

## Supplementary information

### Evidence of the contribution of molecular fluorophores to the luminescence of carbon entities formed by solvothermal treatment of trinitropyrene

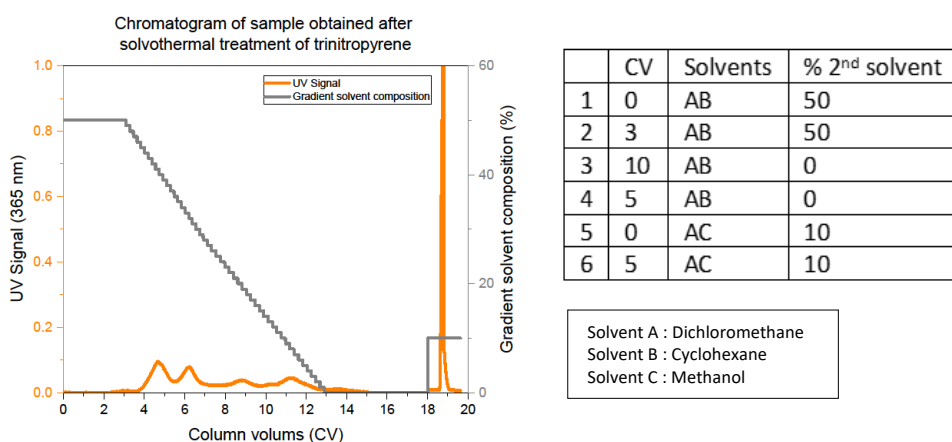
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**Figure S.I.A/** Chromatogram of the sample obtained after solvothermal treatment of TNP. The tables on the right contains information on the steps of the chromatography procedure



### S.I.B/ High Resolution Mass Spectrometry

The peak at  $m/z$  value of 214 must not be considered, it is an artifact. The solvent used for this analysis is dichloromethane. It is to be observed that the samples were not easily ionized.

Left column: positive mode; right column: negative mode

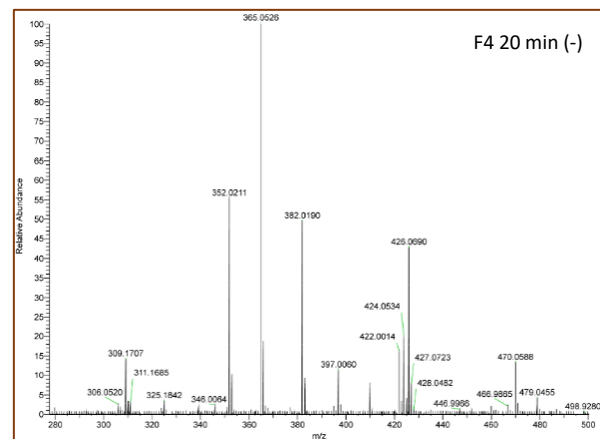
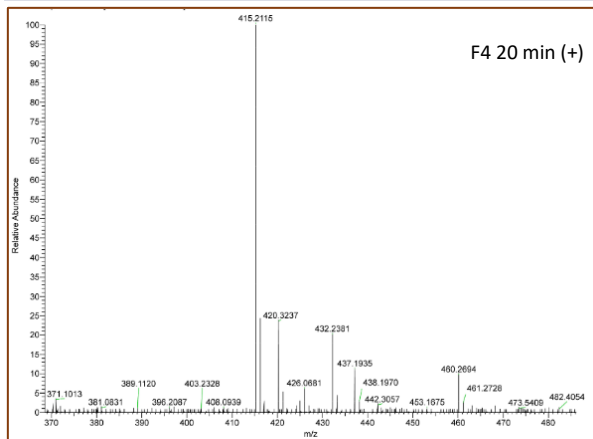
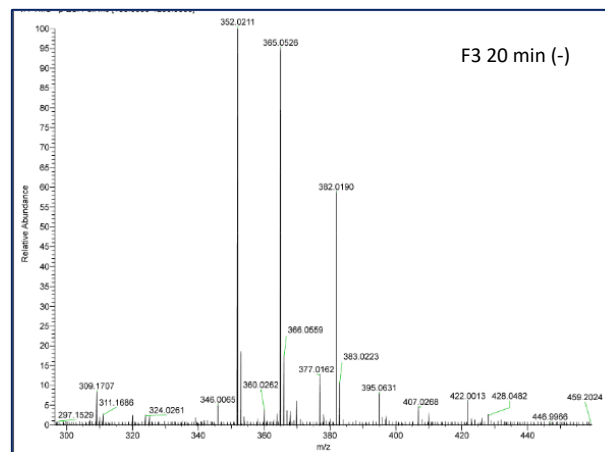
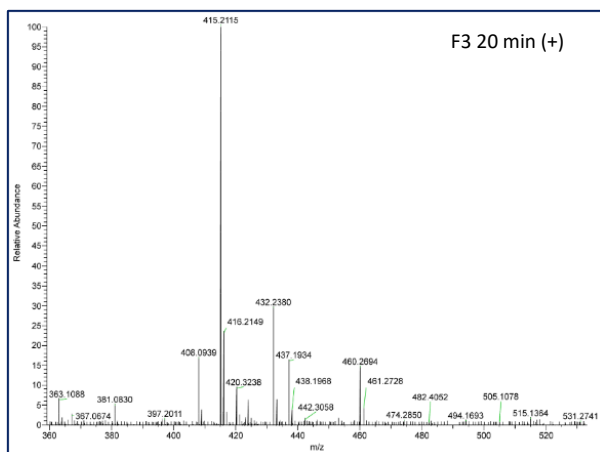
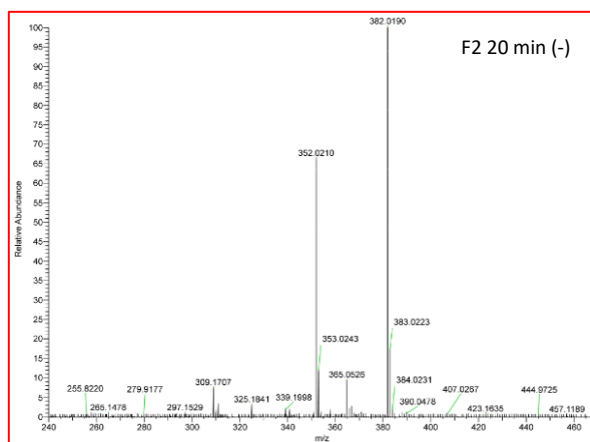
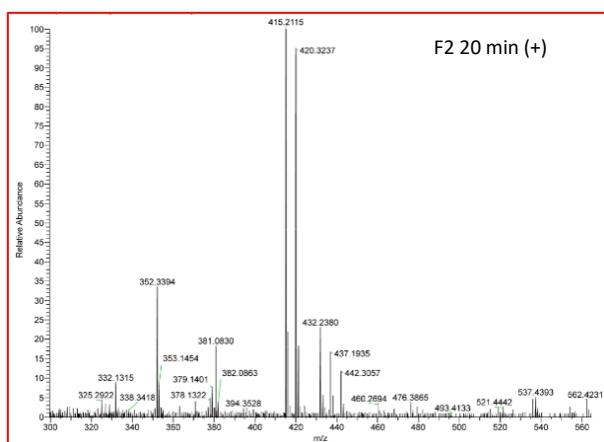
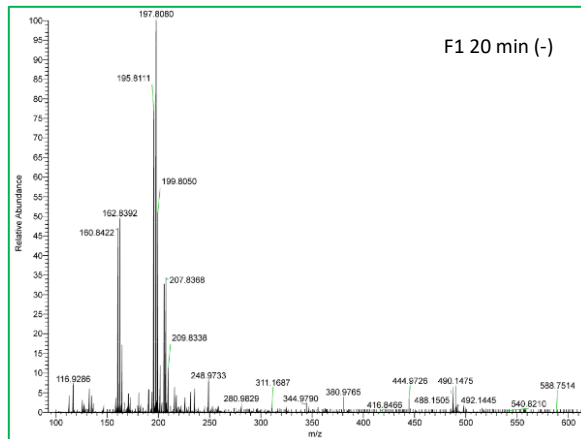
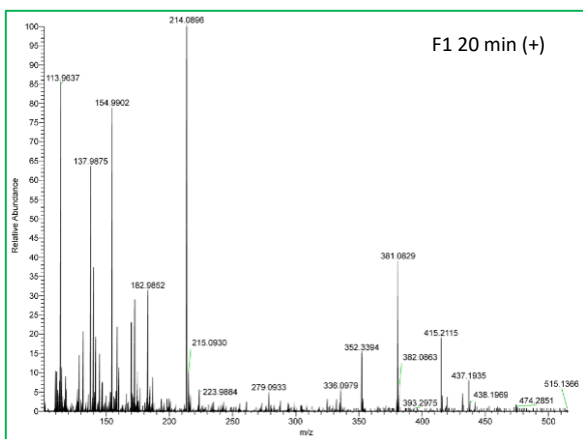
**Table S.I.B/1 :**

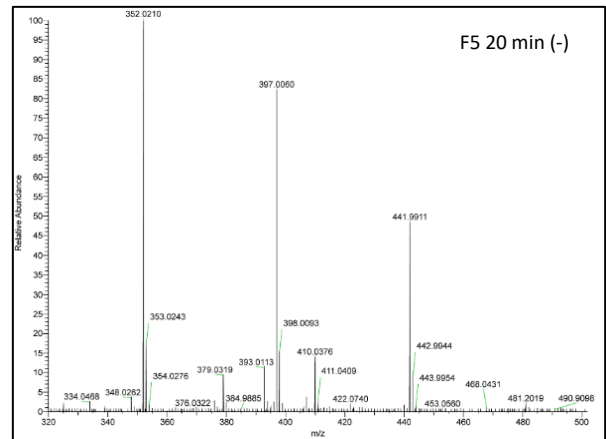
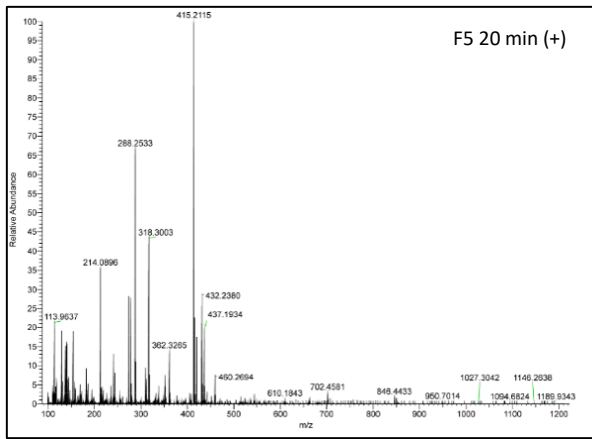
Mass of the pseudomolecular ion : 414			
	Adduct ion	Nominal adduct mass	Adduct mass
	[M+H] <sup>+</sup>	M+1	415
	[M+NH <sub>4</sub> ] <sup>+</sup>	M+18	432
	[M+Na] <sup>+</sup>	M+23	437
	[2M+NH <sub>4</sub> ] <sup>+</sup>	2M+NH <sub>4</sub>	846

Mass of the pseudomolecular ion : 419	Adduct ion	Nominal adduct mass	Adduct mass
	[M+H] <sup>+</sup>	M+1	420
	[M+NH <sub>4</sub> ] <sup>+</sup>	M+18	437
	[M+Na] <sup>+</sup>	M+23	442
	[2M+NH <sub>4</sub> ] <sup>+</sup>	2M+NH <sub>4</sub>	856

