

Supplementary Information for:

Detection of Explosive Simulant via Electrical Impedance Spectroscopy
Utilizing UiO-66-NH₂ Metal-Organic Framework

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Experimental Section

Materials Preparation. UiO-66-NH₂ was received from TDA Research, Inc. and was synthesized by previously described methods and activated under vacuum at 160°C prior to use. The MOF was submerged in solutions of 2,6-DNT in ethanol, which was stirred and allowed to evaporate over a period of a day. The MOF/DNT mixture was subsequently formed into 25 mm pellets using a Carver press. Figures S1-S4 show PXRD patterns, nitrogen isotherm, FTIR spectrum, and TGA results for the material, confirming structural integrity of the MOF.

The MOF was pressed into pellets, and using a parallel plate sample holder, impedance measurements were collected. The MOF was first mixed as a powder with 2,6-dinitrotoluene based on the eventual surface area of the cylindrical pellet, which was calculated to be approximately 10.7 cm² (25 mm diameter, 1.1 mm thickness). Ranging from 10 – 100 μm/cm², powder 2,6-DNT was dissolved in approximately 5 mL of ethanol in a scintillation vial and stirred. To the solution, 500 mg of UiO-66-NH₂ was added. The mixture remained uncapped and the ethanol was allowed to evaporate over the course of a day. After evaporation, the powder was pressed into 25 mm diameter pellets using a Carver press. The pressure used was 10,000 psi. Pellets were then forwarded for impedance analysis.

Measurements. Impedance measurements were collected on all materials using a Solartron Analytical 1260 equipped with a dielectric interface 1296 and sample holder 12962 with brass plates. Voltages ranging from 10 mV to 1V and frequencies ranging from 10⁻² to 10⁶ Hz were used for the measurements. DRIFTS was conducted using a Harrick cell accessory mounted on the internal compartment of a Thermo Nicolet 6700 FTIR spectrometer. Both the UiO-66-NH₂ and 2,6-DNT-exposed UiO-66-NH₂ samples were loosely packed into a ~3 mm diameter stainless steel cup and transferred to the Harrick cell. Once inside the cell, each sample was purged for 20 minutes in CO₂- and H₂O-free air, and the FTIR spectra were collected at a resolution of 2 cm⁻¹ and with an average of 256 interferograms per spectrum. The background spectrum was collected using KBr powder with the same parameters and experimental conditions as the samples. XPS was conducted in a high vacuum (10⁻⁸ Torr) chamber (described elsewhere) using the Al Kα from a dual anode x-ray source (Omicron Nanotechnology, DAR 400) and a hemispherical electron energy analyser (Omicron Sphera).

Modeling. The quantum level calculations on 2,6-DNT (CAS# 606-20-2), UiO-66-NH₂ linker (aminoterephthalic acid, CAS# 10312-55-7), and the complex of 2,6-DNT/UiO-66-NH₂ linker structures were optimized at the B3LYP/Def2-SVPD level of theory using Gaussian 09. The self-consistent field procedure was carried out with a 2-electron integral accuracy set to 10⁻¹³ a.u. on energy and 10⁻¹¹ a.u. on density matrix in combination with an integral grid of -200100. Through vibration frequency analysis (which was carried out with a convergence criterion of 10⁻¹³ a.u. on energy and 10⁻⁹ a.u. on electron density in

combination with an integral pruned (75,302) grid, there was no virtual frequency for the optimized structure, corresponding to the stationary point on the potential energy surface.

	0 $\mu\text{g}/\text{cm}^2$	10 $\mu\text{g}/\text{cm}^2$	50 $\mu\text{g}/\text{cm}^2$	100 $\mu\text{g}/\text{cm}^2$
R1 ($\Omega\cdot\text{cm}$)	2.11(8)E+12	4.5(2)E+11	2.45(5)E+11	1.39(7)E+10
CPE1 (F)	4.7(3)E-12	9.7(9)E-12	7.6(2)E-12	2.2(2)E-11
R2 ($\Omega\cdot\text{cm}$)	2.1(4)E+11	1.6(3)E+11	9.0(11)E+09	7.4(7)E+09
CPE2 (F)	6.2(4)E-12	6.5(6)E-12	1.1(1)E-11	9.4(6)E-12
R3 ($\Omega\cdot\text{cm}$)	8.5(13)E+06	1.1(1)E+07	3.7(6)E+06	6.2(2)E+07
CPE3 (F)	2.6(1)E-11	2.48(6)E-11	2.0(1)E-11	4.79(8)E-12

Table S1. Fit values of resistance and capacitance values, with error values, for resistors R and constant phase elements CPE (respectively) as labelled in Figure 3(a) of the manuscript. These error bars are visualized in Figure S9 below.

