Supporting Information

Smartphone-Assisted Sensing of Trinitrotoluene by Optical Array

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Synthesis of Bodipy probes.

OBEP has been synthetized following a literature protocol.[1]

Synthesis of MBP. 2.38 mL (17.6 mmol, 2 eq.) of 2,4-dimethyl-4-ethyl pyrrole, 0.84 mL (8.8 mmol, 1 eq.) of 3-pyridinecarboxaldehyde were dissolved in dry CH_2Cl_2 (500 mL) under nitrogen atmosphere. A catalytic amount of TFA (5 drops) was added and the reaction mixture was stirred at room temperature overnight. The reaction was monitored by TLC (silica gel, CH_2Cl_2) following the total conversion of the starting aldehyde; then 3 g (13.2 mmol, 1.5 eq.) of DDQ were added. The mixture was stirred at room temperature for 6 hours, then 12 mL of triethylamine and 14 mL of $BF_3(OEt)_2$ were added. The reaction mixture was stirred overnight at room temperature. Then, the solvent was removed under reduced pressure and the mixture was redissolved in CH_2Cl_2 and filtered. The desired Bodipy (yield 17%) was purified by chromatography (silica gel, CH_2Cl_2 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.5 Hz, 6H), 1.28 (s, 6H), 2.30 (q, *J* = 7.8 Hz, 4H), 2.54 (s, 6H), 7.45 (dd, J_1 = 4.9 Hz, J_2 = 2.9 Hz, 2H), 7.64 (t of d, J_1 = 7.8 Hz, J_2 = 2.0 Hz, 1H), 8.56 (dd, J_1 = 2.0 Hz, J_2 = 1.0 Hz, 1H), 8.75 (dd, J_1 = 4.9 Hz, J_2 = 2.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ 14.72, 15.51, 16.11, 17.33, 123.19, 131.10, 131.69, 134.10, 138.95, 145.26, 150.92, 151.36, 156.31. ESI MS: *m/z* 380.04 $[M]^{-1}$ calcd for $C_{22}H_{26}BF_2N_3$.

Synthesis of MBEP. 554 mg of MBP (1.45 mmol) were dissolved in dry CH_3CN under nitrogen atmosphere. Then, 240 mg of dry K_2CO_3 were added and the mixture was heated at 45° C. After 10 minutes, 10 mL of iodoethane were added, and reaction mixture was stirred for 24 h. Total conversion of the starting reagent was monitored by TLC (Al_2O_3, CH_2Cl_2). At the end of the reaction, the solvent was removed under reduced pressure, and the MBEP (yield 62%) was purified by chromatography (Al_2O_3, CH_2Cl_2/CH3OH, from 100/0 to 90/10). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.0 (t, *J* = 7.5 Hz, 6H), 1.34 (s, 6H), 1.8 (t, *J* = 7.3 Hz, 3H), 2.32 (q, *J* = 7.3 Hz, 4H), 2.56 (s, 6H), 5.17 (q, *J* = 7.3 Hz, 2H), 8.4 (m, 2H), 8.51 (d, *J* = 3.7 Hz, 1H), 10.35 (t, *J* = 6.1 Hz, 1H) ppm.

Synthesis of PBP. PBP was synthetized by following the same procedure used for MBP, using the 4-pyridinecarboxaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (d, *J* = 6.0 Hz, 2 H), 7.35 (d, *J* = 6.0 Hz, 2 H), 2.53 (s, 6 H), 2.30 (q, *J* = 7.5 Hz, 4 H), 1.30 (s, 6 H), 0.98 (t, *J* = 7.5 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$) δ 15.23, 15.96, 16.35, 17.11,
124.11, 130.45, 131.55, 132.19, 138.45, 144.29, 151.19, 156.75 ppm.

Synthesis of PBEP. PBEP was synthetized by following the same procedure used for MBEP. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.69 (d, *J* = 6.4 Hz, 2H), 8,05 (d, *J* = 6.4 Hz, 2H), 5.27 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 6H), 2.31 (q, *J* = 7.5 Hz, 4H), 1.84 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 6H), 0.99 (t, *J* = 7.5 Hz, 6H) ppm.

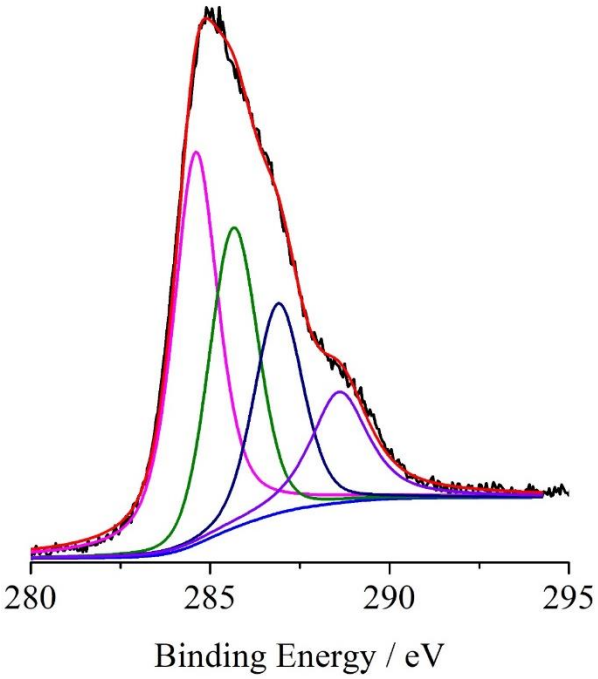

Figure S1. Al-Kα excited XPS of the CDs-C_2-OH sample in the C 1s binding energy region. The magenta, green, navy and violet lines refer to the 284.6, 285.7, 286.9 and 288.6 eV Gaussian components. The blue line refers to the background and the red line superimposed to the black experimental profile refers to the sum of all Gaussian components.