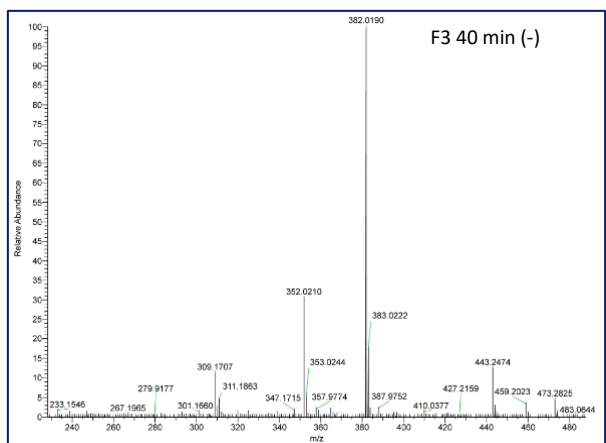
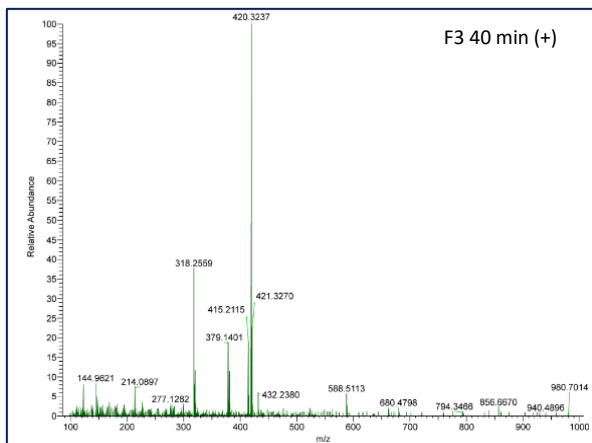
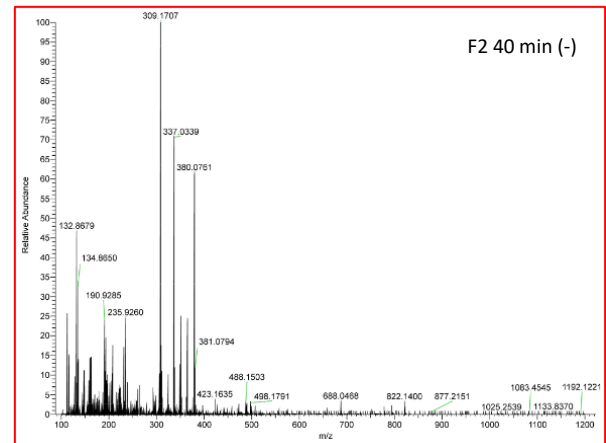
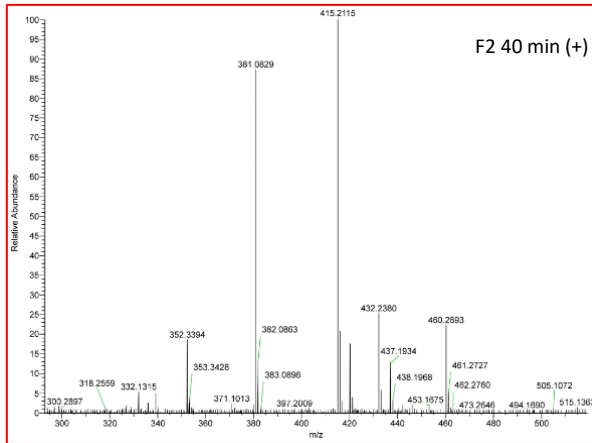
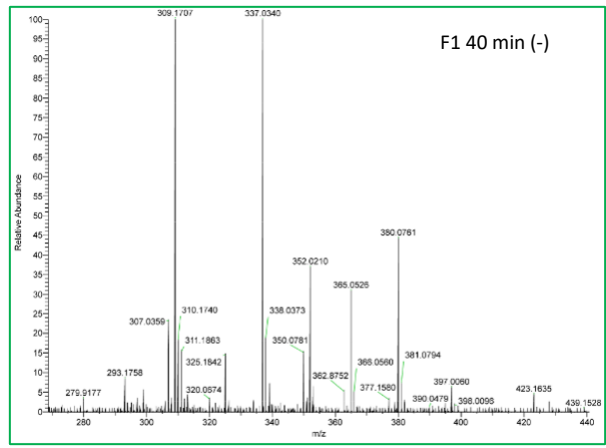
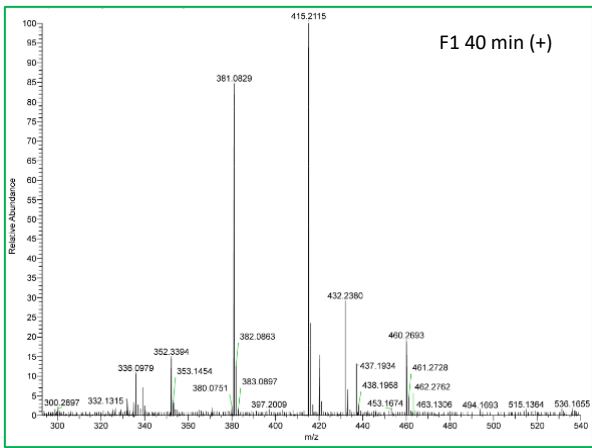
**Figure S.I.B/2** ESI-HRMS Spectra of the fractions in positive and negative mode

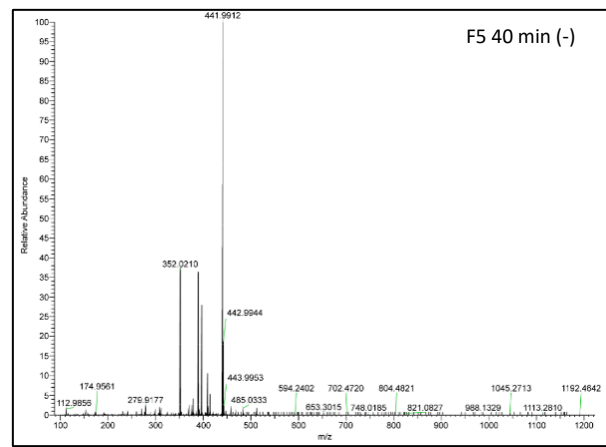
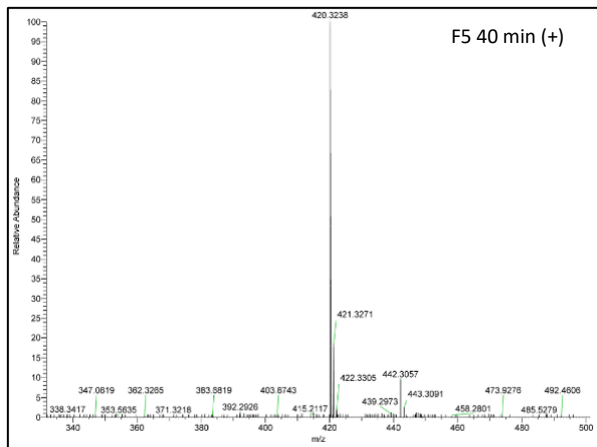
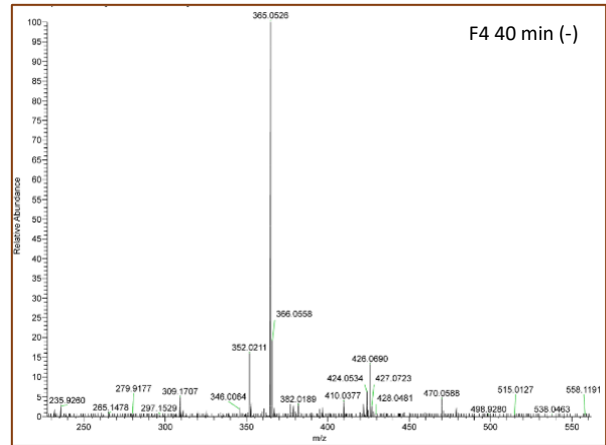
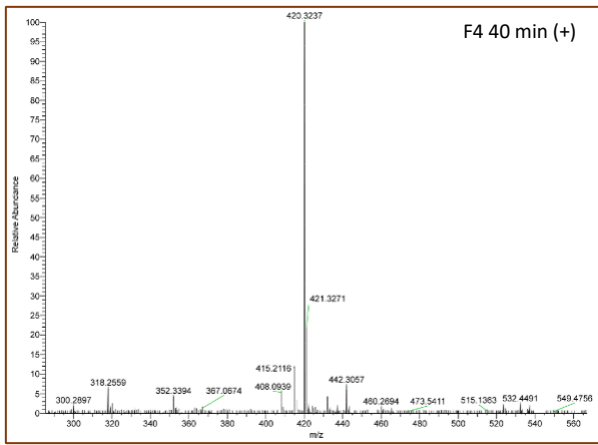
20 min :



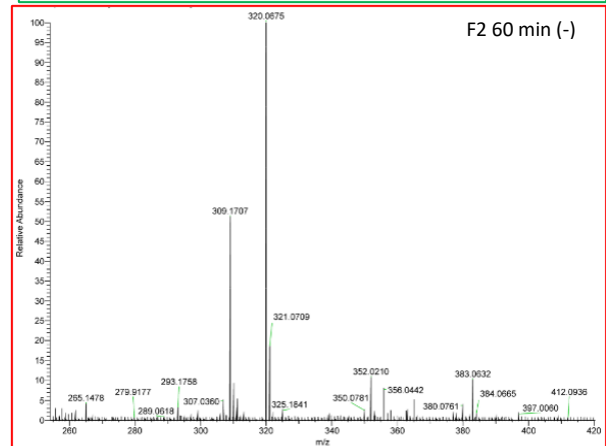
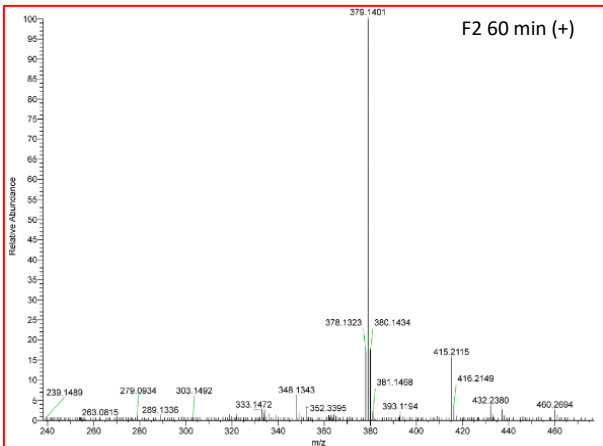
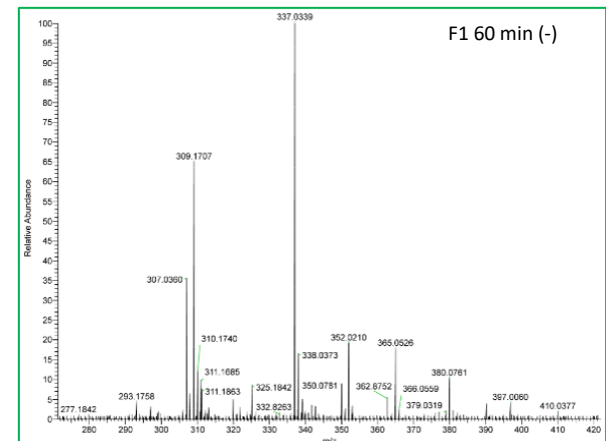
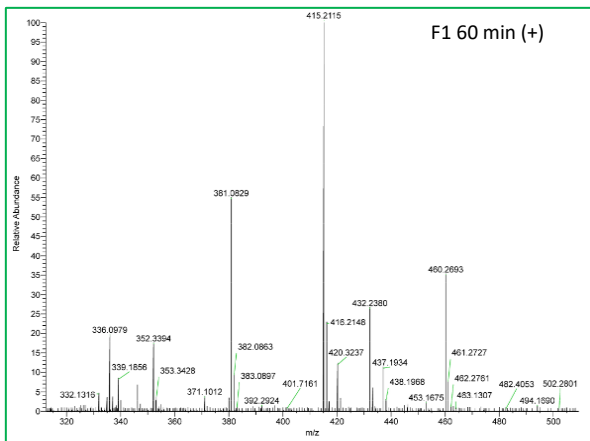


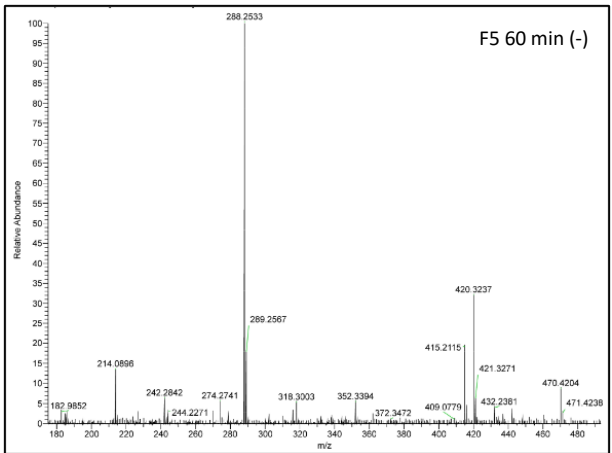
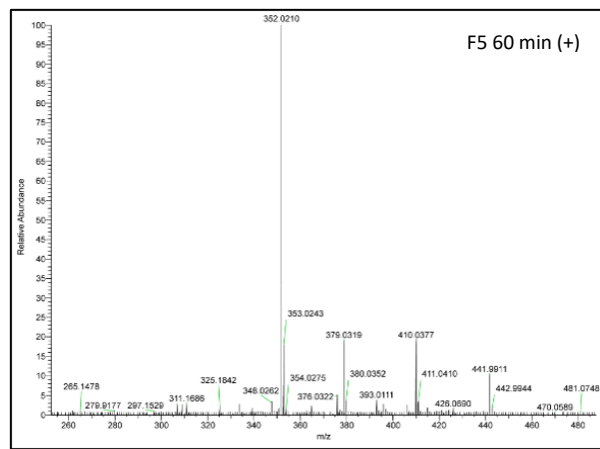
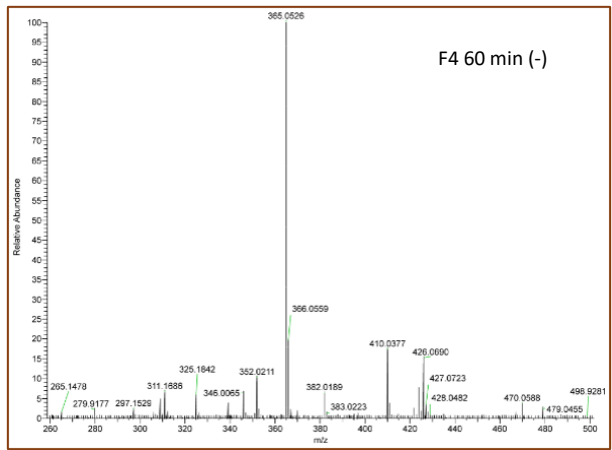
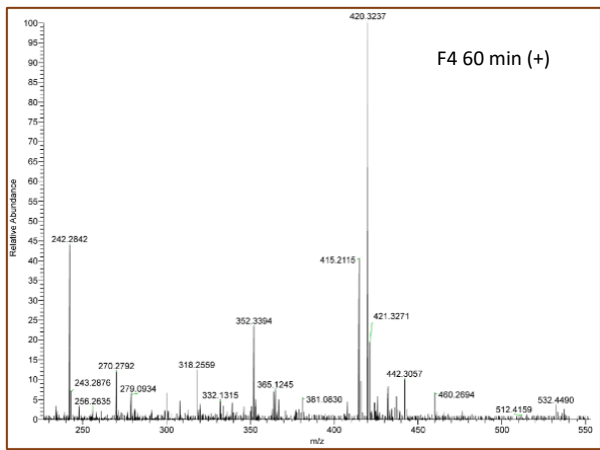
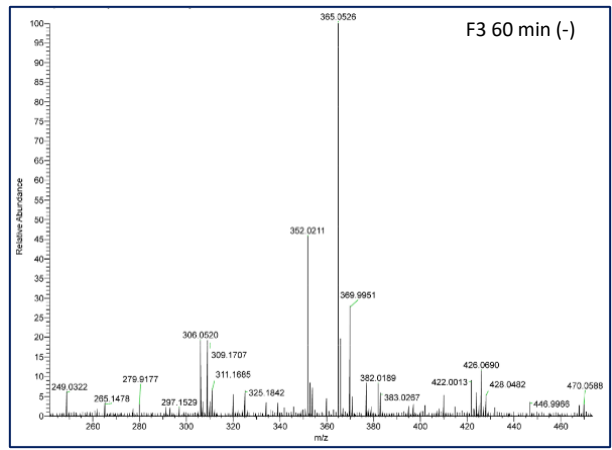
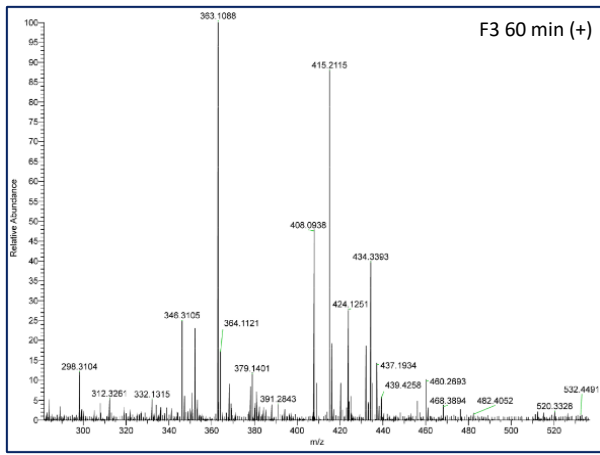
40 min :





