Supporting information

Toward wearable sensors: optical sensor for detection of ammonium nitrate-based explosives, ANFO and ANNM.

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1. Chemicals and Instrumentation

All chemicals were analytical grade and they were used without purification. Fluorescence spectra were measured with an Edinburgh FLS920 single photon counting fluorimeter. Fluorescence images were recorded on a Kodak Image Station 440CF or Kodak Image Station 4000MM PRO instrument. Mass-spectrometry studies were performed using a Shimadzu LCMS-8030 (ESI-3Q) or a Shimadzu Axima Performance (MALDI-TOF) mass spectrometer. The quantum yields were recorded by using a Hamamatsu Quantaurus QY-C11347 absolute quantum yield integrating sphere.

2. Abbreviation used

NM = nitromethane, NE = nitroethane, 1NP = 1-nitropropane, 2NP = 2-nitropropane, AN = ammonium nitrate, PEI = poly(ethyleneimine), H^+ = mineral acid (H_2SO_4 or HCl), TEA = triethylamine, AcOH = acetic acid.

3. Sensors preparation

Preparation of poly(ethyleneimine) solution 7.5%: 5 g of a poly(ethyleneimine) solution (30% in H_2O) was diluted with water (5 mL) and absolute ethanol (10 mL).

Preparation of S1: p-dimethylaminobenzaldehyde (**DMAPC**, 268 mg, 1.79 mmol) was dissolved in absolute ethanol (17.4mL) and 2.6 mL of poly(ethyleneimine) solution (7.5%) were added to get [S1] = 90 mM. The final concentration of poly(ethyleneimine) is 1%.

Preparation of S2: 2-naphthaldehyde (**NapC**, 305 mg, 1.95 mmol) was dissolved in absolute ethanol (17.4 mL) and 2.6 mL of poly(ethyleneimine) solution (7.5%) were added to get [S2] = 98mM. The final concentration of Poly(ethyleneimine) is 1%. A milky suspension is obtained over the course of 2 hours. This suspension is stable for a week.

Preparation of S3: 1-pyrenecarboxaldehyde (**PyrC**, 73 mg, 0.317 mmol) was dissolved in absolute ethanol (17.4 mL). The solution is heated to complete dissolution of the solid and then cooled to room temperature. 2.6 mL of poly(ethyleneimine) (7.5%) are added to get [S3] = 16mM. The final concentration of poly(ethyleneimine) is 1%.

Preparation of S4: 2-fluorenecarboxaldehyde (**FluoC**, 61 mg, 0.314 mmol) was dissolved in absolute ethanol (17.4 mL). 2.6 mL of poly(ethyleneimine) (7.5%) were added to get [S4] = 16mM. The final concentration of poly(ethyleneimine) is 1%.

4. Analytes preparation

Solution of the analytes ([NM] = 458 mM, [NE] = 513 mM, [1NP] = 503 mM, [2NP] = 436 mM) were prepared in 10.0 mL of a water / ethanol mixture (ethanol <5%), to guarantee solubility of the analytes. [AN] = 273 mM and [sulfuric acid] = 15.7 mM were prepared in water (10.0 mL).

