

## SUPPORTING INFORMATION

### **Dye-modified silica-anatase nanoparticles for the ultrasensitive fluorogenic detection of the improvised explosive TATP in an air microfluidic device**

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<b>1.- Characterization of SL-739.....</b>	<b>S2</b>
<b>2.- Solvatochromism tests.....</b>	<b>S4</b>
<b>3.- Water acceptance and pH tests.....</b>	<b>S5</b>
<b>4.- Ions test.....</b>	<b>S6</b>
<b>6.- Typical time for sublimation of TATP samples.....</b>	<b>S9</b>
<b>7.- <sup>1</sup>H NMR Titrations of SL-739 with TATP and MCPBA.....</b>	<b>S9</b>
<b>8.- DLS (Dynamic Light Scattering ) study.....</b>	<b>S10</b>
<b>9.- Interference studies in the vapour phase.....</b>	<b>S13</b>
<b>10.- Stability of the sensing probe before and after the sensing experiment.....</b>	<b>S15</b>
<b>11.- Justification of the optimum airflow and recirculation time.....</b>	<b>S20</b>

# 1.- Characterization of SL-739

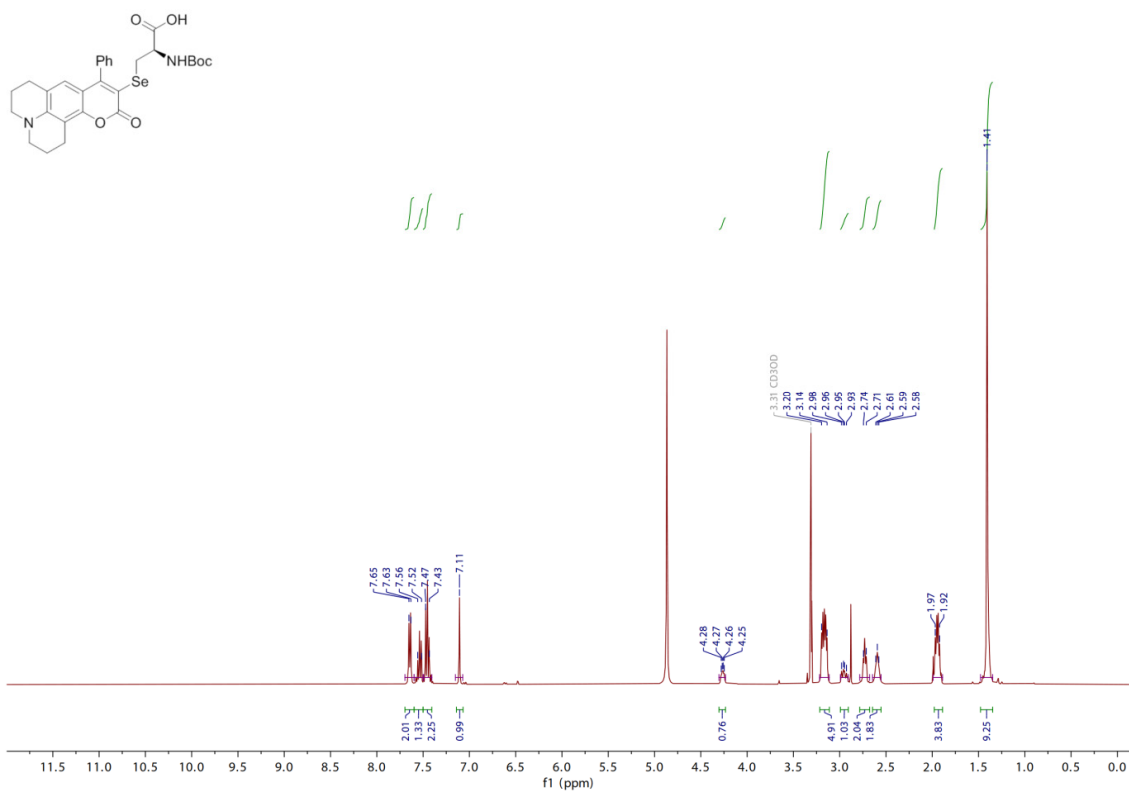


Figure S1: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)

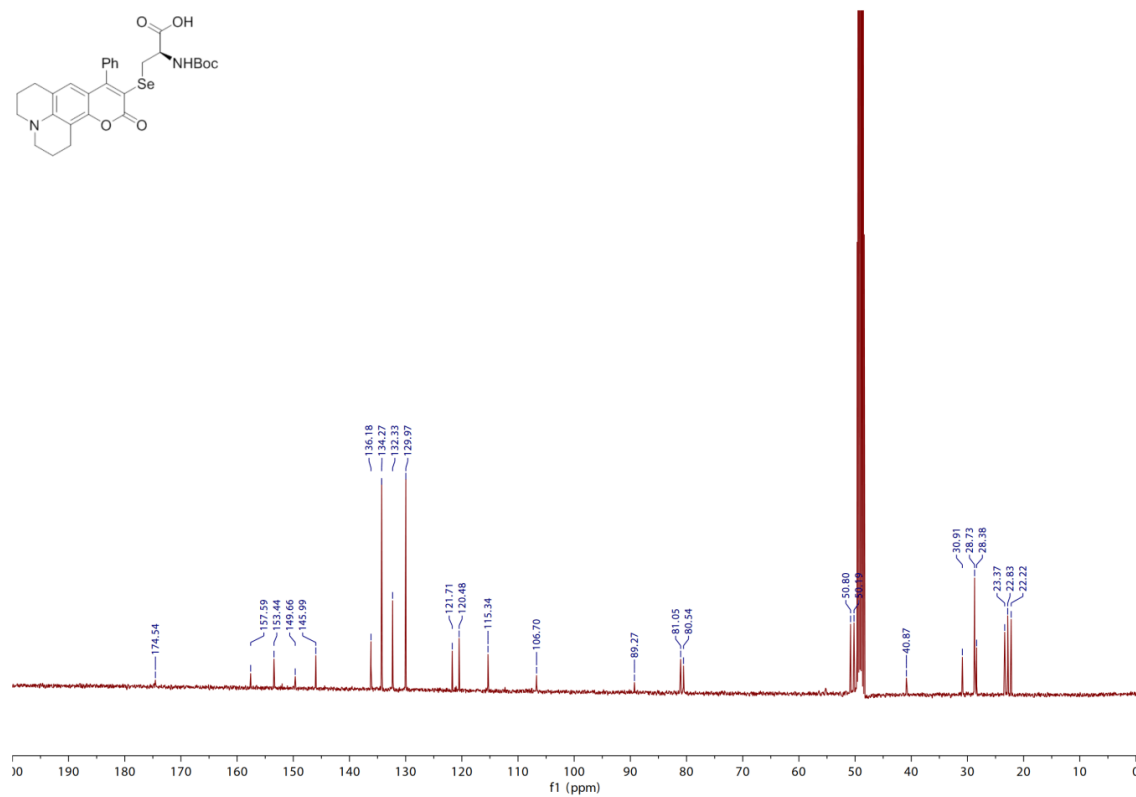
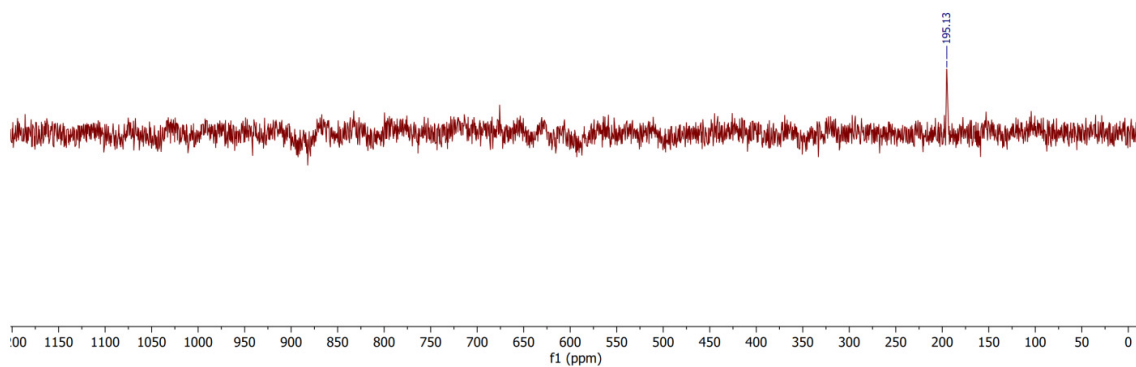
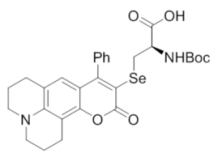
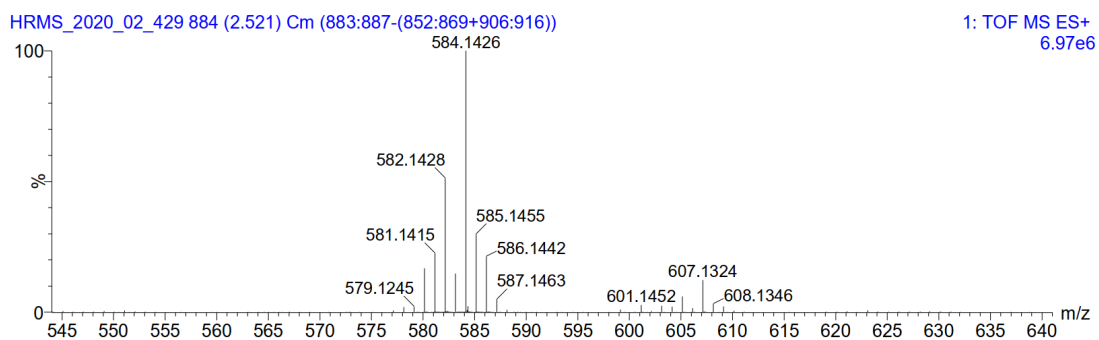
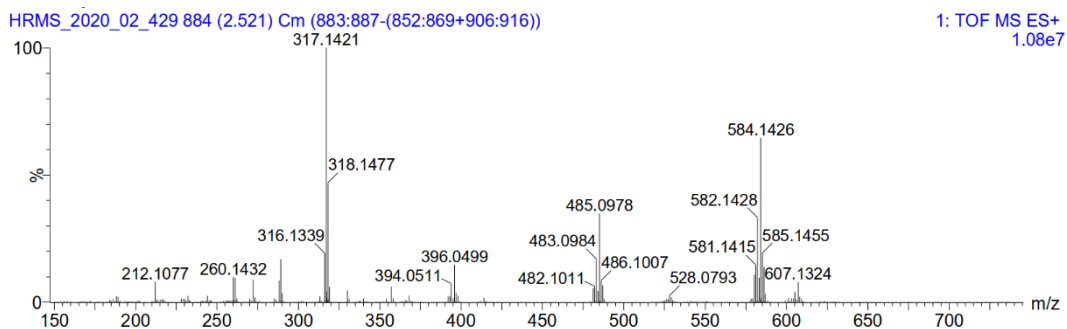


Figure S2: <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>OD)



**Figure S3:  $^{77}\text{Se}$  NMR (76 MHz,  $\text{CD}_3\text{OD}$ )**



**Figure S4: HRMS (ESI/Q-TOF)**

## 2.- Solvatochromism tests

This test is performed at a concentration of  $2 \times 10^{-5}$  M and its objective is to select the most suitable solvent for subsequent tests. The solvents used in carrying out the solvatochromism tests are the ones shown in the following table:

1. H <sub>2</sub> O	2. MeOH	3. DMSO
4. DMF	5. MeCN	6. Acetone
7. EtOAc	8. THF	9. CHCl <sub>3</sub>
10. DCM	11. Toluene	12. Et <sub>2</sub> O
13. Hexane	14. MCH	

Table S1. Solvents used in the solvatochromism test.