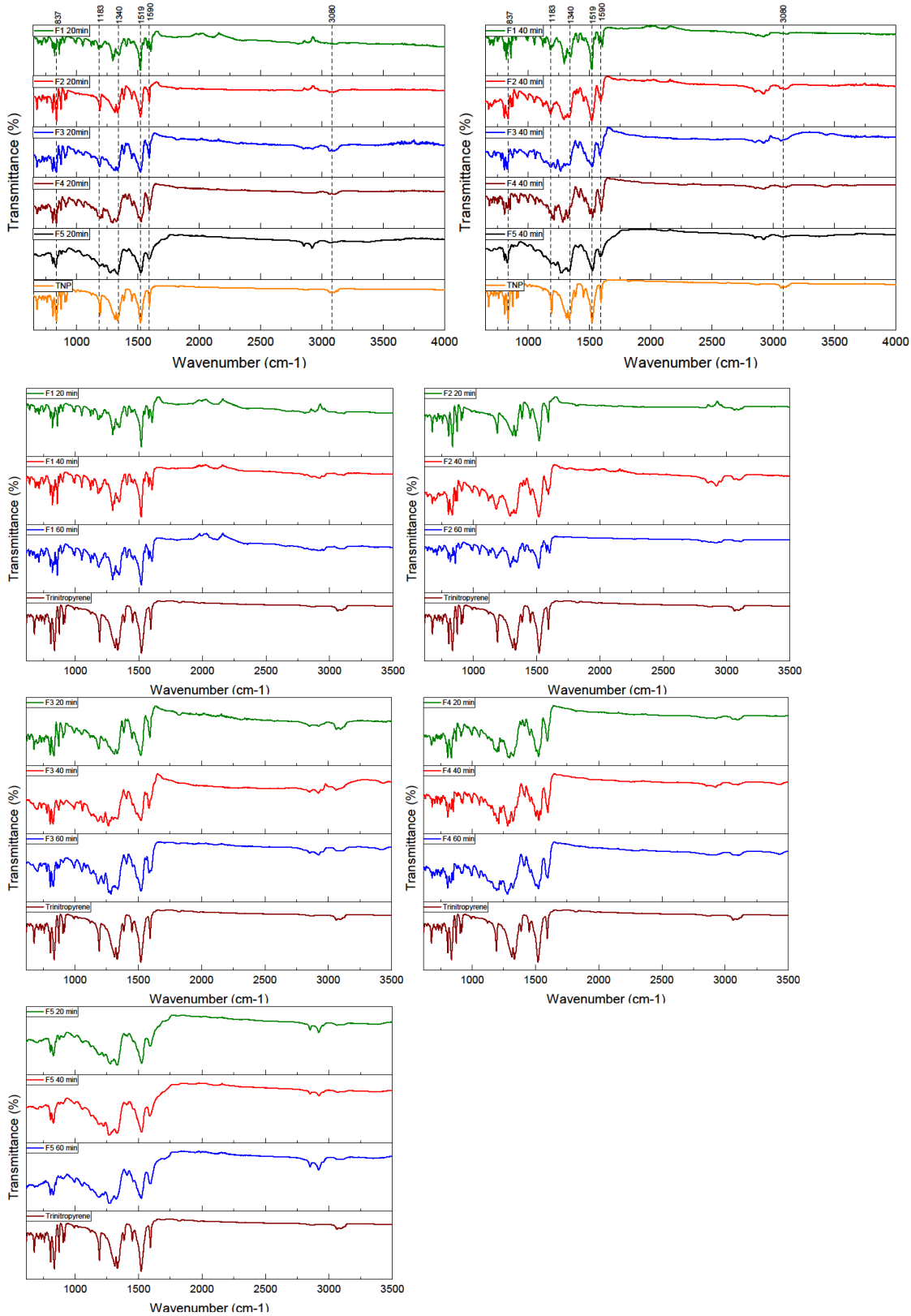
60 min :





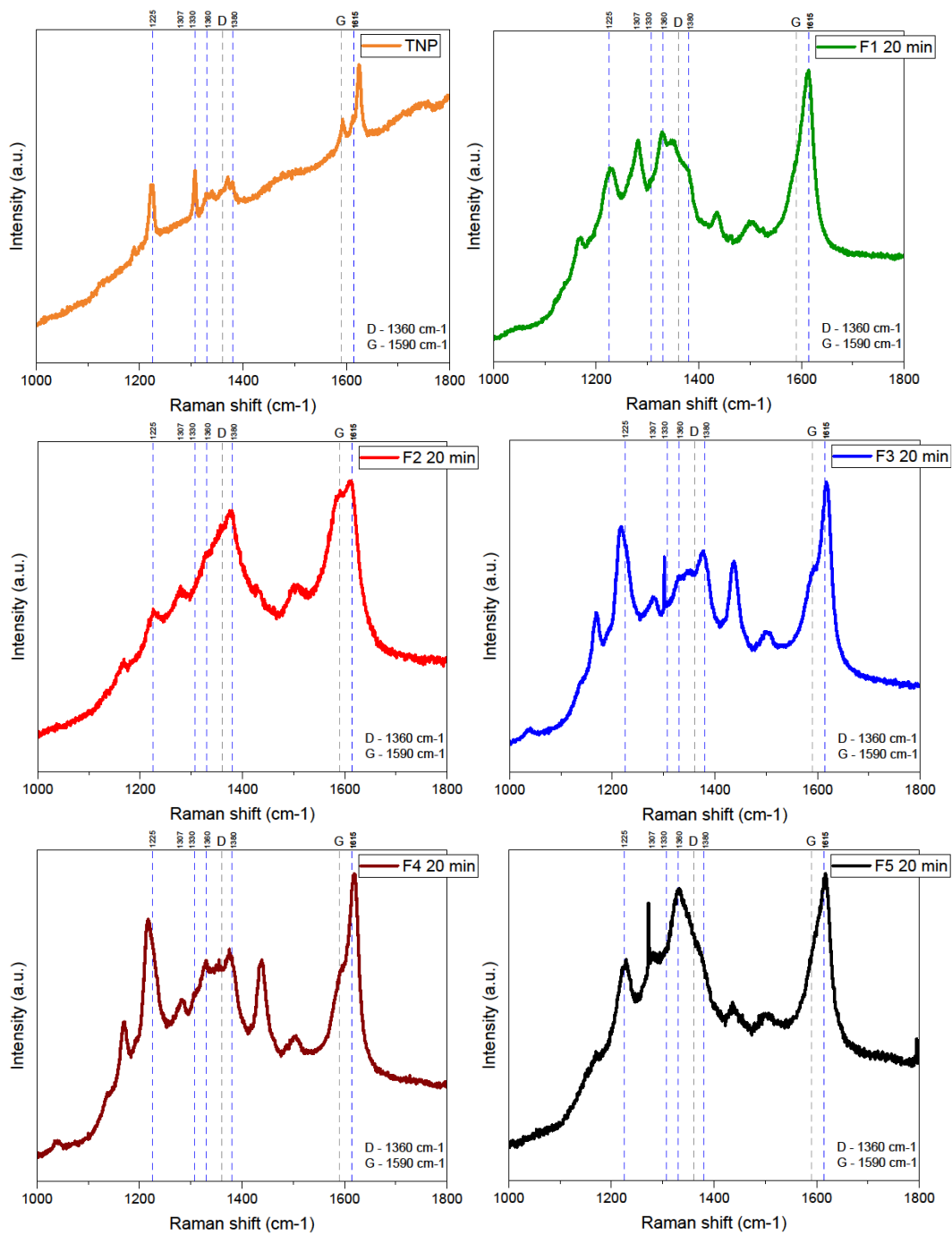
# Figure S.I.C/ Fourier Transform InfraRed spectroscopy

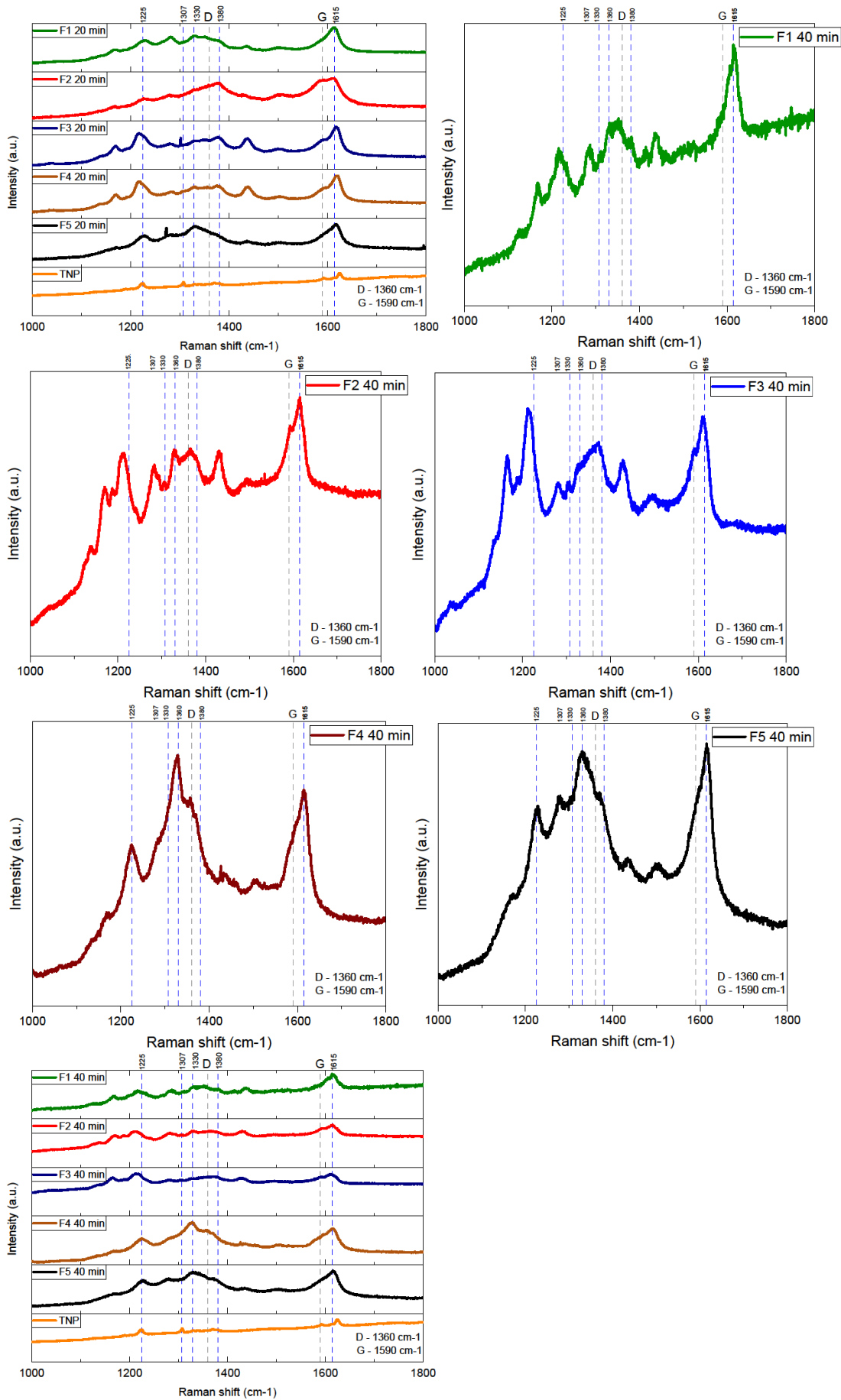
FTIR Spectra of the fractions for 20, 40 and 60 minutes stacked with TNP FTIR spectra



