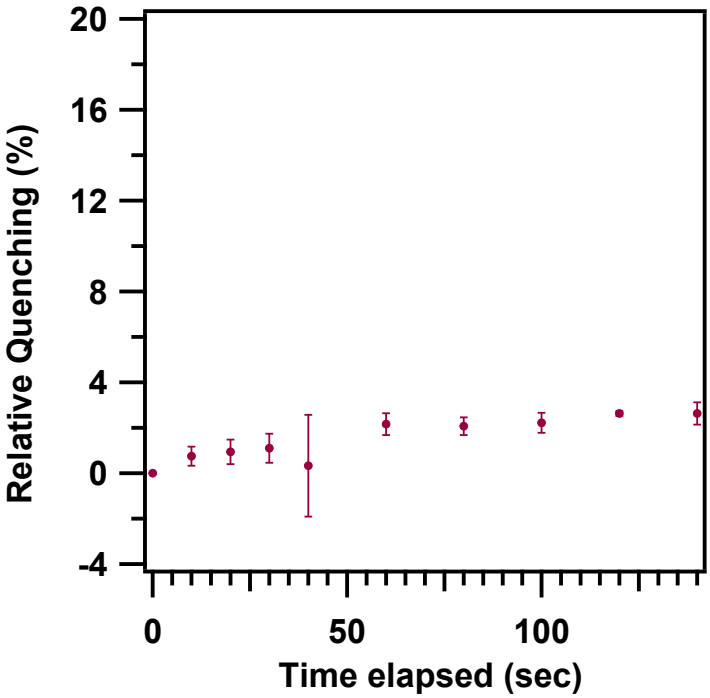


Figure S5 : Time dependent relative quenching % of TPV films grown at 10 mM concentration

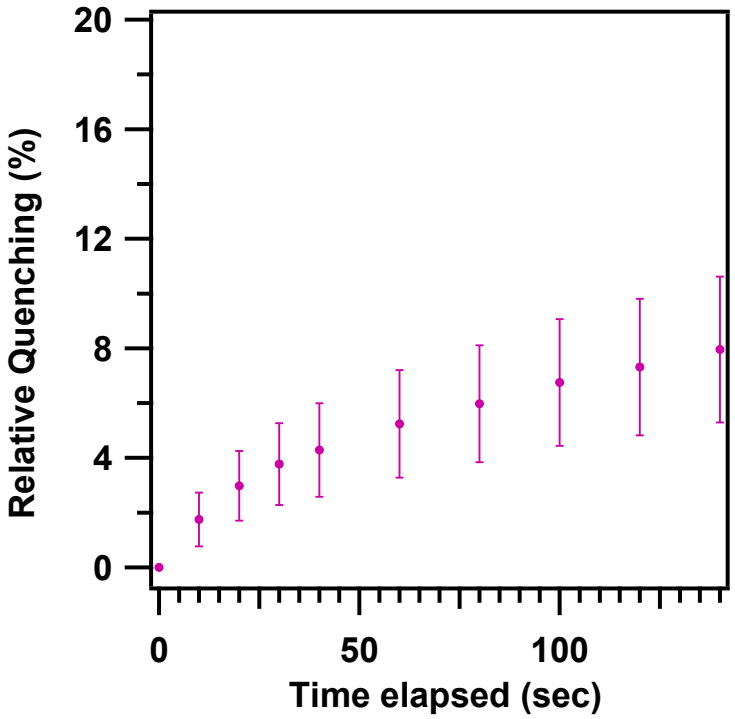


Figure S6 : Time dependent relative quenching % of TPV films grown at 7 mM concentration

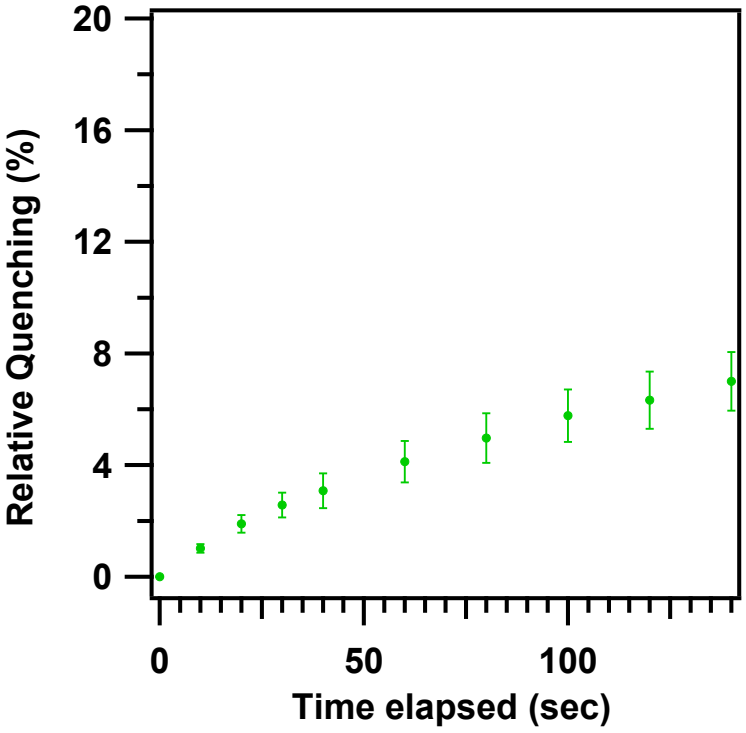


Figure S7 : Time dependent relative quenching % of TPV films grown at 5 mM concentration