5. Sensors-Analyte study

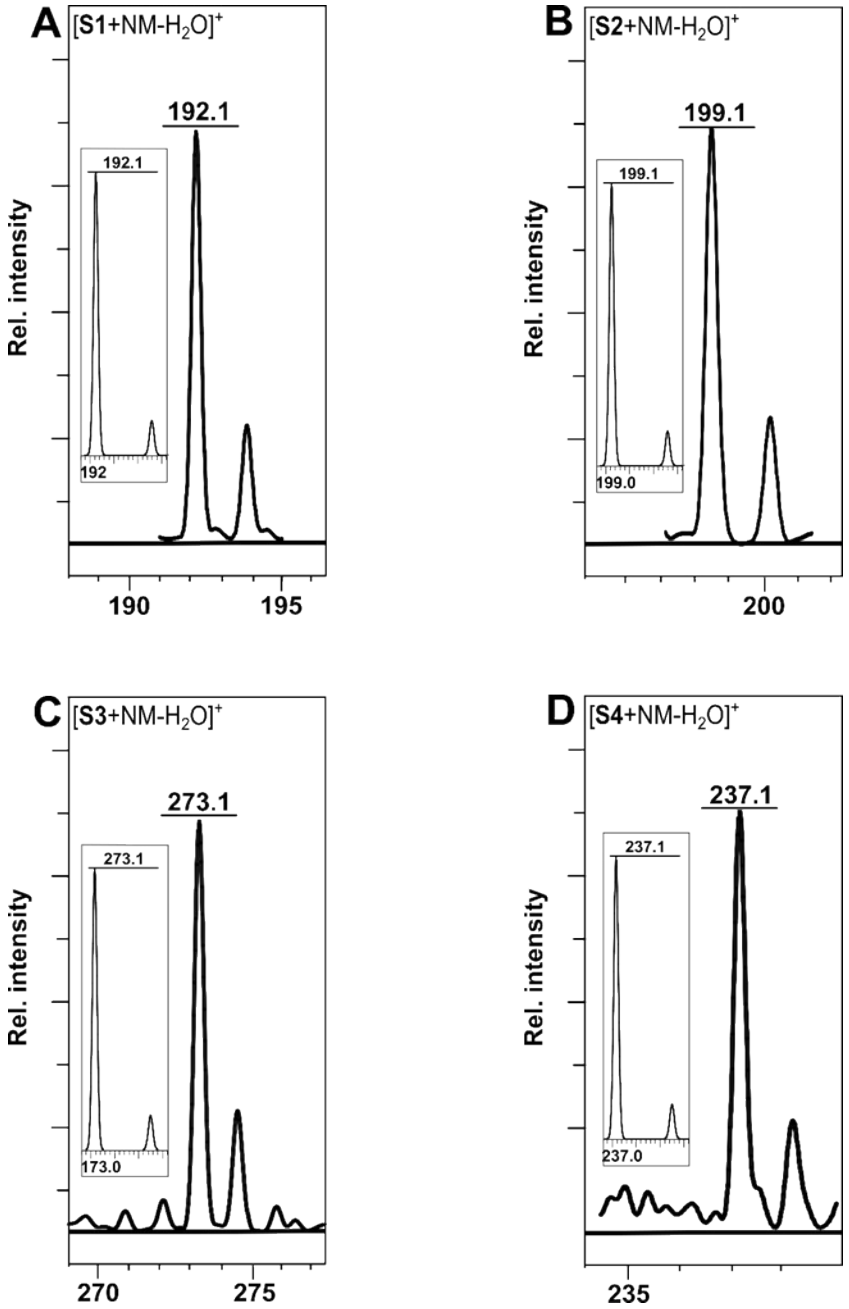


Figure S1. MALDI-TOF mass spectra of A) $[S1+NM-H_2O]^+$ = 192.1, Inset: Calculated isotope pattern for $[S1+NM-H_2O]^+$ = 192.1, B) $[S2+NM-H_2O]^+$ = 199.1, Inset: Calculated isotope pattern for $[S2+NM-H_2O]^+$ = 192.1, C) $[S3+NM-H_2O]^+$ = 273.1, Inset: Calculated isotope pattern for $[S3+NM-H_2O]^+$ = 273.1, D) $[S4+NM-H_2O]^+$ = 237.1, Inset: Calculated isotope pattern for $[S4+NM-H_2O]^+$ = 237.1.

6. Fluorescence studies

6.1 Solid state fluorescence spectra

Solid state fluorescence measurements were performed using a sample holder oriented at a 45° angle on the *x*-*y* plane between the excitation source and the detector and facing upward at a 45° angle from the the *x*-*y* plane to minimize scattering and direct reflection. The sample was prepared by spotting 0.6 μL of **S1**, **S2**, **S3**, and **S4** solutions onto chromatographic paper. Analytes were added by spotting 0.5 μL of their respective solutions.

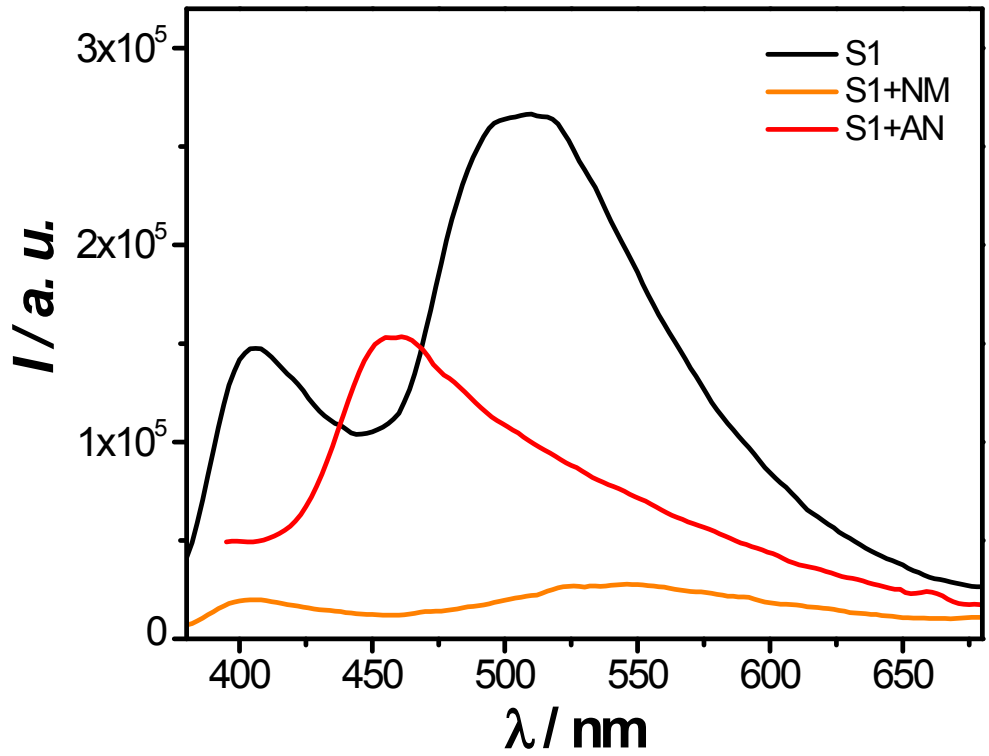


Figure S2. Solid state fluorescence spectra of **S1**, **S1**-NM, **S1**-AN (λ_{exc} = 380 nm).

