FRET- and PET-based Sensing in a Single Material: Expanding the Dynamic Range of an Ultra-sensitive Nitroaromatic Explosives Assay

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Supporting Information

1. EXPERIMENTAL SECTION

1.1 Reagents and Equipment. 1-Pyrenebutyric acid N-hydroxysuccinimide ester (PBANHSE, 97%) and branched PEI (Mw=25,000) were purchased from Sigma–Aldrich. NAC explosives such as TNT (1000 µg/mL in acetonitrile) and 2,4-dinitrotoluene (DNT, analytical standard) were purchased from Sigma-Aldrich, while 2,4,6-trinitrophenylmethylnitramine (Tetryl, 1000 µg/mL in acetonitrile) and nitrobenzene (NB, 1000 µg/mL in acetonitrile) were bought from Ultra Scientific Inc. Aniline, toluene, phenol, and benzonitrile used in interference study were bought from Sigma-Aldrich. All reagents were used as received without further purification. De-ionized water (DI water, 18 MΩ·cm) used in the experiments was obtained from Thermo Scientific Barnstead Water Purification System. Caution: NACs are highly explosive and should be used with extreme care and handled only in small quantities.

Absorption spectra were performed on a Cary 50 UV-vis spectrophotometer (Agilent Technologies), and fluorescence emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (Agilent Technologies). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected using a ZnSe internal reflection element (IRE) obtained on a Nicolet Magna-IR 560 spectrophotometer (Brucker, Germany).

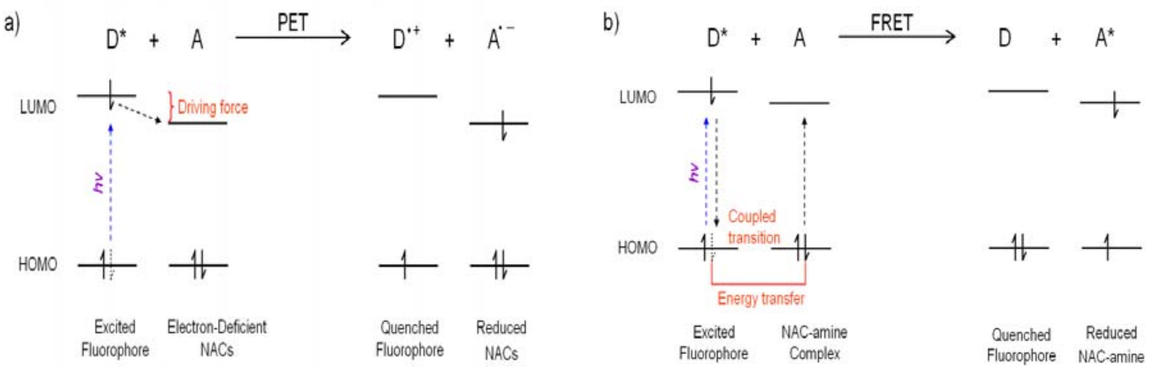
1.2 Polymer Synthesis. Pyrene-PEI was synthesized by aminolysis of PBANHSE with the primary amine groups in branched PEI. Briefly, 0.154 g PBANHSE was dissolved in 6 mL *N,N*-dimethylformamide (DMF) and then mixed with 2.12 g branched PEI, followed by gently stirring at room temperature for 24 h to allow the conjugation to proceed. The formed brown solution was slowly poured into ethyl ether, and the resulting yellow precipitate was extensively washed with THF and H_2O to remove reactant residues. After drying under vacuum for 24 h at room temperature, the final polymer product shows a light yellow color.

1.3 Dispersion of Pyrene-PEI in Water. Due to its poor solubility, pyrene-PEI was sonicated and suspended in DI H_2O for NACs detection. Briefly, 100 mg as-prepared pyrene-PEI was dispersed in 100 mL DI H_2O by a cup-horn sonicator (Cole-Parmer Ultrasonic Processor, 750 W, 100% amplitude) for 30 min in an ice-water bath, followed by centrifuged at 7,200 rpm for 30 min to remove any large particles. The upper 80% supernatant was carefully decanted to ensure well-dispersed pyrene-PEI suspension, and then stored at room temperature for future use.