Figure S1 shows the XPS of a representative CDs-C_2-OH sample in the C 1s binding energy region. An accurate fitting of this spectrum revealed the presence of four components at 284.6, 285.7, 286.9, and 288.6 eV, respectively. The first signal at 284.6 eV is due to the sp^2 component of the graphitic CNPs surface.[2] The peaks at 285.7 and 286.9 and 288.6 eV are due to the C−N and C−OH and −OC−NH− groups, respectively and the presence of some of these signals confirms the covalent functionalization of the nanoparticles with ethanolamine.[3]

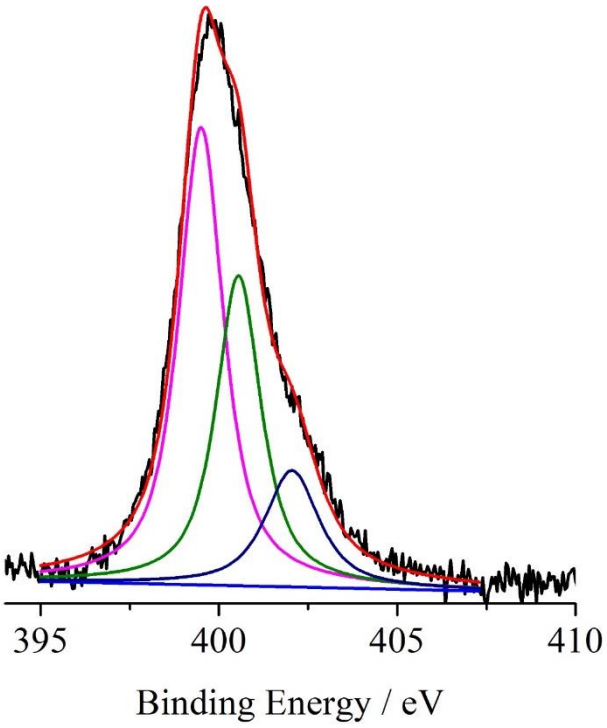

Figure S2. Al-Kα excited XPS of the CDs-C_2-OH sample in the N 1s binding energy region. The magenta, green and navy lines refer to the 399.5, 400.5 and 402.1 eV Gaussian components. The blue line refers to the background and the red line superimposed to the black experimental profile refers to the sum of all Gaussian components.

Figure S2 shows the XPS of a representative CDs-C_2-OH sample in the N 1s binding energy region. The N 1s spectral profile shows components at 399.5 (50 % of the overall signal), 400.5 (34 % of the overall signal) and 402.1 eV (16 % of the overall signal), consistent with the presence of the amine (C-NH-R), the amide (–OC–NH–) and protonated N^+ groups, respectively on the surface of the CDs.[4] On the basis of the intensity ratios, only the 34 % of the starting surface-confined amine was transformed in amide groups while the 16 % of this starting amine was protonated by some HCl generated during the surface-functionalization reaction.

Sensing in solution.

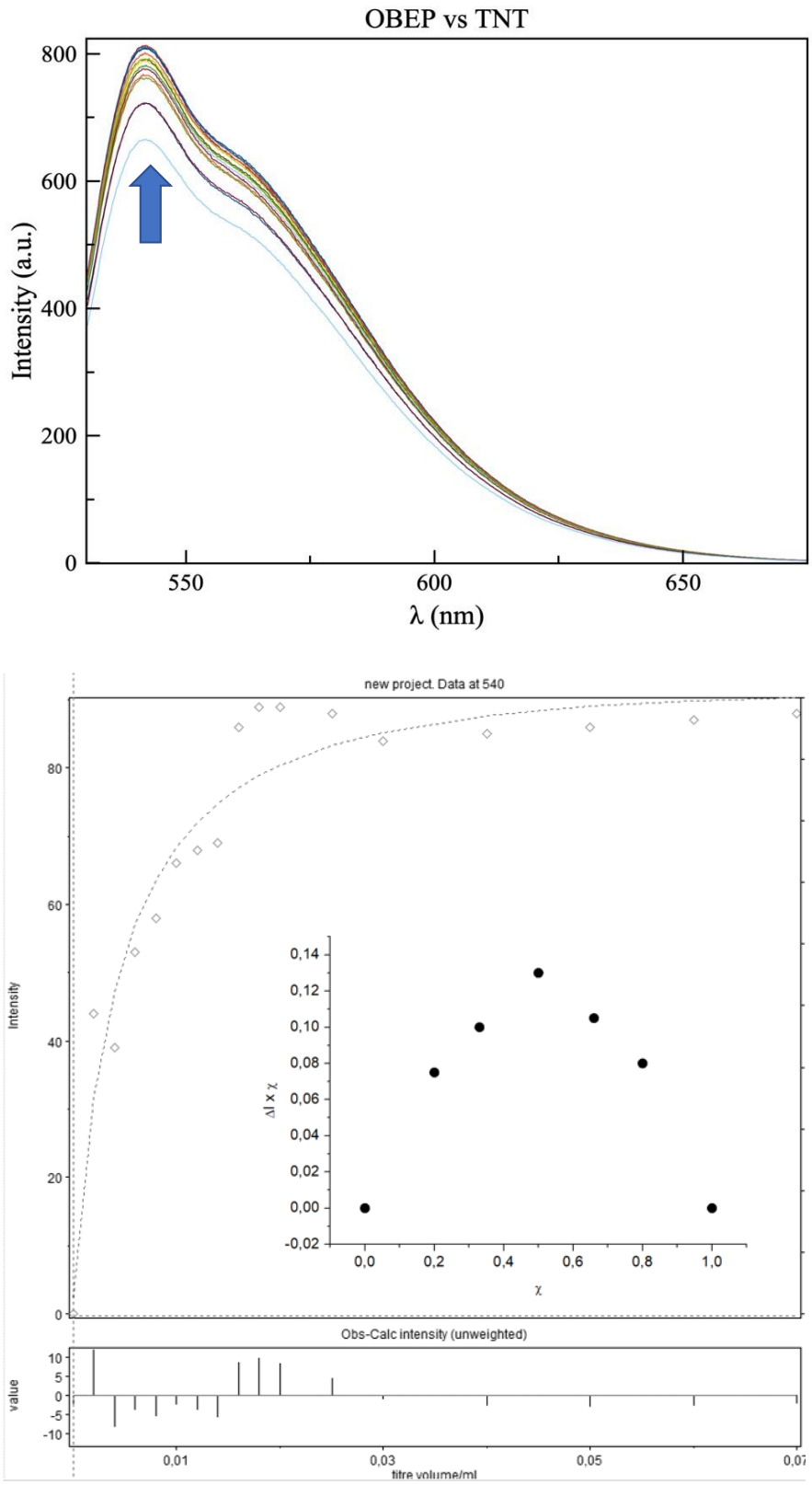

Figure S3. Fluorescence spectra during the titration between OBEP and TNT (inset shows the relative Job's Plot)

