Esta es la versión de autor del artículo publicado en:
This is an author produced version of a paper published in:

Dalton Transactions 47.16 (2018): 5607-5613

DOI: https://doi.org/10.1039/C8DT00083B

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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

We report on the direct formation of 1D nanostructures of two coordination polymers based on copper(I)-iodine double chains decorated with ethyl isonicotinate or 2-amino-5-nitropyridine as terminal ligands. The use of different reaction conditions, e.g. energy of the formation process, solvents, and/or concentration of reactants, have allowed to control the size of the fibres and ribbons directly formed in this process going from micron- to submicron- up to nano-size. We show experiments that direct the formation of materials kinetically versus thermodinamically controlled, adjusting simple experimental parameters. Finally, a morphological study on the Cu(I)-iodine bearing 2-amino-5-nitropyridine nanofibres has confirmed their reversible molecular recognition ability towards acetic acid vapours.

Introduction

Coordination polymers (CPs) encompass a large family of compounds, formed by central metal ions and ligands linked by coordination bonds. Depending on the selected building blocks, CPs give rise to mono, bi or three-dimensional structures. Additionally, the mono- and bi-dimensional structures can extend their networks using supramolecular interactions such as hydrogen bonds or weak interactions such as Van der Waals forces. The building blocks are also determining for the physical and chemical properties of the CPs, suitable combinations give rise to multifunctional or even stimuli response materials.1-3 Thus, CPs decorated with specific organic ligands functionalized with donor-acceptor H-bond groups can incorporate molecular recognition capabilities, hence their potential sensing applications.4,6 Additionally, these functional organic ligands with intrinsic self-assembly capabilities will direct the three-dimensional network and function of CPs, since new intermolecular hydrogen bonds involving the CPs and/or with other molecules will be established. This new scenery is also promising to define novel sensors based on CPs.7 However, the number of CPs decorated with donor-acceptor groups is still scarce.8-11,12-15 Additionally, in this context the study of the materials at the nanoscale increases their potential applications, for instance, giving the possibility to fabricate ultrasensitive sensors based on CP nanostructures. Indeed, this is an interesting aspect towards the use of materials as biological sensors. Therefore, the development of methods for controlling the CP size is a key prerequisite to gain access to a plethora of interesting properties and size-dependent phenomena inherent to CP nanomaterials. In this regard, CPs seem to have, among other interesting advantages, an intrinsic facility to be nanoprocessed, based on the reversible nature of the constituent bonds, coordination bonds.16-20 Thus, in the last years, several CP nanostructures have been obtained using different strategies such as fast-precipitation, interfacial synthesis, hydro-solvothermal, microemulsions or liquid phase exfoliation.21 It is worth mentioning that a small change in the concentration of the reactants, or the addition of a poor solvent to the reaction medium, is sometimes enough to produce a significant change in the size of the final material going from the micron- to the nano-scale. Thus, for instance, in some cases the high insolubility in the reaction medium of the CPs gives rise to their fast precipitation as nanocrystals. However, there are not many studies taking advantage of the facility to create CP nanostructures using these bottom-up
approaches and/or analysing their properties at the nanoscale.22
Here we report on an easy, low cost and fast procedure to reduce the size from micron- to sub-micron and to the nano-
scale of two different CPs based on copper(I)-iodine double
chains bearing either ethyl isonicotinate (EtIN), which presents
optical properties,23 or 2-amino-5-nitropyridine (ANP), a
terminal ligand with molecular recognition capabilities.6, 24 The
syntheses of these two CPs have been optimized varying
different experimental parameters (reaction time, solvents,
reactant concentration...) to produce nanostructures with
control in the size and shape, so as to find the optimal
conditions at which de size reduction is greatest. Finally, a
study of the morphological changes induced by the presence
of acetic acid vapours in the copper(I)-iodine double