For each compound, the normalized absorbance, emission intensity and normalized emission spectra are shown; as well as UV images. The solvent chosen thanks to this test to perform the following ones must be miscible with water and present a fluorescence that allows to clearly observe increases, decreases and any other type of variation. UV and visible images are made for each compound right after the addition.

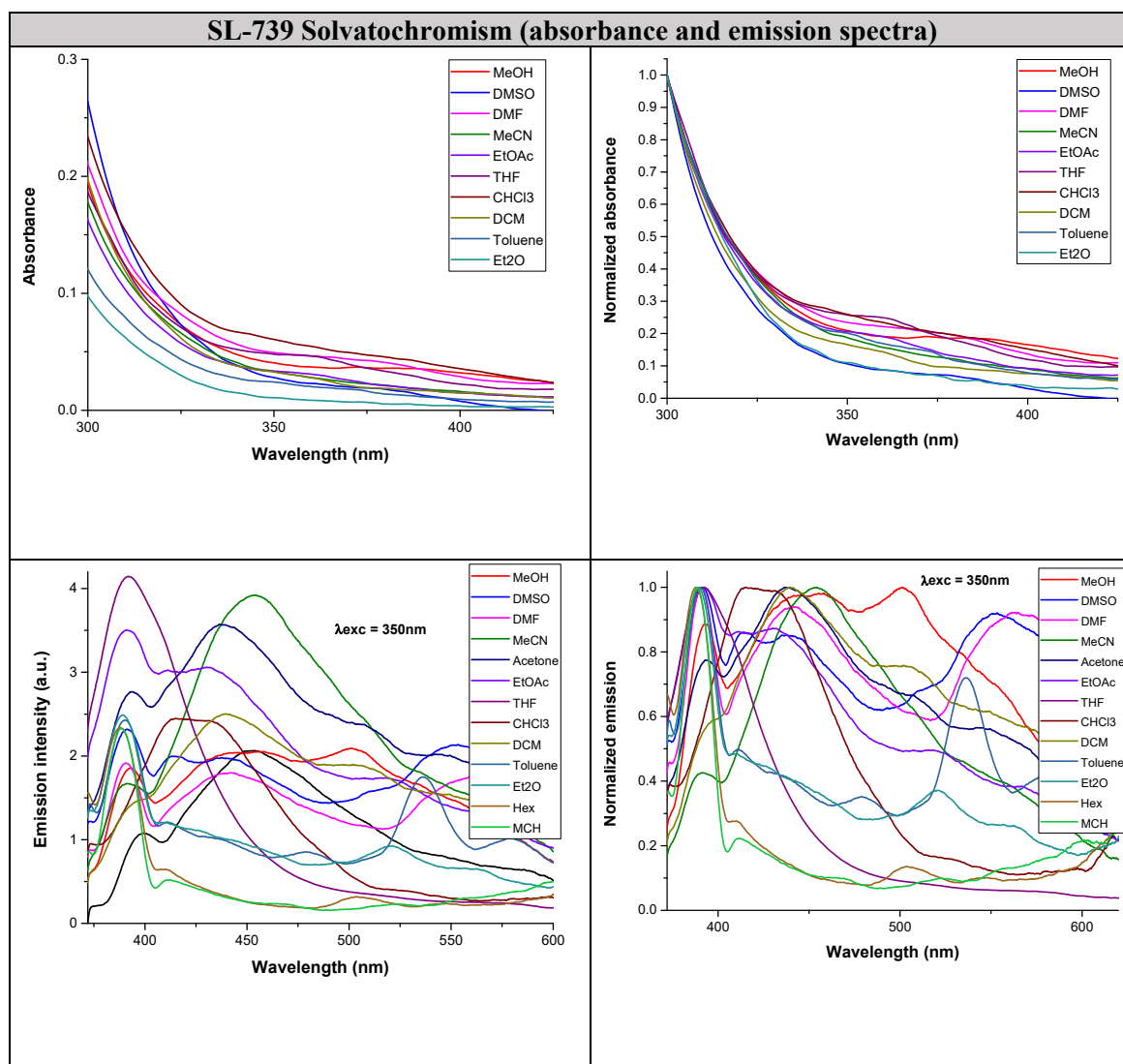


Table S2. SL-739 absorbance and emission spectra.

$\lambda_{exc} = 350$  nm. No clear displacement of the emission bands is observed as a function of the solvent.

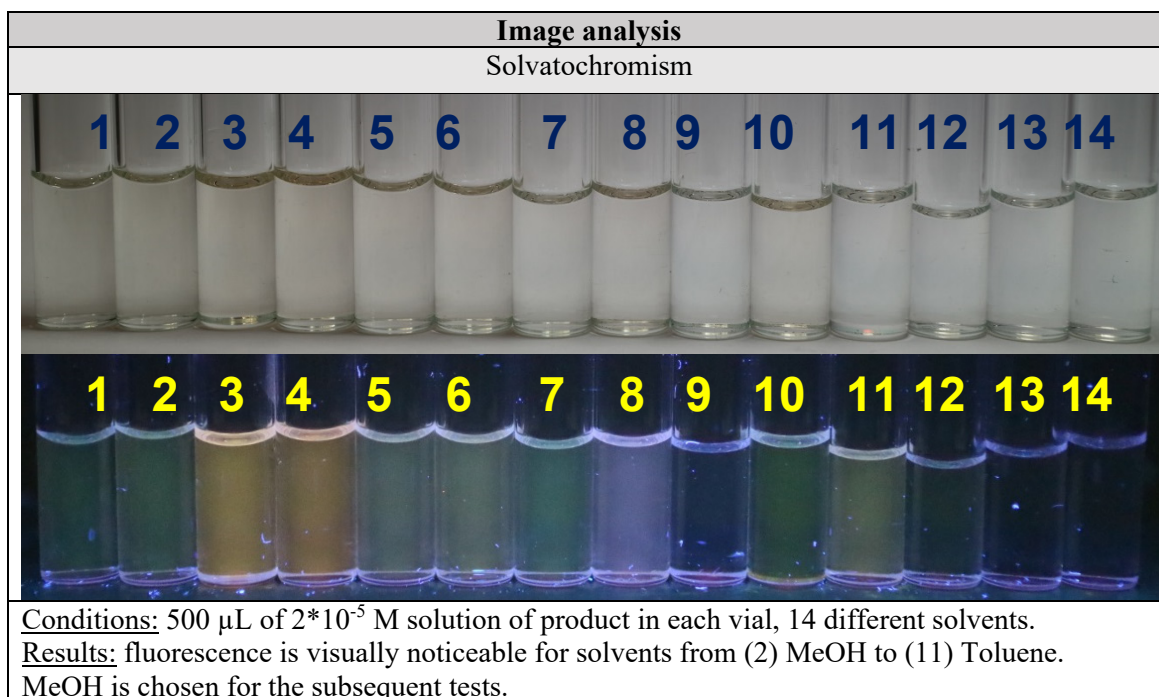


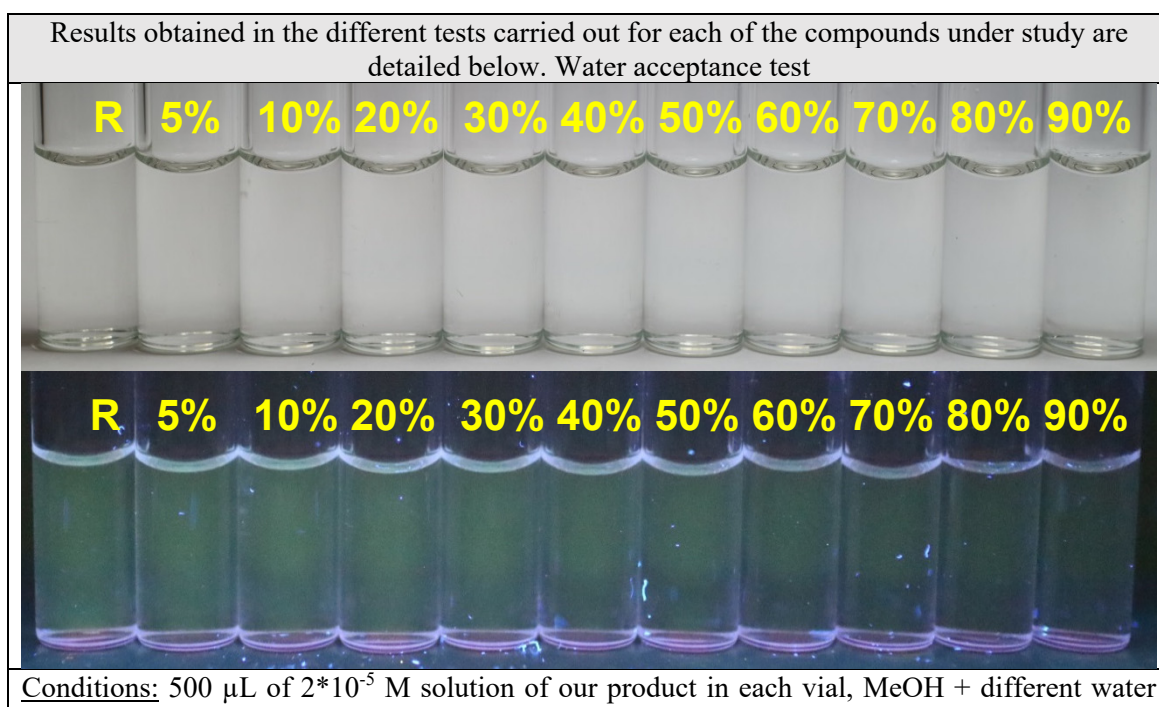
Table S3. SL-739 solvatochromic tests.

### 3.- Water acceptance and pH tests

The water acceptance test consists of the preparation of 11 500 $\mu\text{L}$  vials of a  $2 \times 10^{-5}$  M solution of the compound, with increasing percentages of water (from 0% to 90%). The purpose of this test is to qualitatively determine the maximum water acceptance capacity of our product solution.

