

# **Fast and efficient direct formation of size-controlled nanostructures of coordination polymers based on copper(I)-iodine bearing functional pyridine terminal ligands**

Javier Conesa-Egea, Khaled Hassanein, Marta Muñoz, Félix Zamora,\* Pilar Amo-Ochoa\*

## **Supporting Information**

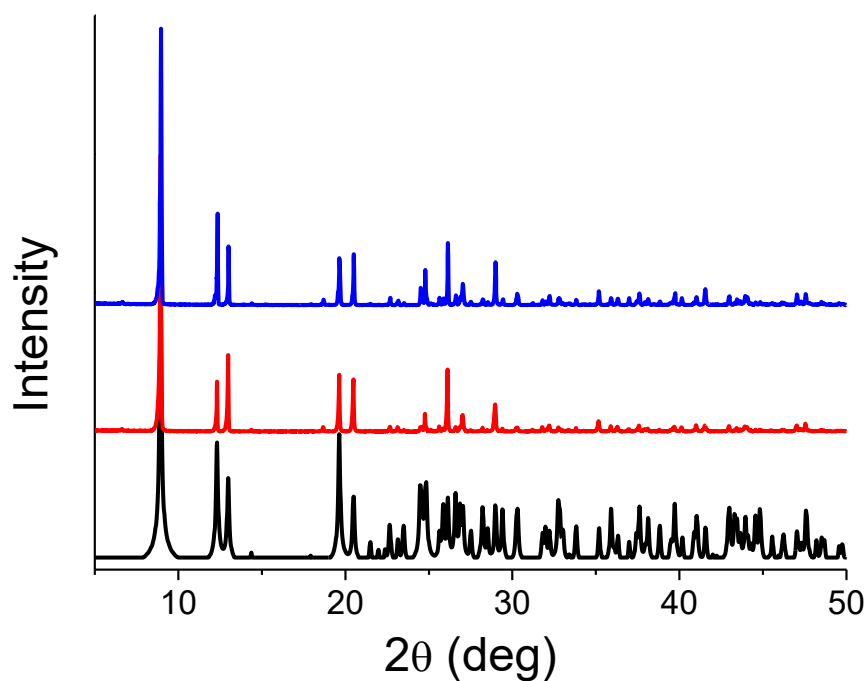
**S1. Structural characterization of 1n and 2n.**

**S2. Morphological Studies.**

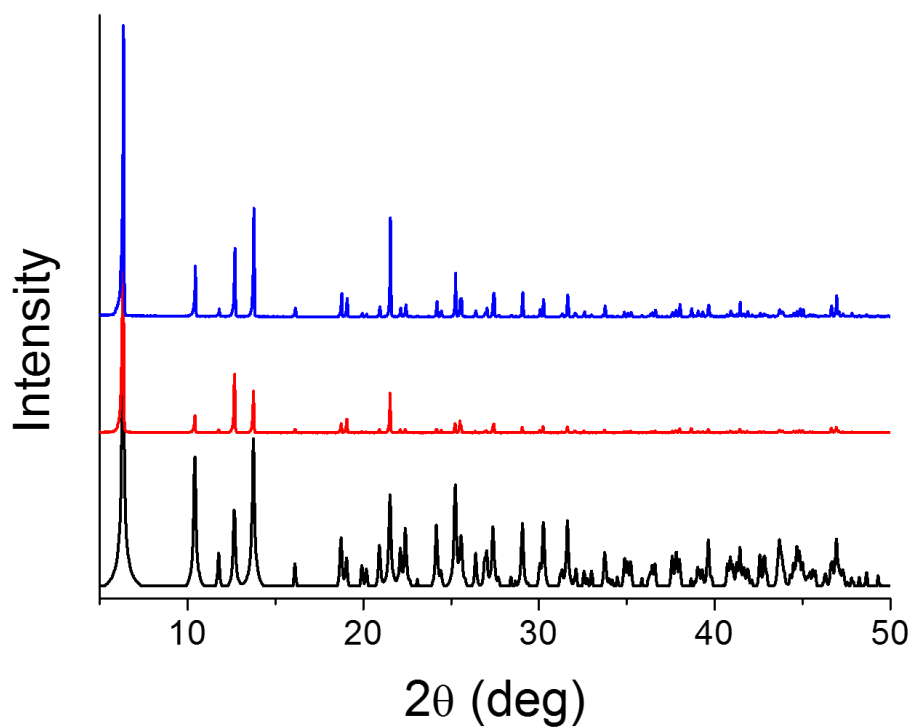
**S2.1 Morphological Studies of 1n and 2n versus time, magnetic stirring and ultrasounds.**