HypSpec output file:

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                     standard

Log beta   value     deviation

AB         5.4804    0.1214
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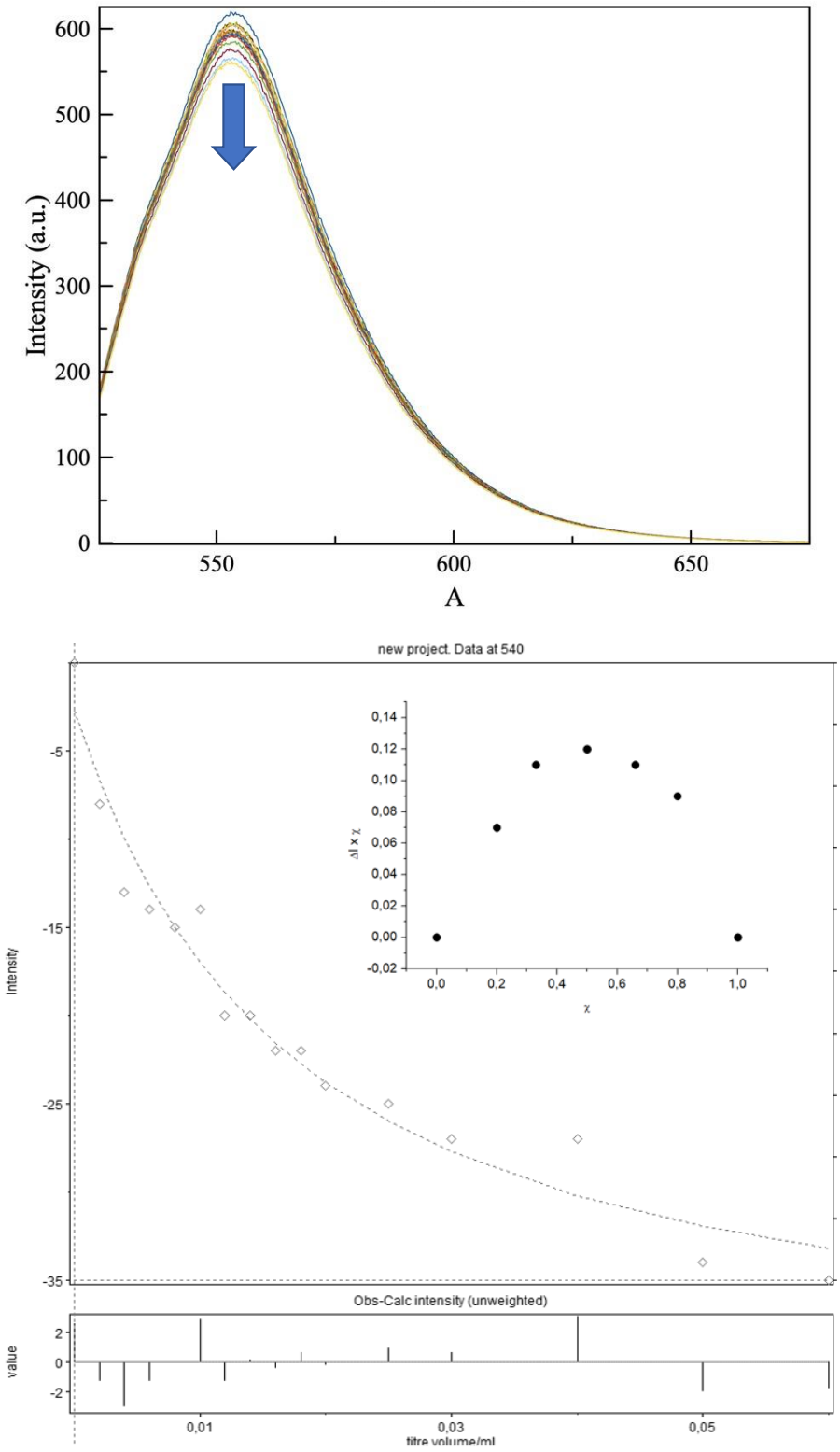

Figure S4. Fluorescence spectra during the titration between MBEP and TNT (inset shows the relative Job's Plot)

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Log beta    value    deviation
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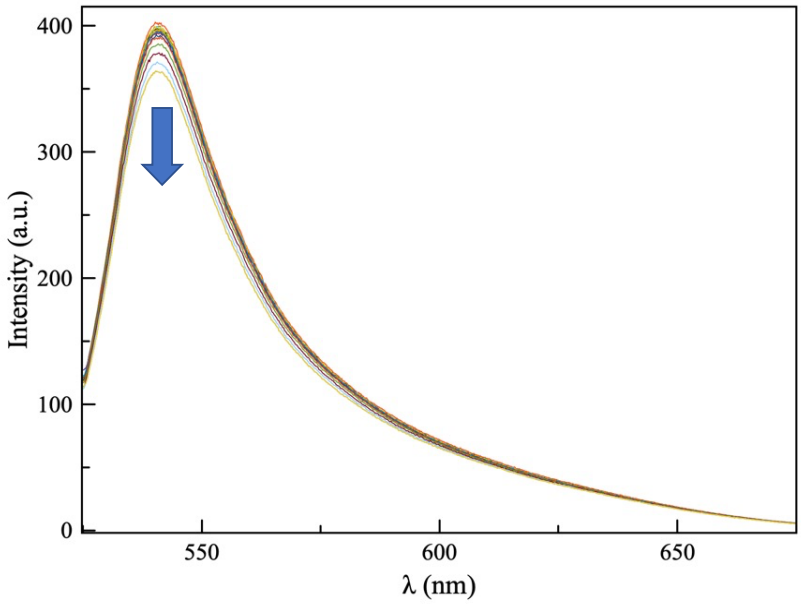
AB 6.7338 0.5687