Results and discussion
Slow evaporation, between three days and a week, at room
temperature of the mother liquor obtained from the direct
reaction between CuI and EtIN or ANP in acetonitrile, gives rise
to the formation of microcrystals of both [Cu(µ-I)(ANP)]n
(1m) (ANP= 2-amino-5-nitropyridine) with dimensions of 22 ± 12 µm
width and 1.0 ± 0.5 mm length, and of [Cu(µ-I)(EtIN)]n (2m)
(EtIN= ethyl isonicotinate) of 61 ± 15 µm width and 1.7 ± 0.4
mm length. Powder X-ray diffraction (PXRD) analysis of
1m and
2m confirm that both materials show the structures already
reported for single crystals of [Cu(µ-I)(ANP)]n and [Cu(µ-I
)(EtIN)]n,23 which consist of 1D-CPs with the copper(I) centre
in a tetrahedral environment coordinated to the iminic
nitrogen of ANP or EtIN terminal ligands and to three bridging
iodides giving rise to CuI2 double chains (Figure 1a and 2a).
In case of [Cu(µ-I)(ANP)]n, the H-bonding acceptor character of
the nitro-substituent of the 2-amino-5-nitropyridine ligand
plays an important role in its supramolecular structure
allowing the assembly of adjacent chains by formation of
hydrogen bonds between the NH2 donor groups and NO2
acceptor groups of the neighbouring chains,25 while the ethoxy
group of ethyl-isonicotinate ligand in [Cu(µ-I)(EtIN)]n
precludes a suitable approach of the chains then avoiding the
formation of hydrogen interchains bonds.23
To have control over size and shape, a rational study of the
reaction parameters such as procedure of reactants
combination (magnetic stirring vs ultrasound), reaction time,
solvents and concentration of reactants has been carried out.

Nanostructure preparation and characterization
The preparation of nanostructures of [Cu(µ-I)(ANP)]n, (1n)
and [Cu(µ-I)(EtIN)]n, (2n) is achieved in a one-pot synthesis. Thus,
1n and 2n are obtained from a solution of the reactants in
acetonitrile-ethanol 2:1 and just acetonitrile, respectively,
within a minute. PXRD and thermogravimetric analysis confirm
that both 1n and 2n correspond to the structures reported for
their single crystals (Figures S1-S4).

The large differences found in the size of 1n and 2n with their
respective microcrystals have been confirmed by AFM and
SEM images (Figures 1b-d and 2b-d). The low magnification of
AFM and SEM images reveals that the precipitates consist of a
quantity of uniform and well dispersed 1D nanostructures
(Figures S5-S8). Thus, SEM images of 1n show a nanofibrillar
structure with lengths longer than 100 µm and widths in the
range 0.348 ± 0.175 µm, while 2n consists of nanoribbons with
dimensions 60 ± 28 µm in length and 3 ± 2 µm in width. The
morphology was confirmed by AFM which allows determining
the heights of both 1n, in the range 50-250 nm, and 2n, in the
range 6-25 nm.