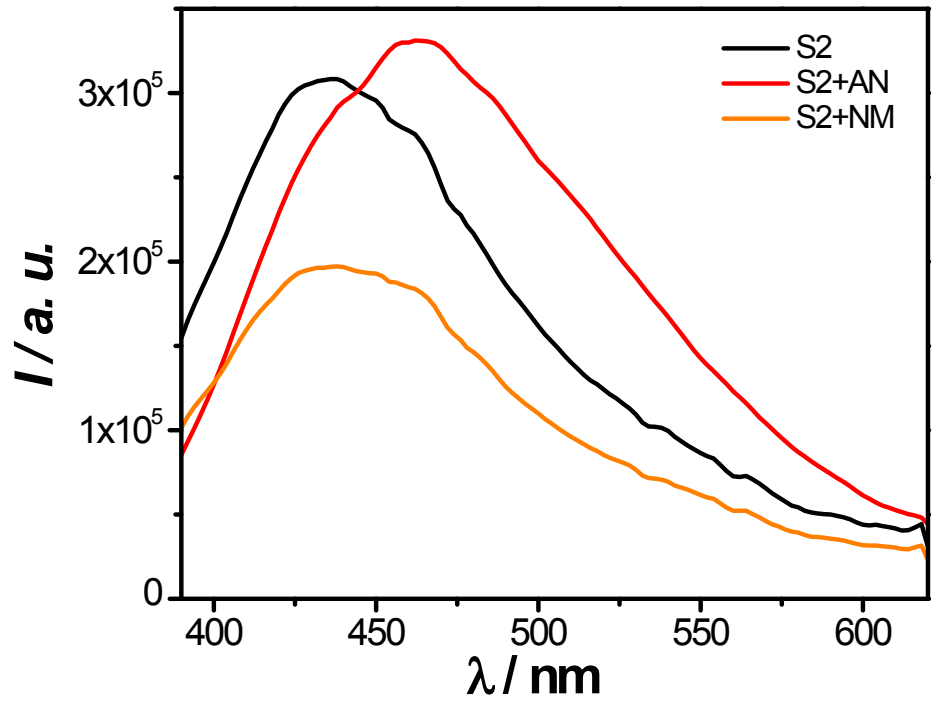


Figure S3. Solid state fluorescence spectra of **S2**, **S2**-NM, **S2**-AN (λ_{exc} = 365 nm).

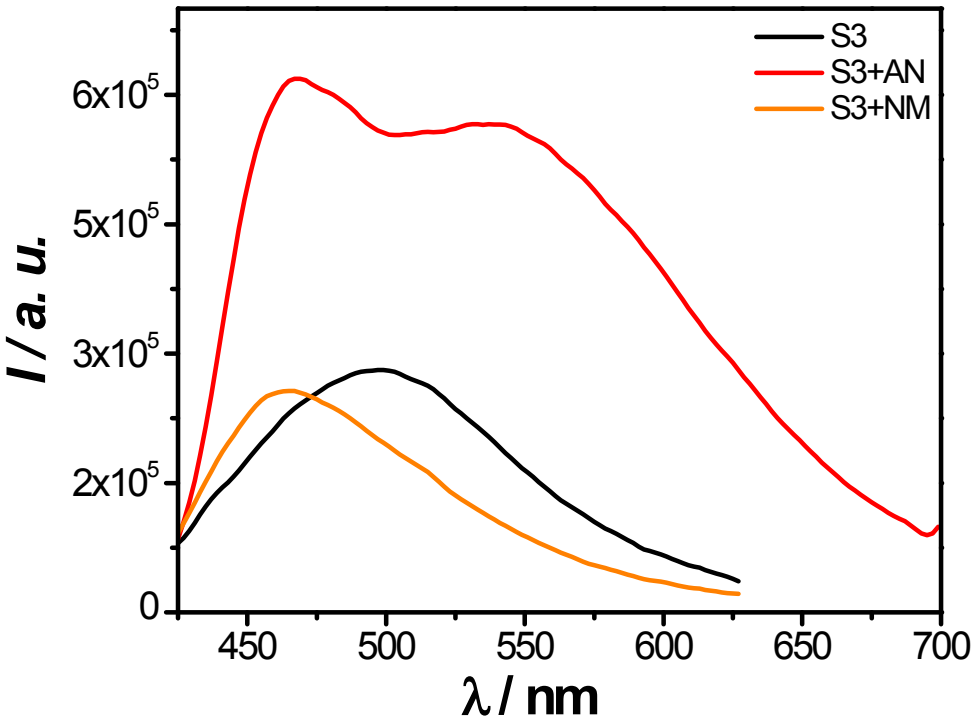


Figure S4. Solid state fluorescence spectra of **S3**, **S3**-NM, **S3**-AN (λ_{exc} = 410 nm).