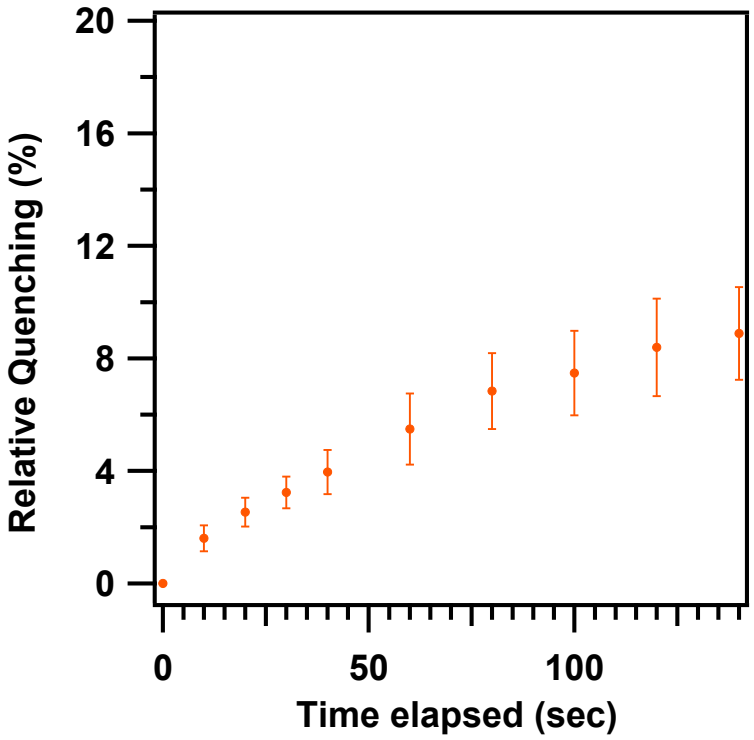


Figure S8 : Time dependent relative quenching % of TPV films grown at 3.5 mM concentration

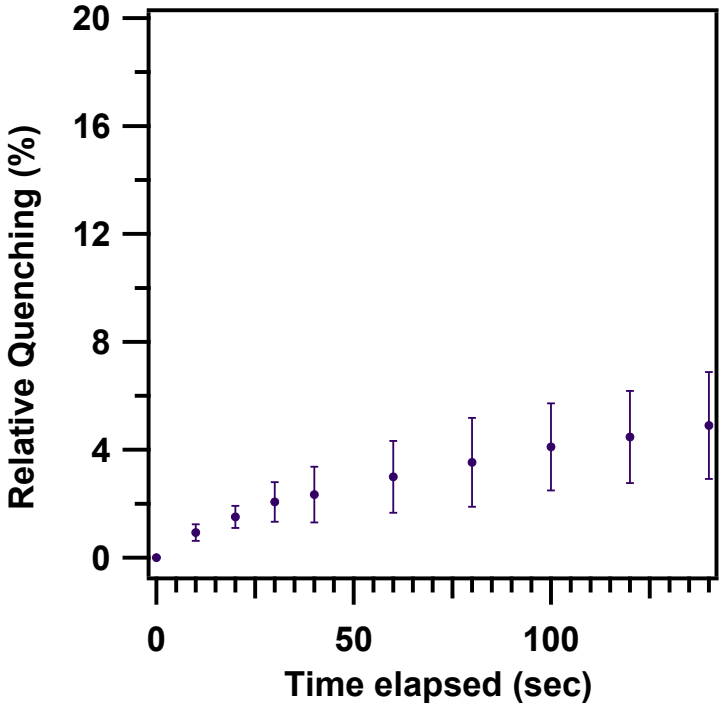


Figure S9 : Time dependent relative quenching % of TPV films grown in 5 mM for 35 min

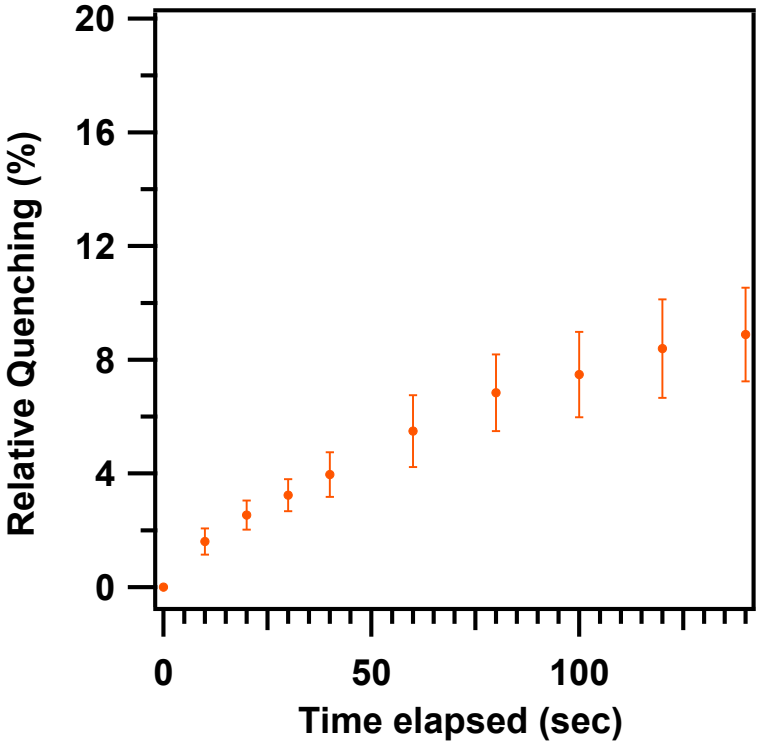


Figure S10 Time dependent relative quenching % of TPV films grown in 5 mM for 2 h