**S2.2 Stability Studies of 1n and 2n versus time.**

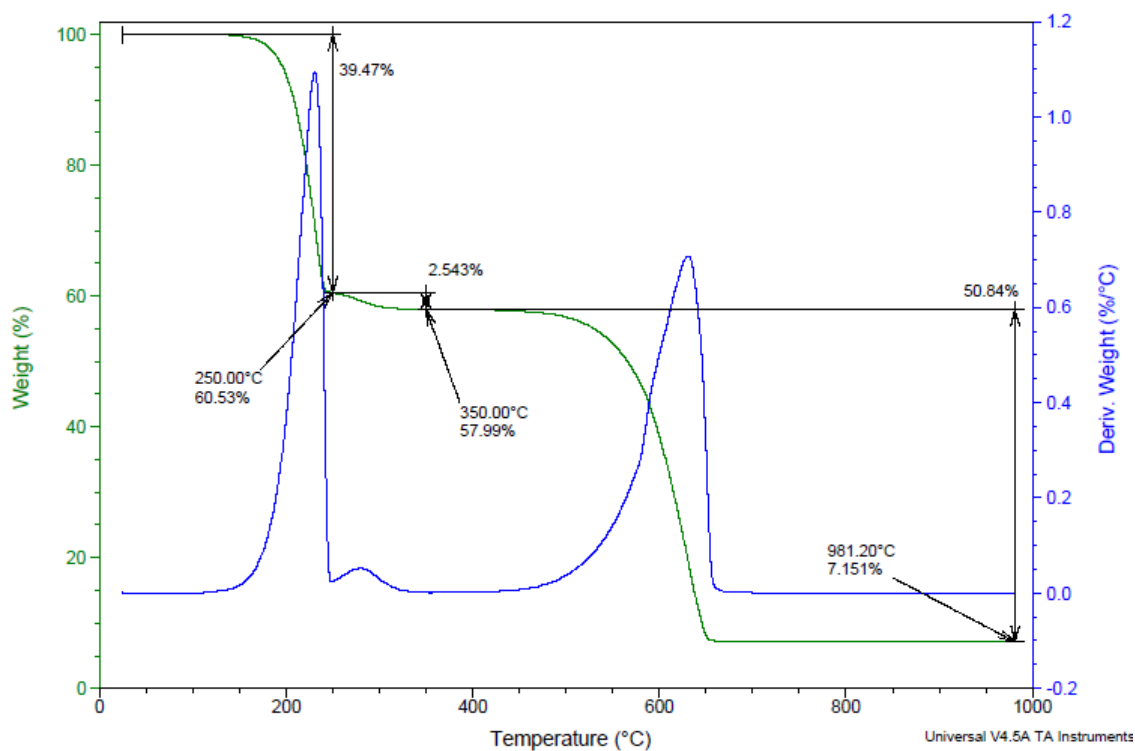
**S1. Structural characterization of 1n and 2n.**