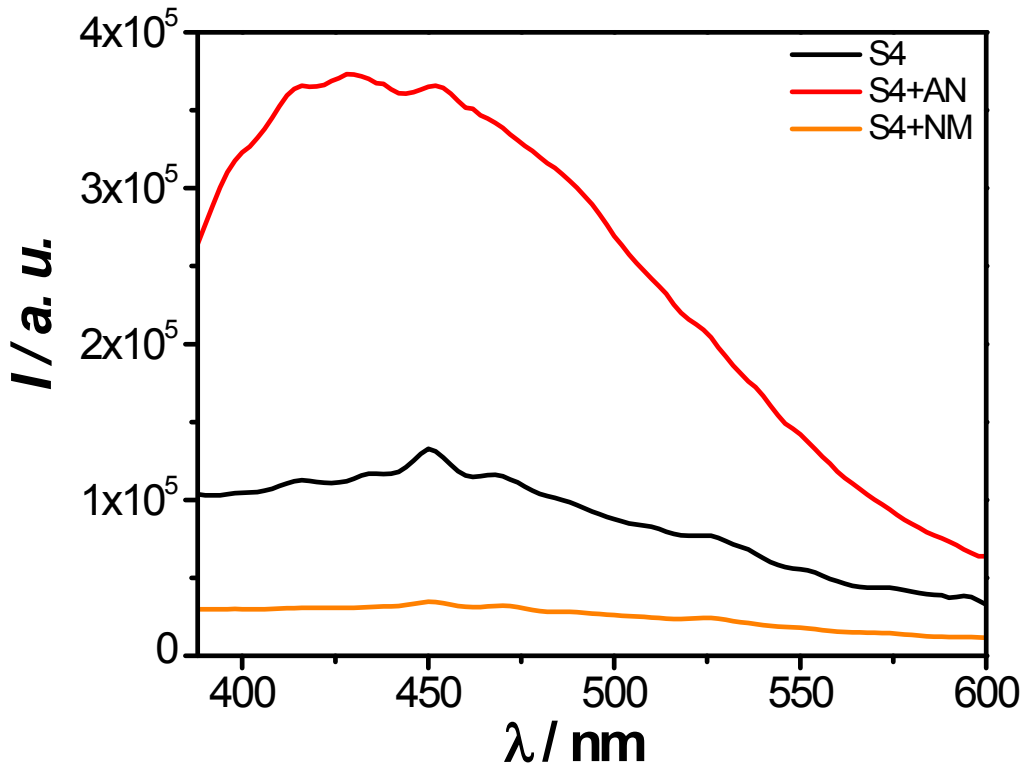


Figure S5. Solid state fluorescence spectra of **S4**, **S4**-NM, **S4**-AN (λ_{exc} = 354 nm).

6.2 Quantum Yields

	Φ / [%]		Φ / [%]
DMAPC *p*-dimethylaminobenzaldehyde	0.43 @ 338 nm	**S1**	0.34% @ 334 nm
NapC 2-naphthaldehyde	4.88% @ 250 nm	**S2**	4.56% @ 250 nm
PyrC 1-pyrenecarboxaldehyde	5.5% @ 287 nm	**S3**	1% @ 346 nm
FluoC 2-fluorenecarboxaldehyde	0.46% @ 317 nm	**S4**	0.96% @ 269 nm

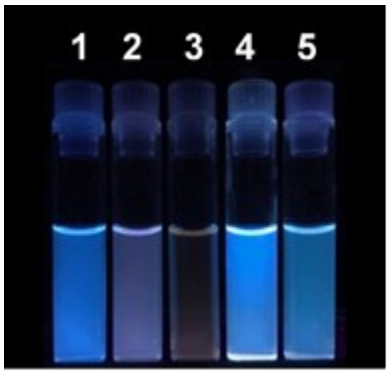
Table S1. Quantum Yields were measured in solutions with A<0.05 at the utilized excitation wavelength. Solutions were prepared in absolute ethanol and the quantum efficiency recorded before and after the addition of PEI.

6.3 Fluorescence titrations in solution

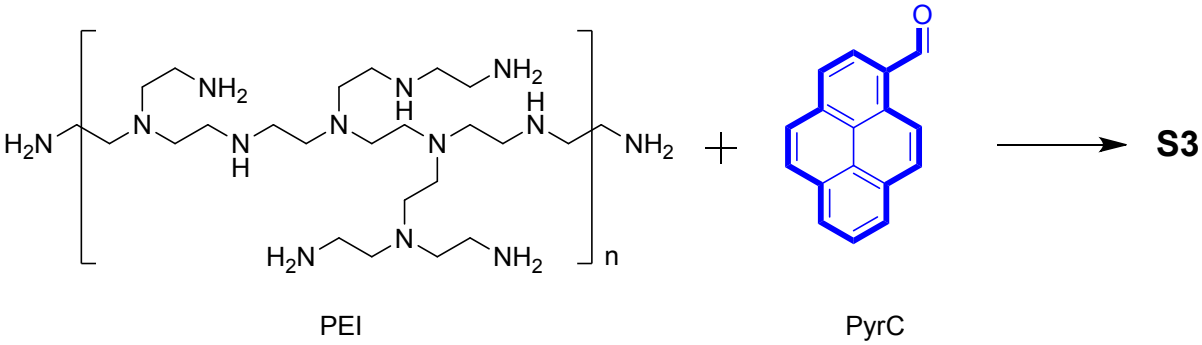
All solutions were prepared in ethanol 96%. The concentrations used were: [**S3**] = 0.1 μM, [AN] = 545 mM, and [NM] = 60 M.