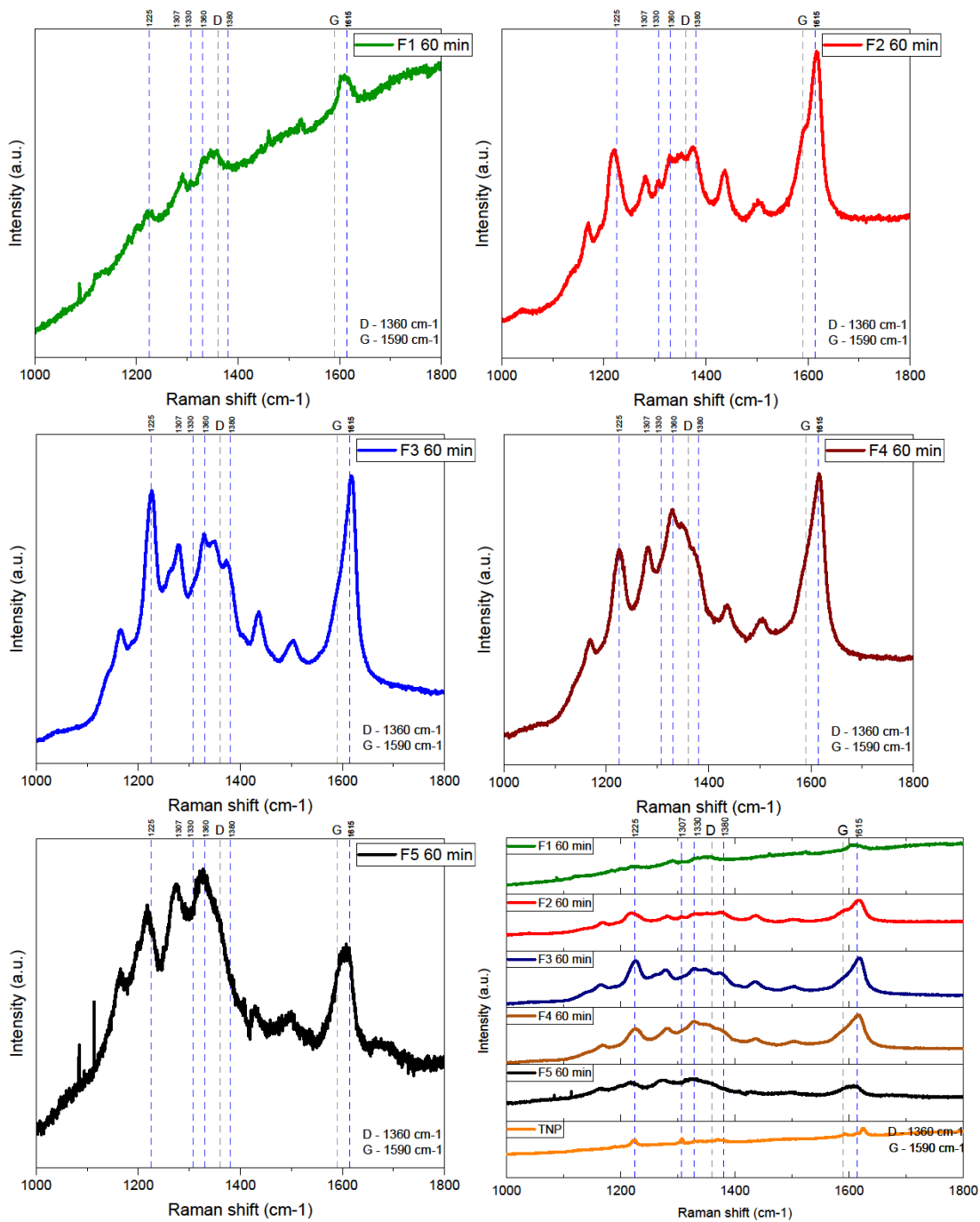
### Figure S.I.D/ Raman spectroscopy

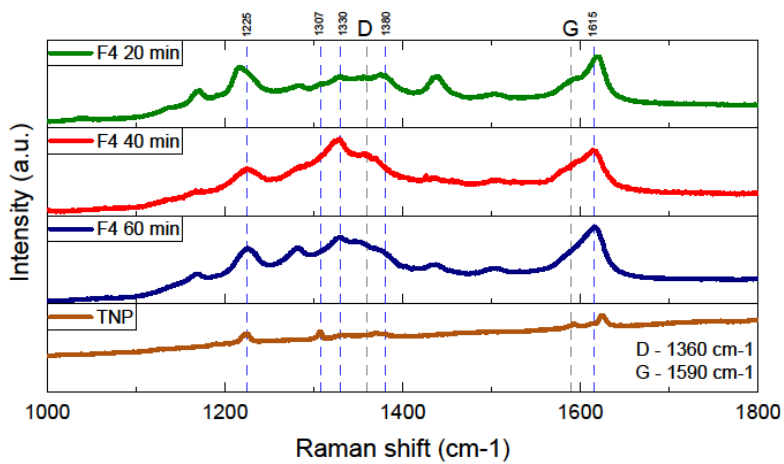
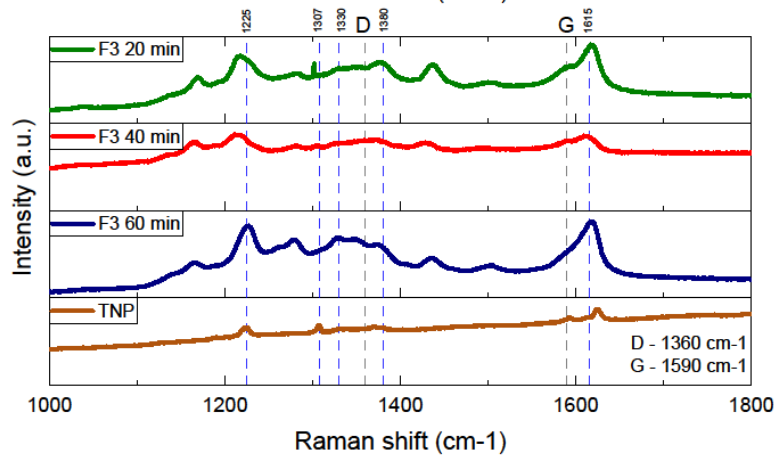
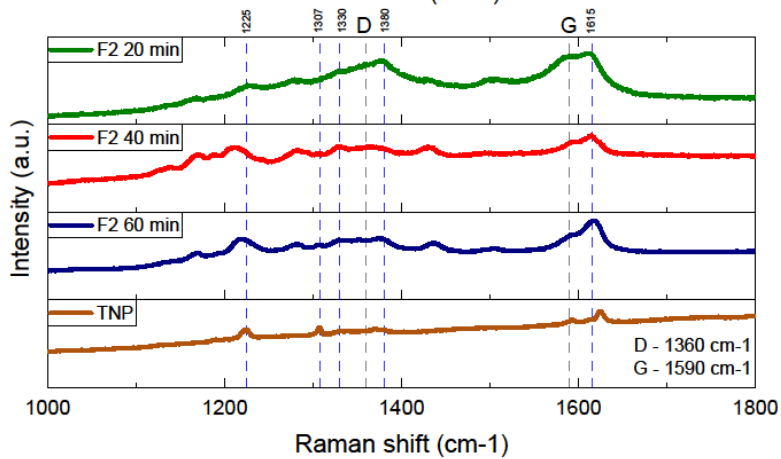
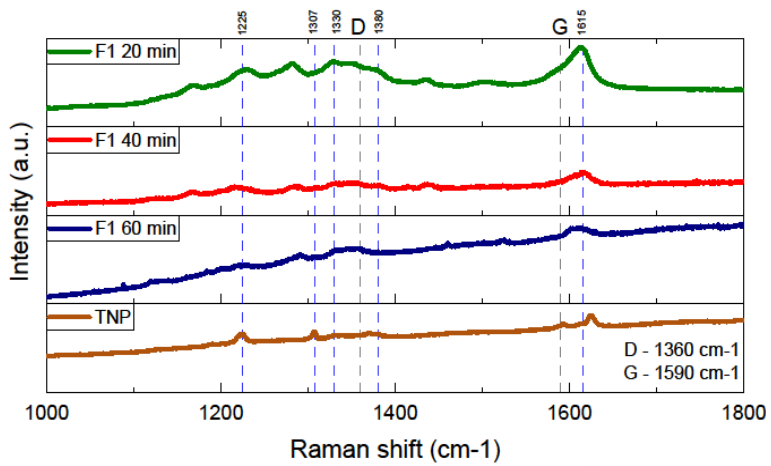
Raman spectra of TNP and the fractions for durations of 20 and 40 minutes of solvothermal treatment