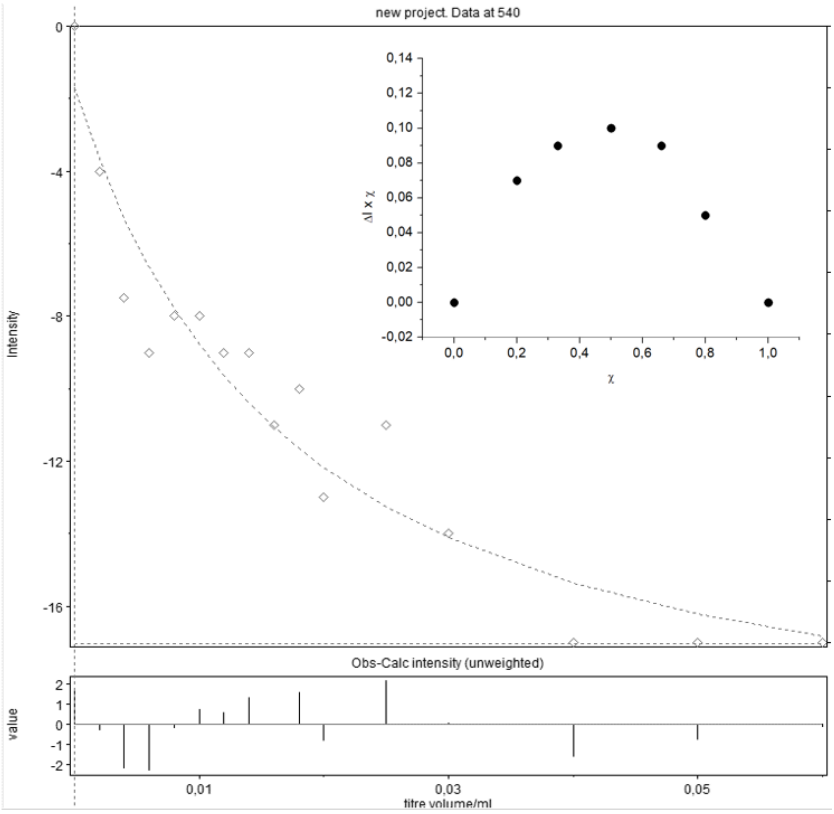


Figure S5. Fluorescence spectra during the titration between PBEP and TNT (inset shows the relative Job's Plot)

HypSpec output file:

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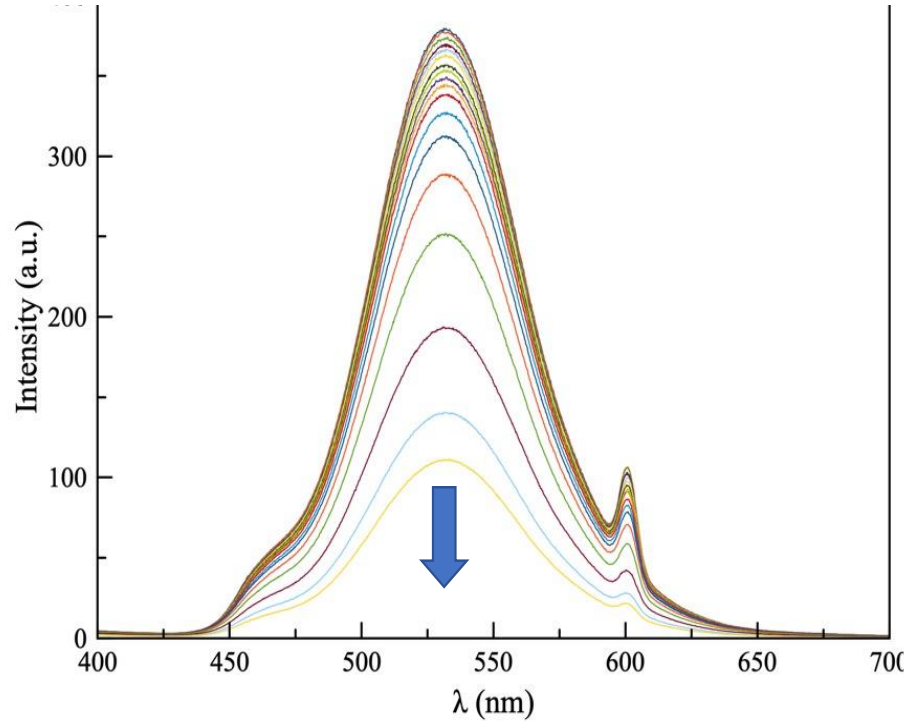
Log beta	value	standard deviation
AB	2.0978	0.1022