7. Reaction schemes

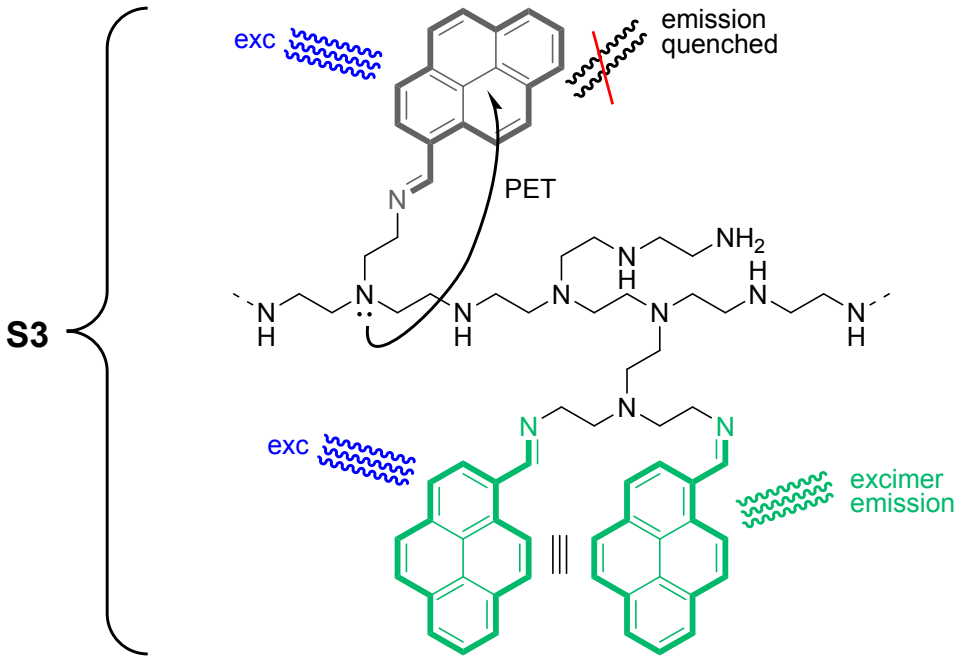
A)



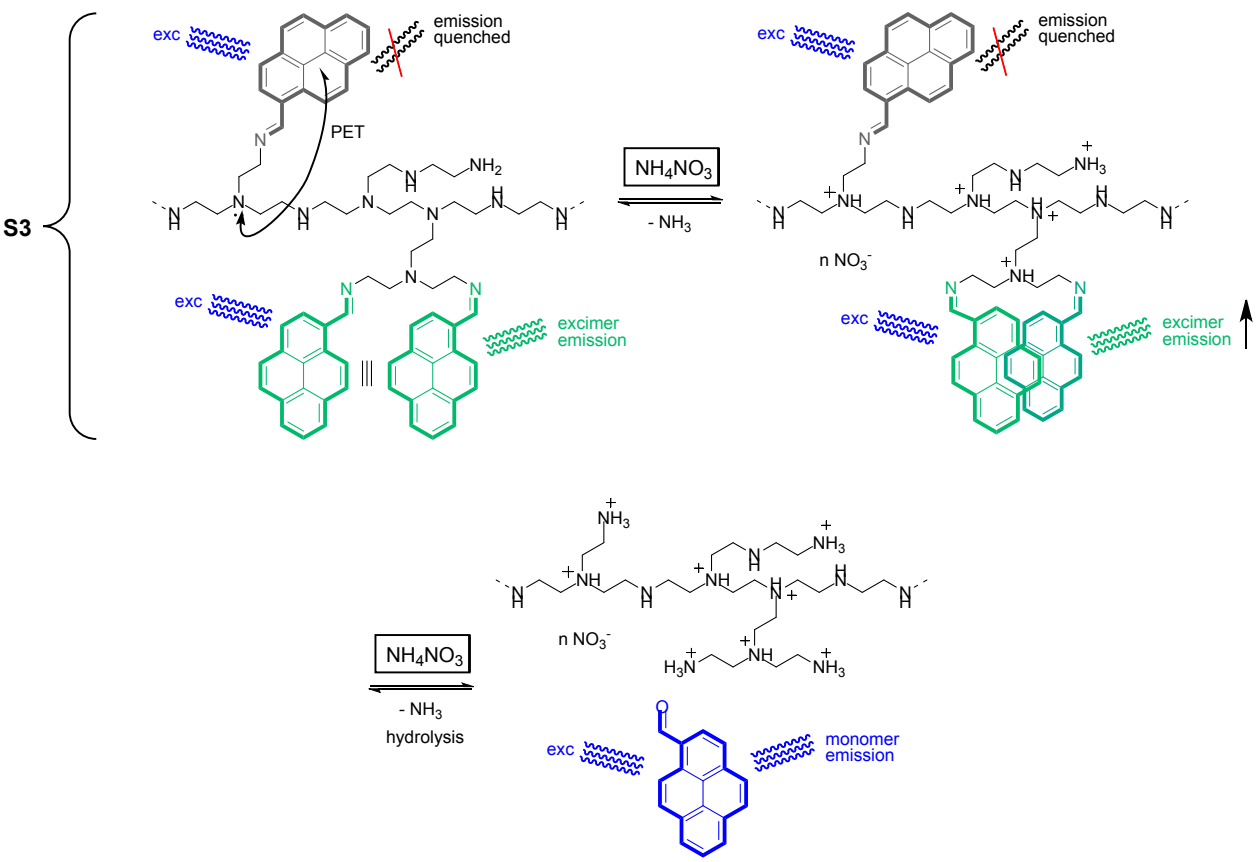
B)