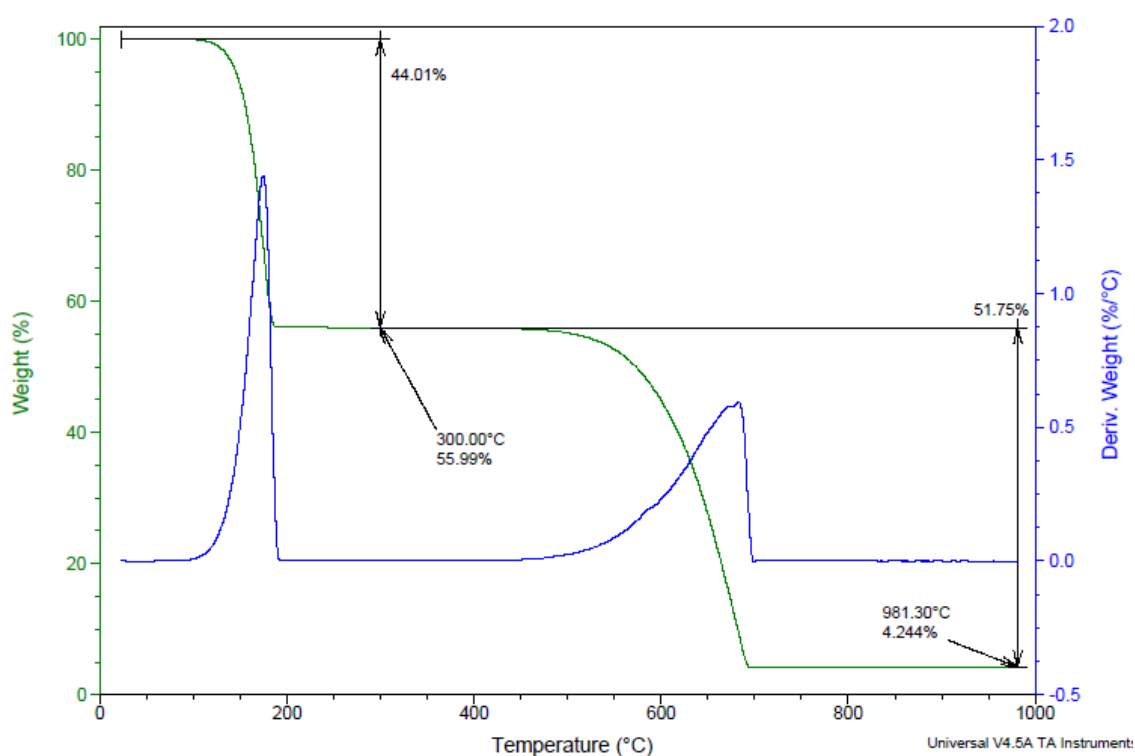
**Figure S1.** Powder X-ray diffractograms of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$ : microcrystals (black), nanofibers prepared by magnetic stirring at 500 rpm (red) and by sonication in ultrasound bath (37 kHz, 380 W, 9 min) (blue).



**Figure S2.** Powder X-ray diffractograms of  $[\text{Cu}(\mu_3\text{-I})(\text{EtIN})]_n$ : microcrystals (black), nanoribbons prepared by magnetic stirring at 500 rpm (red) and by sonication in ultrasound bath (37 kHz, 380 W, 1 min) (blue).



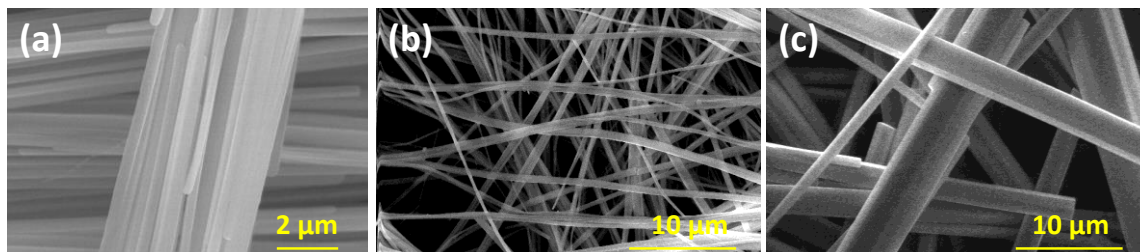
**Figure S3.** Thermogravimetric analysis of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers.