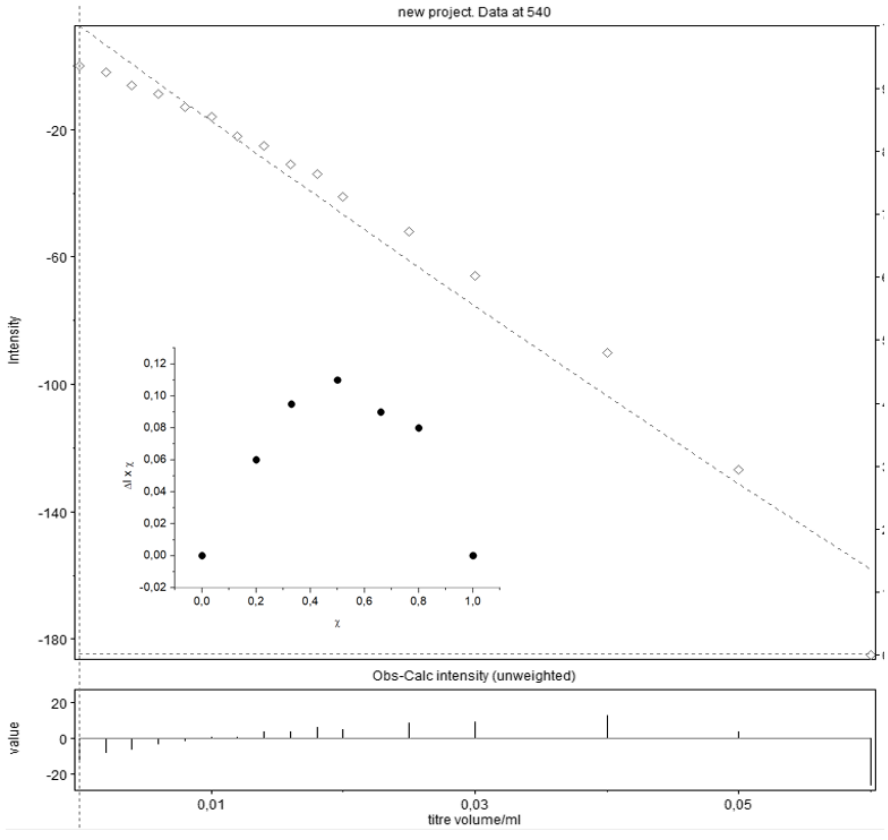


Figure S6. Fluorescence spectra during the titration between Naphthyl-Di-AE and TNT (inset shows the relative Job's Plot)

HypSpec output file:

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Converged in 1 iterations with sigma = 11,890

                    standard
Log beta   value     deviation
AB         4.2997    0.0307
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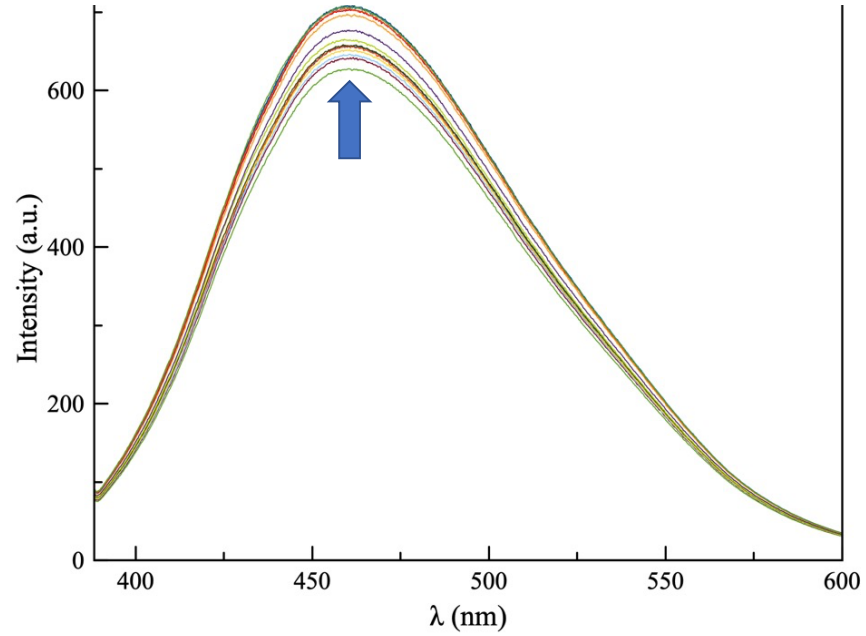

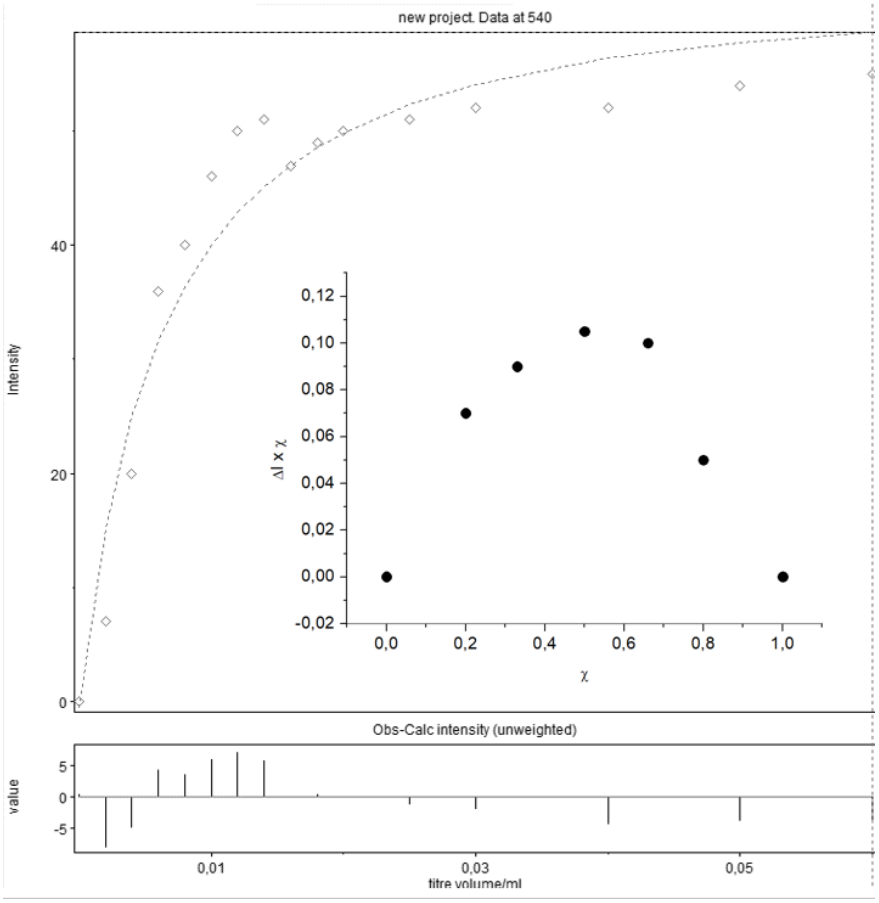

Figure S7. Fluorescence spectra during the titration between CDs-C_2-OH and TNT (inset shows the relative Job's Plot)