1.4 Detection of NACs in aqueous samples. The sensing experiments for NAC explosives were carried out by monitoring the fluorescence quenching behavior of pyrene-PEI upon the addition of target NACs at room temperature. Briefly, 3 mL of pyrene-PEI suspension was placed in a disposal methacrylate cuvette with 1 cm width and then explosives solution was added successively. Each titration was repeated at least three times to ensure good reproducibility. The fluorescence emission data were collected in the wavelength region of 360–600 nm with an excitation wavelength of 343 nm. The fluorescence quenching efficiency was defined as $(I_0\text{-}I)/I_0\times100\%$, where I_0 and I are peak intensities before and after the addition of analytes**.** Similar procedure was applied to investigate the interferences such as toluene, benzonitrile, phenol, and aniline.

2. Fluorescence quenching mechanisms.

In PET process (Scheme S1a), the energy gap between the lowest unoccupied molecular orbital (LUMO) of donor fluorophore and that of the acceptor NACs is approximately the thermodynamic driving force for this oxidative electron transfer process. In FRET process (Scheme S1b), an initially excited molecule (donor) returns to the ground state orbital, while simultaneously the transferred energy promotes an electron on the acceptor to the excited state.[1] If donor emission energies are coincident with acceptor absorption energies, such coupling can permit the resonance transitions to take place. If the donor is a fluorophore but the acceptor is non-emissive, a ‘fluorescence-quenching’ could be observed in a FRET process. Especially when the donor-acceptor distance is less than 10 nm, the FRET would be a dominant process in a fluorescence quenching.



Scheme S1. A comparison of a) PET and b) FRET induced fluorescence quenching.

Reference 1. C. R. Cantor and P. R. Schimmel, *Biophysical Chemistry, Part 2: Techniques for the Study of Biological Structure and Function*, W. H. Freeman and Company, 1980.

3. FT-IR spectra of PEI and pyrene-functionalized PEI.

The IR spectra were analyzed using the software of Omnic 7.2a from Thermo Electron Corporation. The successful functionalization of PEI with pyrenyl units was further demonstrated spectroscopically. As shown in the FT-IR spectra in Figure S1, three new adsorption peaks at 843 cm^{-1} (corresponding to ν_{Pyrene}), 1640 cm^{-1} and 1550 cm^{-1} (both corresponding to the $\nu_{\mathrm{C=O}}$ in NH-C=O) were observed for pyrene-PEI hybrid polymer, indicating the presence of pyrene and the successful linkage between the carbonyl groups from PBANHSE and the amine groups from PEI.

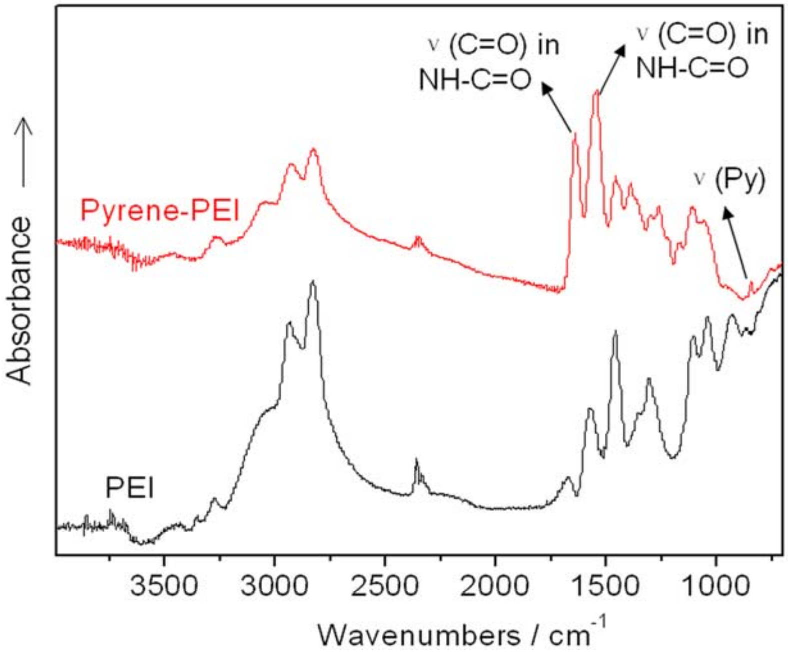


Figure S1. FTIR spectra of PEI and pyrene-PEI.