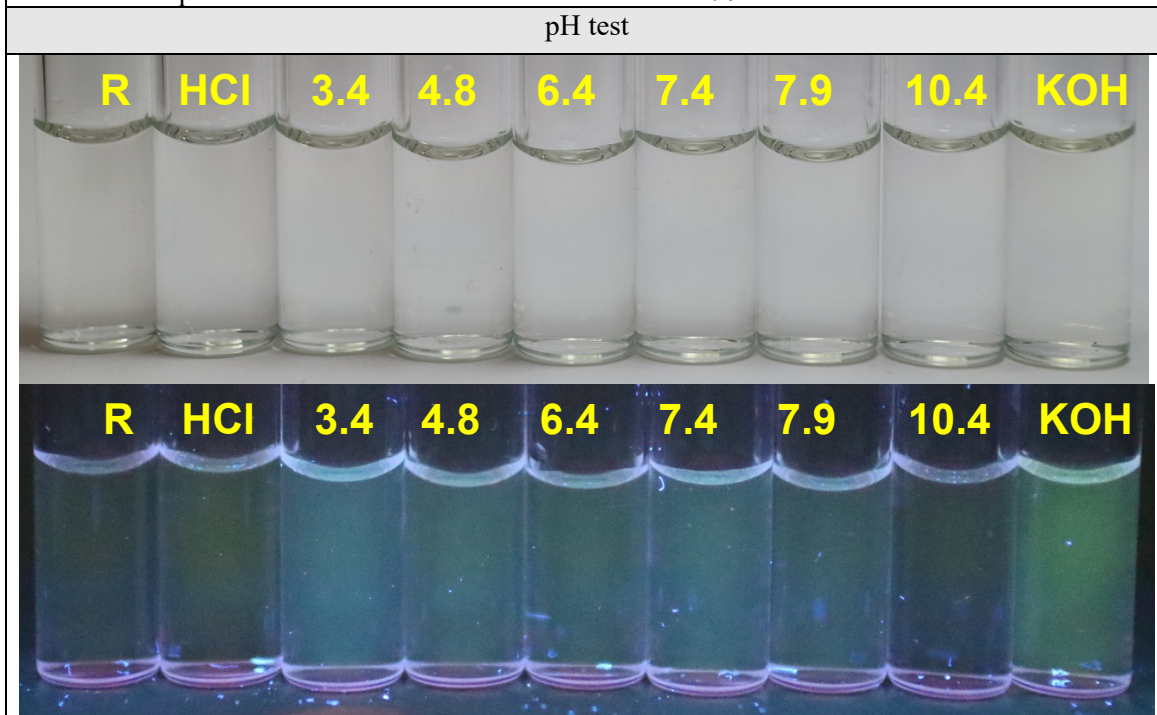
The pH test consists in subjecting our  $2 \times 10^{-5}$  M product solution to different pH conditions by adding 1M HCl, HEPES buffer solutions (pH 3.4, 4.8, 6.4, 7.4, 7.9 and 10.4) and 1M KOH in order to determine variations in fluorescence due to the effect of pH.

UV and visible images are made for each compound right after the addition.



percentages as solvent.

**Results:** a light green fluorescence can be seen. It disappears when a 60-70 water percentage is reached. The pH test is carried out with a water content of 70%.



**Conditions:** 500  $\mu\text{L}$  of  $2 \times 10^{-5}$  M solution of product in each vial, MeOH + 5mM HEPES solution (70% of the total volume) as a solvent.

**Results:** very little increase in fluorescence at pH values between 3.4 and 7.9 and some increase in fluorescence after the addition of concentrated KOH solution.

Table S4. SL-739 water percentage and pH tests.

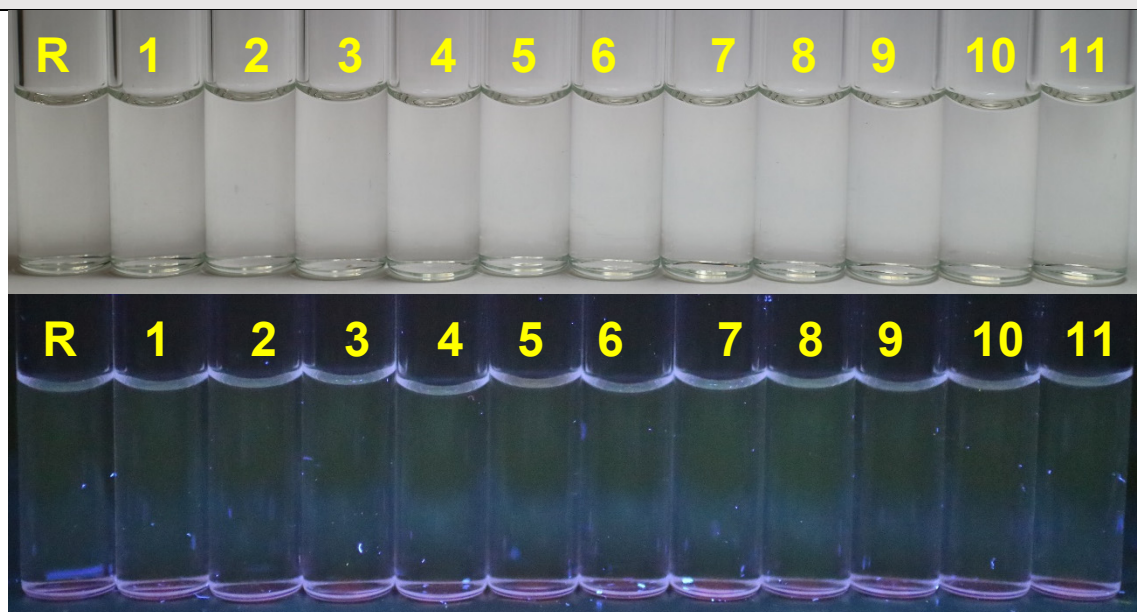
#### 4.- Ions test

This test consists of the addition of 1-2-4-8 eq of solutions corresponding to 11 different anions and cations to the  $2 \times 10^{-5}$  M solution of our compound to qualitatively observe and analyze variations in its fluorescence. The solutions of the different ions are prepared in water, so there is also a reference vial to which equivalent amounts of water are added. The solution of the product we are studying is carried out in the most suitable solvent (or solvent mixture) to correctly visualize changes in fluorescence. This solvent is selected, for each product, from the results obtained by the solvatochromism test. The ions solutions used in carrying out the test are the ones shown in the following table:

Anions			
1. $\text{F}^-$	2. $\text{Cl}^-$	3. $\text{Br}^-$	4. $\text{I}^-$
5. $\text{BzO}^-$	6. $\text{NO}_3^-$	7. $\text{H}_2\text{PO}_4^-$	8. $\text{HSO}_4^-$
9. $\text{AcO}^-$	10. $\text{CN}^-$	11. $\text{SCN}^-$	
Cations			
1. $\text{Ag}^+$	2. $\text{Ni}^{2+}$	3. $\text{Sn}^{2+}$	4. $\text{Cd}^{2+}$
5. $\text{Zn}^{2+}$	6. $\text{Pb}^{2+}$	7. $\text{Cu}^{2+}$	8. $\text{Fe}^{3+}$
9. $\text{Sc}^{3+}$	10. $\text{Al}^{3+}$	11. $\text{Hg}^{2+}$	12. $\text{Au}^{3+}$
13. $\text{Co}^{2+}$	14. $\text{Pd}^{2+}$	15. $\text{Ir}^{3+}$	16. $\text{Cu}^+$
17. $\text{Ru}^{3+}$	18. $\text{Pt}^{2+}$		

Table S5. Ion solutions used in the ion tests.

UV and visible images are made for the compound right after the addition. Anions tests



Conditions: 500  $\mu\text{L}$  of  $2 \times 10^{-5}$  M solution of our product in each vial, MeOH as a solvent. 8eq of each anion solution have been added.

Results: there are no visible variations in the fluorescence of the product as a consequence of the addition of different anion solutions.

Cations tests



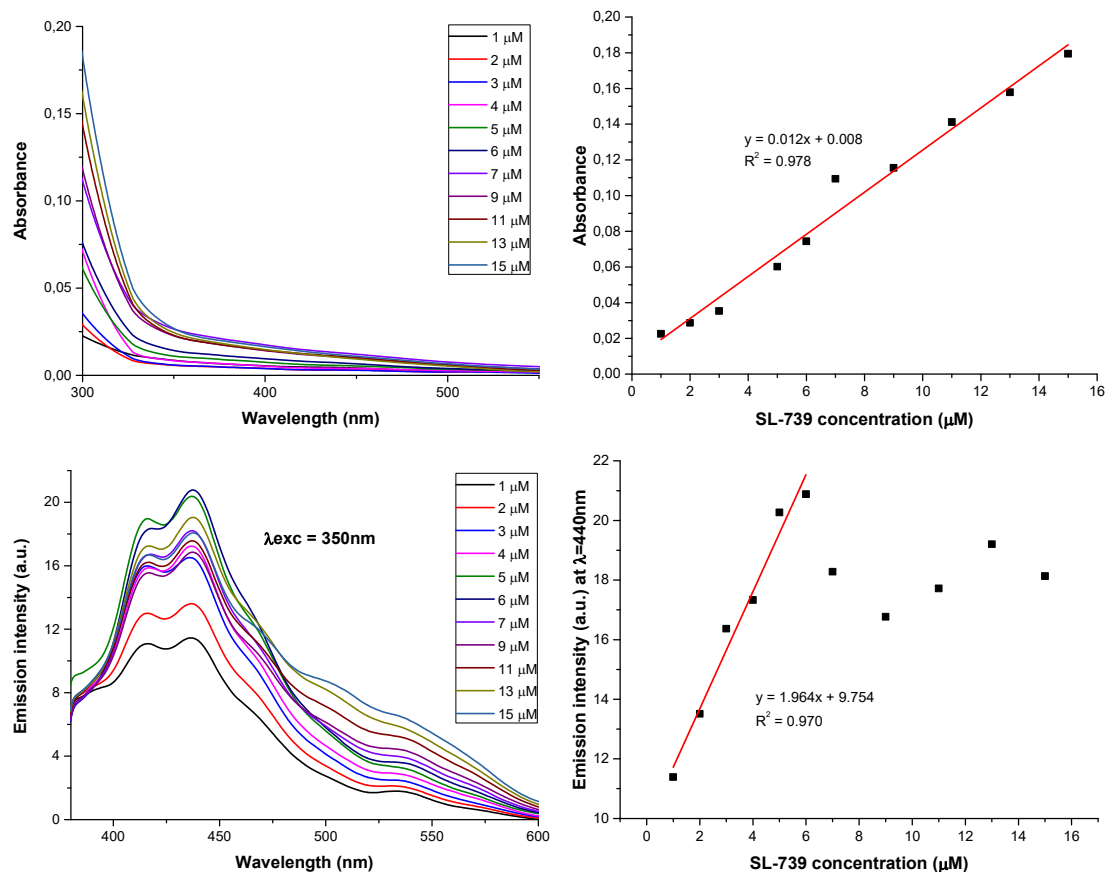
Conditions: 500  $\mu\text{L}$  of  $2 \times 10^{-5}$  M solution of product in each vial, MeOH as a solvent. 8 eq of each cation solution have been added.

Results: A neat increase in fluorescence can be observed after the addition  $\text{Au}^{3+}$  solution (12).

Table S6. SL-739 ions tests.

## 5.- Work concentration

In order to choose an optimum concentration for a quantitative studio, the absorbance and fluorescence of the probe were checked to be linear while concentration changes are small (**Figure 1**). Studied in  $\text{CHCl}_3:\text{MeOH}$  (9:1 v:v):



**Figure S5.** Absorbance (up) and fluorescence (down) of **SL-739** solution in  $\text{CHCl}_3:\text{MeOH}$  9:1, under increasing concentrations of **SL-739**,  $\lambda_{\text{exc}} = 350 \text{ nm}$  (down).

The work concentration ideally should stay at 0.1 of absorbance or less, to avoid inner filter effects, possible dynamic quenching or stacking processes. It implied a concentration below 7  $\mu\text{M}$ . Taking the results into account, the chosen concentration was 2.5  $\mu\text{M}$ , value around which the Lambert-Beer law (or pseudo-Lambert-Beer linear behaviour for fluorescence) was fulfilled.