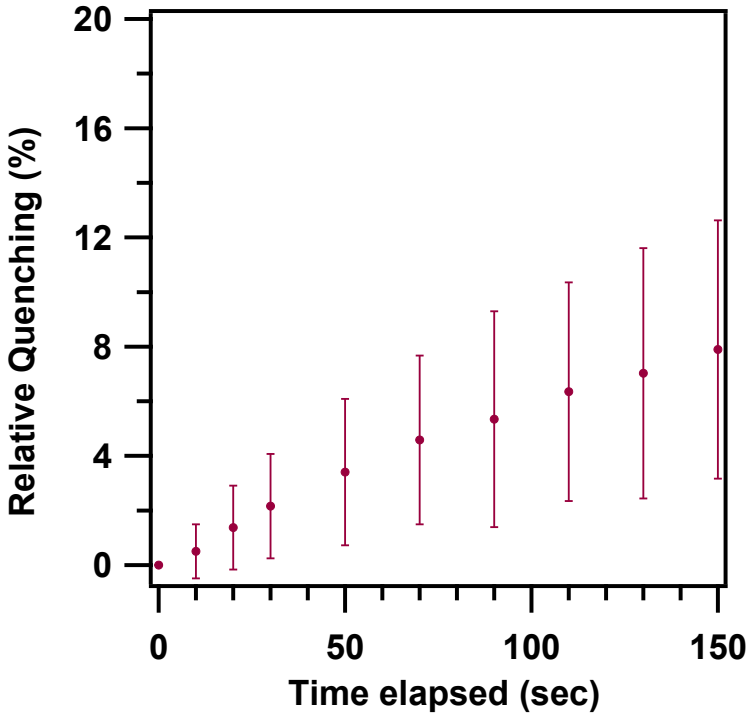


Figure S11 Time dependent relative quenching % of TPV films grown in 5 mM for 16 h

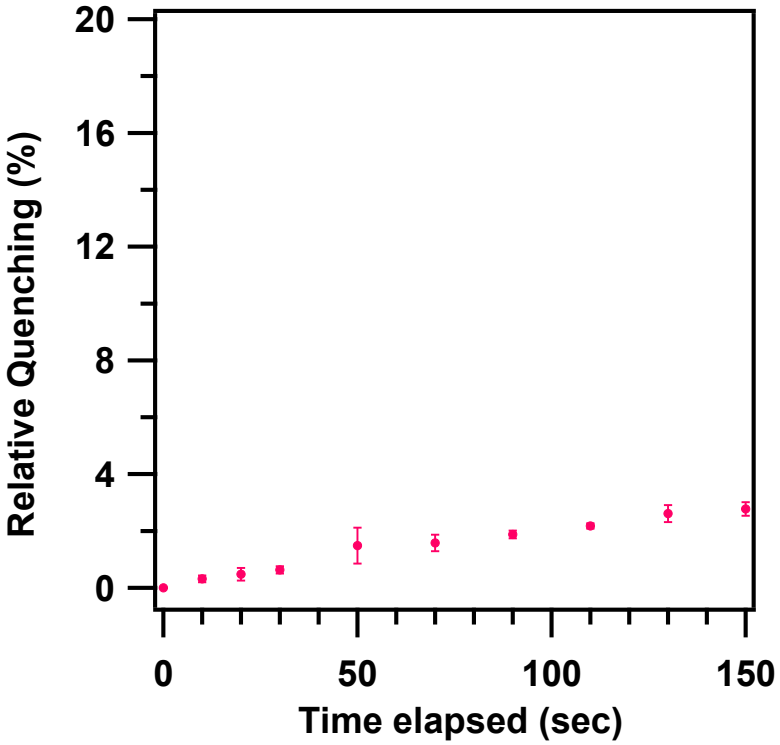


Figure S12 Time dependent relative quenching % of TPV films grown in 5 mM for 24 h

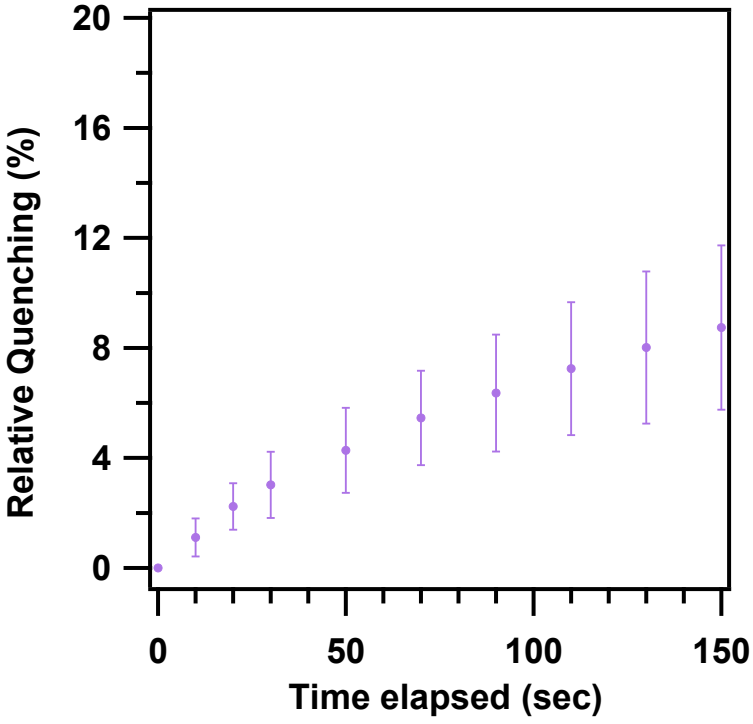


Figure S13 : Time dependent relative quenching % of TPV films grown in 5 mM for 48 h