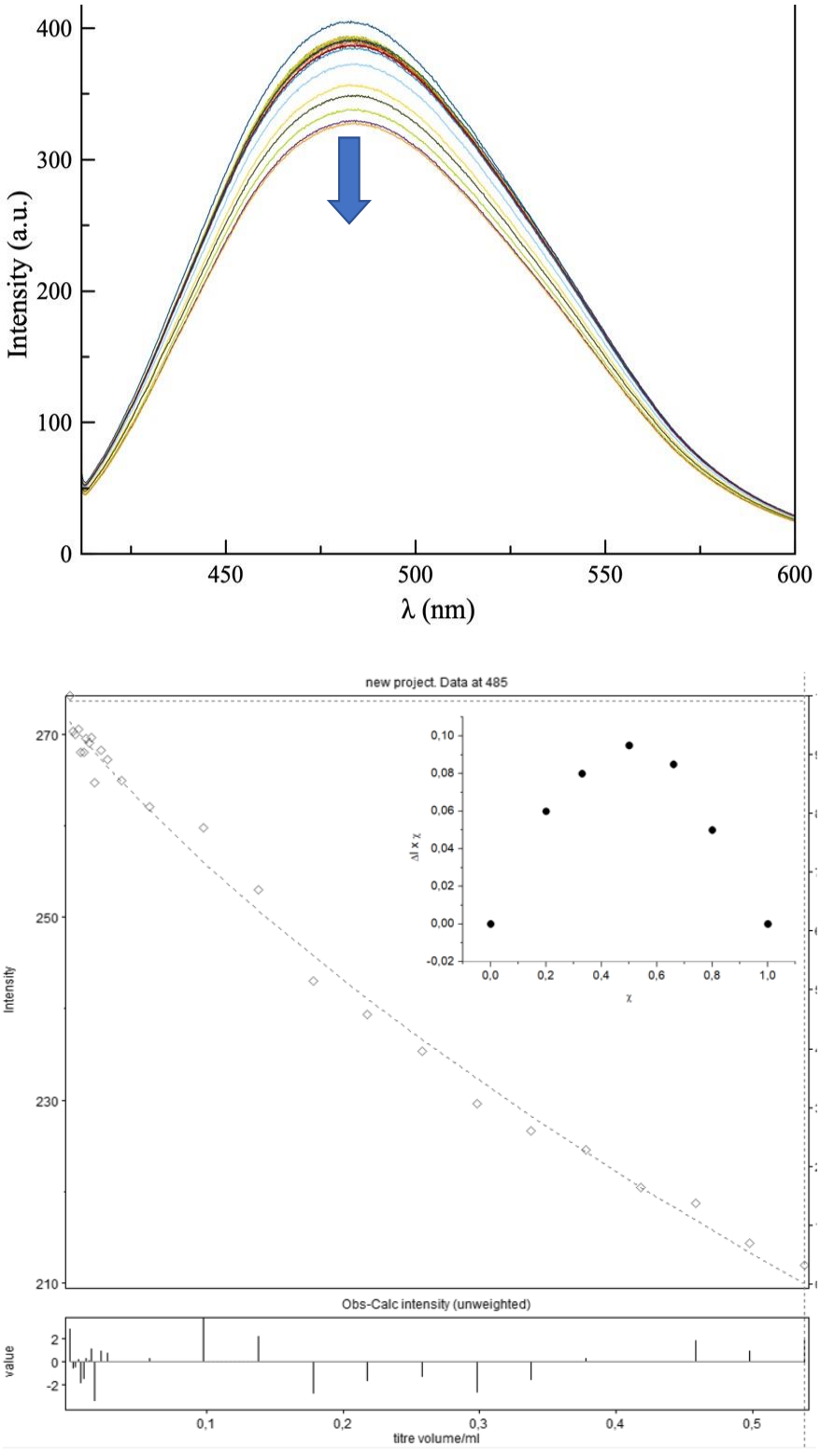

Figure S8. Fluorescence spectra during the titration between CDs-C_3-OH and TNT (inset shows the relative Job's Plot)