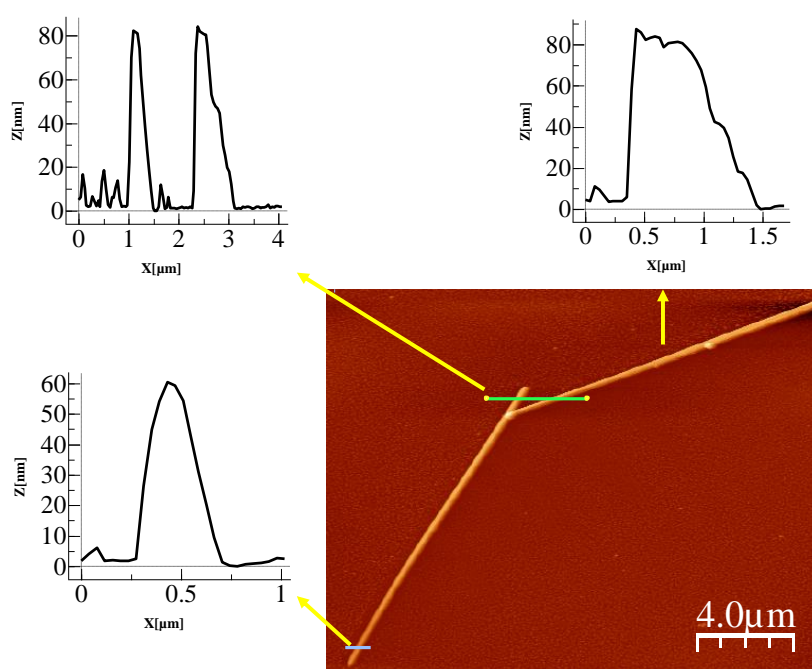
**Figure S4.** Thermogravimetric analysis of  $[\text{Cu}(\mu_3\text{-I})(\text{EtIN})]_n$  nanoribbons. Both compounds, in micro<sup>1, 2</sup> and nanoscale as well, decompose following the same mechanism: from about 85 °C to 300 °C, the ligand is lost. The second weight loss, which occurs from 400 °C to 700 °C, corresponds to iodine and some copper volatile compounds.

## S2. Morphological Studies.

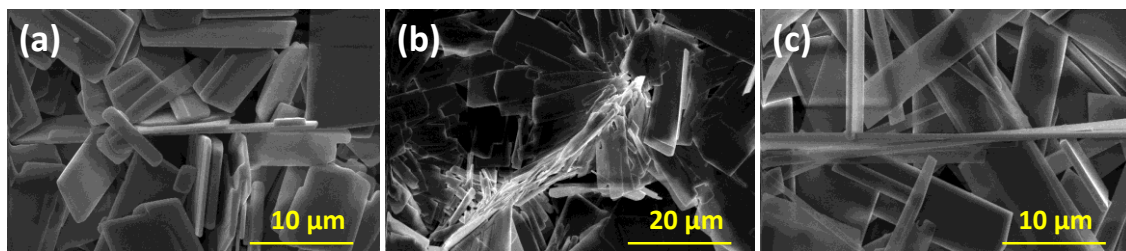
### S2.1 Morphological Studies of 1n and 2n versus time, solvent, magnetic stirring and ultrasounds.



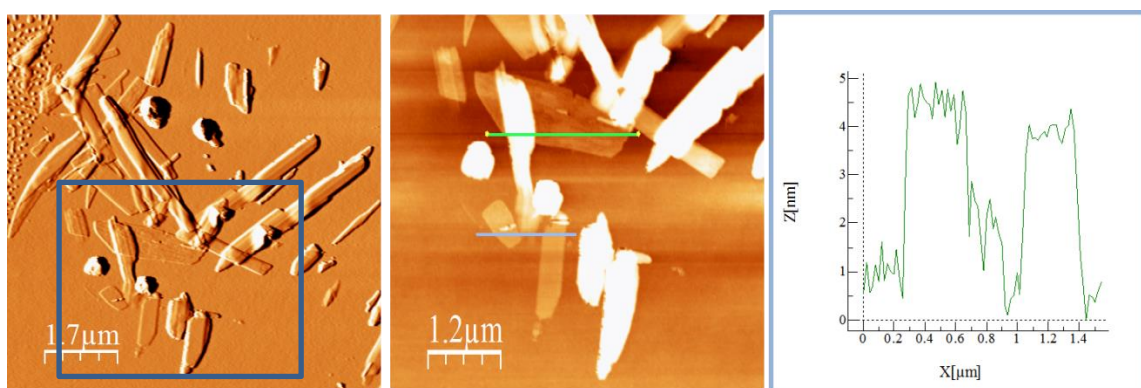
**Figure S5.** (a) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers obtained after 1 minute of magnetic stirring (500 rpm) of a 35 mM mixture of copper(I) iodide and ANP. (b) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers obtained after 9 minutes of magnetic stirring (500 rpm) of a 35 mM mixture of these reactants. (c) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers obtained after 9 minutes of sonication in an ultrasound bath (Elma, 37 kHz, 380 W) of a 70 mM mixture of these reactants.