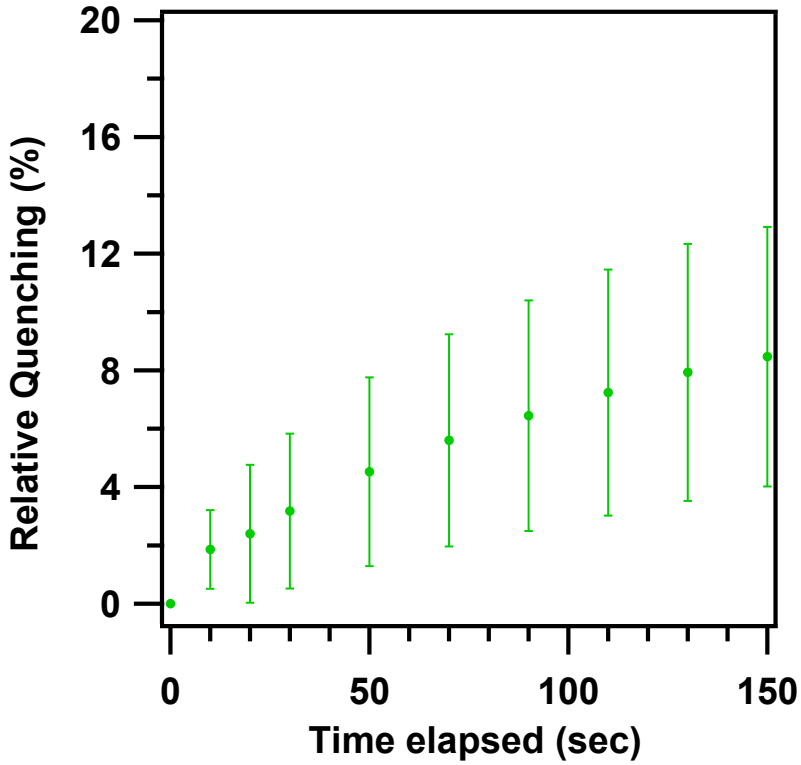


Figure S14 : Time dependent relative quenching % of TPV films grown in 5 mM for 72 h

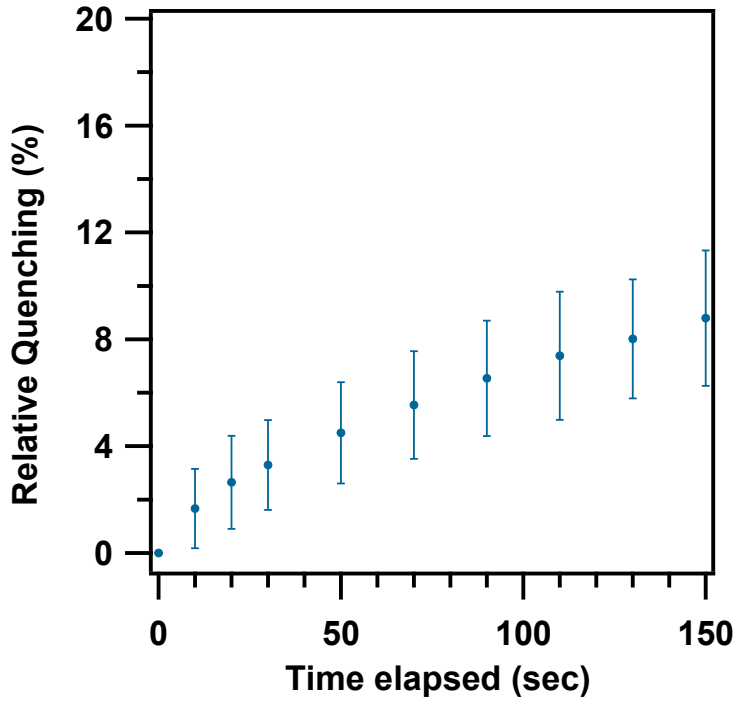
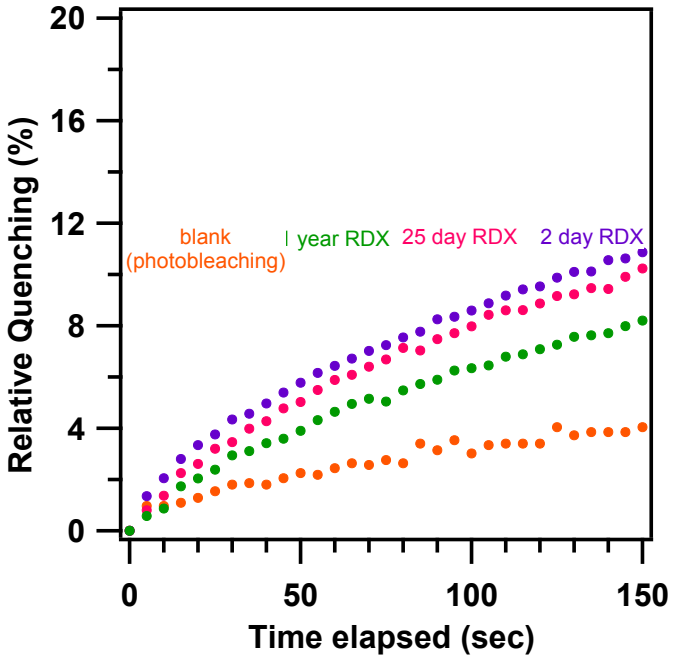


