

## COMMUNICATION

## Efficient and environmentally friendly electrochemical synthesis of the metallacalixarene [Cu(1,3-bdc)·DMF]·2H<sub>2</sub>O†

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**A two-dimensional metallacalixarene-type coordination polymer [Cu(1,3-bdc)·DMF]·2H<sub>2</sub>O was synthesised by an electrochemical method for the first time. This method provided the expected phase within 8 minutes in a high yield, whereas the slow diffusion of reactants in an organic solvent produced the desired product in a small quantity only after 6 months.**

In the past two decades, the interest in coordination polymers and their potential applications is growing at an exponential rate, which is reflected in the number of new structures deposited in the CCDC, which is actually around 37 241. One of the class of coordination polymers are metallacalixarenes, structures resulting from the self-assembly of the organic aromatic ligands having two coordination sites forming an angle of 120° (as in the structure of 1,3-bdc) and the metal entity (Secondary Building Unit, SBU) of square-planar geometry.<sup>1</sup> Their calixarene-like cavity structure is responsible for hosting neutral molecules such as solvents and gases. Moreover, metallacalixarenes possess magnetic, optical and catalytic properties thanks to the metal ion present in their structure.<sup>1</sup> The presence of the coordinatively unsaturated metal centers in the structure of metallacalixarenes is very attractive for enhancing hydrogen adsorption capacity.

Recently, many research efforts have been focused on optimising the synthetic conditions leading to the formation of the desired pure-phase product.<sup>2</sup> The difficulty lies in the great number of factors that affect the structure of the final product, such as time and temperature of reaction, pH, the

ligand to metal ratio, the nature of the counterion, the type of solvent, *etc.*<sup>3</sup> Typically, coordination polymers can be synthesised by hydrothermal or solvothermal methods or by the slow diffusion at room temperature of solutions containing metal salts and organic ligands. However, those methods, in addition to providing products in a small yield, they are relatively slow and the crystallisation process requires from days up to a few months.<sup>4</sup> Although some successful microwave-assisted syntheses of coordination polymers have been reported, high reaction temperature and pressure are still needed.<sup>5,6</sup>

A few reports may be found concerning an electrochemical synthesis of coordination polymers.<sup>7,8</sup> The main advantages of this synthetic route over the conventional methods are reducing the time to several minutes, no need to use metal salts as the source of cations, mild conditions of synthesis, large-scale production and high yields.

So far, only the conventional hydrothermal and slow diffusion methods, requiring from 3 days up to 6 months, have been applied for preparation of metallacalixarenes.<sup>9–11</sup> In this communication, we present for the first time, an electrochemical synthesis of copper metallacalixarene [Cu(1,3-bdc)·DMF]·2H<sub>2</sub>O, which was obtained in a very short time.

The synthesis was performed in the electrochemical cell, in which 6.02 mmol of 1,3-H<sub>2</sub>bdc (1 g) was dissolved in 40 ml of DMF and then the supporting electrolyte (0.1 M NaNO<sub>3</sub>) in 40 ml of distilled water was added. After the complete dissolution, two copper electrodes were immersed into the electrochemical cell and the reaction was kept at room temperature under stirring and constant current for 8 min to complete the reaction. The resultant blue powder of [Cu(1,3-bdc)·DMF]·2H<sub>2</sub>O (1.271 g – 92%, based on isophthalic acid) was collected by filtration, washed with DMF and distilled water and dried on air.

IR (KBr pellet,  $\nu/\text{cm}^{-1}$ ): 3435 (br), 2924 (w), 1630 (vs), 1385 (vs), 734 (w), 489 (w).

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Elemental analysis: found: C, 38.97%; H, 4.60%; N, 3.88. Calc. for  $[\text{Cu}(1,3\text{-bdc})\cdot\text{DMF}]\cdot 2\text{H}_2\text{O}$ : C, 39.20%; H, 4.45%; N, 4.16%.