Influence of ultrasound, reaction time and solvent
concentration mediated synthesis over the [Cu(µ-I)(ANP)]n and
[Cu(µ-I)(EtIN)]n nano fibres and nanoribbons morphology and
size.
Table 1 collects the results obtained using different reaction
conditions. Starting with magnetically stirring variations in the
reaction time do not favour aggregation in 1n, but 2n is slightly
broadened (Figures S5 and S7, Table 1 experiments b1, c1
and b2). Additionally, the variation in the reactants
concentration shows that an increase of concentrations
produces a slight increase in the fibres width in 1n, but no
changes in 2n (Table 1 experiments b1, c1, b2 and c2).
Although it has been described that high reactant
concentration leads to high supersaturation, which results in a
faster nucleation rate and thereby smaller particles; high
 supersaturation also speeds up agglomeration promoting
production of bigger particles This enhancement in the width
of 1n can indicates that agglomeration prevails over nucleation
at high reactant concentrations.26 This aggregation is favoured
in CP 1n due to its possibility to form intermolecular H-bonds.
Table 1. Effect of the reaction time, concentration, solvent and stirring method in the widths of [Cu(μ3-I)(ANP)]n, (1) nanofibres and [Cu(μ3-I)(EtIN)]n, (2) nanoribbons at 20 °C for magnetic stirring and between 20 and 30 °C for ultrasound bath.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>reaction method</th>
<th>Solvent</th>
<th>Reaction Time (min.)</th>
<th>[Cu] and [ANP] or [EtIN] mM</th>
<th>Mean fibre width (µm)</th>
<th>Mean fibre length (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>Magnetic stirring</td>
<td>CH₃CN/EtOH</td>
<td>1</td>
<td>35</td>
<td>0.3 ± 0.2</td>
<td>&gt;100</td>
</tr>
<tr>
<td>b1</td>
<td>Magnetic stirring</td>
<td>CH₃CN/EtOH</td>
<td>9</td>
<td>35</td>
<td>0.3 ± 0.1</td>
<td>&gt;100</td>
</tr>
<tr>
<td>c1</td>
<td>Magnetic stirring</td>
<td>CH₃CN/EtOH</td>
<td>9</td>
<td>70</td>
<td>0.5 ± 0.1</td>
<td>&gt;100</td>
</tr>
<tr>
<td>d1</td>
<td>Ultrasound bath</td>
<td>CH₃CN/EtOH</td>
<td>1</td>
<td>35</td>
<td>0.3 ± 0.2</td>
<td>&gt;100</td>
</tr>
<tr>
<td>e1</td>
<td>Ultrasound bath</td>
<td>CH₃CN/EtOH</td>
<td>9</td>
<td>35</td>
<td>1.3 ± 0.7</td>
<td>&gt;100</td>
</tr>
<tr>
<td>f1</td>
<td>Ultrasound bath</td>
<td>CH₃CN/EtOH</td>
<td>9</td>
<td>70</td>
<td>2 ± 1</td>
<td>&gt;100</td>
</tr>
<tr>
<td>g1</td>
<td>Ultrasound bath</td>
<td>CH₃CN/H₂O</td>
<td>9</td>
<td>35</td>
<td>0.6 ± 0.4</td>
<td>65 ± 28</td>
</tr>
<tr>
<td>a2</td>
<td>Magnetic stirring</td>
<td>CH₃CN</td>
<td>1</td>
<td>35</td>
<td>3 ± 2</td>
<td>60 ± 28</td>
</tr>
<tr>
<td>b2</td>
<td>Magnetic stirring</td>
<td>CH₃CN</td>
<td>9</td>
<td>35</td>
<td>7 ± 3</td>
<td>31 ± 18</td>
</tr>
<tr>
<td>c2</td>
<td>Magnetic stirring</td>
<td>CH₃CN</td>
<td>9</td>
<td>70</td>
<td>7 ± 2</td>
<td>20 ± 4</td>
</tr>
<tr>
<td>d2</td>
<td>Ultrasound bath</td>
<td>CH₃CN</td>
<td>1</td>
<td>35</td>
<td>7 ± 2</td>
<td>23 ± 5</td>
</tr>
<tr>
<td>e2</td>
<td>Ultrasound bath</td>
<td>CH₃CN</td>
<td>9</td>
<td>35</td>
<td>5 ± 3</td>
<td>46 ± 5</td>
</tr>
<tr>
<td>f2</td>
<td>Ultrasound bath</td>
<td>CH₃CN</td>
<td>9</td>
<td>70</td>
<td>9 ± 3</td>
<td>22 ± 7</td>
</tr>
<tr>
<td>g2</td>
<td>Ultrasound bath</td>
<td>CH₃CN/H₂O</td>
<td>9</td>
<td>35</td>
<td>2 ± 0.6</td>
<td>9±2</td>
</tr>
</tbody>
</table>

The means and standard deviations were calculated from values corresponding to 60 fibres (1) or ribbons (2).

Finally, the most significant change is observed in the width of 1n when ultrasound is used vs magnetic stirring for their preparation. Table 1, experiment b1 versus e1, shows a more significant enhancement which is even more prominent when higher reactants concentrations are used in agreement with our previous observations, experiment e1 versus f1 (Figure S5c). In order to rationalize this observation it has to be taken into account that ultrasound can induce supramolecular self-assembly for molecules showing donor-acceptor H-bonding sites.27, 28 Even though the process it is still not fully understood; it is suggested in the literature that sonication and time provide suitable energy to favour intramolecular H bonds speed formation.28, 29 Our experiments for 1n are in agreement with this observation. Thus, longer sonication times induce fibre aggregation probably as a consequence of a slight increase in the reaction temperature, from 20 to 30 °C, upon sonication. This produces an increase in the hydrogen bonds speed formation (Table 1, experiments a1 and e1). Moreover, saturation also speeds up agglomeration promoting production of bigger particles (experiments e1 and f1). The effect of sonication on the widths of the nanofibres in compound 1n is not observed for compound 2n. This is expected since this compound does not have the capacity to
form intermolecular hydrogen bonds and helps us confirm our theory (Table 1, experiments a2, b2, c2, d2, e2, f2).