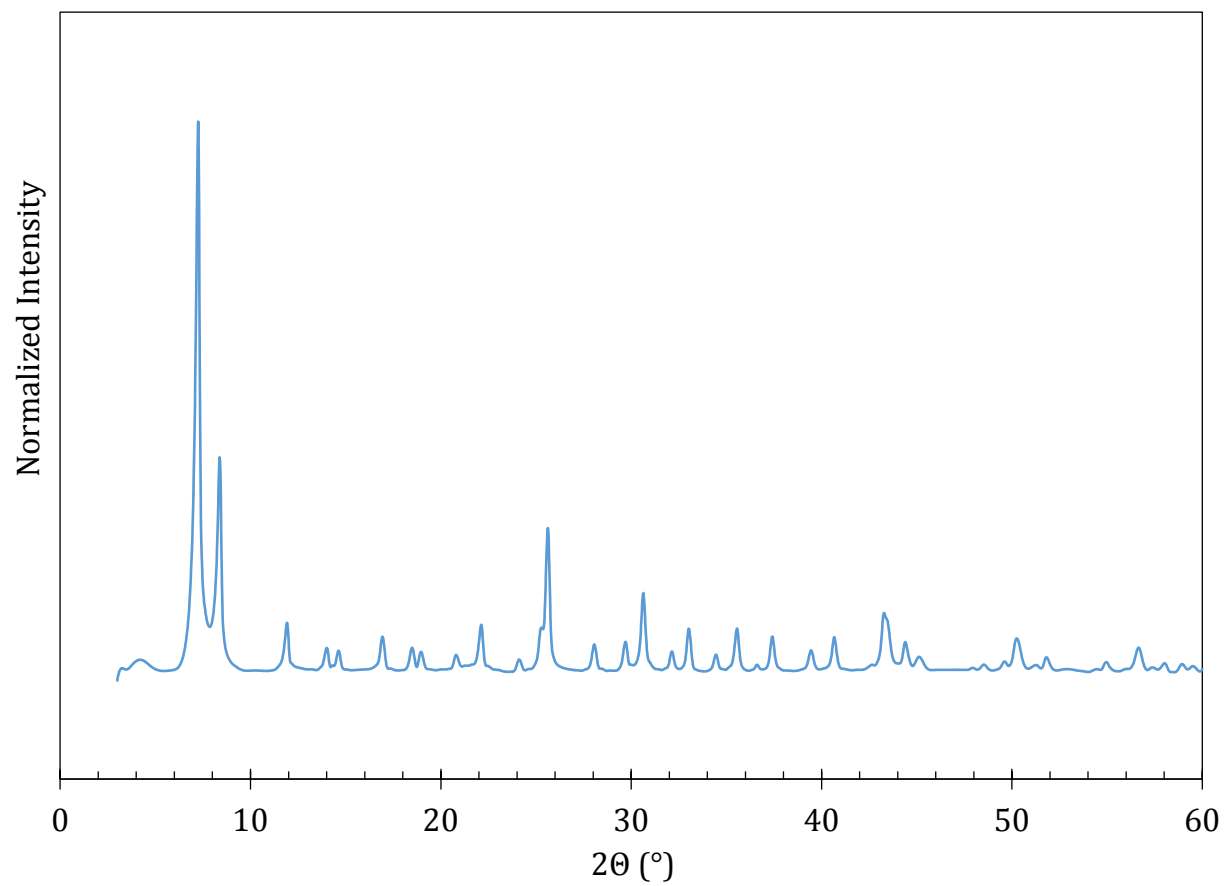


Figure S1. Powder X-ray diffraction pattern of UiO-66-NH₂.