## 6.- Typical time for sublimation of TATP samples

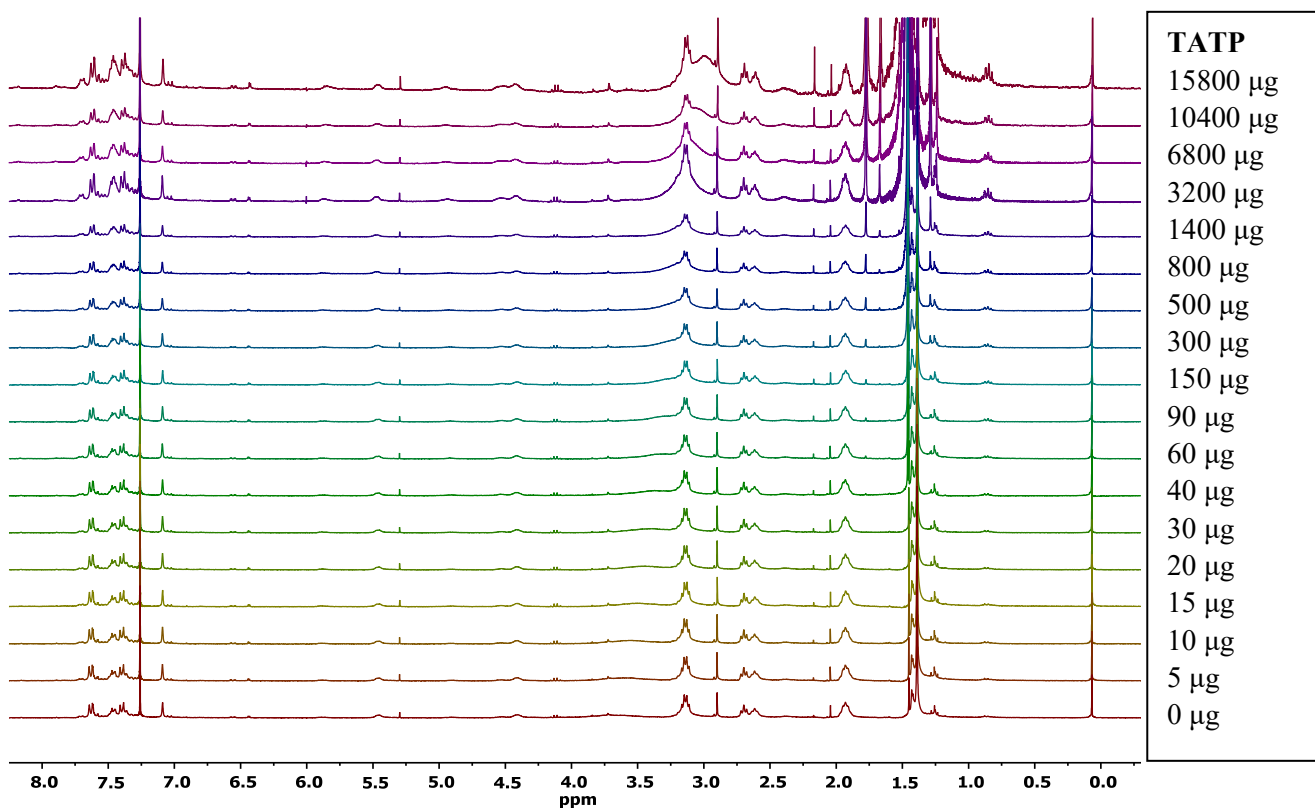
Typical time for sublimation of TATP samples in the gas-solid experiments:

TATP (mg)	Sublimation time
0.032	1'41''
0.048	1'45''
0.083	2'14''
0.114	2'42''
0.158	3'10''
0.203	3'21''
0.247	3'57''
0.333	4'26''
0.483	5'03''
0.800	7'45''
1.000	11'23''
1.400	13'13''
2.100	19'37''

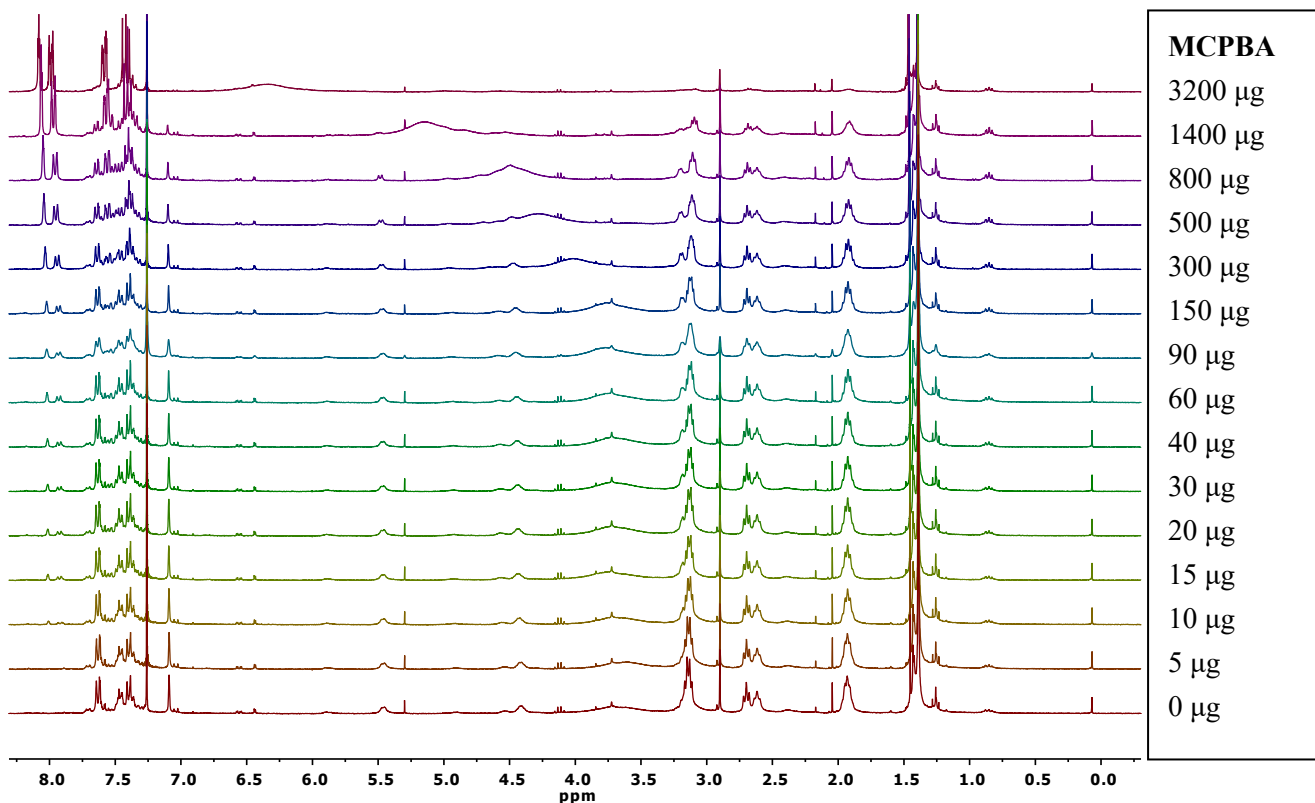
\*10 minutes recirculation after evaporation of TATP samples.

*Table S7. Typical time for sublimation of TATP samples in the gas-solid experiments.*

## 7.- <sup>1</sup>H NMR Titrations of SL-739 with TATP and MCPBA



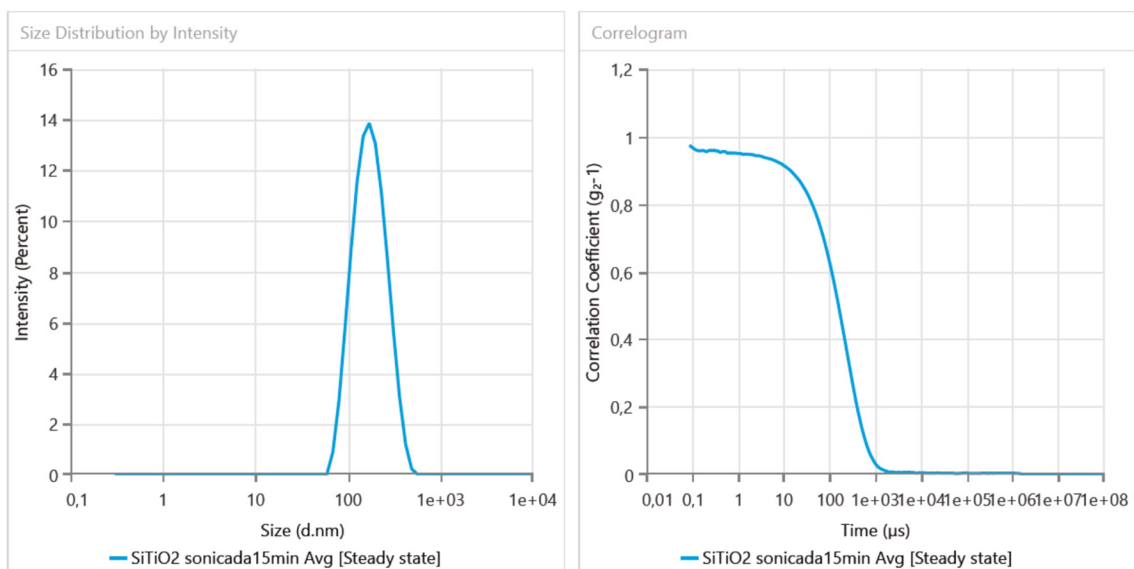
**Figure S6:** <sup>1</sup>H NMR Titration of SL-739 with TATP, 3 mg SL-739 in 0.5 mL CDCl<sub>3</sub> as solvent, 5 µg to 15.8 mg TATP. Inset: Total amount of added TATP in each step.

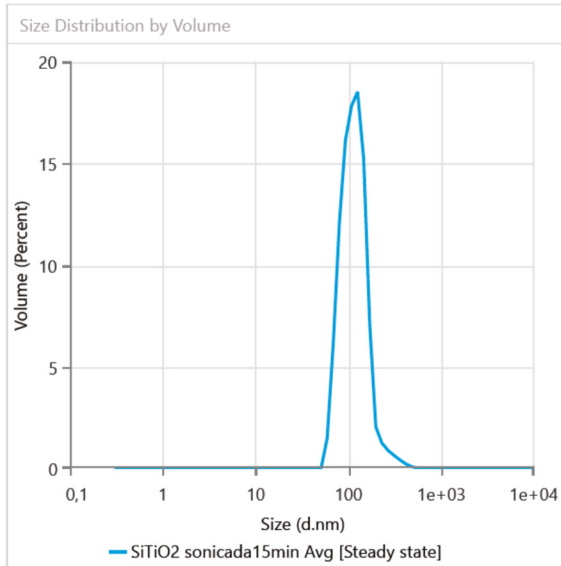
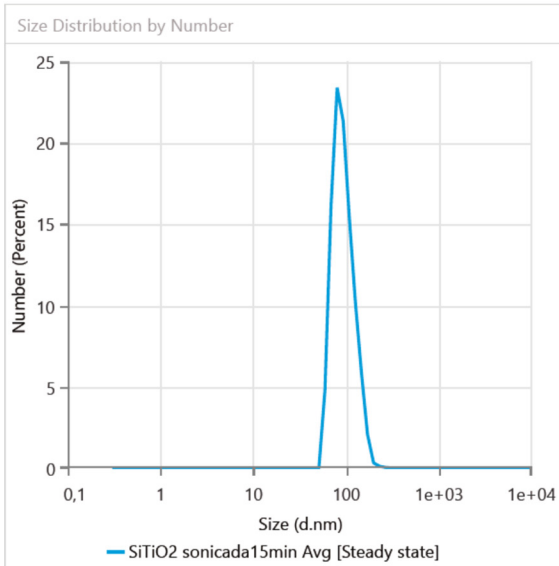


**Figure S7:**  $^1\text{H}$  NMR Titration of **SL-739** with MCPBA, 3 mg **SL-739** in 0.5 mL  $\text{CDCl}_3$  as solvent, 5 µg to 3.2 mg TATP. Inset: Total amount of added MCPBA in each step.