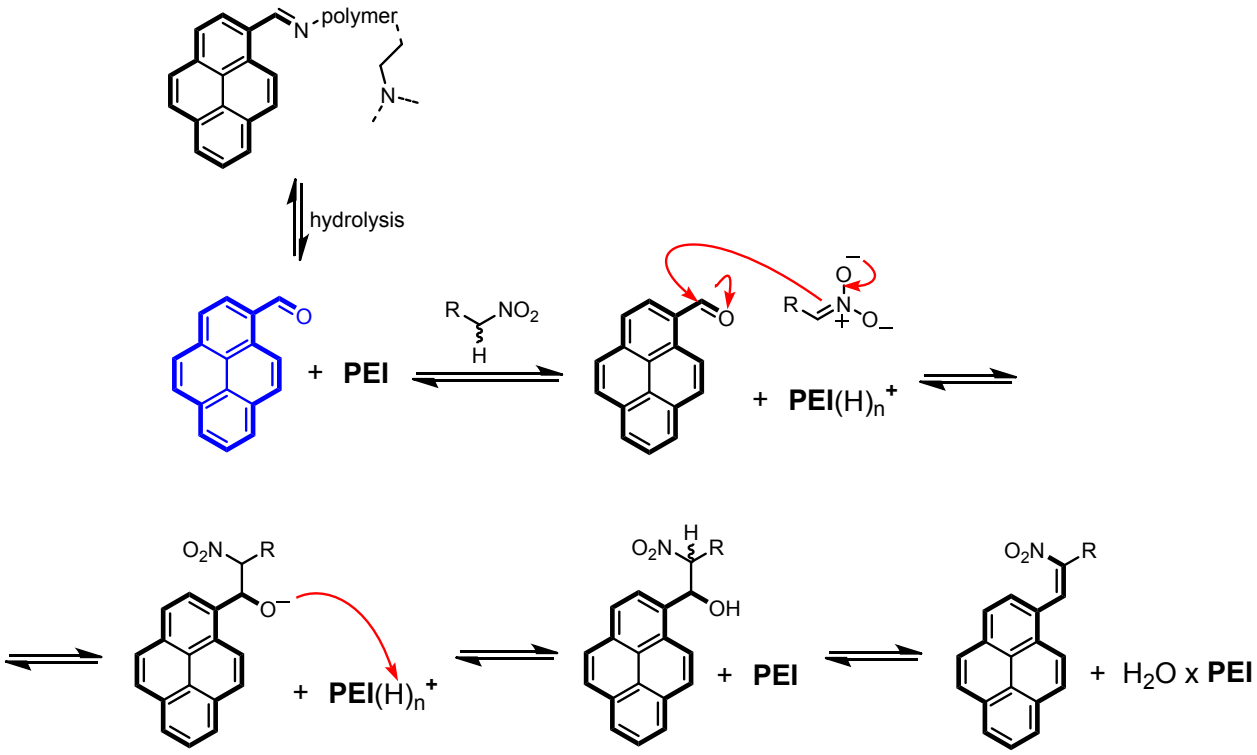
PEI PyrC



C)


S3
exc
emission quenched
PET
NH2
NH4NO3
- NH3
n NO3-
exc
excimer emission
NH4NO3
- NH3
hydrolysis
exc
monomer emission

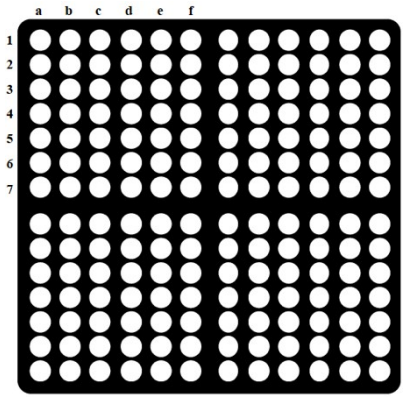
D)



Scheme S6. A) The fluorescence photographs of 1) PyrC, 2) **S3**, 3) **S3**+NM, 4) **S3**+AN, 5) **S3**+ANNM under black light illumination. B) Formation of **S3** from PyrC and PEI. C) Proposed mechanism for **S3**+AN: in the presence of NH_4^+ part of the free amines of PEI are protonated and the pyrene excimer formation is favoured. In the presence of excess of NH_4^+ the hydrolysis of the imine bond becomes the dominant process and the monomeric emission of PyrC is restored. D) **S3**+NM, PEI-promoted formation of the nitroaldol and nitroalkene products leads to a non-fluorescent product.

8. Paper microzone plates study

8.1 Paper microzone plates for Linear Discriminant Analysis (LDA) in solution.



The plates were printed on chromatography paper (Whatman) with a Xerox ColorQube model 8570 wax printer. The diameter of a zone on the paper microzone plate was 2.95 ± 0.04 mm and the total size of the plate was 51.2 ± 0.36 × 53.1 ± 0.17 mm. After printing, it was baked in an oven for 4.5 minutes at 110 ^{o}C to allow for the penetration of wax into the paper. Finally, the back side of the paper was covered with tape. These plates were utilized for qualitative classification of analytes using water as the solvent. 600 nL of S1, S2, S3, and S4 solutions were applied to the zones.

For qualitative analysis, [NM] = 458 mM, [NE] = 513 mM, [1NP] = 503 mM, [2NP] = 436 mM were prepared as described before. [AN] = 273 mM and [H^+] = 15.7 mM (H_2SO_4) were dissolved in H_2O. Then 500 nL of each analyte were added on the zones and the fluorescence images were recorded. Fluorescence intensities were classified by using Linear Discriminant Analysis (LDA). Validation of the analysis was confirmed with cross validation and 100% classification was achieved (Table S1).