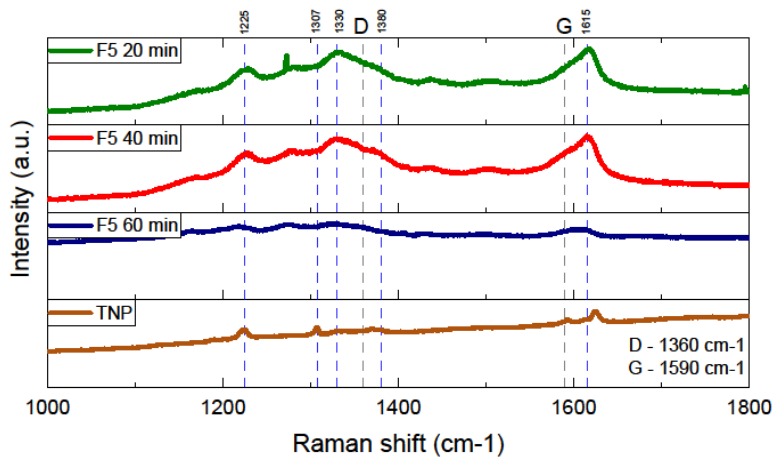






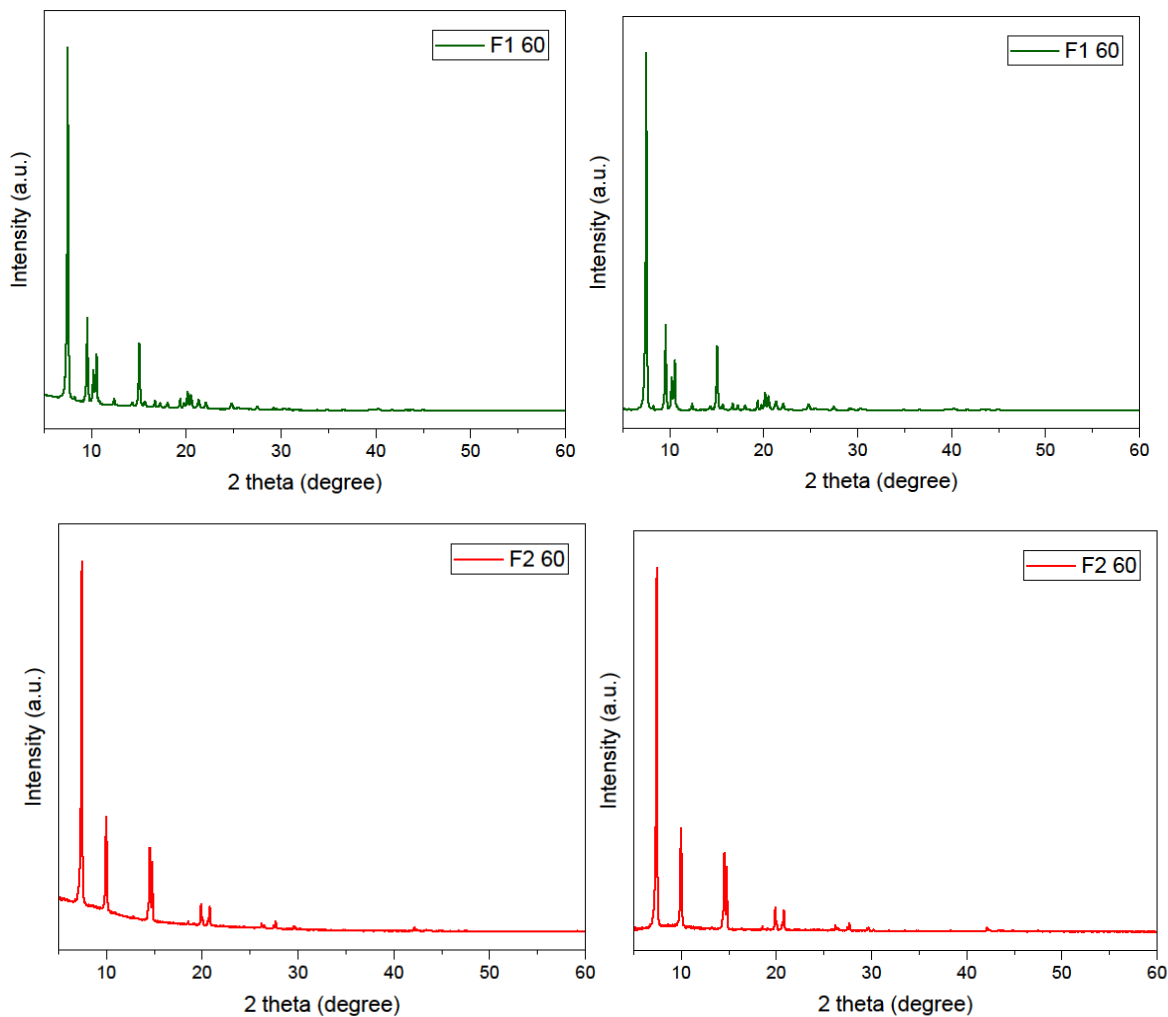


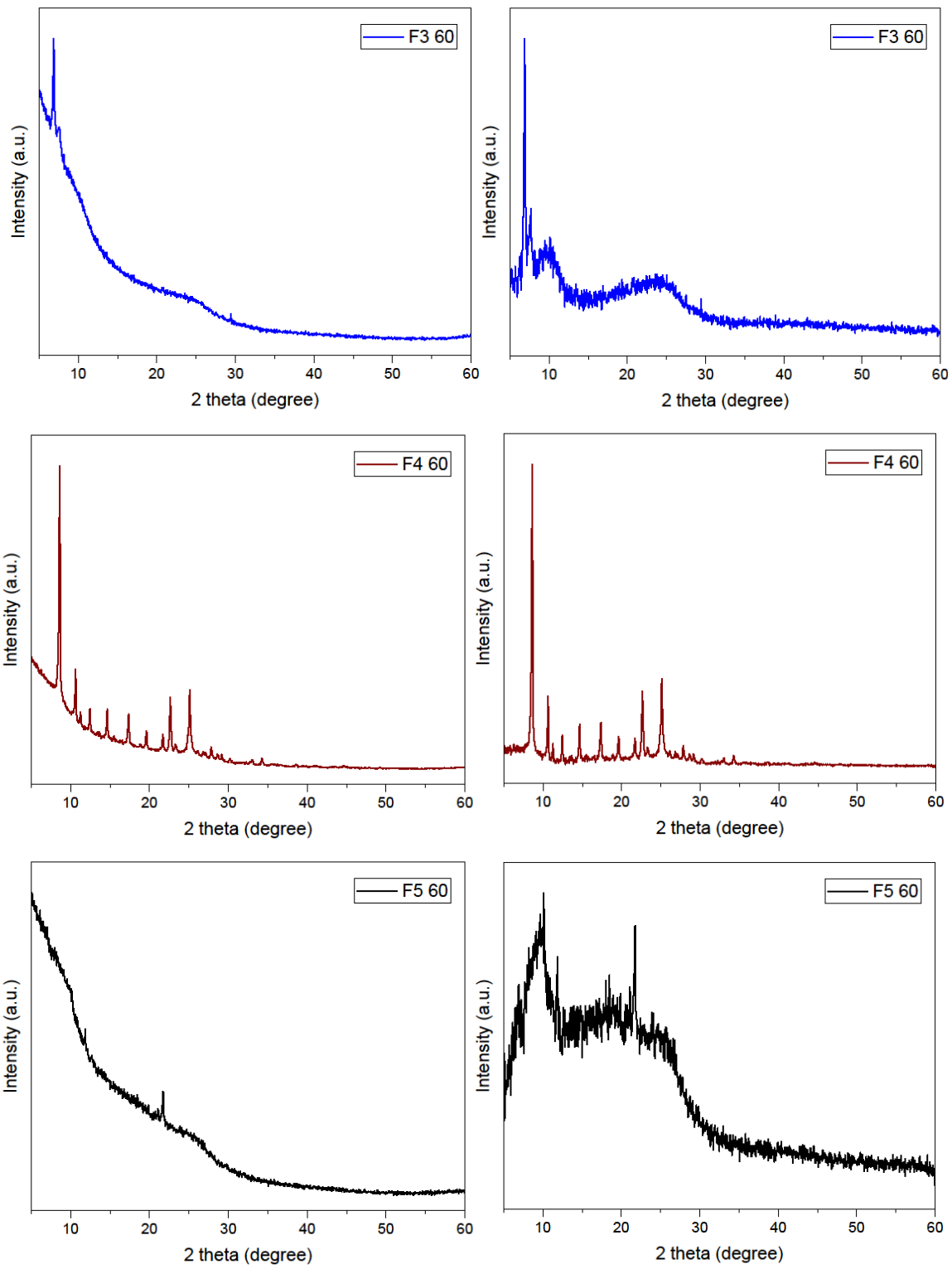


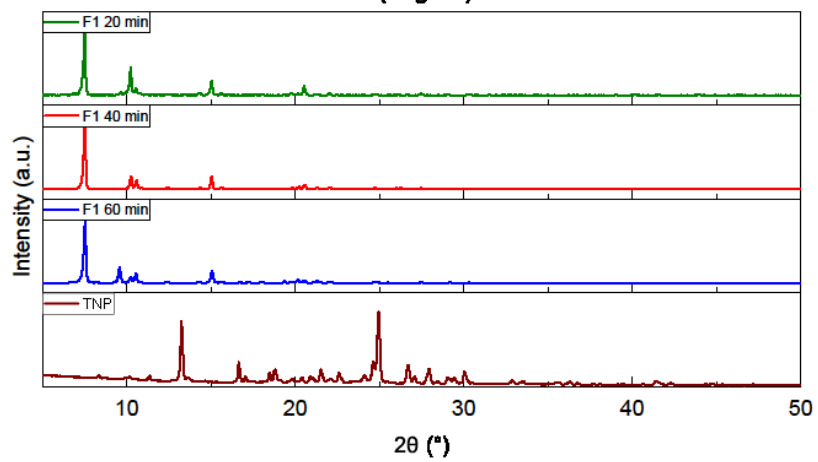
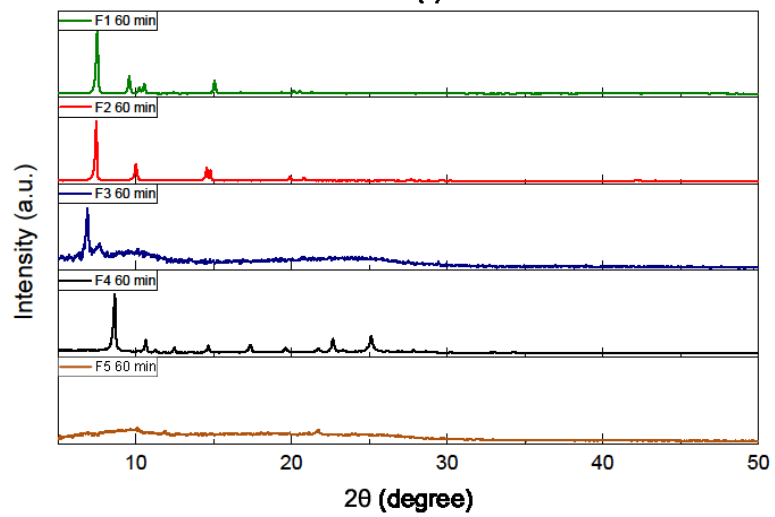
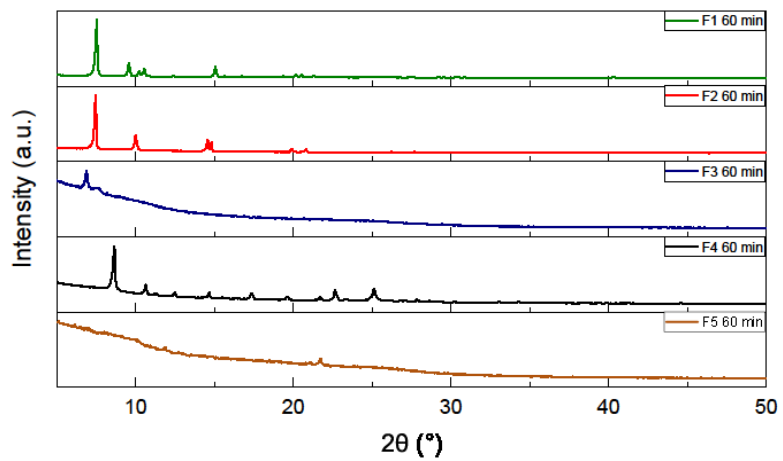


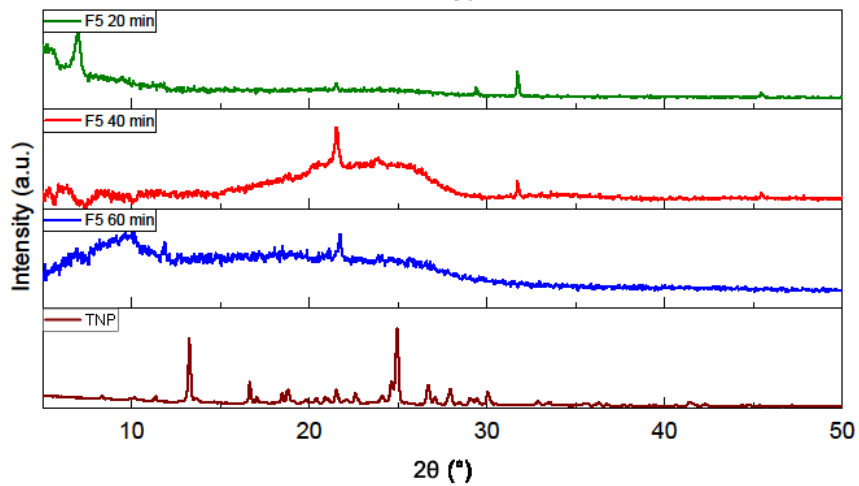
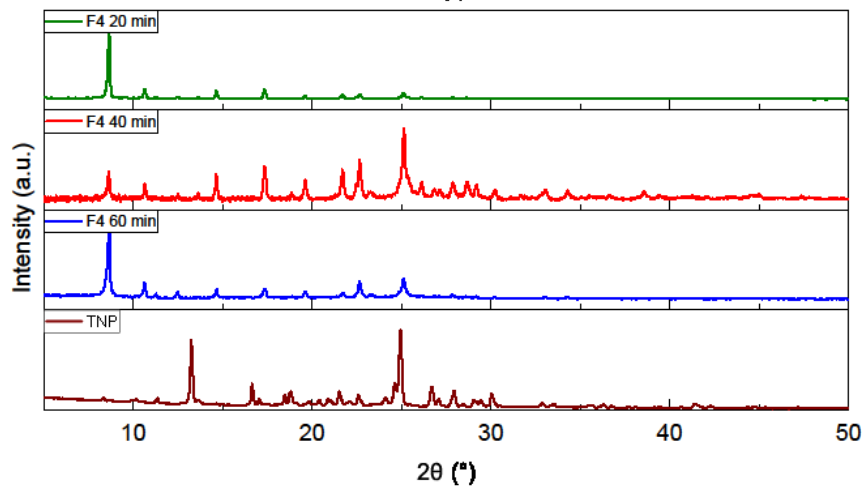
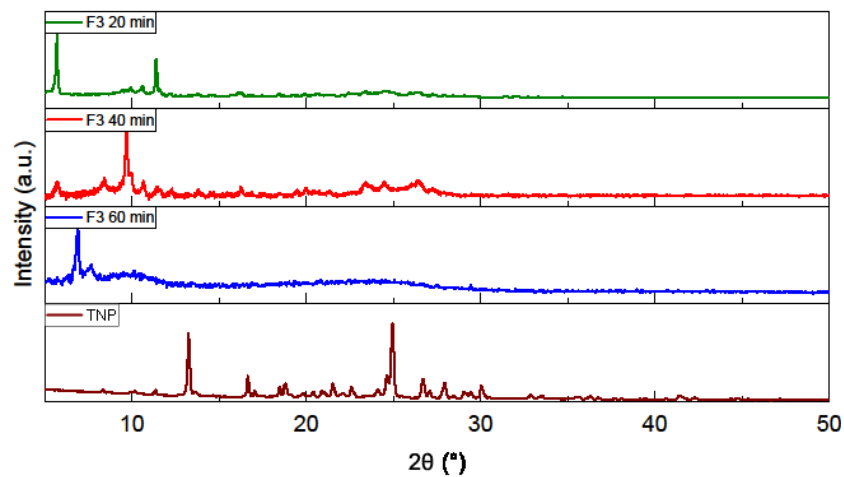
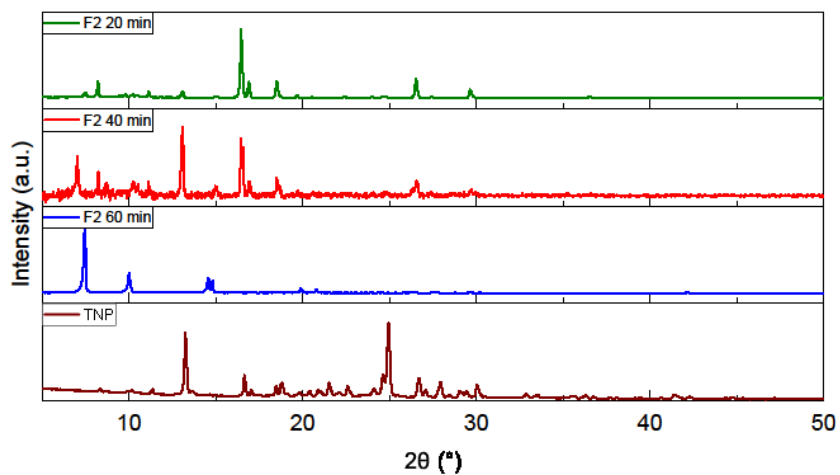
**Figure S.I.E. X-ray Diffraction**

Diffraction pattern (individual and stacked) of the fractions F1 to F5 with (left column) and without (right column) the background (60 minutes duration of solvothermal treatment)