4. Fluorescence quenching efficiency of pyrene-PEI for TNT at 376 nm band in Figure 3B

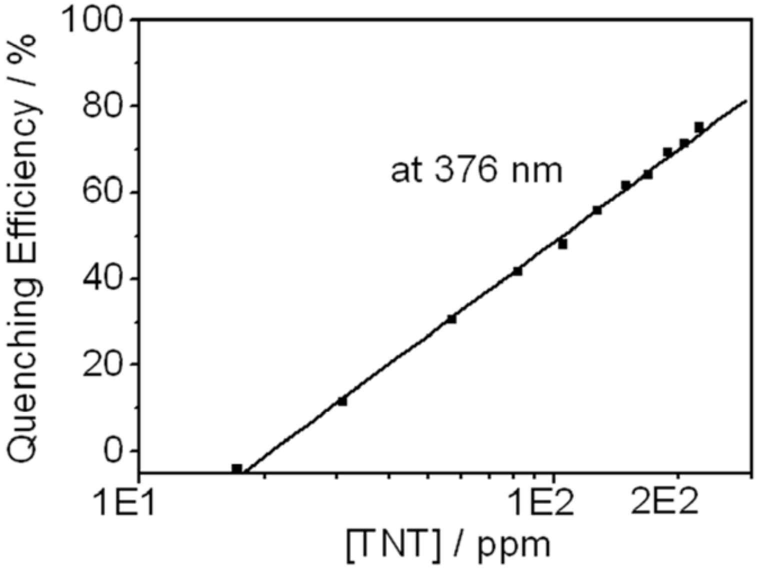


Figure S2. Semi-log plot of fluorescence quenching efficiencies of pyrene-PEI at 376 nm emission band with increasing TNT concentration to 225 ppm.

5. Fluorescence quenching efficiency of pyrene-PEI for Tetryl

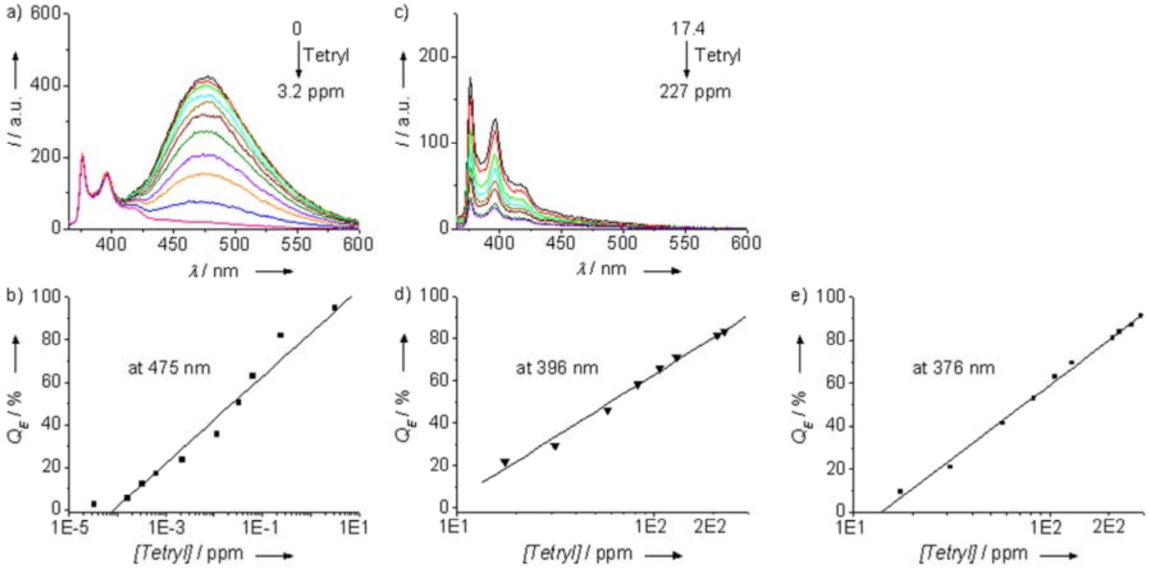


Figure S3. Fluorescence emission spectra of an aqueous pyrene-PEI suspension upon titration with Tetryl ($\lambda_{excitation}$ = 343 nm). A) Low Tetryl concentration range. B) Semi-log plot of the fluorescence quenching efficiency of the pyrene excimer emission (475 nm) with increasing Tetryl concentration. C) Moderate to high Tetryl concentration range. D and E) Semi-log plots of the fluorescence quenching efficiency of the pyrene monomer fluorescence bands (396 nm and 376 nm) of the pyrene-PEI polymer with increasing Tetryl concentration.