**8.- DLS (Dynamic Light Scattering ) study, samples prepared in water 1 mg/mL.**

**Average, three repeats:**





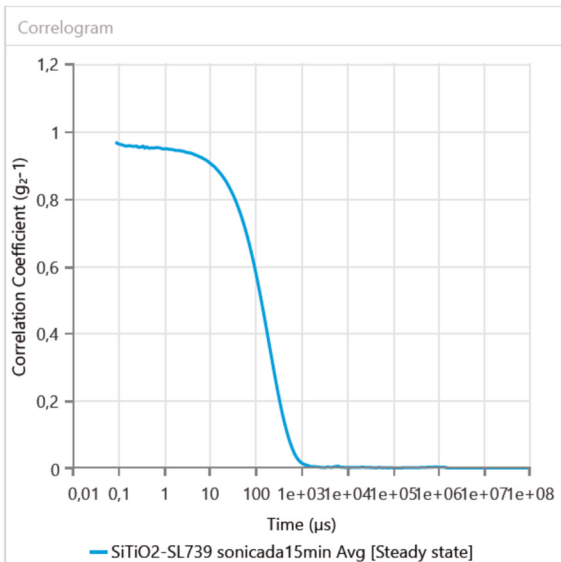
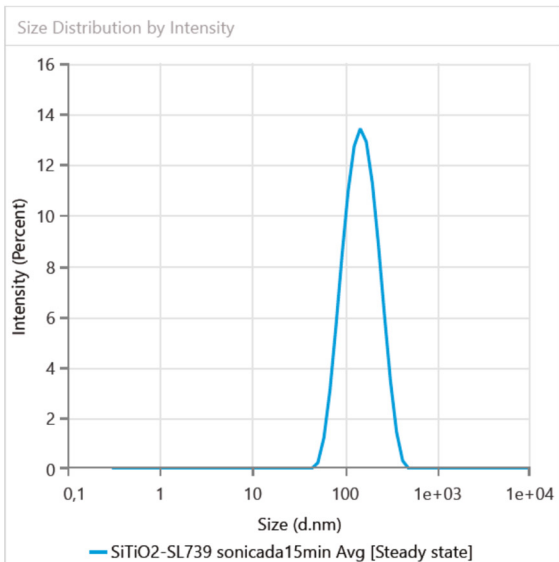
Parameter List

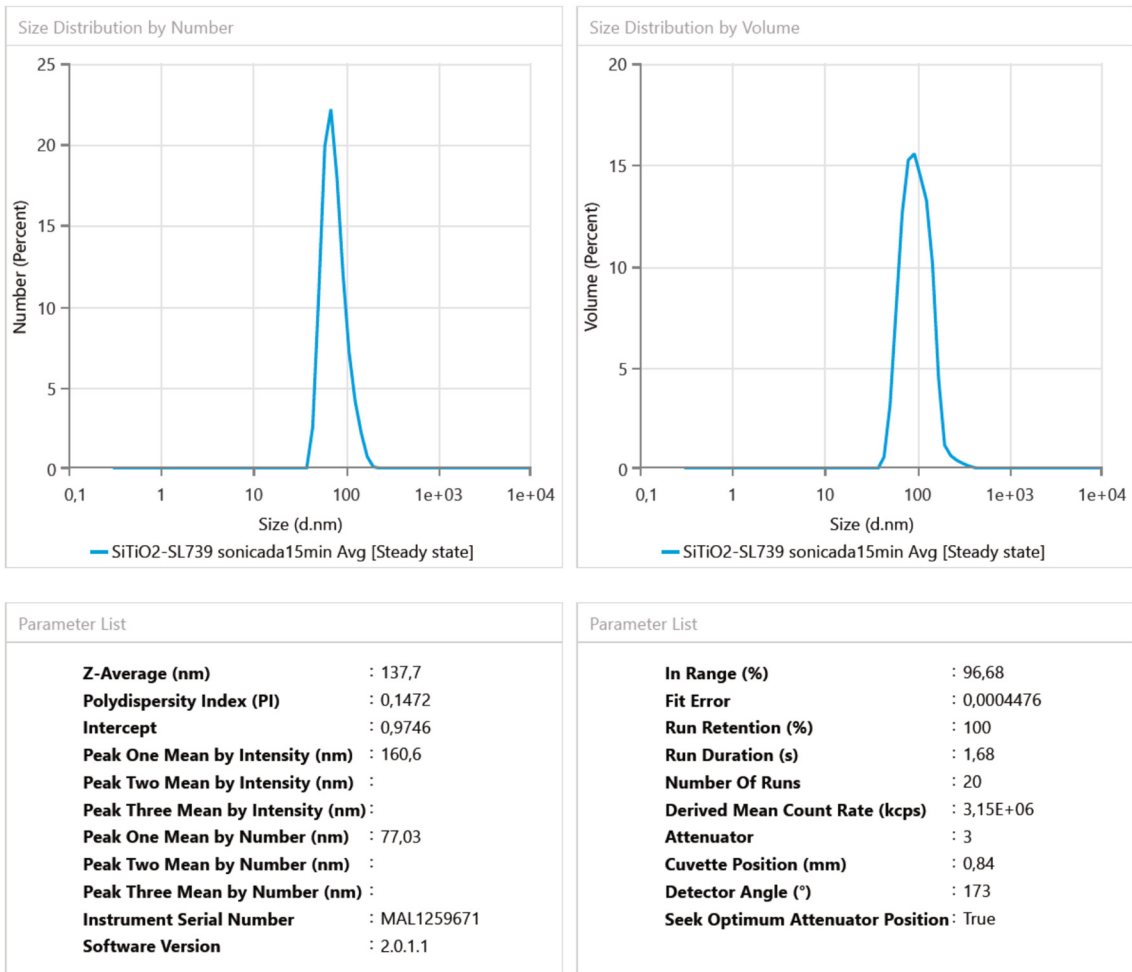
<b>Z-Average (nm)</b>	: 161,8
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<b>Intercept</b>	: 0,975
<b>Peak One Mean by Intensity (nm)</b>	: 184,2
<b>Peak Two Mean by Intensity (nm)</b>	:
<b>Peak Three Mean by Intensity (nm)</b>	:
<b>Peak One Mean by Number (nm)</b>	: 95,44
<b>Peak Two Mean by Number (nm)</b>	:
<b>Peak Three Mean by Number (nm)</b>	:
<b>Instrument Serial Number</b>	: MAL1259671
<b>Software Version</b>	: 2.0.1.1

Parameter List

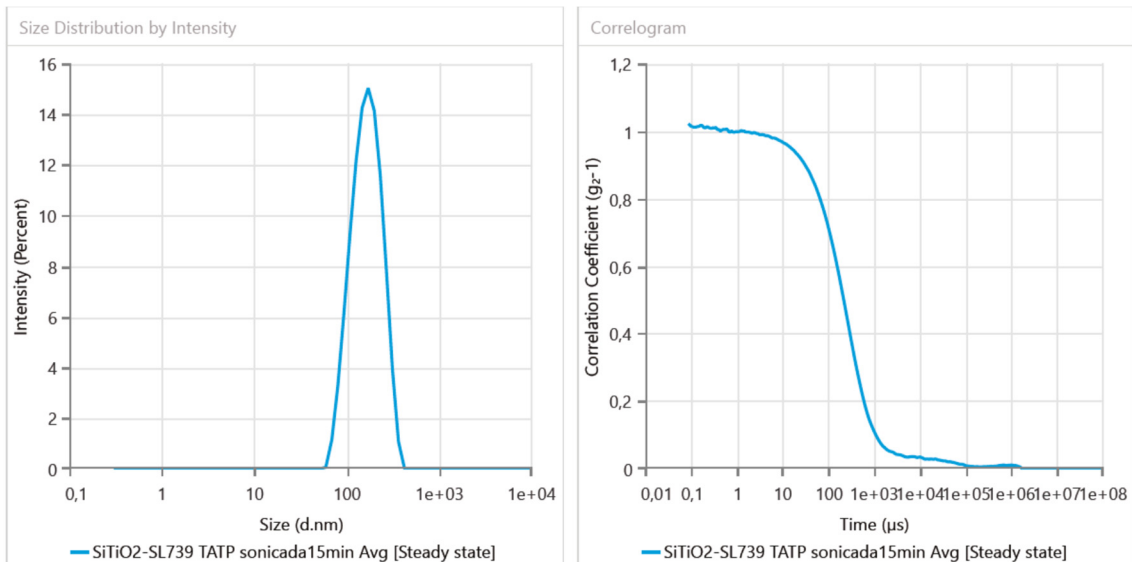
<b>In Range (%)</b>	: 95,81
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<b>Run Retention (%)</b>	: 98,89
<b>Run Duration (s)</b>	: 1,68
<b>Number Of Runs</b>	: 20
<b>Derived Mean Count Rate (kcps)</b>	: 2,774E+06
<b>Attenuator</b>	: 3
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<b>Detector Angle (°)</b>	: 173
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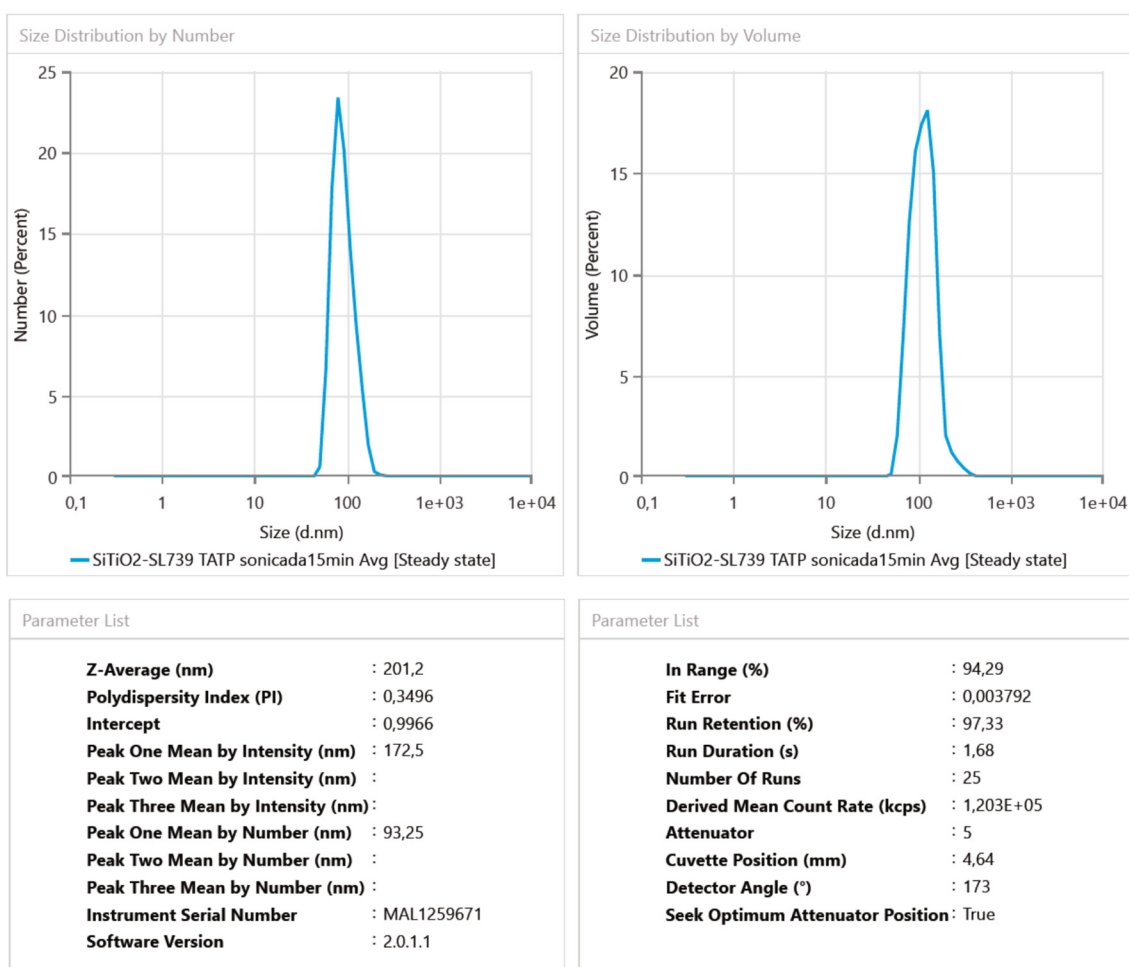
**Figure S8: DLS results, sample of SiTiO<sub>4</sub> prepared in water 1 mg/mL.**