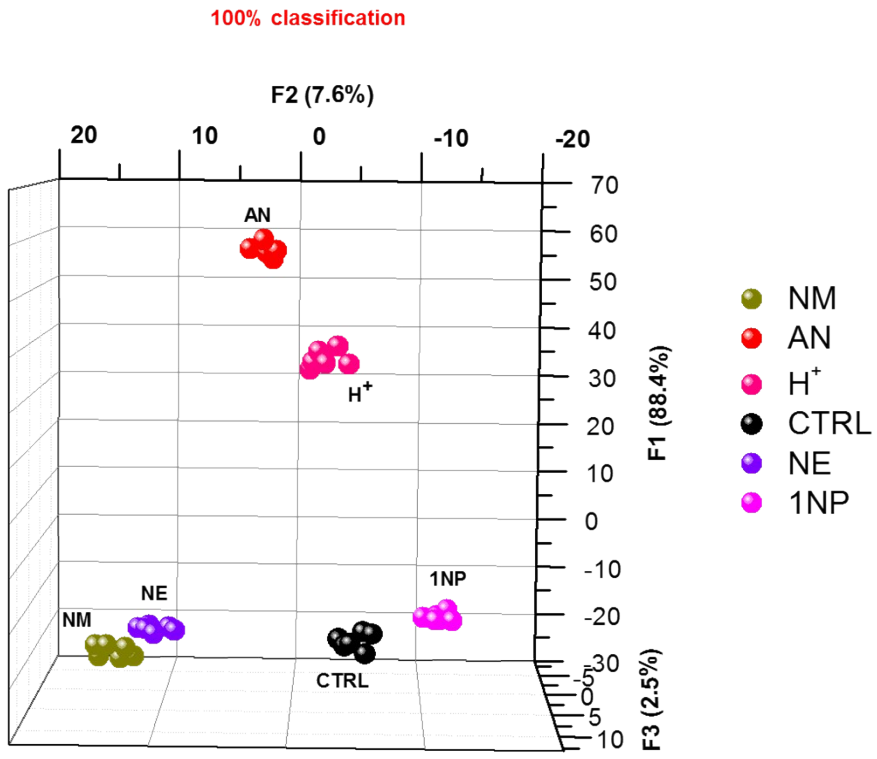


Figure S7. LDA score plot for the fluorescence response patterns showing discrimination among six separate analytes.

Jackknifed Classification Matrix

	1NP	AN	Blank	H^+	NM	NE	%correct
1NP	6	0	0	0	0	0	100
AN	0	6	6	0	0	0	100
Blank	0	0	0	6	0	0	100
H+	0	0	0	0	6	0	100
NM	0	0	0	0	0	6	100
NE	0	0	0	0	0	0	100
Total	6	6	6	6	6	6	100

Table S2. The jackknifed classification matrix for qualitative analysis in the solid state

8.2 Paper microzone plates for vapor sensing.

In qualitative analysis, 600 nL of S1, S2, S3, S4 were applied on microzones of paper. Then 20 μL of each analyte were applied to the zones and allowed to equilibrate with the air. The microzone plates were introduced in the jars and exposed to the vapors of the analyte for 5 minutes. The fluorescence images of the microzone plates exposed to analyte vapors were acquired. The fluorescence intensities were classified by using Linear Discriminant Analysis (LDA). Validation of the analysis was confirmed with cross validation and 100% classification was achieved (Table S2). The analytes used were ammonia (NH_3, as NH_4OH), acetic acid (AcOH), triethylamine (TEA), 1-nitropropane (1NP), 2-nitropropane (2NP), nitroethane (NE), nitromethane (NM).

Jackknifed Classification Matrix

	1NP	**2NP**	**AN**	**AcOH**	**Blank**	**NE**	**NH_3**	**NM**	**TEA**	**%correct**
1NP	5	0	0	0	0	0	0	0	0	100
2NP	0	5	0	0	0	0	0	0	0	100
AN	0	0	5	0	0	0	0	0	0	100
AcOH	0	0	0	5	0	0	0	0	0	100
Blank	0	0	0	0	5	0	0	0	0	100
NE	0	0	0	0	0	5	0	0	0	100
NH_3	0	0	0	0	0	0	5	0	0	100
NM	0	0	0	0	0	0	0	5	0	100
TEA	0	0	0	0	0	0	0	0	5	100
Total	5	5	5	5	5	5	5	5	5	100

Table S3. The jackknifed classification matrix for qualitative analysis in solution.

9. Hierarchical clustering analysis (HCA)

HCA was performed to quantify differentiability among analytes. In this research, we used the most common clustering criterion (Ward's minimum variance) method, which takes into consideration the minimum amount of variance between analytes to define a cluster. There is clear discrimination among all ten analytes. The resultant dendrogram shows connectivity and distance between each analytes. (Figure S11)