6. Fluorescence quenching efficiency of pyrene-PEI for DNT and NB

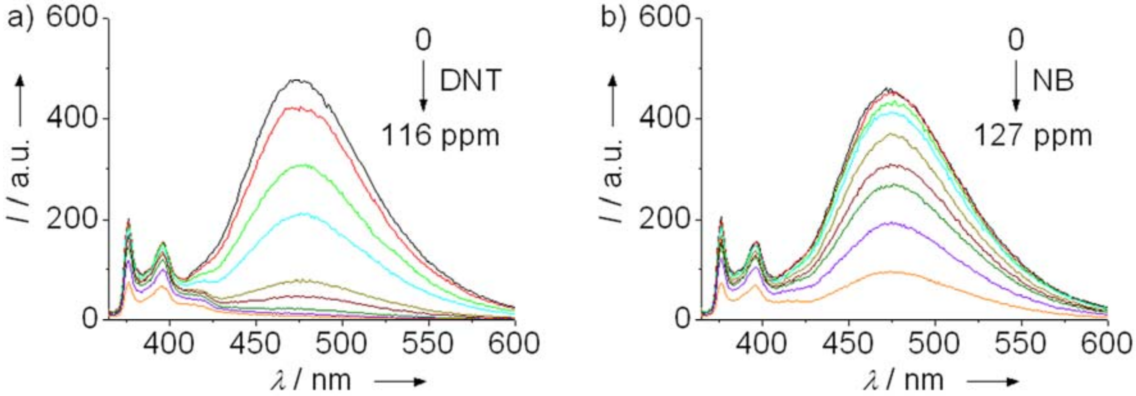


Figure S4. Fluorescence emission spectra ($\lambda_{excitation}$ = 343 nm) of an aqueous pyrene-PEI suspension upon titration with a) DNT ([DNT] = 0, 1.18, 3.37, 12.55, 20.1, 35.4, 34.4, 65.7, and 116 ppm) and b) NB ([NB] = 0, 1.32, 3.22, 12.8, 22.1, 34.4, 65.4, and 127 ppm).

7. Water Test Strips based on pyrene-PEI printed filter paper

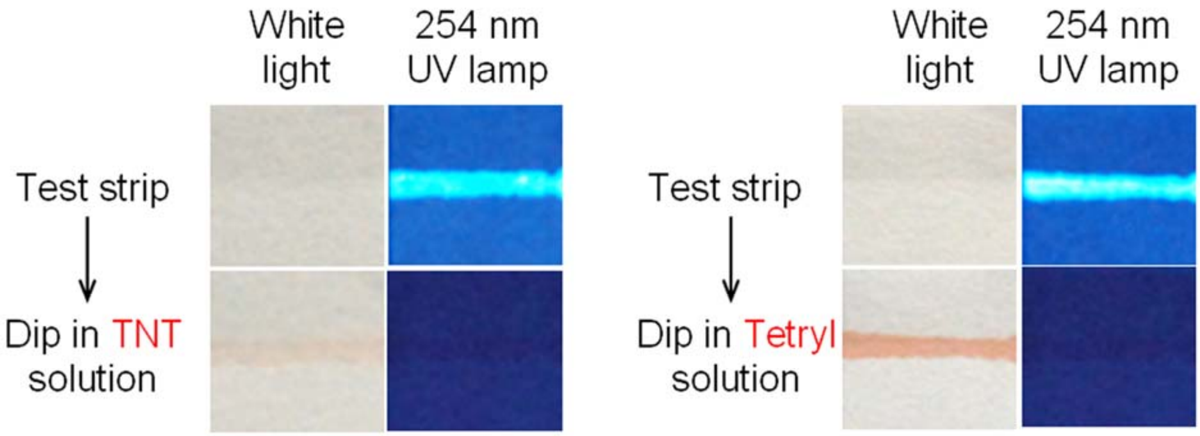


Figure S5. Pyrene-PEI polymer brought onto a cellulose filter paper, followed by dipping in TNT and Tetryl solutions.