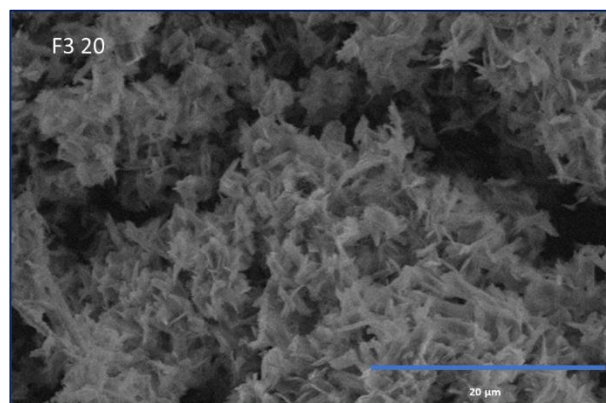
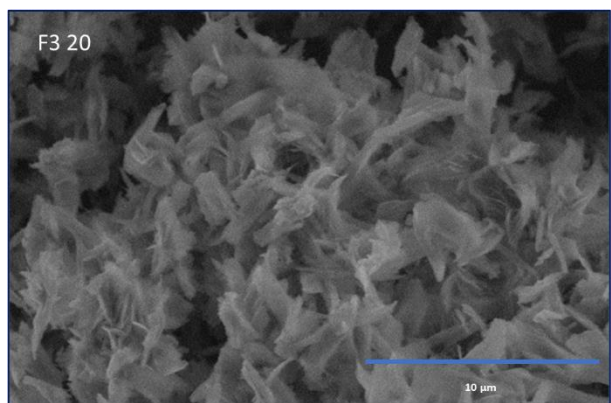
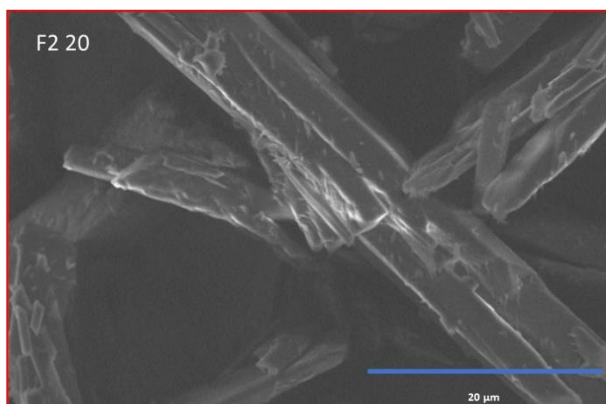
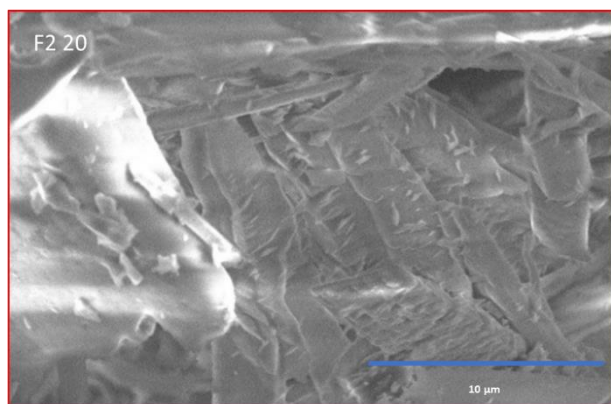
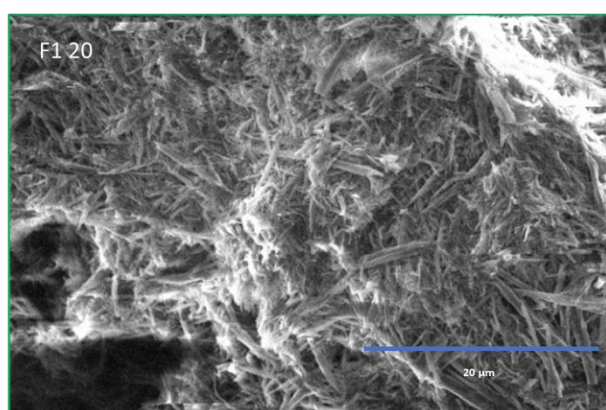
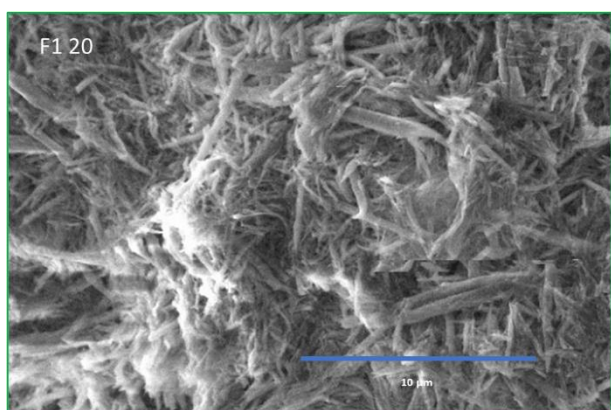


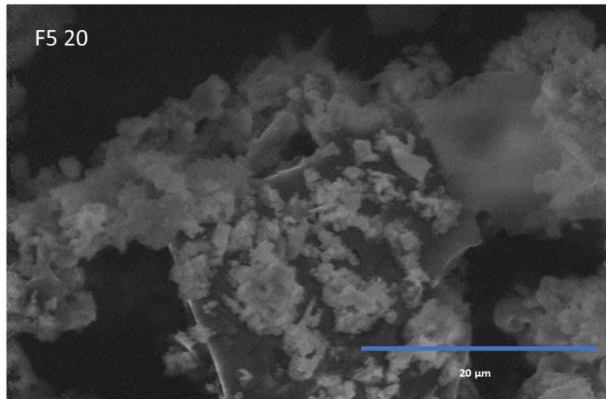
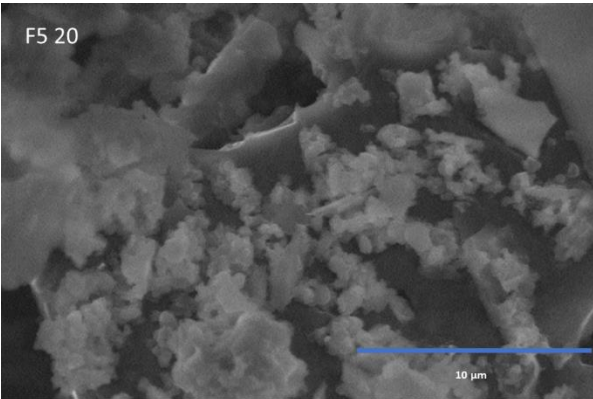
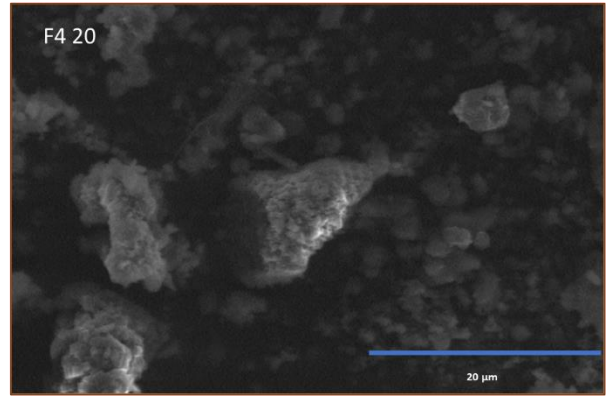
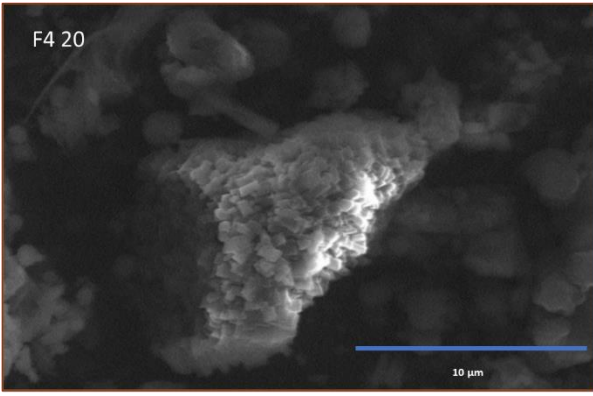
## S.I.F/ SEM

For 20 min synthesis, the fraction  $F_1$  20 shows tangled, stacked thread-like structure of various size ( $\mu\text{m}$  size) and diameter. Some of the threads are bent. Fraction  $F_2$  20 displays straight rods-like. They are regular and larger than the thread from  $F_1$  20. If we focus on the surface of the rods, we observe smaller stacked pieces and irregularities. Fractions  $F_3$  20 and  $F_4$  20 exhibit small pieces of irregular size and shape.  $F_5$  20 displays small and large pieces of irregular size and shape. Some of them look like the other four fractions. Overall, the fractions are  $\mu\text{m}$  size. For 40 min synthesis, the fraction  $F_1$  40 shows tangled, stacked thread-like structure of various size ( $\mu\text{m}$  size) and diameter similarly to the  $F_1$  20. Some of the threads are bent. Fraction  $F_2$  40 displays rods and sheet-like structure.  $F_2$  40 structure is very different from  $F_2$  20. They are irregular and similar in size to  $F_1$  40. If we focus on the surface of the rods, we observe smaller stacked pieces and irregularities. Fractions  $F_3$  exhibit stacked spike-like structure of varying size.  $F_4$  does not have a clear morphology as it contains rods, threads, and sheets-like pieces. Overall, some fractions display quite regular structure. This imply that the sample structure is organized on a long range. This is in accordance with the XRD results that suggest that these samples are quite crystalline. This is not something expected for carbon dots but these morphologies are expected for organic molecules. Moreover, reports of pyrene derivatives that self-assembled to form supramolecular object such as nanorods have been made<sup>1,2,3</sup>. This suggest, like the XRD and the HRMS results, that the samples are more likely composed of a pool of molecular fluorophores.

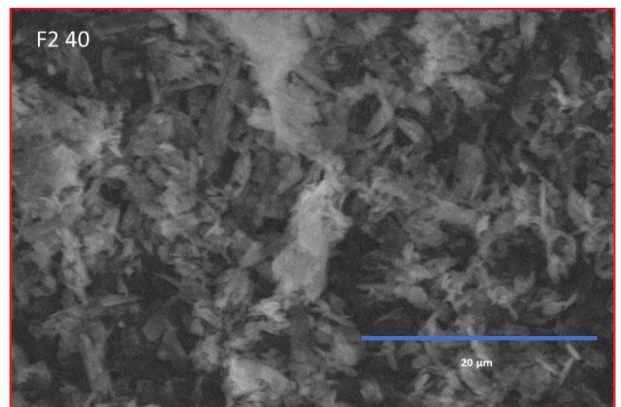
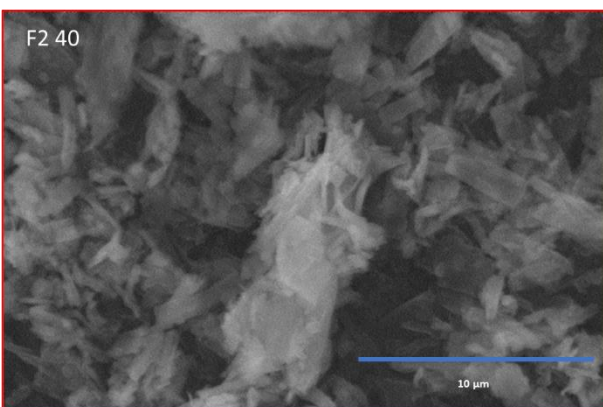
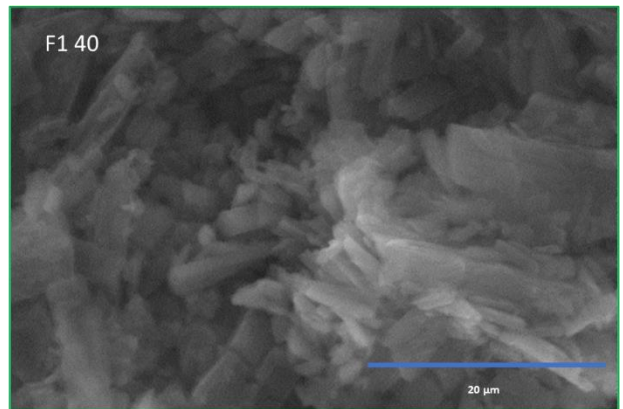
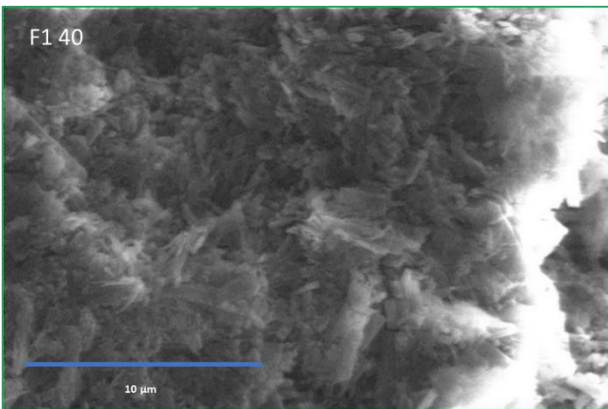
**Figure S.I.F/1** SEM images of the fractions from F1 to F5 for 20, 40 and 60 minutes of solvothermal treatment

20 min :

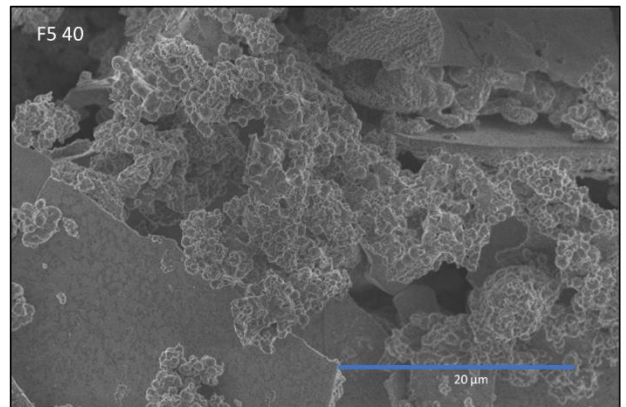
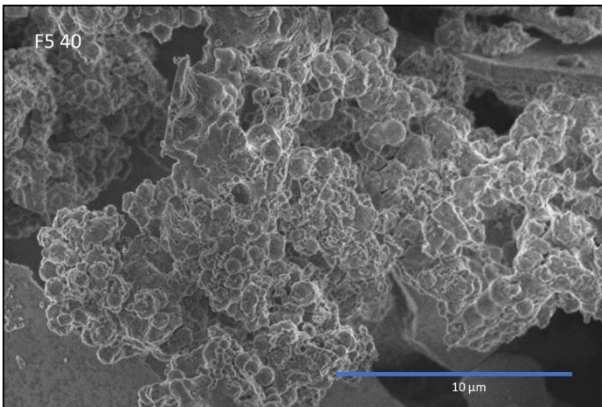
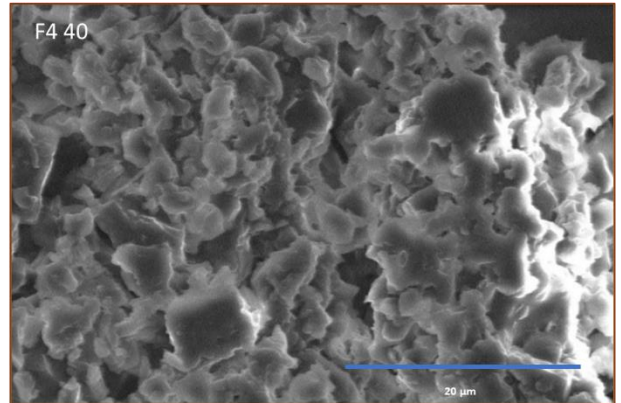
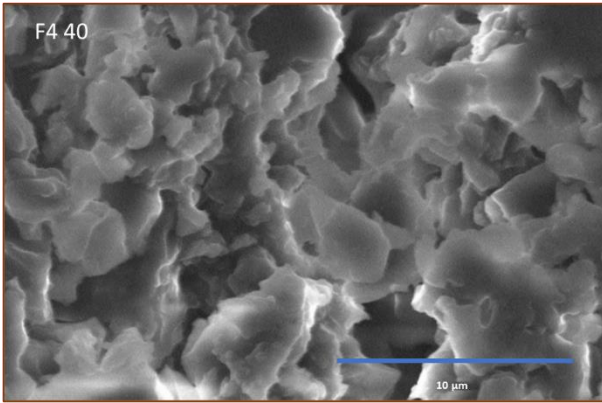
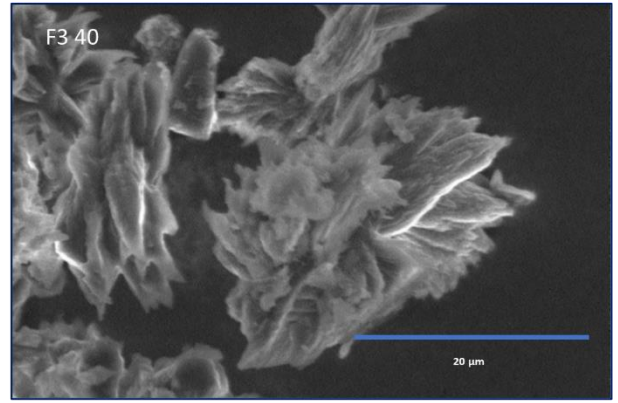
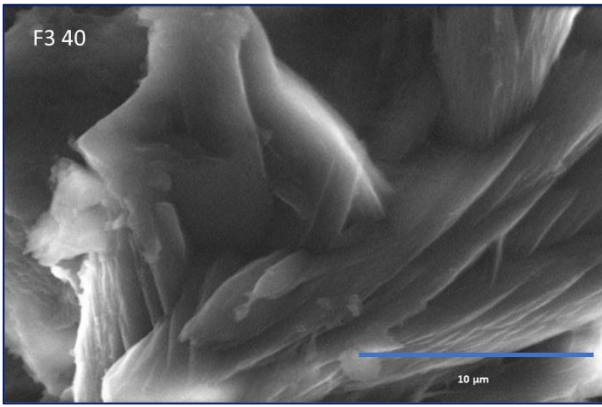