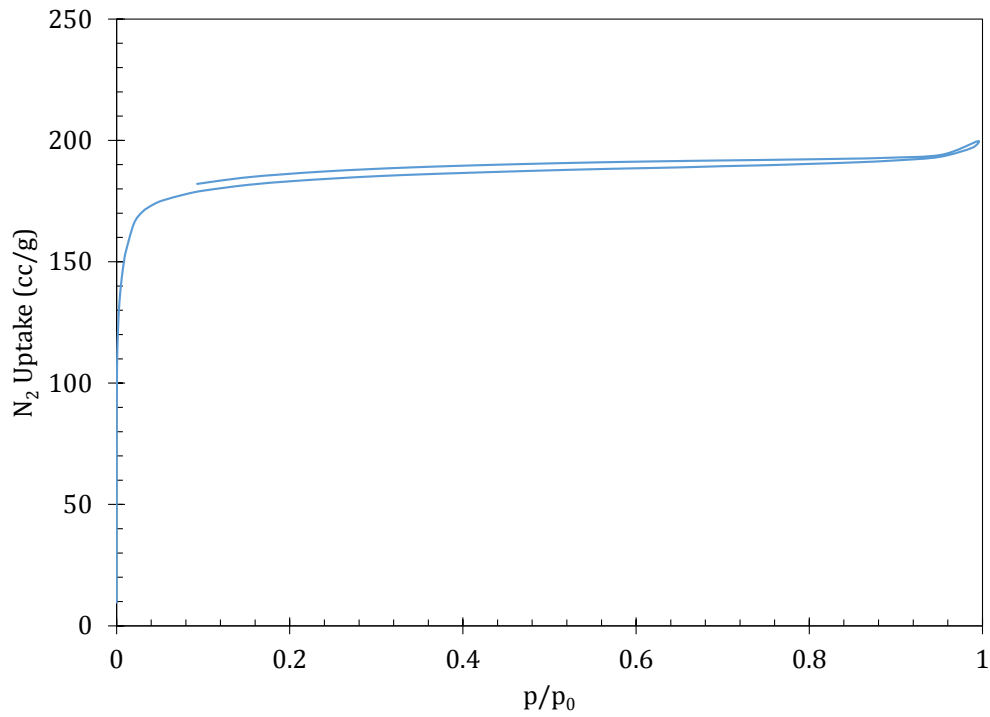


Figure S2. Nitrogen isotherm for UiO-66-NH₂.

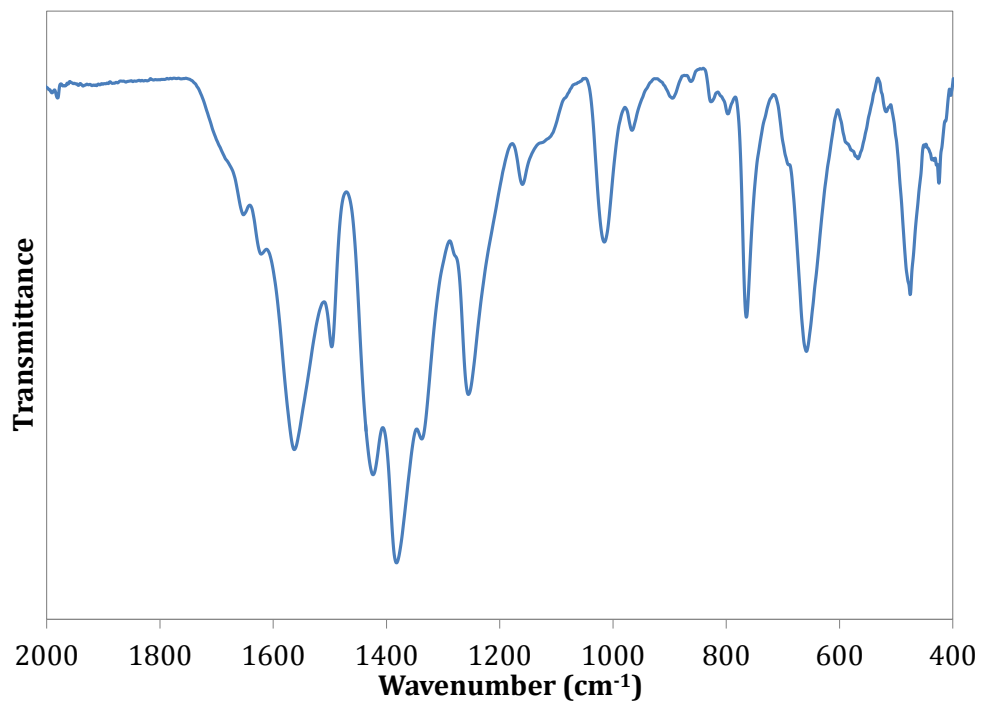


Figure S3. Attenuated total reflectance Fourier transform infrared spectrum of UiO-66-NH₂.

