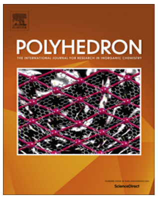
Polyhedron 115 (2016) 236–241

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



# Metal–organic frameworks based on copper(I) iodide and pyridine-3,5-dicarboxylic acid: Synthesis, crystal structures and luminescent properties

Selçuk Demir [a],*, Hamide Merve Çepni [a], Nuray Bilgin [a], Małgorzata Hołyńska [b], Fatih Yilmaz [a]

[a] *Faculty of Arts and Sciences, Department of Chemistry, Recep Tayyip Erdoğan University, 53100 Rize, Turkey*
[b] *Department of Chemistry, Philipps University Marburg, 35043 Marburg, Germany*

ARTICLE INFO

*Article history:*
Received 29 February 2016
Accepted 4 May 2016
Available online 14 May 2016

*Keywords:*
Metal–organic framework
Pyridine-3,5-dicarboxylic acid
Porosity
Luminescent
Cluster

ABSTRACT

Two metal–organic frameworks (MOFs) with pyridine-3,5-dicarboxylic acid ($H_2pdc$), $\{[Cu^{I}I][Cu^{II}(pdc)(H_2O)]\cdot 1.5MeCN\cdot H_2O\}_n$ (**1**) and $\{[Cu(MeCN)_4]\cdot 2[Cu^{I}I]\cdot 2[Cu^{II}_2(pdc)_2(H_2O)_{1.5}(OH)_{0.5}]\cdot MeCN\cdot 4AcOH\cdot 8H_2O\}_n$, (**2**) (MeCN = acetonitrile, AcOH = acetic acid), containing both $[Cu_xI_x]$ ($x = 4$ for **1** and $x = 2$ for **2**) and $Cu_2(COO)_4$ clusters at the same time, were synthesized solvothermally and characterized by means of spectroscopic and X-ray diffraction techniques. These MOFs are constructed of $Cu^+/Cu^{2+}$ cations, pyridine-3,5-dicarboxylate and iodide anions and water molecules as terminal ligands. $[Cu(MeCN)_4]^+$ complex cations are embedded in the channels of 7.7 × 9.2 Å diameter in between the columns of the $[Cu_2I_2]$ units of the compound **2**. The Brauner–Emmett–Teller specific surface areas are of 498 and 515 $m^2/g$ for **1** and **2**, respectively. While **1** and **2** show cluster-based luminescence, the luminescent property of **2** is "on" after 2-nitrotoluene loading.

## 1. Introduction

Metal–organic frameworks (MOFs) are crystalline organic/inorganic hybrid materials which have permanent porosity and significant interest in this field has been reported during the last two decades [1]. MOFs are usually composed of metal ions as nodes and polycarboxylic acids as linkers. There are many review papers about the synthesis, characterization and application areas of MOFs probably because they could be used in every field which a scientist could imagine [1–8].

Because of the coordination geometry of Cu(I) and the potential bridging capability of the iodide anion, CuI has capability to form clusters such as a rhomboid $Cu_2I_2$ dimer, cubane or stepped-cubane $Cu_4I_4$ tetramer, prismane $Cu_6I_6$ hexamer, and double-cubane $Cu_8I_8$ octamer [9]. Though discrete [10–15], 1D [13,16], 2D [12,16–19] and 3D [9,19,20] compounds of the CuI clusters are common, MOF materials, with porosity confirmed by surface area measurements or adsorption experiments, consisting of CuI clusters and organic struts, are very rare [21,22].

These clusters transmit rigidity to the framework and also can impart the desired photophysical properties of the framework [16]. For instance, due to the presence of the weak Cu···Cu interactions in the copper-iodo cluster nodes, these compounds may show attractive photoluminescence properties [9–14,16,17,20,23–26].

In order to combine the photophysical properties and cluster forming capability of copper iodide with copper carboxylate building unit which is well-known in MOF chemistry, we chose pyridine-3,5-dicarboxylic acid ($H_2pdc$) as an organic linker. Because $H_2pdc$ is a multifunctional ligand which can bridge metal centers through different bridging modes with M–O and M–N bonds [27,28] and pyridylcarboxylates can form +1, +2 or mixed-valent copper compounds [29], that is a challenging alternative way to increase the possibility of obtaining interesting MOFs with promising properties.