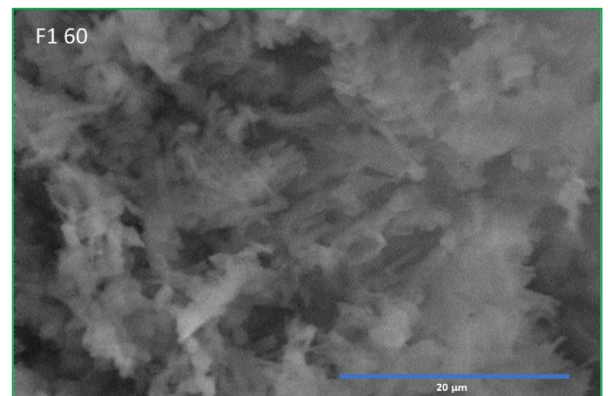
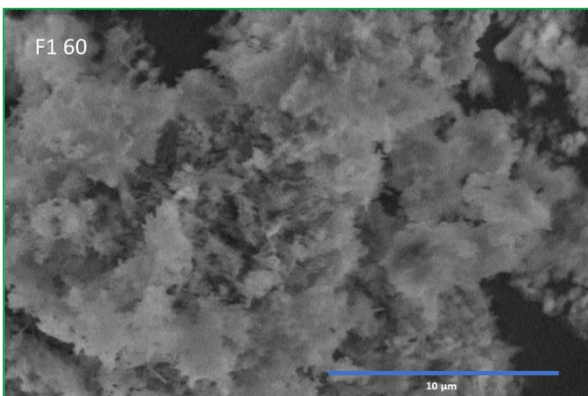
40 min :

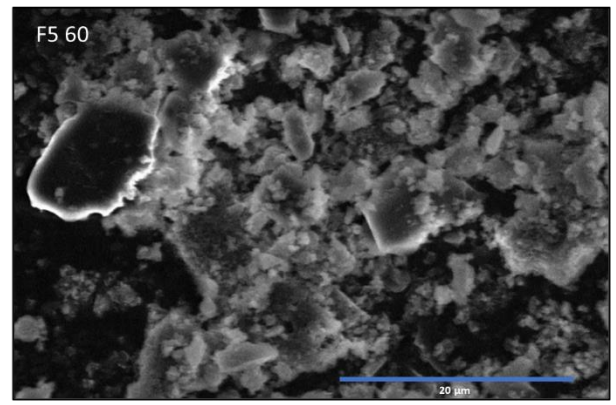
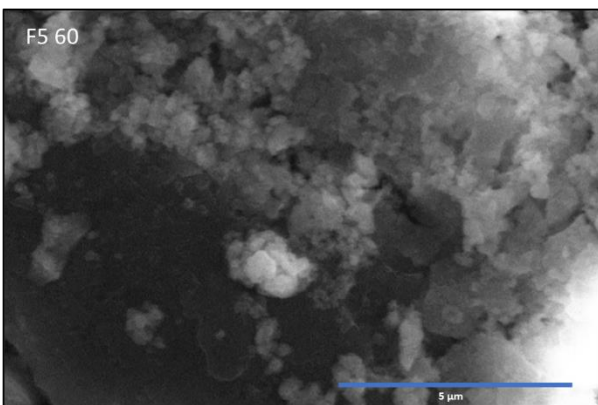
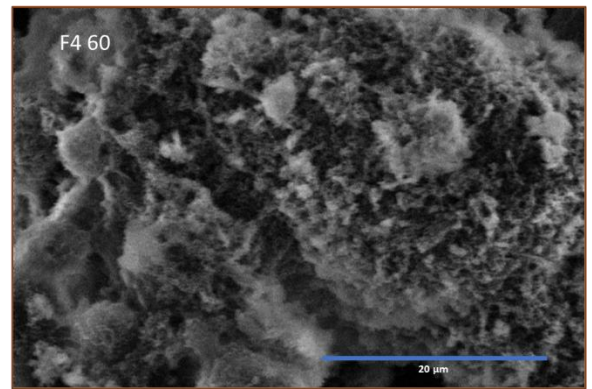
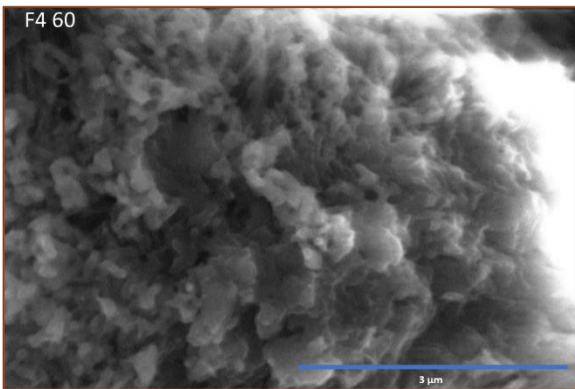
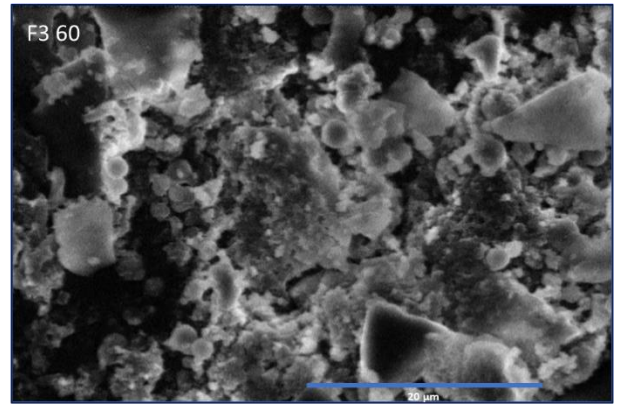
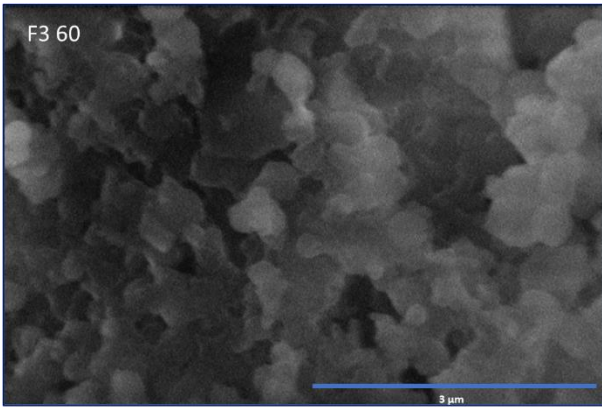
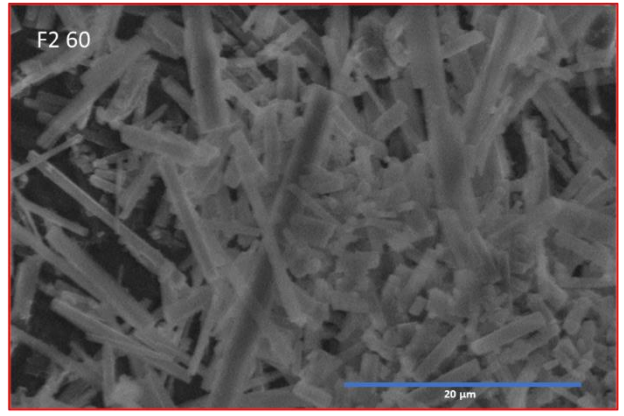
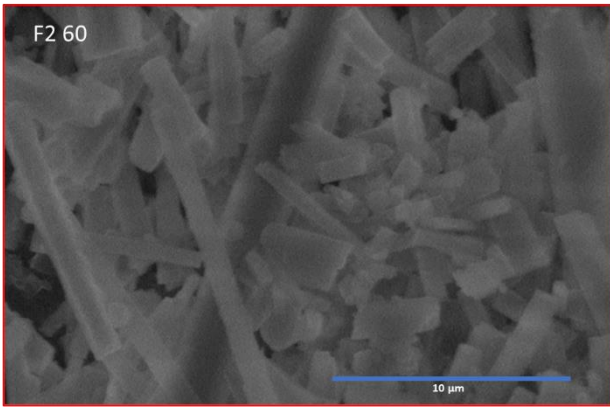






60 min :

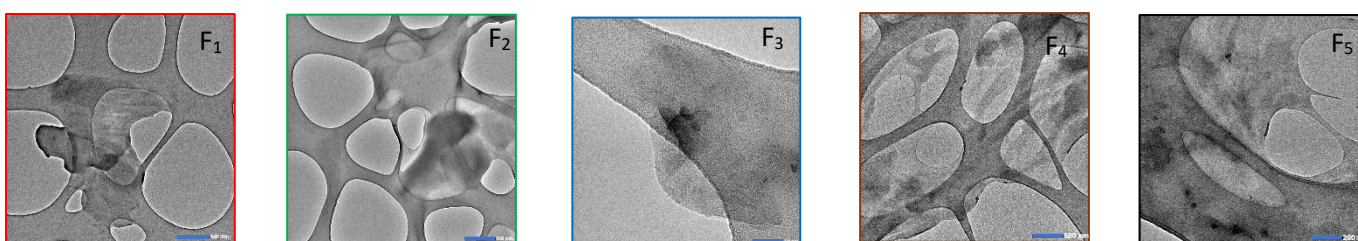




## S.I.G/ TEM

Figure S.I.G/1 TEM images of the fractions from F1 to F5 for 20, 40 and 60 minutes of solvothermal treatment

TEM micrographs of the fractions for the synthesis at 60 min. doesn't show particle features specific or analogous to CDs. Structures or varying morphologies are observed. The fractions all display a kind of membrane or coating-like morphology that extend beyond the grid, in the space between corresponding to the holes of the grid. Such morphologies are likely the result of the aggregation of molecular fluorophore<sup>4,5</sup>. However, some nanoparticles can be observed in the fraction F<sub>5</sub>. The size of this carbon particles is several tens of nanometers. This suggest that this carbon nanomaterial isn't carbon dots but rather a by-product significantly larger. It can explain the origin the signal signal of amorphous carbon powder we observed in powder x-ray diffraction and molecular fluorophores could be adsorbed to this by-product, endowing it with fluorescent properties. These relatively big carbon nanomaterials may also be responsible for the cloudy solution, to a certain extent, that we observe in the case of the fraction F<sub>5</sub>. Overall, The fractions from F<sub>1</sub> to F<sub>4</sub> don't display the structures expected for carbon dots but rather appear as aggregated molecular fluorophores, a kind of supramolecular association of organic fluorophores. In addition to this, some relatively big carbon nanomaterial structures are observed in the fraction F<sub>5</sub>.