**Figure S9: DLS results, sample of SL-739@TiSiO<sub>4</sub> prepared in water 1 mg/mL.**





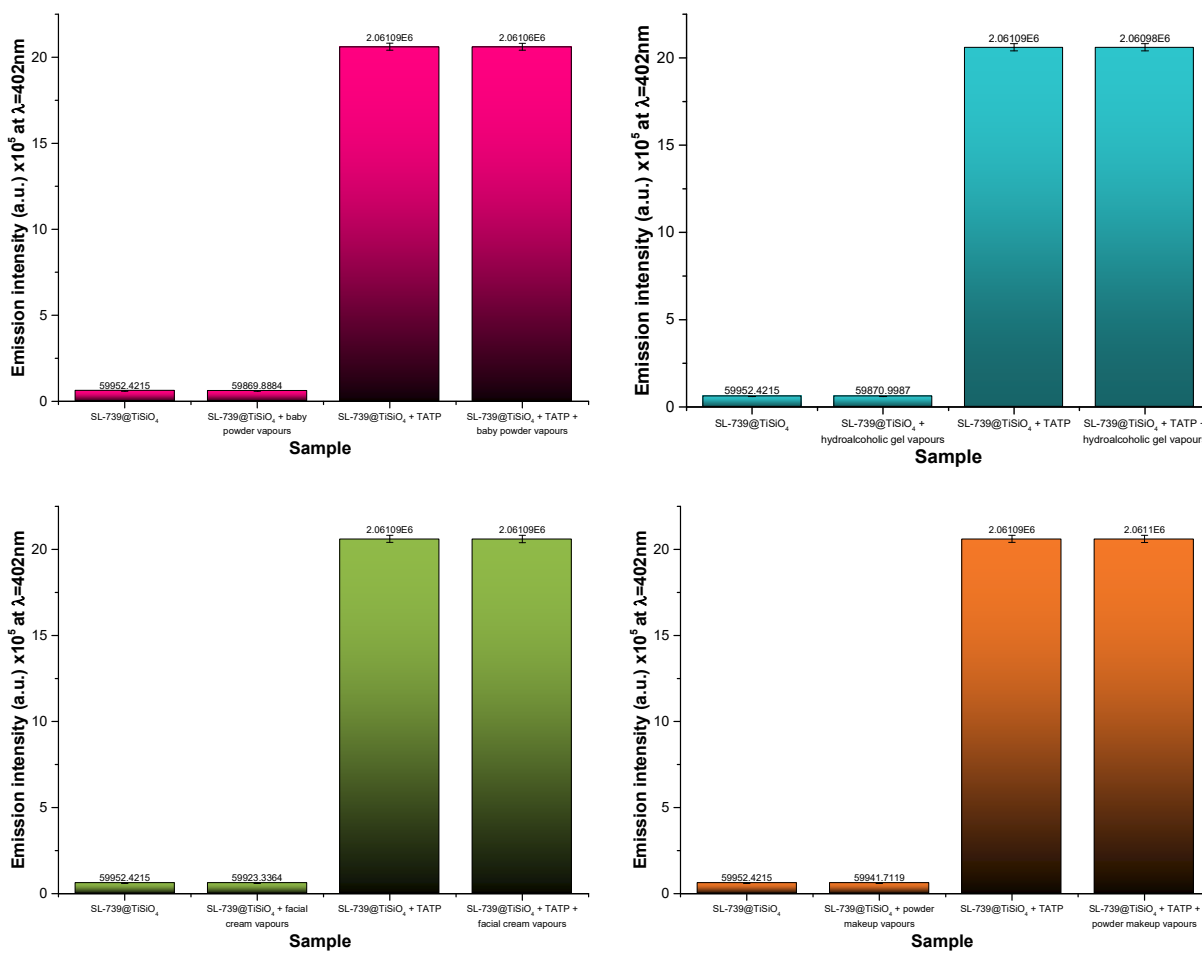
**Figure S10: DLS results, sample of SL-739@TiSiO<sub>4</sub>+TATP prepared in water 1 mg/mL.**

## 9.- Interference studies in the vapour phase.

As substances capable of generating vapours that could interfere with the sensing system and that could be present in the environment, we have selected baby powder, hydroalcoholic gel, facial cream and makeup.

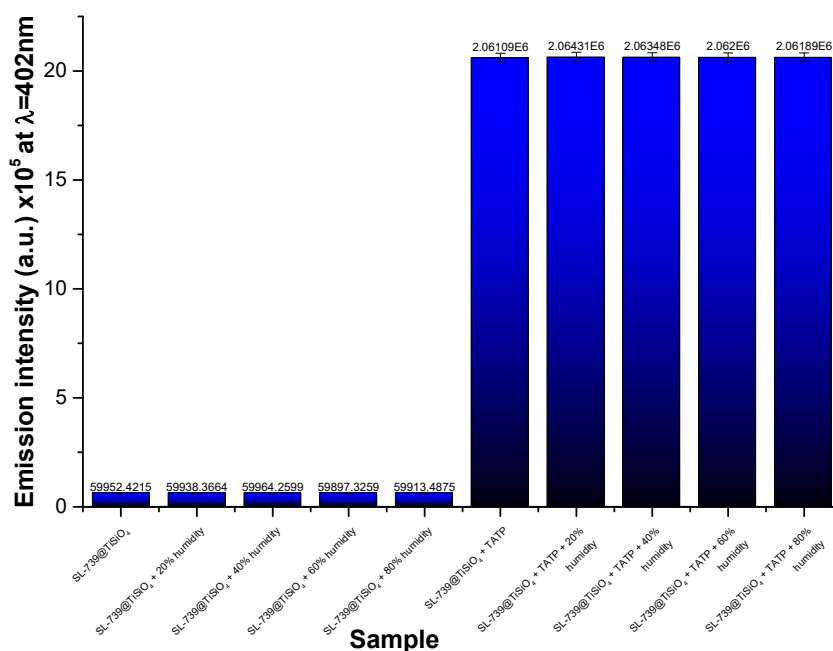
The study is carried out by subjecting SL-739@TiSiO<sub>4</sub> to a vapour flow of the different possible interferents equivalent to that of TATP: 2 mg of each of the different substances are evaporated, the air flow is set at 100 cm<sup>3</sup>/min and the recirculation time is set at 10 minutes. In the cases that TATP is included, the evaporated quantity is also 2 mg (maximum point of the titrations and the quantity used as excess in all the tests).

In the histograms of **Figure S11** we can see that there is no interference with the sensing system for the substances already mentioned, since, for all cases, the emission (taken for the 402 nm wavelength) of SL-739@TiSiO<sub>4</sub> and SL-739@TiSiO<sub>4</sub> + TATP remained unchanged.



*Figure S11. Histograms representing the emission of SL-739@TiSiO<sub>4</sub> and SL-739@TiSiO<sub>4</sub> + TATP at 402nm vs. baby powder vapours, hydroalcoholic gel vapours, facial cream vapours and powder makeup vapours.*

Analogously, SL-739@TiSiO<sub>4</sub> and SL-739@TiSiO<sub>4</sub> + TATP (2 mg) have been subjected to increasing percentages of humidity, from 0 to 80%. In the histogram of **Figure S12** we can see that there is no interference with the sensing system for the percentages already mentioned.



*Figure S12. Histogram representing emission of SL-739@TiSiO<sub>4</sub> and SL-739@TiSiO<sub>4</sub> + TATP at 402 nm vs. increasing humidity percentages.*

## 10. Stability of the sensing probe before and after the sensing experiment.

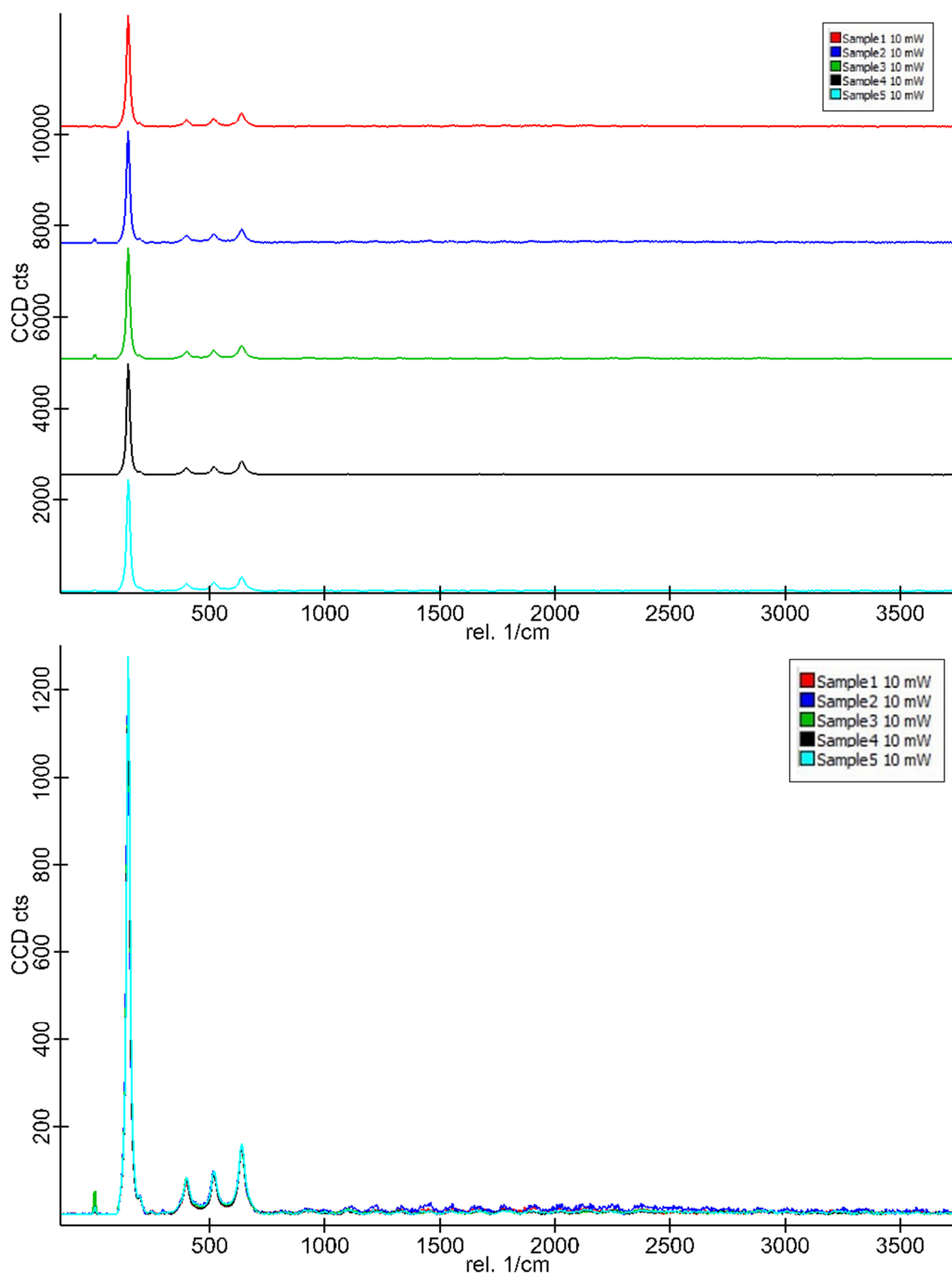
To study the stability of the sensor system, the following tests have been carried out: Raman spectroscopy, excitation and emission spectra and thermogravimetric analysis.