**Figure S6.** AFM images of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers obtained after 1 minute of magnetic stirring (500 rpm) of a 35 mM mixture of copper(I) iodide and 2-amino-5-nitropyridine.



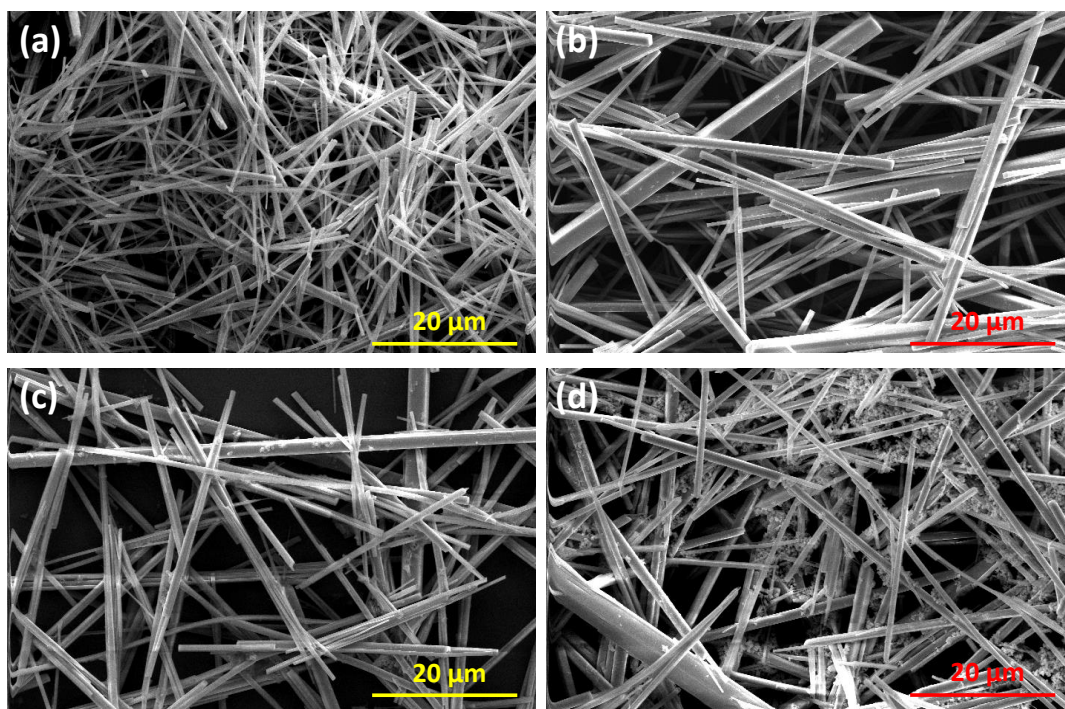
**Figure S7.** (a) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{EtIN})]_n$  nanofibers obtained after 1 minute of magnetic stirring (500 rpm) of a 35 mM mixture of copper(I) iodide and ethyl isonicotinate. (b) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{EtIN})]_n$  nanofibers obtained after 1 minute of magnetic stirring (500 rpm) of a 70 mM mixture of these reactants. (c) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{EtIN})]_n$  nanofibers obtained after 1 minute of sonication in an ultrasound bath (Elma, 37 kHz, 380 W) of a 70 mM mixture of these reactants.