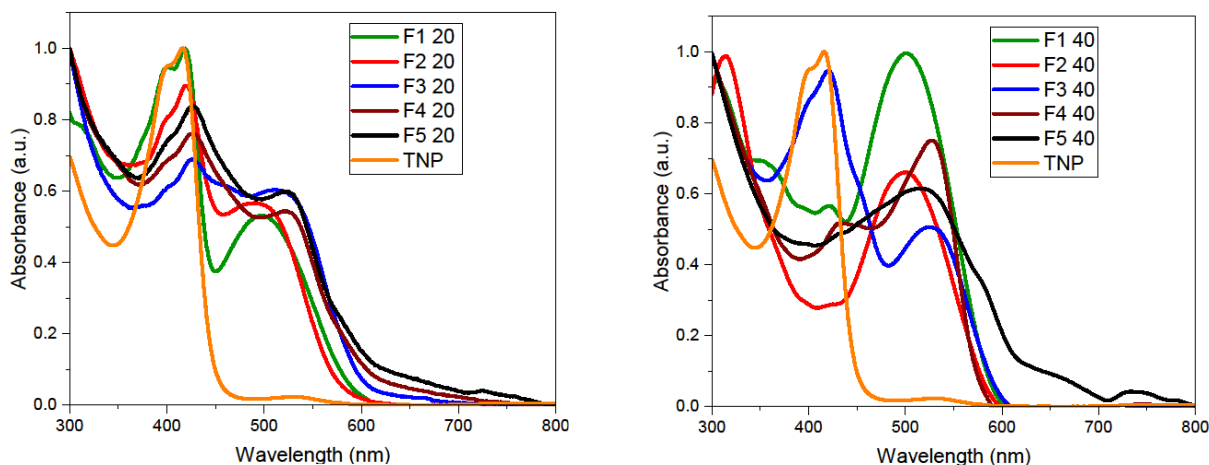


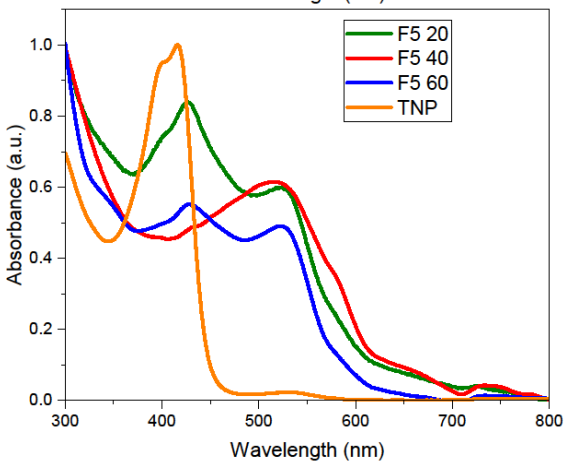
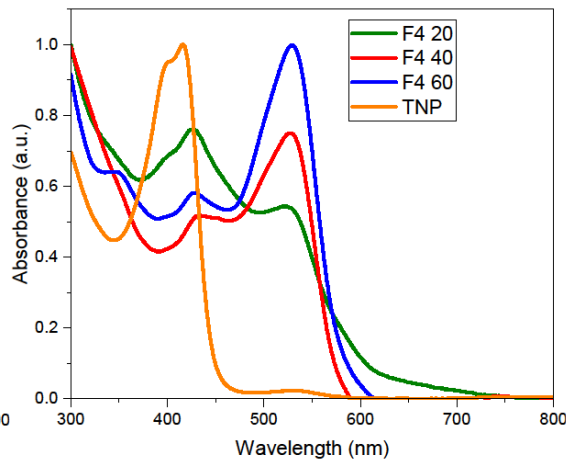
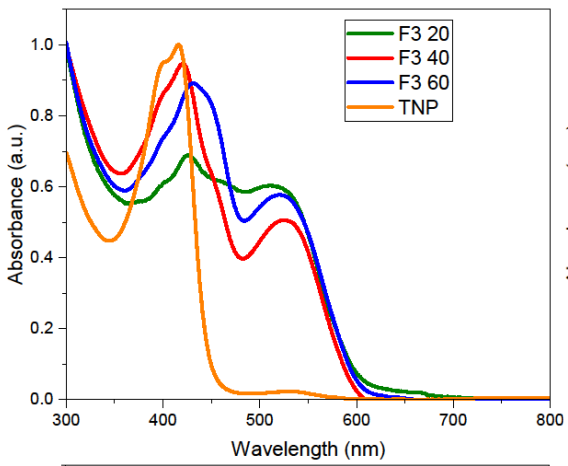
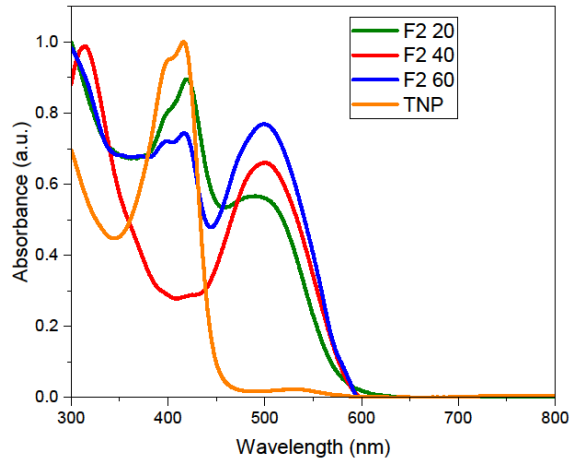
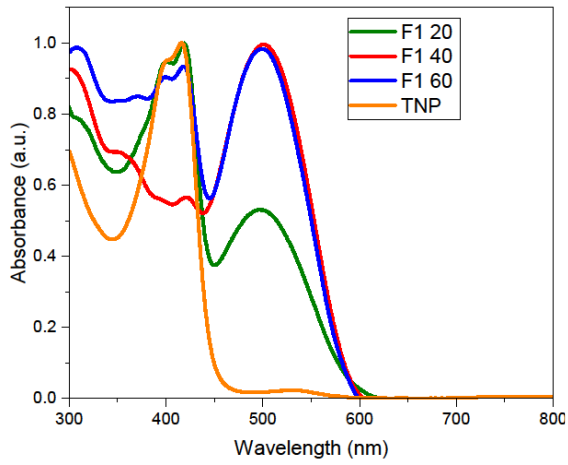
## Optical properties

The UV-Vis spectra of the samples were recorded. For all the fractions, pronounced absorption is observed at around 300 nm, 400 nm and 500 nm. For a given fractions, the absorption spectra are fairly similar even when the duration of the synthesis varies. The F5 absorption spectra extend to slightly longer wavelength. Around 400 nm and 500 nm, significant absorption bands are observed. The absorption spectra of the fractions exhibit close shapes with the TNP absorption spectrum, in particular around 400 nm. It contrasts with the expected large UV-Vis absorption for carbon dots and rather suggests to some kind of molecular fluorophores derived from trinitropropane. Emission spectra was also recorded. From F1 to F4, brightly luminescence can be observed under 365 nm UV, lamp. Luminescence slightly less intense. The fractions display similar emission around 600 nm. From F<sub>1</sub> to F<sub>5</sub>, the maximum wavelength emission seems to shift slightly to the shorter wavelength, 618 nm for F<sub>1</sub> to around 580, close to the TNP maximum wavelength emission spectrum.

## S.I.H/ Ultraviolet-visible spectroscopy

Figure S.I.H/1 UV-visible absorbance spectra of TNP and the fractions obtained for durations of 20 and 40 minutes of solvothermal treatment

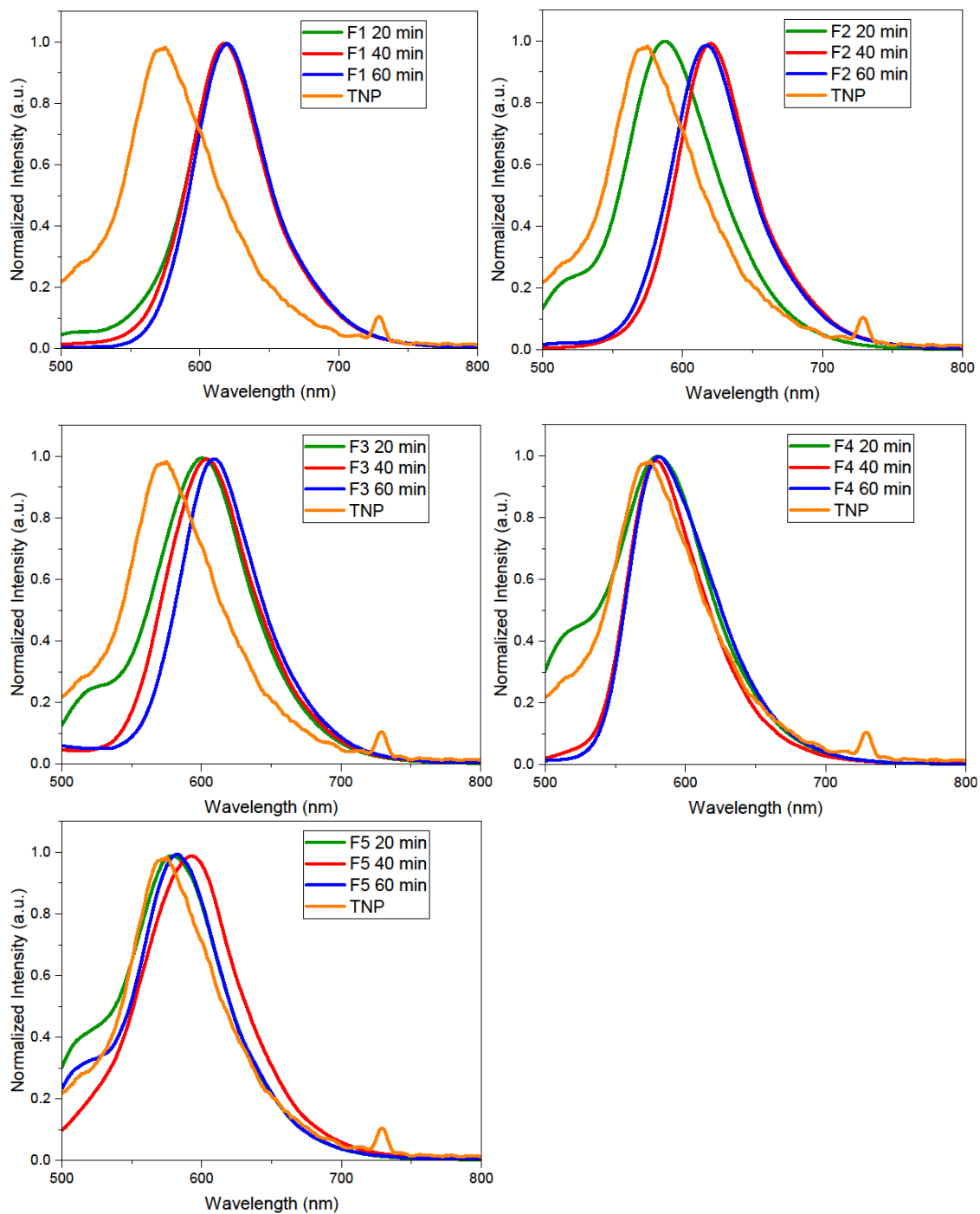


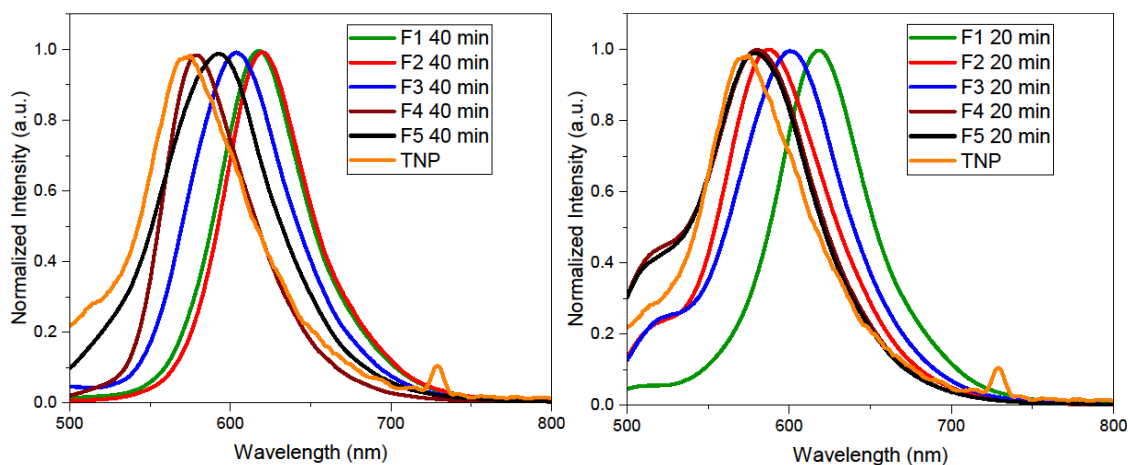


## S.I.J/ Fluorescence spectroscopy

**Figure S.I.J/1** Fluorescence spectra of the fractions for durations of 20, 40 and 60 minutes of solvothermal treatment

The small peak around 730 nm for the TNP emission spectra is due to 2<sup>nd</sup> order diffraction but doesn't change the overall fluorescence of the TNP spectra.





**Table S.I.K/ Main structural information on the fractions F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub> and F<sub>5</sub> obtained for a 60 min microwave-assisted solvothermal treatment of TNP in DMF**

		F1	F2	F3	F4	F5
<b>Techniques</b>	<b>XRD</b>	7.47°, 9.52°, 10.3°, 15.1° smaller peaks at 8.29°, 12.4° - rather crystalline phase	7.47°, 10°, 14.5°, 14.8° smaller peaks at 19.9°, 20.8°, 12.4° - rather crystalline phase	A few sharp peaks at low 2θ values and low intensity underlying large peaks around 10° and 20°	8.6°, 10.6°, 14.65°, 22.65°, 25.1°, 17.35°, smaller peaks at 11.26°, 12.45°, 19.63°, 21.69° - rather crystalline phase	Large peak at around 10° and 20°, rather amorphous phase
	<b>SEM</b>	Stacked thread-like structure of various size (μm size) and diameter	Rods structures of odd length (μm size)	Irregular sheets and sphere-shaped pieces	No distinct morphology	No distinct morphology
	<b>FTIR spectroscopy</b>	Peaks around 1516 cm <sup>-1</sup> and 1346 cm <sup>-1</sup> attributed to the asymmetric and symmetric stretching of the NO <sub>2</sub> bond, sp <sup>3</sup> C-H stretching (3100 cm <sup>-1</sup> ), C-H stretching (2920 cm <sup>-1</sup> ), C=C stretching (1590 cm <sup>-1</sup> ) and NO <sub>2</sub> shearing (860 cm <sup>-1</sup> )				
	<b>Raman spectroscopy</b>	1590 cm <sup>-1</sup> and 1279 cm <sup>-1</sup> can be attributed to NO <sub>2</sub> asymmetric stretching and symmetric stretching, 1000-1300 cm <sup>-1</sup> are associated to CH in-plane bending vibrations.				

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