Figure S15 : Time dependent relative quenching % of TPV films based on age of RDX crystals (Each data point indicates the average response of 3 different films)



F. Fluorescence Response of TPV films

Figure S16 : Fluorescence response of film to attogram quantities of RDX

5 mM – 35 min growth

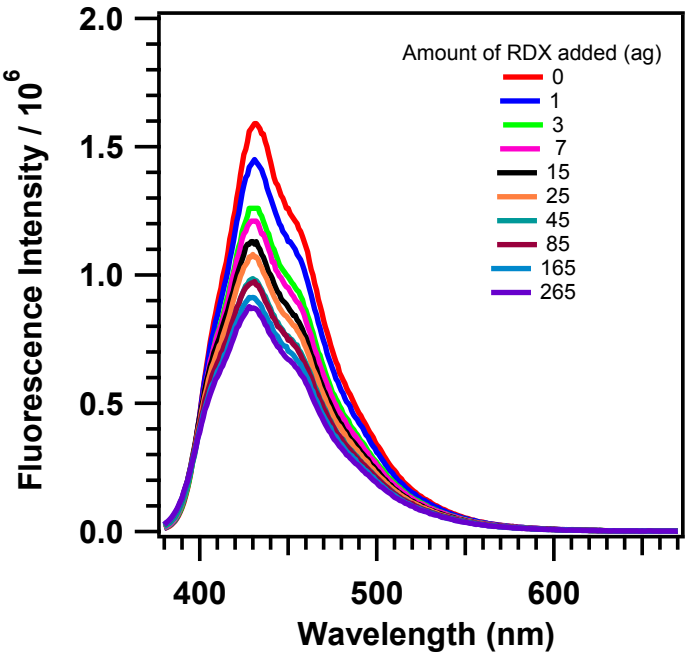


Figure S17 : Fluorescence response of film to attogram quantities of RDX

70 mM- 72 h growth

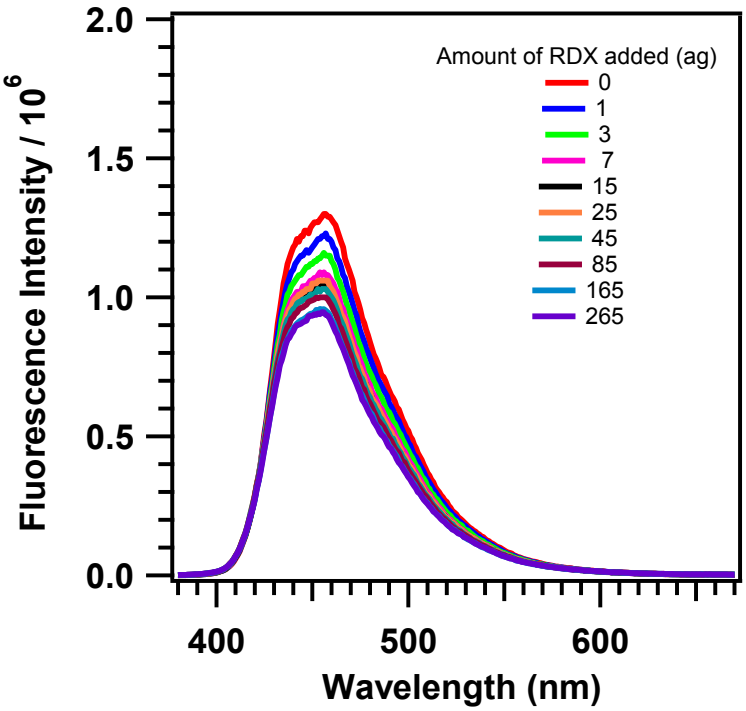