Test conditions and the correspondence of the samples are as follows:

- **Sample 1:** SL-739@TiSiO<sub>4</sub> adsorption + measurement.
- **Sample 2:** SL-739@TiSiO<sub>4</sub> + 3 days waiting + measurement.
- **Sample 3:** SL-739@TiSiO<sub>4</sub> + TATP vapours (2 mg of TATP, 100 cm<sup>3</sup>/min airflow, 10 minutes as recirculation time) + measurement.
- **Sample 4:** SL-739@TiSiO<sub>4</sub> adsorption + TATP vapours (2 mg of TATP, 100 cm<sup>3</sup>/min airflow, 10 minutes as recirculation time) + 3 days waiting + measurement.
- **Sample 5:** SL-739@TiSiO<sub>4</sub> adsorption + 3 days waiting + TATP vapours (2 mg of TATP, 100 cm<sup>3</sup>/min airflow, 10 minutes as recirculation time) + measurement.

## Raman spectra

Measurements in **Figure S13** were made using a 532 nm laser and 10 mW power.



*Figure S13. Raman spectra, separated (up) and combined (down) of Samples 1-5 measured using a 532 nm laser and 10 mW power.*



## Excitation and emission spectra

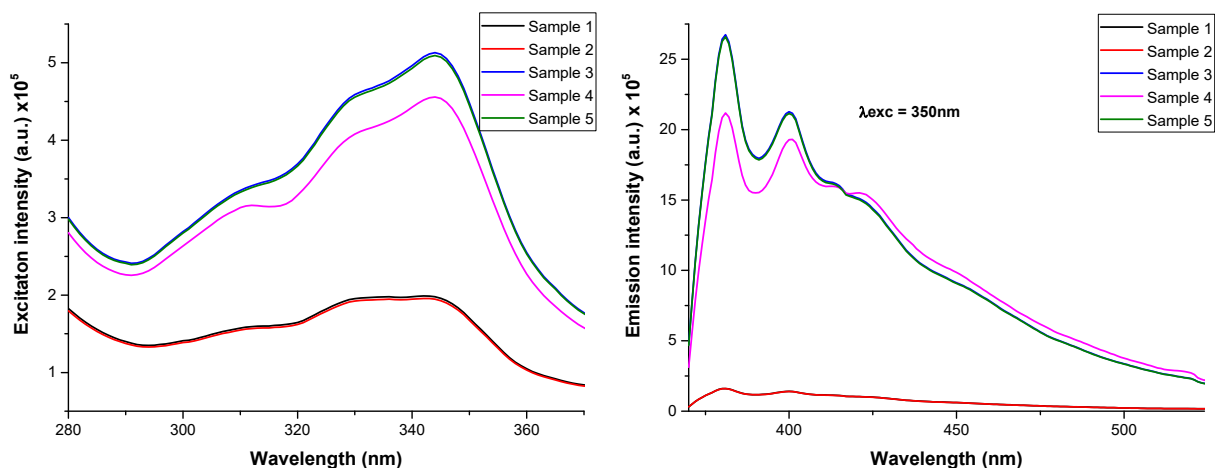
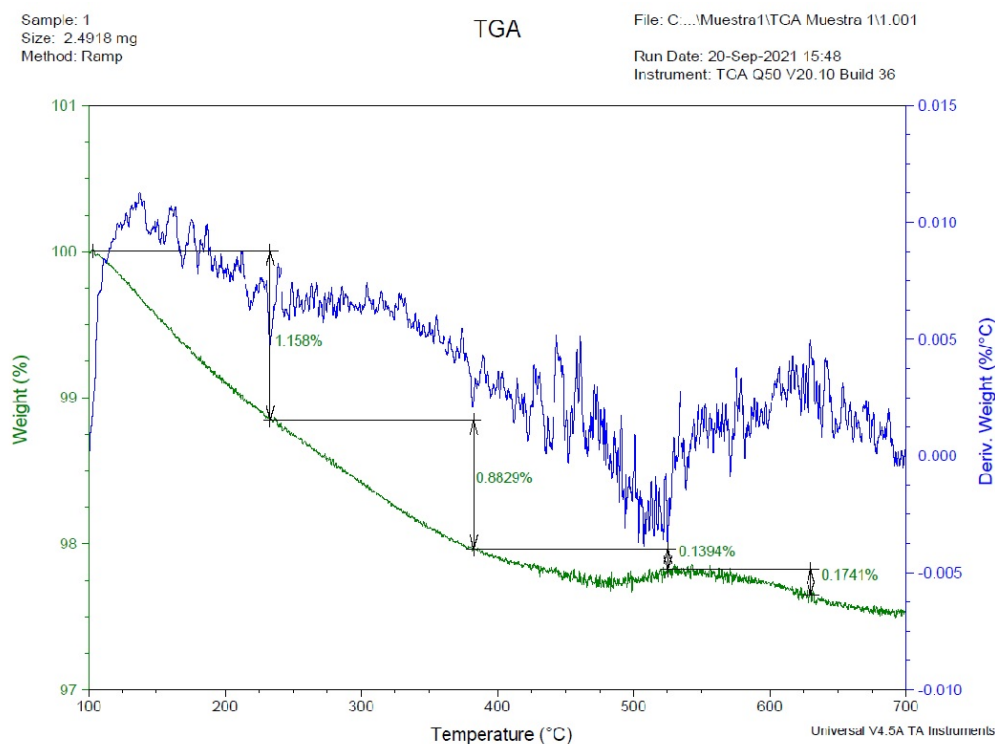


Figure S14. Excitation (left) and emission (right) spectra of Samples 1-5.  $\lambda_{exc} = 350$  nm.

## Thermogravimetric analysis

### Method Log:

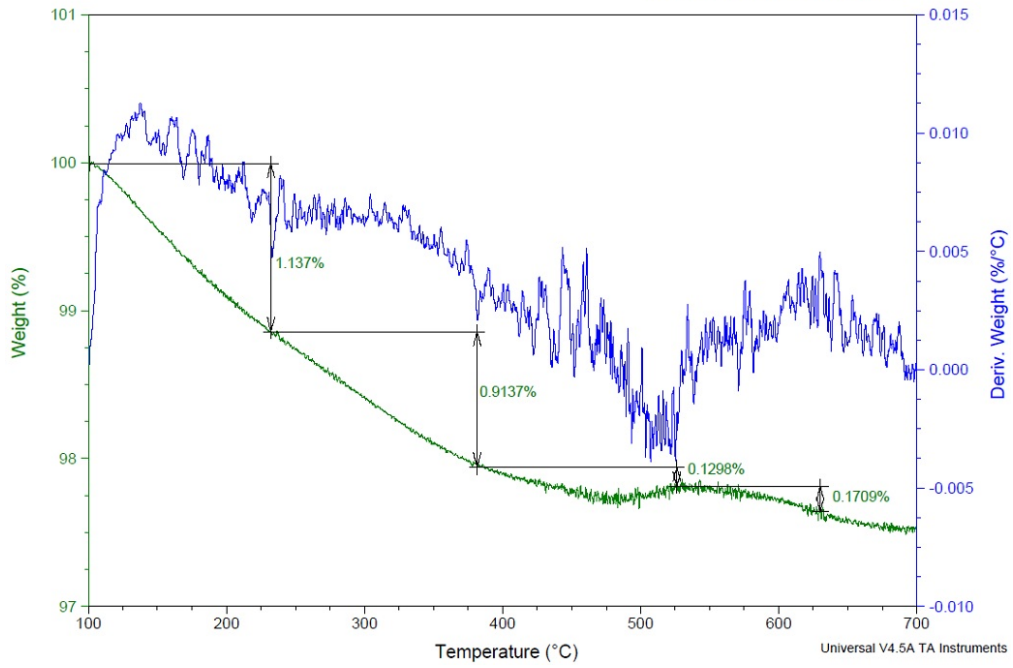
1: Select Gas: 1 2: Ramp 10.00°C/min to 100.00°C 3: Isothermal for 15.00 min 4: Mark end of cycle 1 5: Ramp 10.00°C/min to 800.00°C 6: Mark end of cycle 2 7: Select Gas: 2 8: Isothermal for 15.00 min 9: End of method.