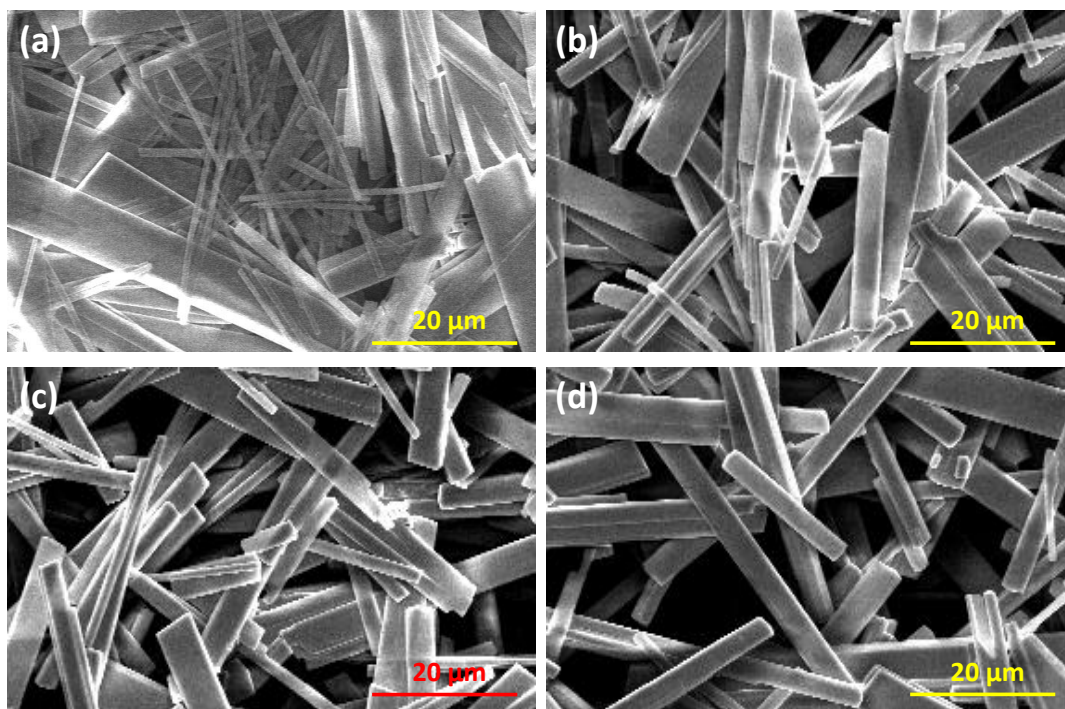
**Figure S8.** AFM images of  $[\text{Cu}(\mu_3\text{-I})(\text{EtIN})]_n$  nanoribbons obtained after 1 minute of magnetic stirring (500 rpm) of a 70 mM mixture of copper(I) iodide and ethyl isonicotinate.



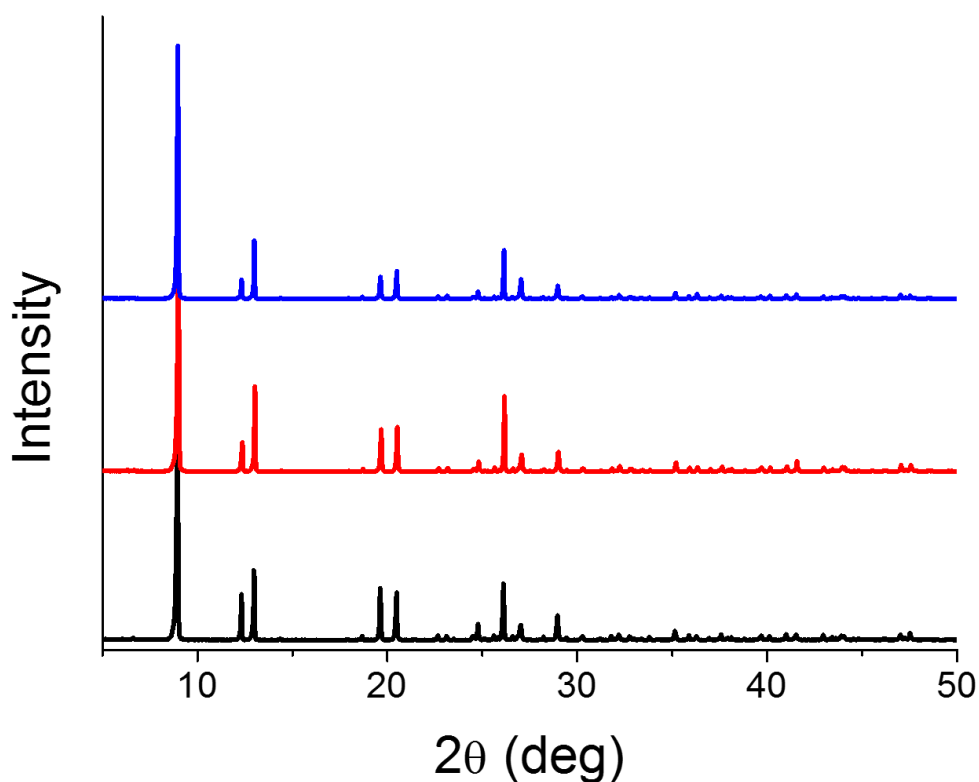
## S2.2 Stability Studies of 1n and 2n versus time.