Figure S18 : Fluorescence response of film to attogram quantities of HMX- film 1

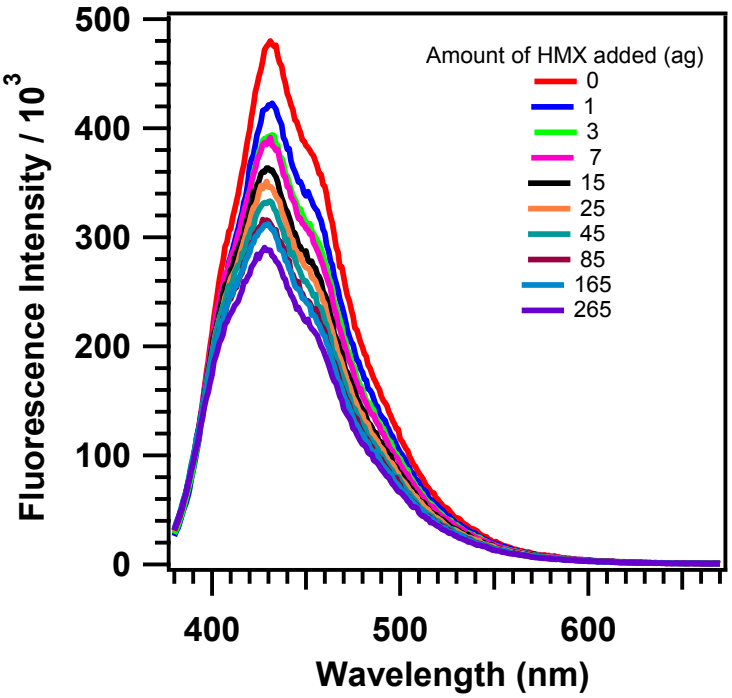


Figure S19 : Fluorescence response of film to attogram quantities of HMX- film 2

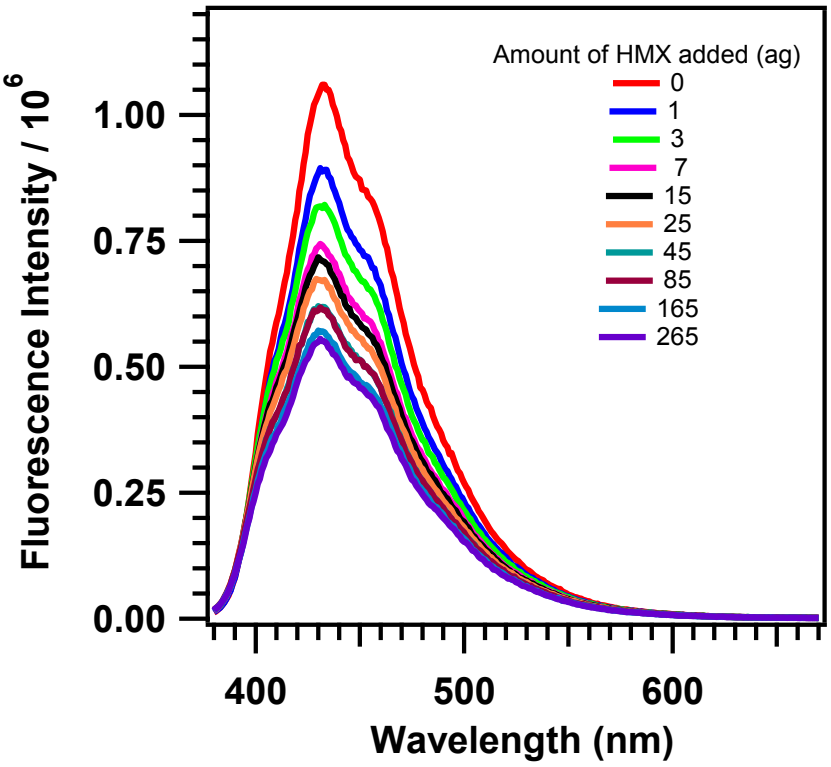


Figure S20 : Fluorescence response of film to attogram quantities of HMX- film 3

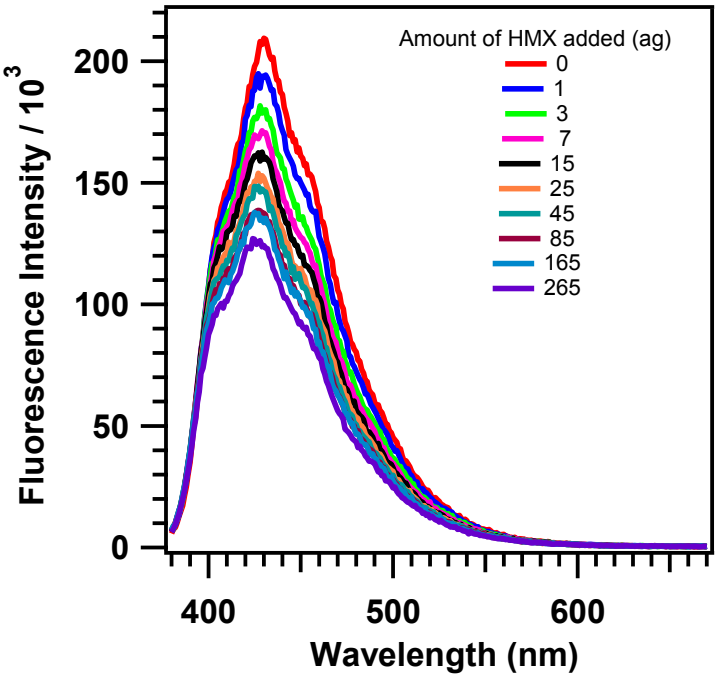


Figure S21 : Fluorescence response of film to vapors of 2,4-dinitrotoluene (DNT)