Sample: 2  
Size: 2.4919 mg  
Method: Ramp

### TGA

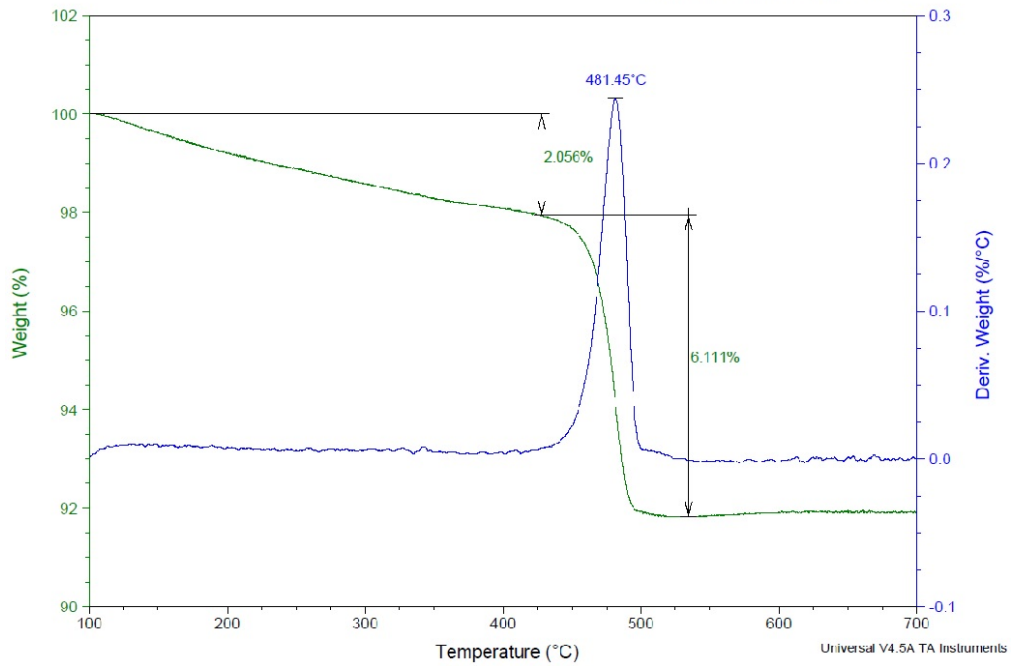
File: C:\...Muestra2\TGA Muestra 2\2.001  
Run Date: 20-Sep-2021 15:48  
Instrument: TGA Q50 V20.10 Build 36



Sample: 3  
Size: 3.1308 mg  
Method: Ramp

### TGA

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Run Date: 21-Sep-2021 13:02  
Instrument: TGA Q50 V20.10 Build 36

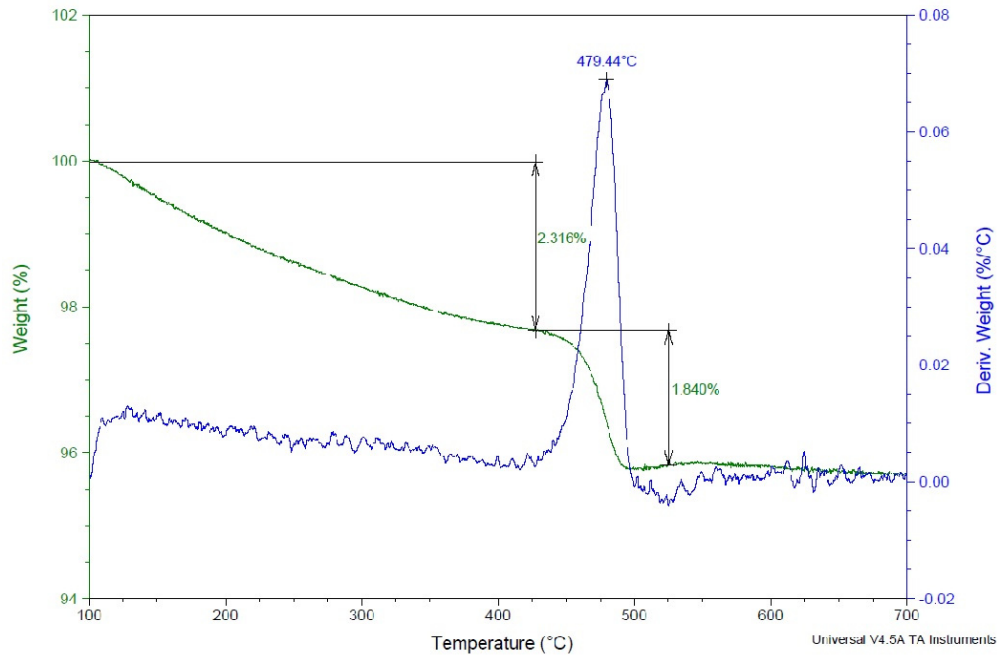


Sample: 4  
Size: 2.3749 mg  
Method: Ramp

TGA

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Instrument: TGA Q50 V20.10 Build 36

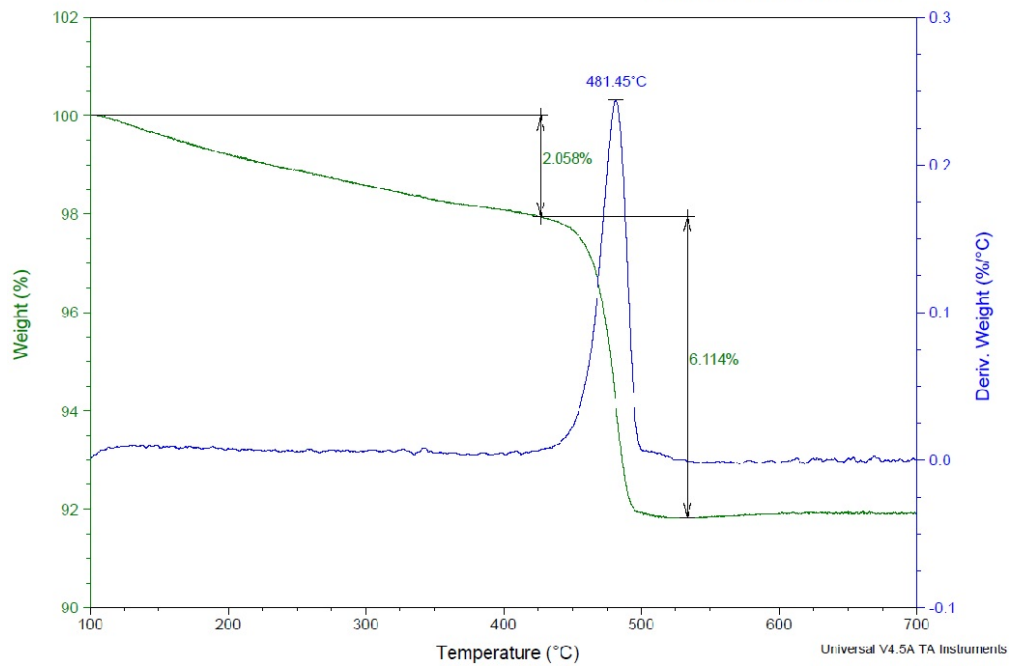


Sample: 5  
Size: 3.1308 mg  
Method: Ramp

TGA

File: C:\...Muestra5\TGA Muestra 5\5.001

Run Date: 21-Sep-2021 13:02  
Instrument: TGA Q50 V20.10 Build 36



*Figure S15. Thermogravimetric analysis of Samples 1-5.*

From the thermogravimetric analysis and the excitation and emission spectra, it can be concluded that there are 3 differentiated behaviours:

- Samples 1 and 2 (SL-739@TiSiO<sub>4</sub>) regardless of the time that elapses between adsorption and measurement).

- Samples 3 and 4 (SL -739@TiSiO<sub>4</sub> + TATP) measured just after exposure to vapours, regardless of the time elapsed between adsorption and exposure to vapours.
- Sample 4 (in which the measurement is made days after exposure to TATP vapours).

## 11. Justification of the optimum airflow and recirculation time.

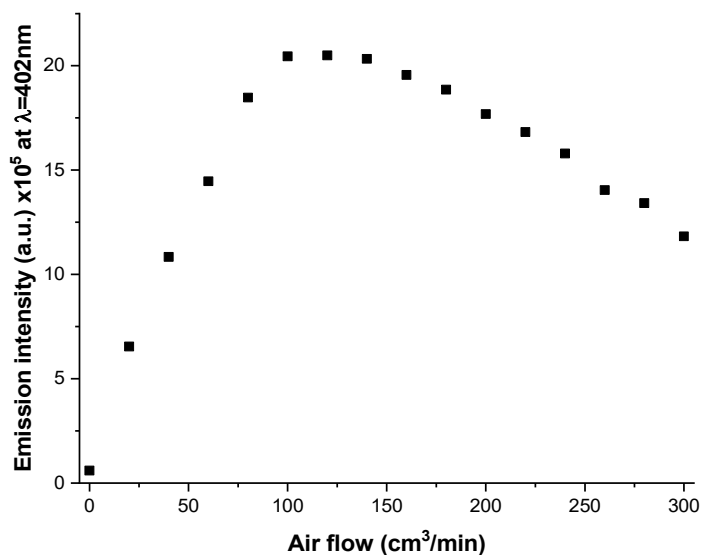
### 11.1. Airflow

A specific amount of TATP has been chosen to perform the study, 2mg, the maximum studied. This quantity is kept constant, and the variable is the flow. The graph represents the emission of SL-739@TiSiO<sub>4</sub> + TATP (taken for the 402nm wavelength) versus the flow.

At point 0, as there is no recirculation, there is no TATP vapours-probe contact, so the emission value at that point is the one that would correspond to SL-739@TiSiO<sub>4</sub> itself.

The flow values reach up to 300 cm<sup>3</sup>/min, which is three times the amount chosen for the experiments. Emission value has dropped considerably at that point, based on the fact that when recirculating that quickly, the TATP vapours-probe contact time is shorter, and therefore the emission is diminished.

The maximum has been established at the value of 100 cm<sup>3</sup>/min, and the corresponding emission value has been taken from the SL-739@TiSiO<sub>4</sub> + TATP titration.



*Figure S16. Emission intensity (at  $\lambda = 402 \text{ nm}$ ) as a function of the air flow.*

### 11.2. Recirculation time

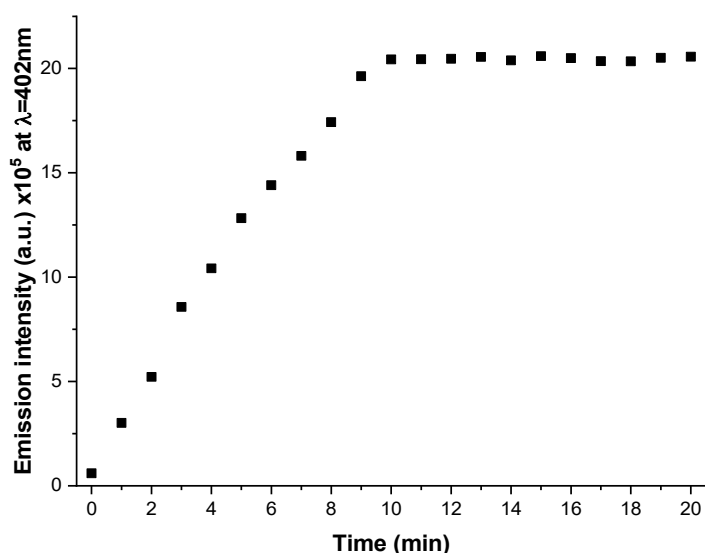
A specific amount of TATP has been chosen to perform the study, 2 mg, the maximum studied. This quantity is kept constant, same as flow (100cm<sup>3</sup>/min), and the

variable is the recirculation time. The graph represents the emission of SL-739@TiSiO<sub>4</sub> + TATP (taken for the 402nm wavelength) versus the time.

The time whose choice is discussed is the time that passes from when the evaporation of TATP has been completed until the recirculation of air has stopped (and therefore it is the time during which TATP vapours have been circulating so that they come into contact with the probe). This time has been set at 10 minutes.

At point 0 we assume that, as air recirculation has not yet started, there is no TATP vapours-probe contact, so the emission value at that point is the one that would correspond to SL-739@TiSiO<sub>4</sub> itself. After 10 minutes, emission is maximum and the corresponding emission value has been taken from the SL-739@TiSiO<sub>4</sub> + TATP titration.

From 10 to 20 minutes there are small oscillations around the maximum emission value, so the behaviour stabilizes, and therefore it is not worth prolonging recirculation beyond 10 minutes.



*Figure S17. Emission intensity (at  $\lambda = 402 \text{ nm}$ ) as a function of the time.*