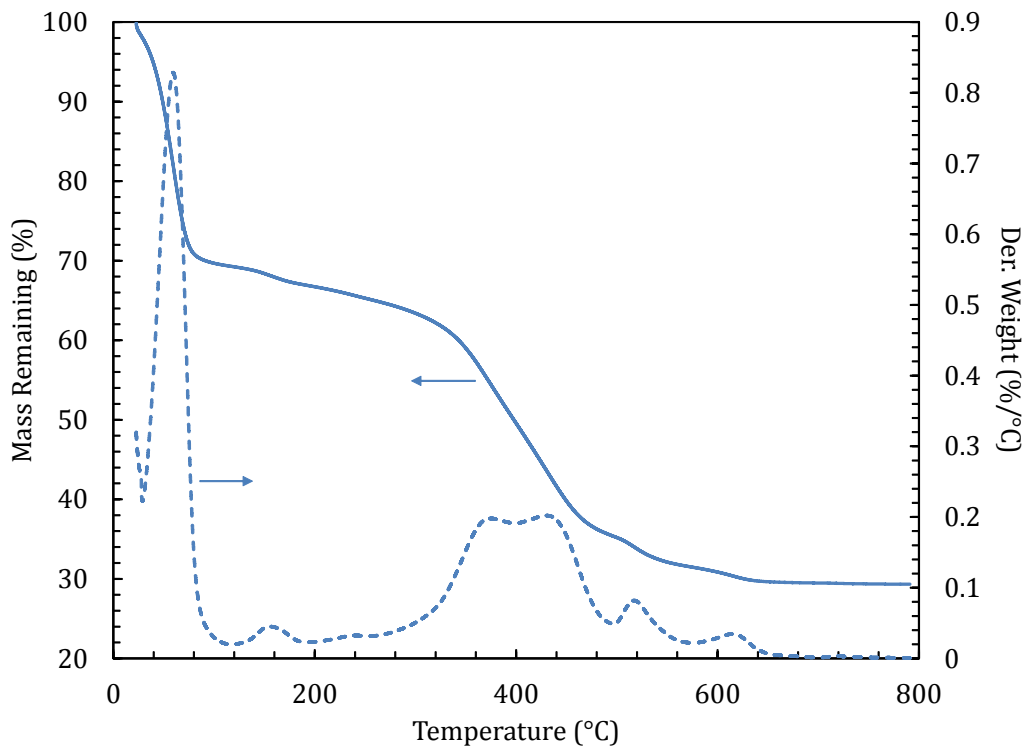


Figure S4. Thermogravimetric analysis profiles for UiO-66-NH₂. Results taken after mixing with ethanol, which accounts for the initial weight loss.