Although the changes in the reaction parameters (ultrasound vs magnetic agitation, reaction time and concentration) did not show significant effect on the length of 1n and 2n, the use of a mixture of solvents containing water (CH₃CN:H₂O; 1:1) for these reactions produces a significant decrease in the lengths of 1n and 2n (Table 1, experiments g1 and g2). Therefore, the use of a poor solvent seems to play a central role in the fast precipitation of the CPs once they are formed in these water containing media. Indeed, size reduction using a poor solvent is well-known for nanoparticles of CP, including MOFs; however, it is little studied for CPs with one-dimensional structures.30, 31

Evolution of 1n and 2n nanostructures through time in their reaction medium

The presence of functional groups with hydrogen bonds capacity and molecular recognition capability in the \([\text{Cu}(\mu_3-I)(\text{ANP})]_n\), produces a different behaviour with the reaction time compared to that observed for the \([\text{Cu}(\mu_3-I)(\text{EtIN})]_n\) in which chains do not interact through via H-bonds. Thus, when the suspensions of 1n and 2n obtained at 500 rpm for 9 min., using concentrations of the two reagents of 35 mM in acetonitrile ethanol 2:1 (compound 1n) or just in acetonitrile, 2n, are allowed to react for a period of a week, a widening of the fibres of the 1n can be observed probably as a result of the formation of hydrogen bonds between them (Figures S9 and S10). However, compound 2n nanoribbons do not suffer significant changes in their dimensions over reaction time, as expected based on the absence of H-bond capabilities in its structure. Moreover, \([\text{Cu}(\mu_3-I)(\text{EtIN})]_n\) is more insoluble than \([\text{Cu}(\mu_3-I)(\text{ANP})]_n\) in its reaction medium, so nanoribbons with a fixed size are formed immediately.

Effect of acetic acid vapours on 1n

The flexible structure of \([\text{Cu}(\mu_3-I)(\text{ANP})]_n\) and the presence of ANP as ligand, with available donor and acceptor H-bond groups makes this CP a potential stimuli-response material. Thus, when a microcrystalline powder of \([\text{Cu}(\mu_3-I)(\text{ANP})]_n\), is immersed in glacial acetic acid, a sorption process takes place, and the crystals change from yellow to orange, becoming amorphous. Noticeable, this is a reversible change giving rise the original microcrystals upon exposition of the amorphous material to air.25 The change in the electrical conductivity of \([\text{Cu}(\mu_3-I)(\text{ANP})]_n\) upon exposition to vapours of different molecules was also studied confirming a selective recognition of those molecules showing H-bonding donor capabilities, including acetic acid.23 Moreover, the structure of \([\text{Cu}(\mu_3-I)(\text{ANP})]_n\cdot\text{CH}_3\text{COOH}\) confirmed the hydrogen bonds interactions between the NH₂ functional group of the ANP and the carboxylic group of the acetic acid.25 The ability of \([\text{Cu}(\mu_3-I)(\text{ANP})]_n\) to respond to this chemical external stimulus is attributed to the softness of the double Cu₂I₂ chains, which makes these chains very dynamic, leading to significant structural changes that translate to its electrical conductivity. Thus the ANP terminal ligand directly connected to the Cu₂I₂ chains acts as an antenna for the external chemical stimulus.
Finally, the reversibility of the acetic acid adsorption by 1n was studied. Thus 1n×HAcO was allowed to stay in air for 30 days. The SEM characterization of the new material shows lateral dimensions of 600 ± 497 nm which are slightly thinner in width than 1n×HAcO but wider than the initial 1n. IR spectrum at this state still shows the vibration assigned to the carboxylic group (Figure S13). Desorption of HAcO molecules from 1n×HAcO is fully completed upon heating at 50 °C for 2 hours. IR spectroscopy confirms the absence of carboxylic groups (Figure S13). Morphological characterization of the desorbed crystalline material shows widths of 443 ± 332 nm (Figure 3) which compares with those observed in the initial non-treated 1n fibres.