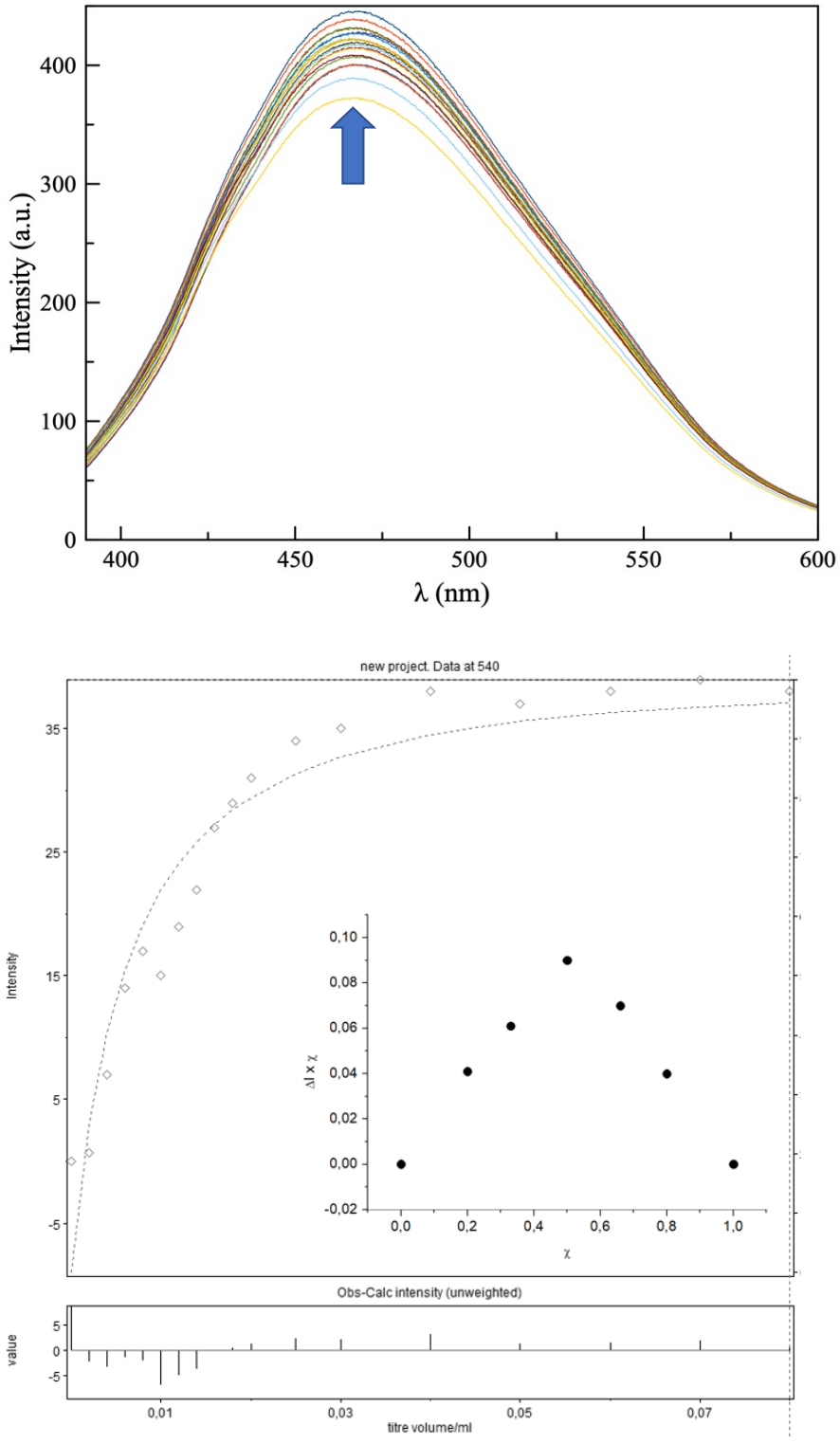

Figure S9. Fluorescence spectra during the titration between CDs-C_4-OH and TNT (inset shows the relative Job's Plot)

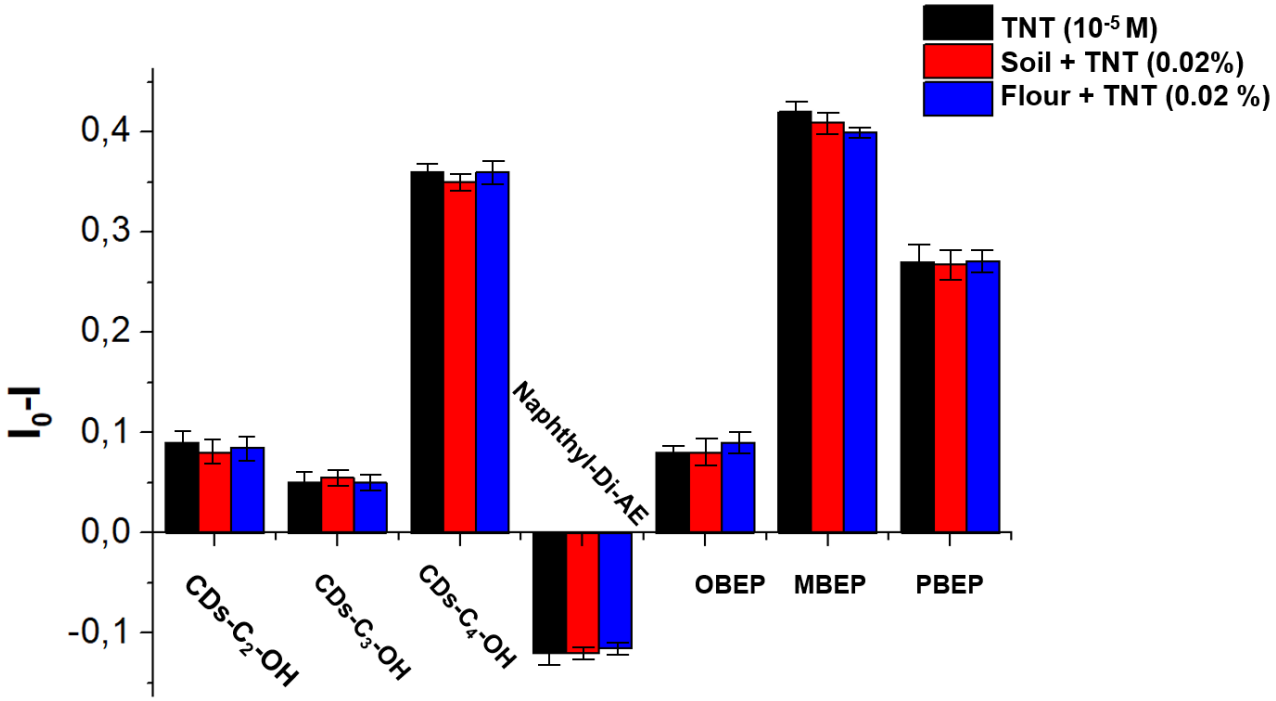

Figure S10. Normalized emission responses (I_0-I) and relative standard deviations of the probes to TNT (black bars, 1 x 10^{-5} M in H_2O/CH_3CN 50/50), 1 g of Agricultural Soil containing the 0.02% of TNT (red bars) and 1 g of Food Flour containing the 0.02% of TNT (blue bars) extracted with 20 mL of H_2O/CH_3CN 50/50.