**Figure S9.** FESEM images of freshly prepared nanofibers of compound **1n** sample (a) and after 1 day (b), 2 days (c) and 7 days (d).

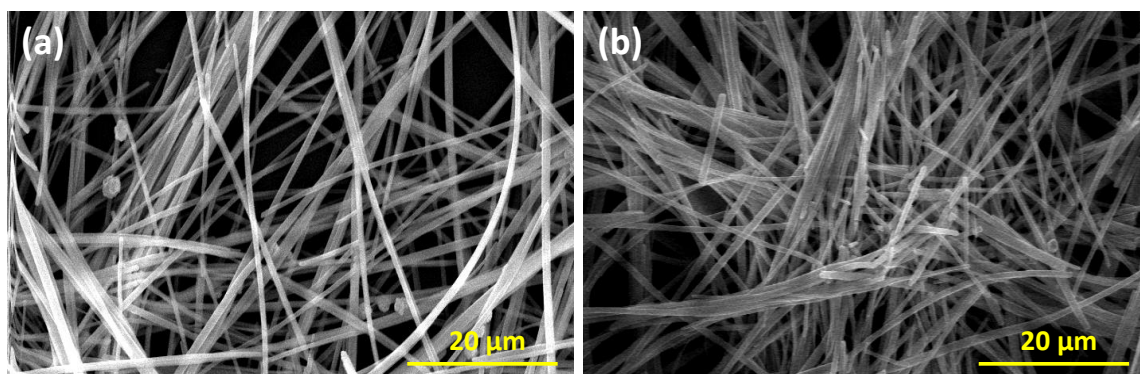


**Figure S10.** FESEM images of freshly prepared sub-microribbons of compound **2n** sample (a) and after 1 day (b), 2 days (c) and 7 days (d).