**Conclusions**

The integrity of the double-chain structures of 1 and 2 is directed by the dynamic Cu-I coordination bonds, however additional supramolecular H-bonds act packing double-chains in 1. Therefore, the aggregation to produce large nanostructures in these CPs will be dominated by the thermodynamic equilibrium of the systems while shortening of these structures will be achieved under kinetic control in the formation reaction. Additionally, in 1 the thermodynamic vs kinetic could allow a control of the width of the material. These are important considerations towards the modification of synthetic experimental parameters to gain control over the material dimensions. Indeed, we have observed that it is possible to modulate the dimensions of both materials upon slight selected changes in some experimental parameters. Thus, modification of the energetic reaction conditions in the preparation of 1 (magnetic agitation versus sonication) produces a widening under more energetic conditions when either the time (Table 1, experiment d1 vs e1) or concentration (Table 1, experiment e1 vs f1) enhance, at the time that the length is over hundreds of microns, leading to morphologies thermodynamically controlled. In the case of compound 2, thermodynamically controlled material undergoes a clear increase in the length while the width, dominated only by Van der Waals interactions, is almost unaffected. Here, at short reaction times, more energetic conditions favour the kinetic control over the thermodynamic one; at longer reaction times the thermodynamic control occurs, whereas higher reactant concentrations produce the kinetic control, due to the high insolubility of this CP (Table 1, experiment a2 vs d2, b2 vs e2 and c2 vs f2).

It is worth mentioning that in both reactions the increase in the concentration produces a fast precipitation; this induces a kinetically controlled material, therefore leading to a reduction in the length of the structures for 2. However, this also favours the formation of H-bonds, hence a thermodynamically controlled material and an increase in the width of the fibres for 1. Similar results are obtained when water, a poor solvent, is incorporated in both reactions: kinetically controlled structures are obtained leading to reduction in shortening of the structures of 1 and 2.

To sum up, by means of a simple method, in a single step at room temperature based on the high insolubility in the reaction medium of the PCs 1 and 2, we can control the dimensions of the fibres of one-dimensional coordination polymers of Cu(I) with different types of terminal ligands. The presence of organic ligands with molecular recognition capability able to form H-bonds, as in 1, is a key to create sensors for compounds with H-bonds capacity. In this context, we have showed the effect of acetic acid vapours to aggregate fibres of 1n in a reversible way. Since the selected CPs of this study show luminescent properties, they could act as sensors to detect volatile organic compounds. Additionally, their control of size could allow their integration in opto-electronic nanodevices for sensing.

We envision that studies focusing on the reduction and control of size in CPs are still necessary to gain knowledge and allow the processability of this novel materials for the construction of nanodevices. This work provides preliminary results in the nanoprocessing of two functional PCs showing that small modifications in the reaction conditions (time, agitation method, solvent, concentration of reagents, etc.) lead to significant changes in the final material dimensions.

**Experimental Section**

**Materials and Methods**

All reagents and solvents were purchased from standard chemical suppliers and used as received. IR spectra were recorded on a PerkinElmer 100 spectrophotometer using a Pike Technologies MiRacule Single Reflection Horizontal ATR Accessory from 4000-600 cm⁻¹. Elemental analysis was performed on an LECO CHNS-932 Elemental Analyzer. Powder X-ray diffraction has been collected using a Diffractometer PANalyticalX’Pert PRO θ/2θ primary monochromator and detector with fast X’Celerator. The samples have been analysed with scanning electron microscope.