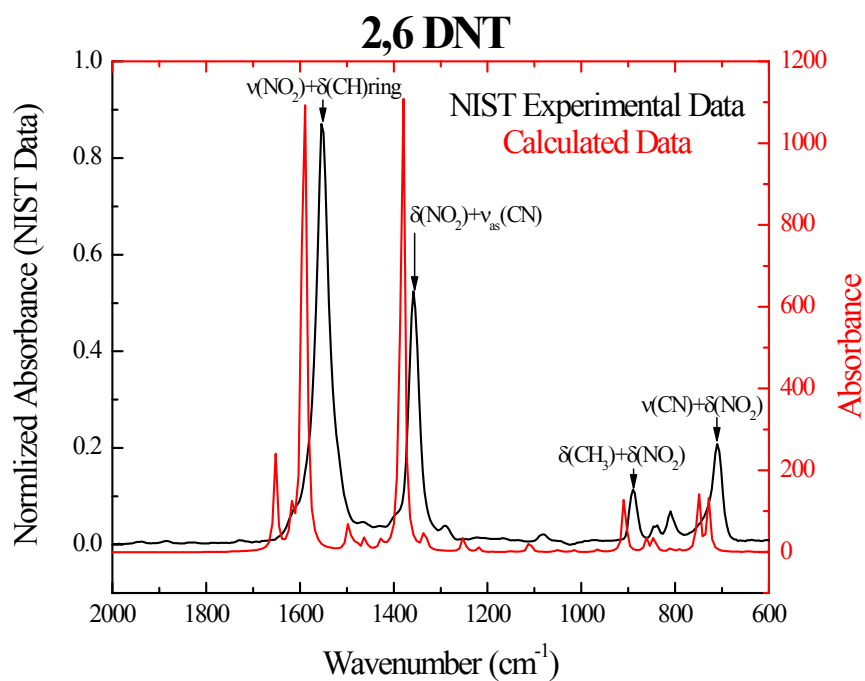


Figure S5. NIST infrared spectra.

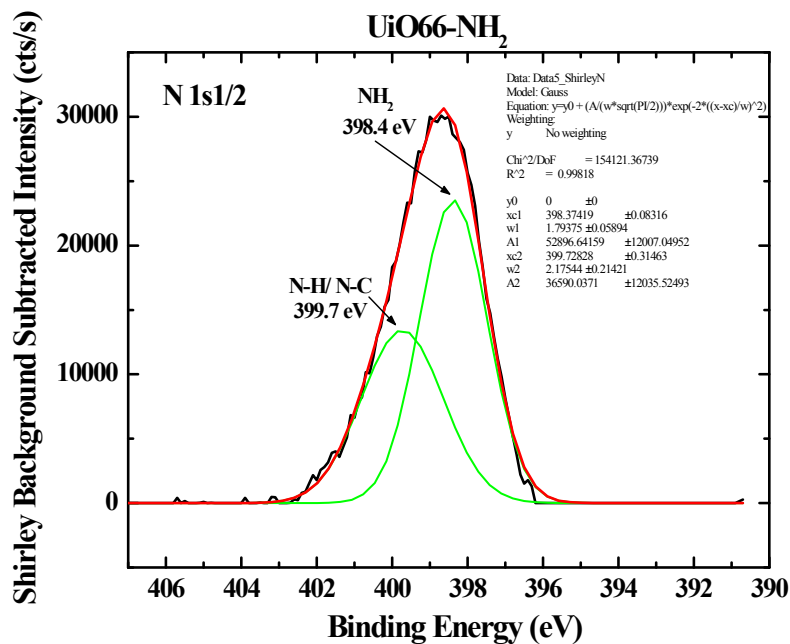


Figure S6. X-ray photoelectron spectroscopy spectrum showing the nitrogen 1s region for baseline UiO-66-NH₂ sample.

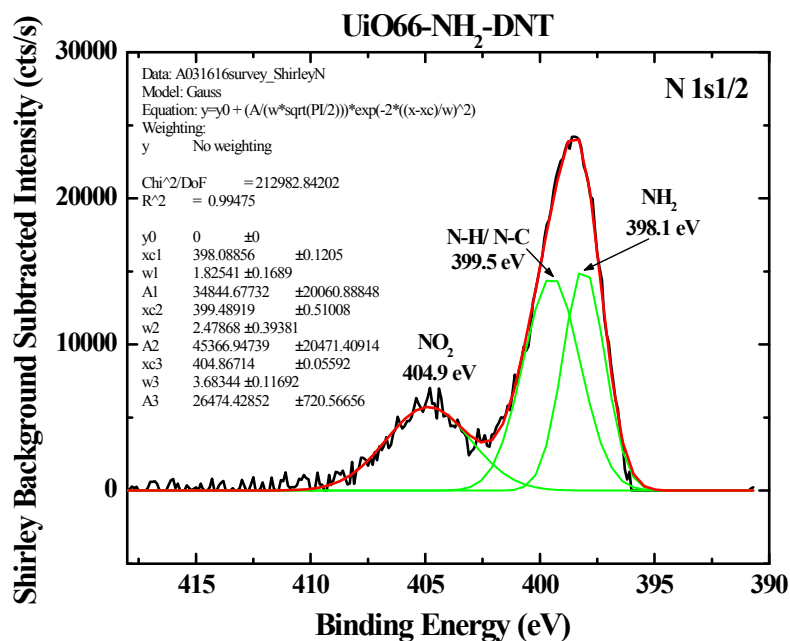


Figure S7. X-ray photoelectron spectroscopy spectrum showing the nitrogen 1s region for 2,6-dinitrotoluene exposed sample.