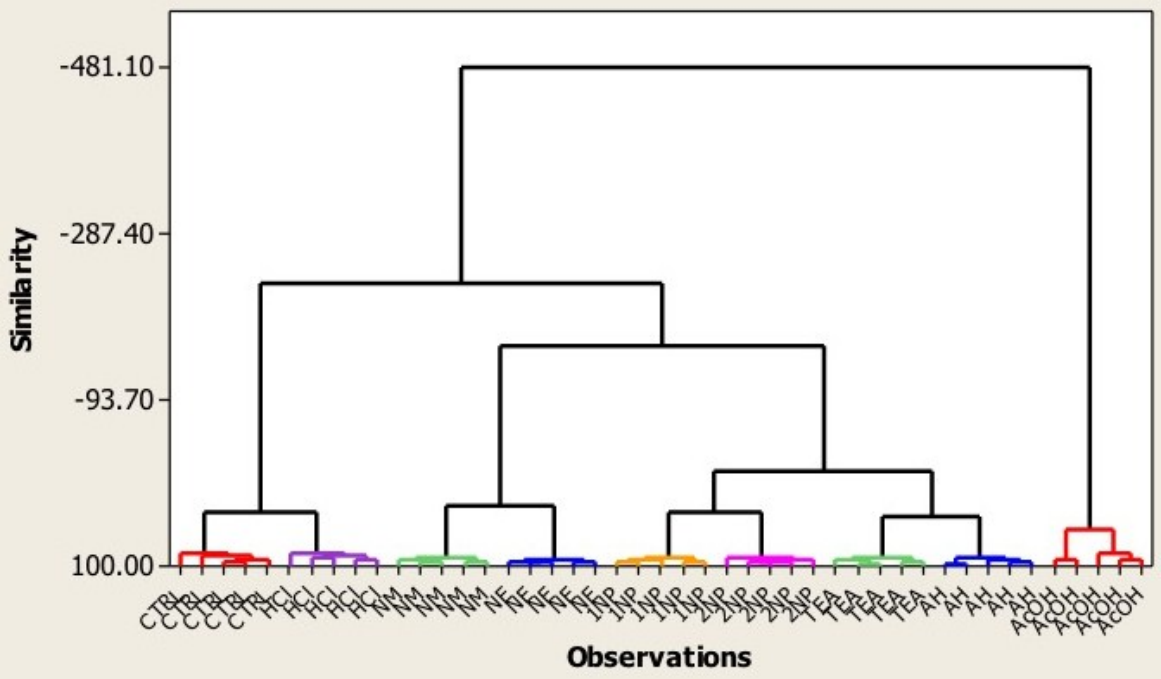


Figure S8. Dendrogram of euclidean distance between 10 samples with ward linkage.

10. Optical sensor array

The plates were printed on chromatography paper (Whatman) with a Xerox ColorQube model 8570 wax printer. The diameter of a zone on paper microzone plates was 2.95 ± 0.04 mm and the total size of the plate was 23.1 ± 0.36 × 21.3 ± 0.17 mm. After printing, it was baked in an oven for 4.5 minutes at 110 °C to allow for the penetration of wax into the paper. The back side of the microzone plate was covered with tape. 600 nL of the sensors ([S3], [S4] = 16 µM), Rhodamine B (3 µM, H_2O), and Fluorescein (3 µM, EtOH) were added on the microzones, then 200 nL of NM, AN, ANNM (60:40) added on the microzones (Figure S12). The picture was taken under a handheld Uv-vis lamp using a compact camera.

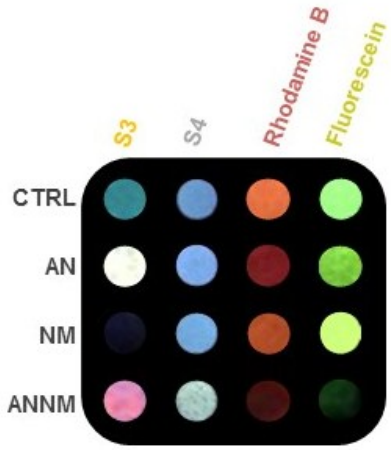


Figure S9. The sensor array's fluorescence under black light (365 nm). Different maps showing the optical sensor array response to NM, AN, and ANNM.

11. Deposition of non-woven nanofiber mats through a shadow mask

11.1 Preparation of non-woven nanofiber mats

S3 fibers were electrospun from a solution containing **S3** (50 mM), TDMACl (50 μM), and 12% w/w of Tecoflex™ (EG-80A, from Lubrizol®) in THF/EtOH 2:1. **S3** solution was electrospun from an 8.5 cm height target-to-collector. A typical voltage applied was 5.5 kV and the injection rate was set to 0.198 mL/h. A shadow mask was utilized to electrospin **S3** on top of four microscope slides (Figure13A). Then, a few drops of nitromethane were applied to **S3** fibers on the microscope slides for 5 minutes (Figure13B). The **S3** fiber's fluorescence under black light (256 nm) was quenched upon exposing to nitromethane. **S3** fibers exposed to the ammonium nitrate solution (in water) (Figure13C). After 5 minutes' exposure, its fluorescence was enhanced. A mixture of ANNM was applied on the S3 microscope slide that fluorescence under black light (256 nm) was different from A, B and C (Figure13D).

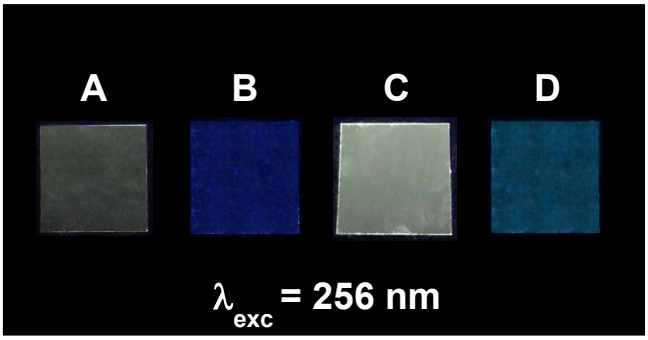


Figure S10. Non-woven nanofiber mats: nanofiber mat deposited on a microscope slide A) **S3** mat fluorescence under black light (256 nm) B) **S3** mat exposed to NM; resulting in fluorescence quenching as seen under black light. C) **S3** mat exposed to AN (in water); resulting in fluorescence enhancement as seen under black light. D) **S3** mat exposed to the ANNM.