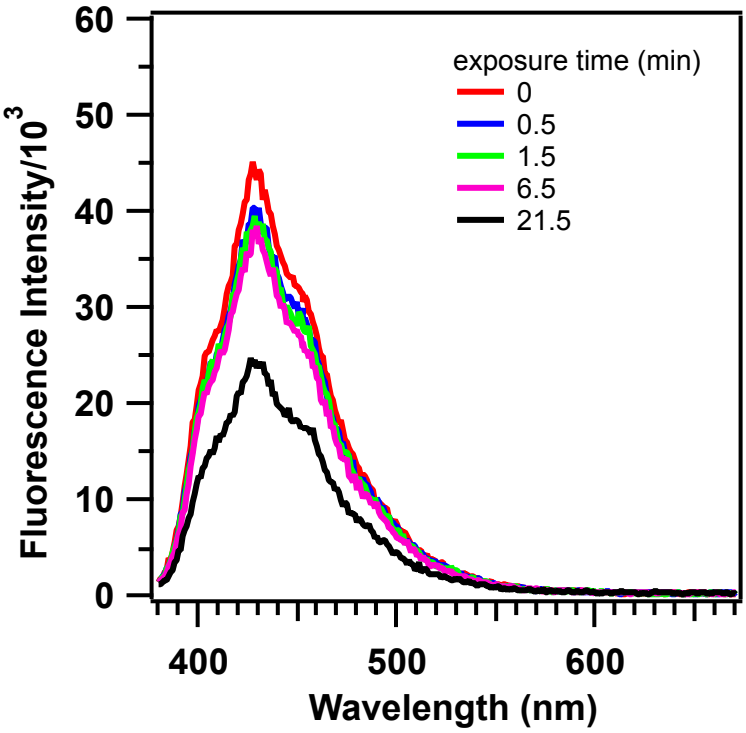
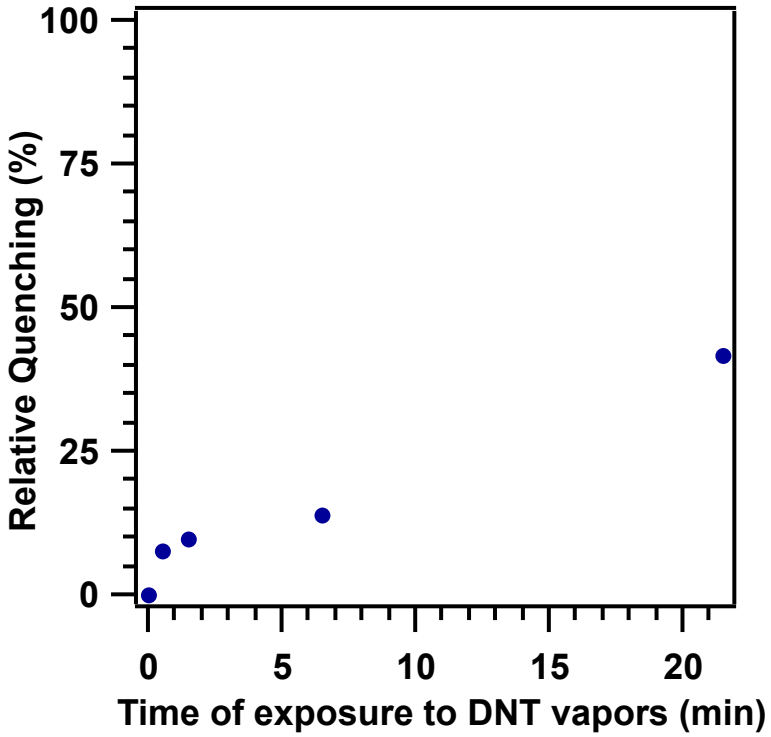


Figure S22 : Rate of quenching of TPV fluorescence on exposure to DNT vapor



G. Fluorescence control experiments

Figure S23 : Photobleaching of films grown in 5 mM concentration for 35 min

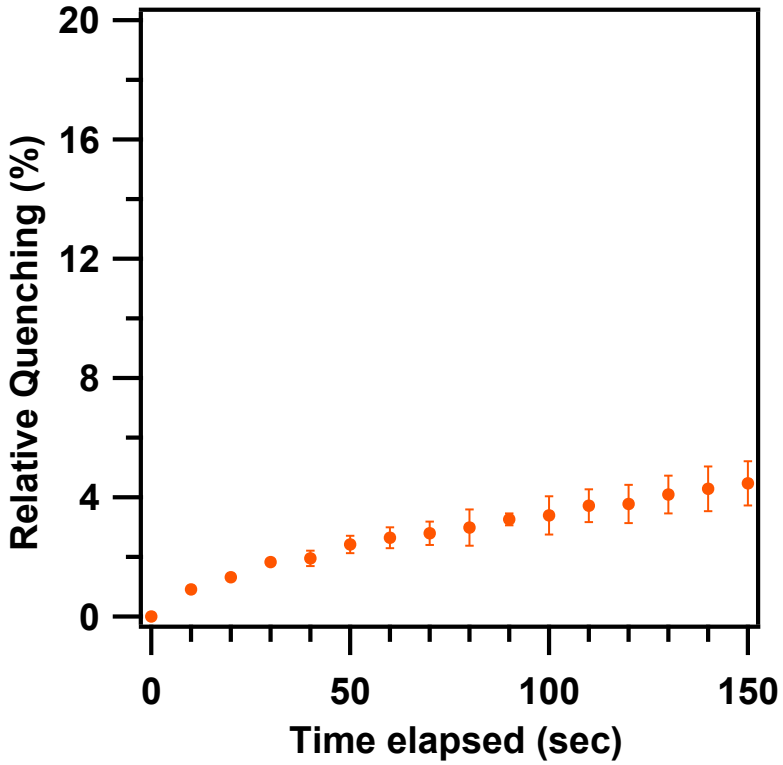


Figure S24 : Relative quenching % of film with addition of vapors of CH_3CN without RDX