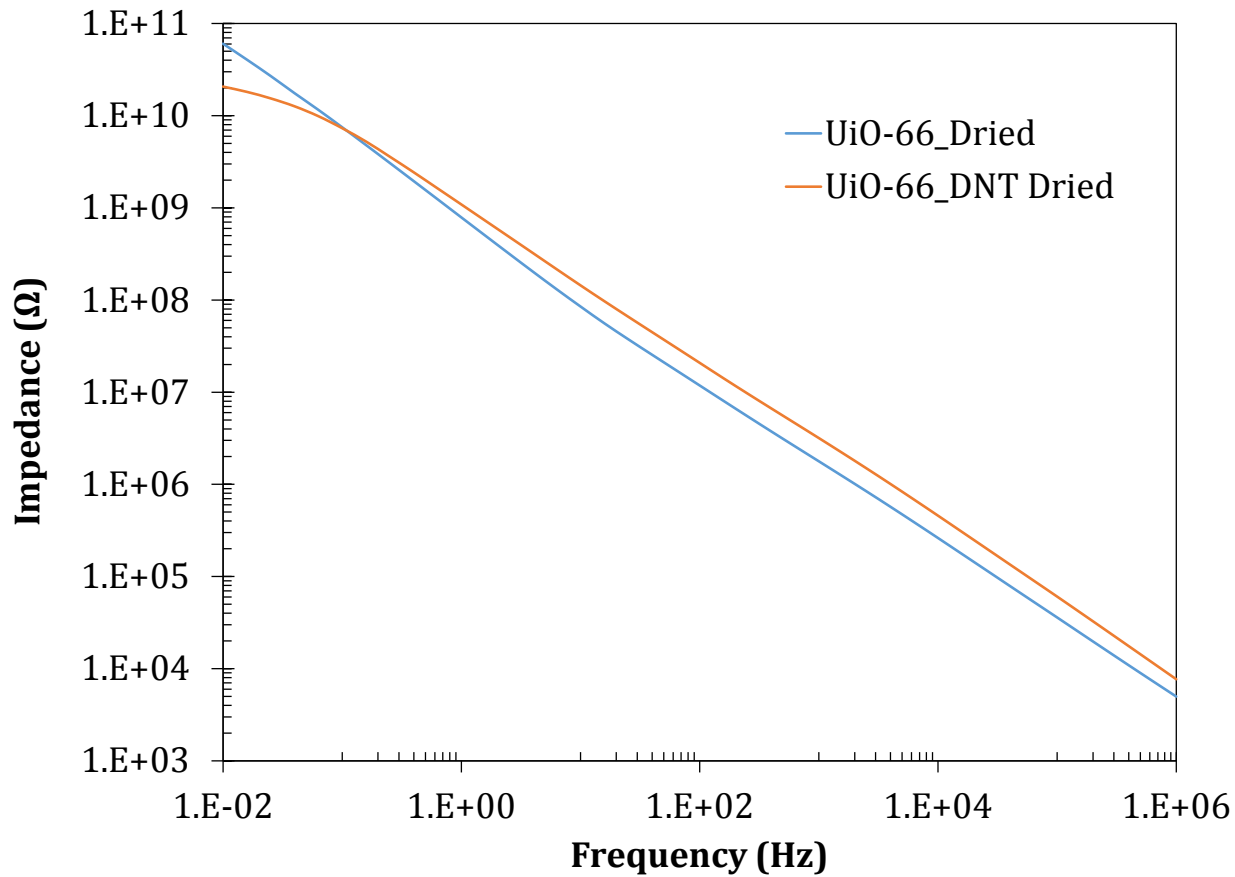


Figure S8. Impedance spectra for baseline UiO-66 and UiO-66 exposed to 1300 μg of 2,6-dinitrotoluene.