**SEM samples preparation of [Cu[μ-I](ANP)]ₙ (1n).** A mixture of 0.53 mmol of copper(I) iodide dissolved in 10 mL of acetonitrile and 0.53 mmol of 2-amino-5-nitropyridine (ANP) dissolved in 5 mL of ethanol was magnetically stirred (500 rpm) at 20 °C. After 1 min., an orange suspension was formed. 20 µL of this suspension were dispersed onto freshly prepared (15 min sonicated in acetone and 15 min sonicated in 2-
proton-doped SiO$_2$ substrates and left to adsorb until the drop completely evaporated (15 min.). The samples were covered with a 10 nm-thick layer of conductive Cr to improve the resolution of the images.

**SEM samples preparation of [Cu($\mu$-I)(EtIN)$_2$]$_n$ (2n).** A mixture of 0.53 mmol of copper(I) iodide dissolved in 15 mL of acetonitrile and 0.53 mmol of ethyl isonicotinate (EtIN) was magnetically stirred (500 rpm) at 20 °C. After 1 min., a yellow suspension was formed. 20 µL of this suspension were dispersed onto freshly prepared (15 min sonicated in acetone and 15 min. sonicated in 2-propanol) glass substrates and left to adsorb until the drop completely evaporated (15 minutes). The samples were covered with a 10 nm-thick layer of conductive Cr to improve the resolution of the images.

**AFM samples preparation of [Cu($\mu$-I)(EtIN)$_2$]$_n$ (2n).** A mixture of 0.53 mmol of copper(I) iodide dissolved in 10 mL of acetonitrile and 0.53 mmol of 2-amino-5-nitropyridine (ANP) dissolved in 5 mL of ethanol was magnetically stirred (500 rpm) at 20 °C. After 1 min., an orange suspension was formed. 40 µL of this suspension were diluted with 3960 µL of bidistilled water, and 15 µL of the new suspension were drop-cast onto freshly prepared (15 min sonicated in acetone and 15 min. sonicated in 2-propanol) doped SiO$_2$ substrates. After 3 min. of adsorption, the surfaces were dried under an Argon flow.

**AFM samples preparation of [Cu($\mu$-I)(EtIN)$_2$]$_n$ (2n).** A mixture of 0.53 mmol of copper(I) iodide dissolved in 15 mL of acetonitrile and 0.53 mmol of ethyl isonicotinate (EtIN) was magnetically stirred (500 rpm) at 20 °C. After 1 min., a yellow suspension was formed. 400 µL of this suspension were diluted with 3600 µL of bidistilled water, and 15 µL of the new suspension were drop-cast onto freshly prepared (15 min sonicated in acetone and 15 min. sonicated in 2-propanol) doped SiO$_2$ substrates. After 3 minutes of adsorption, the surfaces were dried under an argon flow. Atomic Force Microscopy (AFM) images were acquired in dynamic mode using a Nanotec Electronica system operating at room temperature in ambient air conditions. For AFM measurements, Olympus cantilevers were used with a nominal force constant of 0.75 N/m and a resonance frequency of about 70 kHz. The images were processed using WSxM. The surfaces used for AFM were SiO$_2$ 300 nm thickness (IMS Company). SiO$_2$ surfaces were sonicated in ultrasound bath at 37 kHz and 380 W, for 15 min. in acetone, 15 min. in 2-propanol and then dried under an argon flow.

Synthetic procedures

**Synthesis of [Cu($\mu$-I)(ANP)$_2$]$_n$ (1n).** Orange needle-like microcrystals of this coordination polymer have been prepared following the method already described in the literature.

**Synthesis of nanostructures of [Cu($\mu$-I)(ANP)$_2$]$_n$ (1n).** Two solutions of 0.53 mmol (100 mg) of copper(I) iodide in 10 mL of acetonitrile and 0.53 mmol (73 mg) of 2-amino-5-nitropyridine (ANP) in 5 mL of ethanol were prepared at 30 °C, and then mixed with magnetic stirring at 500 rpm. Immediately, the solution turned from yellow to orange and a solid precipitate as nanocrystals after 1 min. The solid was filtered off and dried in vacuum. Yield: 62 mg, 26 % based on Cu. Elemental analysis Calcd (found) % for Cu$_2$H$_3$Cu$_2$N$_2$O$_2$: C 25.26 (25.75), N 2.84 (2.75). Selected IR data υ (cm$^{-1}$): 3323 (m), 3087 (w), 3056 (w), 1625 (s), 1601 (m), 1570 (m), 1491 (s), 1421 (m), 1329 (s), 1285 (s), 1161 (w), 1124 (m), 941 (m), 869 (w), 826 (vs), 760 (m), 723 (m), 667 (w). The homogeneity of the sample was confirmed by X-ray powder diffraction (Figure S1).