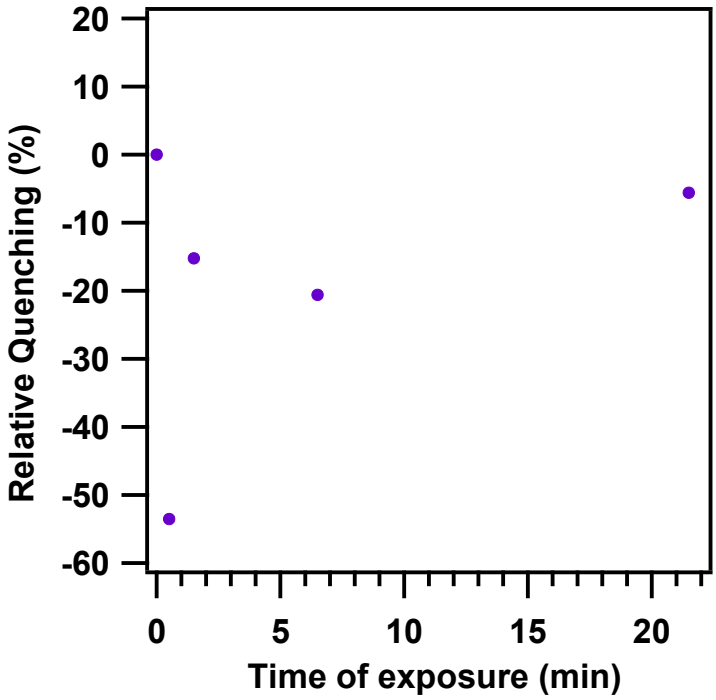


Figure S25 : Relative quenching % of films grown in 5 mM concentration for 35 min to CH_3CN

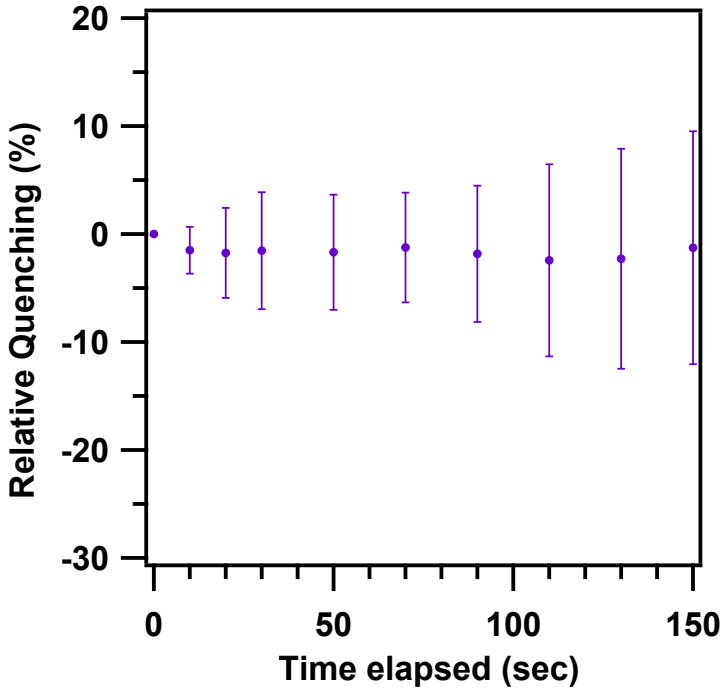


Figure S26 : Relative quenching % of films grown in 5 mM concentration for 35 min to perfume

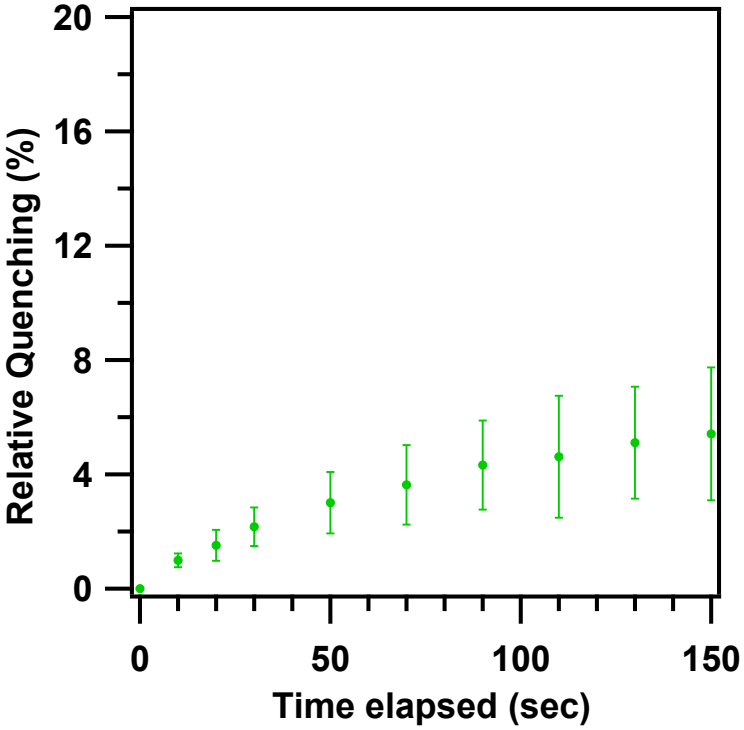


Figure S27 : Relative quenching % of films grown in 5 mM concentration for 35 min to HMX vapors