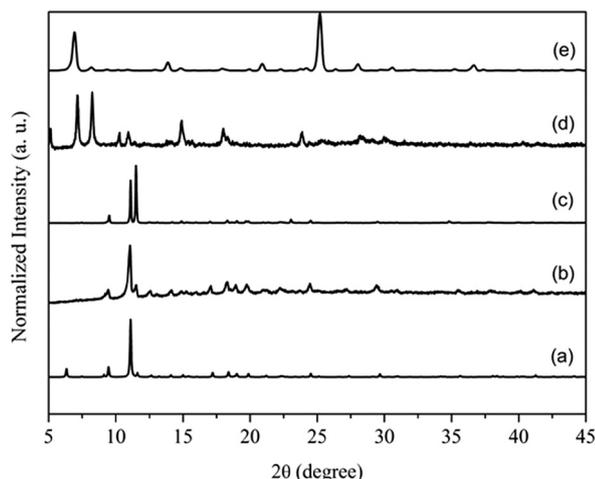
Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. The morphology of the samples was verified using a scanning electron microscope Model: XL-30 – ESEM Phillips and a 20 kV electron beam. Thermogravimetric analyses (TGA) were performed on a Shimadzu DTG-60H thermal analysis system in a continuous nitrogen flow atmosphere. Elemental analysis was performed on CE Instruments CHNS-O EA 1110. FT-IR spectra were obtained by using a Bruker spectrometer (model IFS66) and KBr pellets.

The electrochemical synthesis led to the formation of the desired product within 8 minutes. The diffraction pattern of the electrochemically synthesised Cu-metallalixarene (Fig. 1b) is in good agreement with the simulated pattern obtained from the literature data (Fig. 1a).<sup>10</sup>

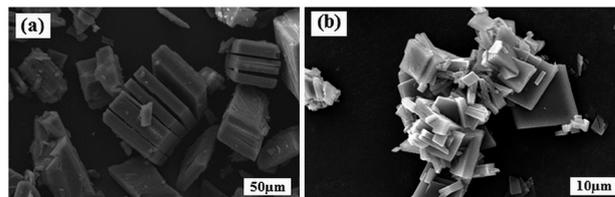
For comparison, we have tried to obtain the same structure *via* different methods such as the slow diffusion of reactants in solution at room temperature, microwave irradiation and conventional solvothermal reaction in an oven. Only the slow diffusion of reactants provided the expected product, nevertheless, the product was obtained after 6 months. Thus, there is no doubt that the electrochemical synthesis is very advantageous, since the reaction time was reduced to only a few minutes giving a pure-phase structure in a high yield (92%).

Elemental analysis indicates that there is one molecule of DMF bound to the Cu-cluster and two water molecules, which is consistent with IR results, where the broad band observed in the  $3100\text{--}3600 \text{ cm}^{-1}$  region indicates the presence of water molecules in the structure (see ESI†).

Fig. 2 presents the SEM images of the copper metallalixarene prepared by the electrochemical method and for comparison *via* slow diffusion confirming the phase purity of the samples.



**Fig. 1** XRD patterns (a) simulated from the crystallographic data structure of  $\text{Cu}_2(1,3\text{-bdc})_2(\text{DMF})(\text{DMF})\cdot\text{H}_2\text{O}\cdot(\text{EtOH})_{0.5}$ <sup>10</sup> and samples prepared *via* (b) electrochemical method at room temperature, (c) slow diffusion at room temperature, (d) microwave irradiation, and (e) conventional method in oven at  $90 \text{ }^\circ\text{C}$ .



**Fig. 2** SEM images of Cu-metallalixarene prepared *via*: (a) slow diffusion method and (b) electrochemical synthesis.

As it can be observed, the micro-crystals of  $[\text{Cu}(1,3\text{-bdc})\cdot\text{DMF}]\cdot 2\text{H}_2\text{O}$  prepared by the electrochemical synthesis have a size of  $10 \text{ }\mu\text{m}$  and are around five times smaller than those synthesised using the slow diffusion method ( $50 \text{ }\mu\text{m}$ ).

## Conclusions

In this communication, we report for the first time, the electrochemical synthesis of the 2-D coordination polymer, metallalixarene  $[\text{Cu}(1,3\text{-bdc})\cdot\text{DMF}]\cdot 2\text{H}_2\text{O}$ . Mild synthetic conditions, no need to use metal salts as the source of cations, short reaction time (8 minutes) and production of the pure-phase in a large scale, make this method extremely advantageous compared with traditional synthesis methods of coordination polymers. Such an approach to synthesise metallalixarenes and other coordination polymers is very promising and studies on optimisation of the experimental conditions are currently in progress.

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