**Synthesis of nanostructures of [Cu($\mu$-I)(EtIN)$_2$]$_n$ (2n) in aqueous medium.** Two solutions of 0.53 mmol (100 mg) of copper(I) iodide in 15 mL of acetonitrile and 0.53 mmol (73 mg) of 2-amino-5-nitropyridine (ANP) in 15 mL of distilled water were prepared at 30 °C, and then mixed in an ultrasound bath (Elma, 37 kHz, 380 W). Immediately, the solution turned from yellow to orange and a solid precipitate as nanocrystals after 1 min. After 9 minutes, the solid was filtered off and dried in vacuum. Yield: 137 mg, 58 % based on Cu. Elemental analysis Calcd (found) % for Cu$_2$H$_3$Cu$_2$N$_2$O$_2$: C 25.26 (25.75), N 2.84 (2.75). Selected IR data υ (cm$^{-1}$): 3323 (m), 3087 (w), 3056 (w), 1625 (s), 1601 (m), 1570 (m), 1491 (s), 1421 (m), 1329 (s), 1285 (s), 1161 (w), 1124 (m), 941 (m), 869 (w), 826 (vs), 760 (m), 723 (m), 667 (w). The homogeneity of the sample was confirmed by X-ray powder diffraction (Figure S1).

**Synthesis of nanostructures of [Cu($\mu$-I)(EtIN)$_2$]$_n$ (2n).** Yellow needle-like microcrystals were obtained following the method described in the literature. To a 15 mL of an acetonitrile solution of copper(I) iodide, 0.53 mmol (100 mg), 0.53 mmol (80 µL) of ethyl-isonicotinate (EtIN) were added and magnetically stirred at 500 rpm. Immediately, a yellow solid was formed. The solid was filtered off and dried in vacuum. Yield: 110 mg, 61 % based on Cu. Elemental analysis Calcd (found) % for Cu$_2$H$_3$Cu$_2$N$_2$O$_2$: C 25.26 (25.75), N 2.84 (2.75). Selected IR data υ (cm$^{-1}$): 3444 (m), 3323 (m), 3087 (w), 3056 (w), 1625 (s), 1601 (m), 1570 (m), 1491 (s), 1421 (m), 1329 (s), 1285 (s), 1161 (w), 1124 (m), 941 (m), 869 (w), 826 (vs), 760 (m), 723 (m), 667 (w). The homogeneity of the sample was confirmed by X-ray powder diffraction (Figure S2).

**Synthesis of nanostructures of [Cu($\mu$-I)(EtIN)$_2$]$_n$ (2n) in aqueous medium.** To a 15 mL of an acetonitrile solution of copper(I) iodide, 0.53 mmol (100 mg), 0.53 mmol (80 µL) of ethyl-isonicotinate (EtIN) were added and magnetically stirred at 500 rpm. Immediately, a yellow solid was formed. The solid was filtered off and dried in vacuum. Yield: 110 mg, 61 % based on Cu. Elemental analysis Calcd (found) % for Cu$_2$H$_3$Cu$_2$N$_2$O$_2$: C 25.26 (25.75), N 2.84 (2.75). Selected IR data υ (cm$^{-1}$): 3444 (m), 3323 (m), 3087 (w), 3056 (w), 1625 (s), 1601 (m), 1570 (m), 1491 (s), 1421 (m), 1329 (s), 1285 (s), 1161 (w), 1124 (m), 941 (m), 869 (w), 826 (vs), 760 (m), 723 (m), 667 (w). The homogeneity of the sample was confirmed by X-ray powder diffraction (Figure S2).
Conflicts of interest
There are no conflicts to declare”.

Acknowledgements
We thank financial support from the Spanish Ministerio de Economía y Competitividad (MAT2013-46502-C2-2P, BES-2015-071534). Also to the scientific computing center (CCC) of the Autónoma University of Madrid for their time.

Notes and references