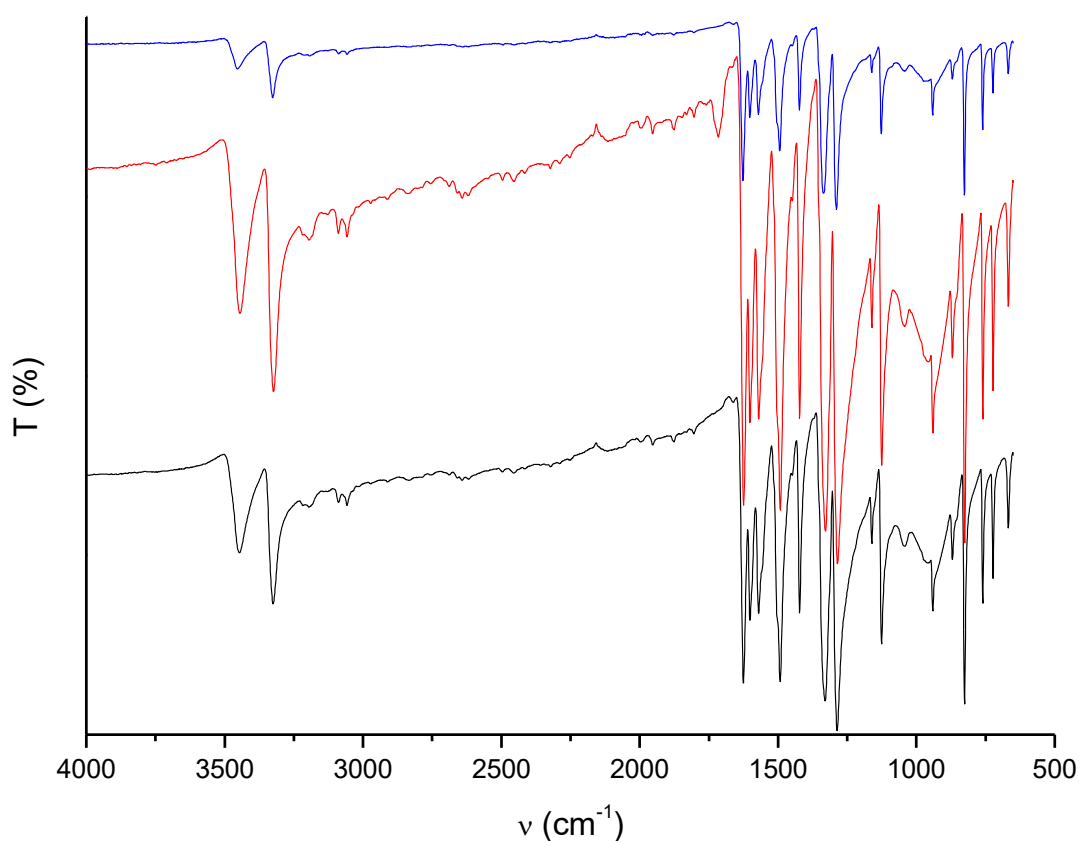


**Figure S11.** Powder X-ray diffractograms of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers pristine (black), exposed to acetic acid vapours for 72 hours (red) and exposed to acetic acid vapours for 72 hours and heated at 50 °C for 2 hours (blue).

To check whether the electrical response of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  is due to a change in the fibre morphology and size, three samples of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  were prepared and deposited on  $\text{SiO}_2$  substrates; each sample was placed inside a vial with methanol, ethanol or acetic acid, respectively, and left to adsorb the solvent vapours for 72 hours. After that, the samples were studied by SEM. The samples exposed to ethanol and methanol, with mean dimensions of  $(369 \pm 113)$  nm and  $(392 \pm 187)$  nm respectively, show no significant changes from the original samples (**Figure S12**).



**Figure S12.** (a) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers after being exposed to EtOH vapours for 72 hours. (b) SEM image of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers after being exposed to MeOH vapours for 72 hours.



**Figure S13.** IR spectra (ATR) of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers: pristine (black), exposed to acetic acid vapours for 72 hours (red) and exposed to acetic acid vapours for 72 hours and heated at 50 °C for 2 hours (blue).

**Table S1.** Elemental analysis of  $[\text{Cu}(\mu_3\text{-I})(\text{ANP})]_n$  nanofibers after exposition to acetic acid vapours for 72 hours:

%	% Experimental	% calculated for $[\text{Cu}(\text{ANP})\text{I}]_n$	% calculated for $[\text{Cu}(\text{ANP})\text{I}]_n \times 0.1\text{AcOH}$
C	18.36	18.22	18.31
H	1.7	1.52	1.62
N	12.68	12.75	12.52

## References

1. P. Amo-Ochoa, K. Hassanein, C. J. Gomez-Garcia, S. Benmansour, J. Perles, O. Castillo, J. I. Martinez, P. Ocon and F. Zamora, *Chem. Commun.*, 2015, **51**, 14306-14309.
2. K. Hassanein, J. Conesa-Egea, S. Delgado, O. Castillo, S. Benmansour, J. I. Martinez, G. Abellan, C. J. Gomez-Garcia, F. Zamora and P. Arno-Ochoea, *Chem. Eur. J.*, 2015, **21**, 17282-17292.