Table S1. List of substances used that we defined as 'no TNT' each associated with the Euclidean distance with centre of maximum density of 'TNT' samples in the t1-t2-t3

SAMPLES REPLICA	DISTANCE
AMATOL1	3.77
AMATOL2	4.28
AMATOL3	4.02
AVERAGE AMATOL	**4.02**
NITROMETHANE1	6.47
NITROMETHANE2	6.02
NITROMETHAN3	3.50
AVERAGE NITROMETHAN	**5.33**
CHLOROBENZENE1	4.55
CHLOROBENZENE2	3.35
CHLOROBENZENE3	4.99
AVERAGE CHLOROBENZENE	**4.30**
NITROBENZENE1	5.83
NITROBENZENE2	7.11
NITROBENZENE3	2.16
AVERAGE NITROBENZENE	**5.04**
DYNAMITE1	4.03
DYNAMITE2	3.82
DYNAMITE3	3.61
AVERAGE DYNAMITE	**3.82**
PEP1	5.61
PEP2	5.60
PEP3	3.89
AVERAGE PEP	**5.04**
ANFO1	4.26
ANFO2	5.08
ANFO3	4.44
AVERAGE ANFO	**4.60**
PREMEX1	4.28
PREMEX2	4.29
PREMEX3	4.20
AVERAGE PREMEX	**4.26**

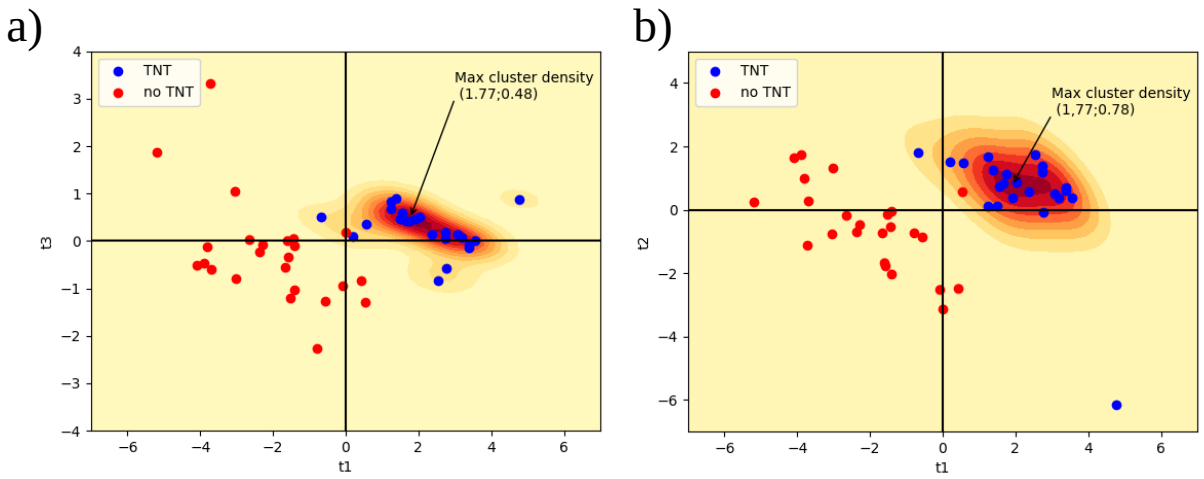

Figure S11. PLS-DA model results. a) Scores plot t1 vs t2, b) t1 vs t3 of the binary PLS-DA model. Blue dots are referred to TNT tests, Red dots represent no-TNT samples class. False color contour plots represent the density of TNT dataset in the plane.

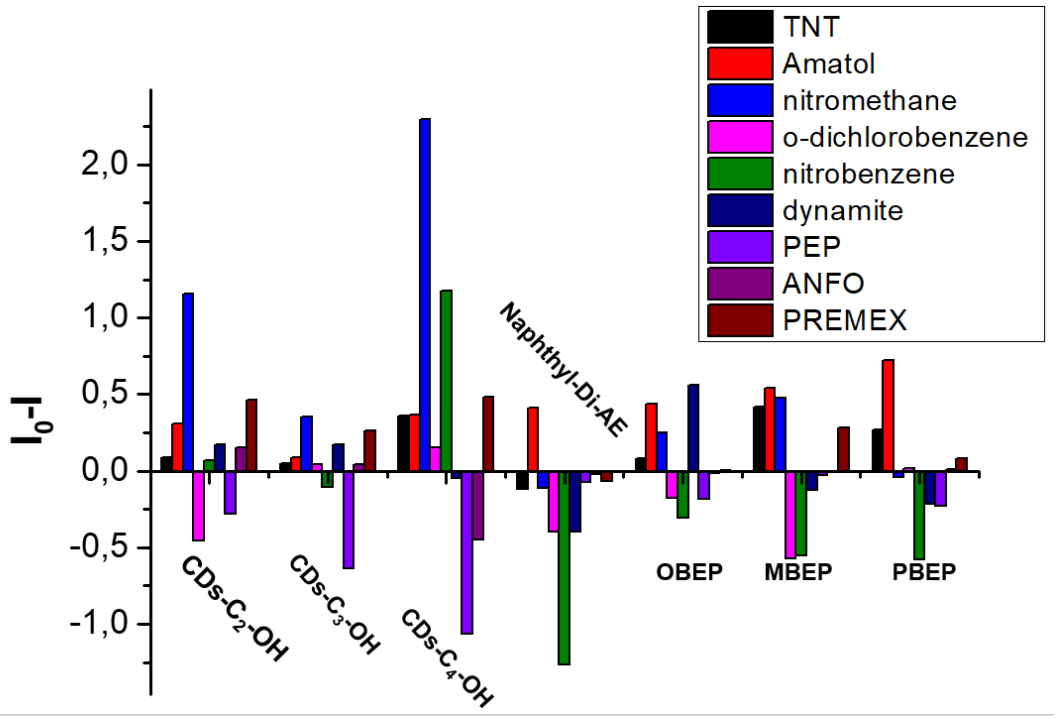

Figure S12. Normalized emission responses (I_0-I, where I_0 and I are the Gray channel emission values before and after the exposition to the analyte, respectively) of the probes to TNT, Amatol, nitromethane, o-dichlorobenzene, nitrobenzene, dynamite, PEP, ANFO and PREMEX (1 x 10^{-5} M in H_2O/CH_3CN 50/50).

References

[1] M. l. Giuffrida, E. Rizzarelli, G. A. Tomaselli, C. Satriano, G. Trusso Sfrazzetto *Chem. Commun.*, 2014, **50**, 9835–9838

[2] (a) Briggs, D.; Grant, J. T. Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy; Surface Spectra Ltd.: Manchester, U.K. 2003. (b) Gulino, A. Structural and electronic characterization of self-assembled molecular nanoarchitectures by X-ray photoelectron spectroscopy. *Anal. Bioanal. Chem*. 2013, **405**, 1479−1495.

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