Herein we present the results of the synthesis and characterization of two MOFs, $\{[Cu^{I}I][Cu^{II}(pdc)(H_2O)]\cdot 1.5MeCN\cdot H_2O\}_n$ (**1**) and $\{[Cu(MeCN)_4]\cdot 2[Cu^{I}I]\cdot 2[Cu^{II}_2(pdc)_2(H_2O)_{1.5}(OH)_{0.5}]\cdot MeCN\cdot 4AcOH\cdot 8H_2O\}_n$, (**2**) constructed of copper iodide metal clusters and $Cu_2(COO)_4$ paddlewheel as nodes. The MOFs were synthesized solvothermally and characterized by single crystal X-ray diffraction, elemental analysis, infrared (IR spectroscopy), thermal analysis (TG/DTA), and low temperature surface area measurements. Furthermore, photoluminescence spectra indicate that the compounds exhibit cluster-based emissions.

---

* Corresponding author. Tel.: +90 464 223 6126; fax: +90 464 223 5376.
*E-mail address:* selcuk.demir@erdogan.edu.tr (S. Demir).

http://dx.doi.org/10.1016/j.poly.2016.05.008
0277-5387/

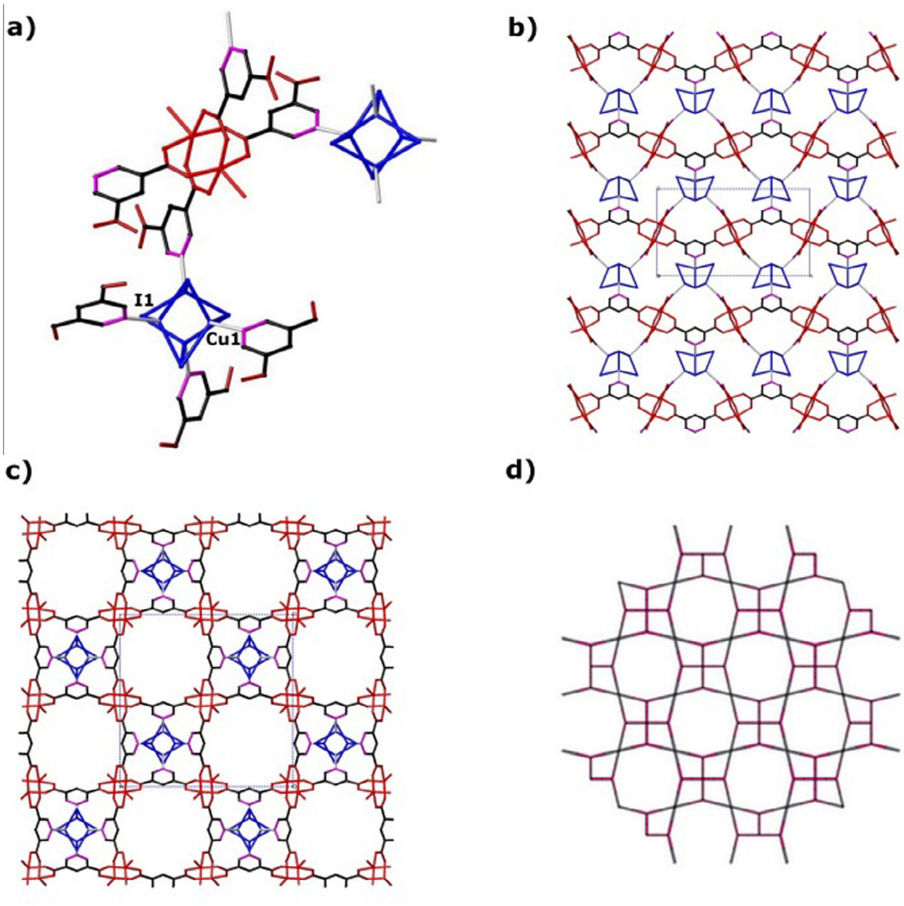


**Fig. 1.** Description of **1**: (a) The basic building blocks of **1**; (b) view of **1** along the *b* direction; (c) view of the **1** along the *c* direction; (d) the corrugated topology network.

## 2. Experimental

### 2.1. Experimental procedures

All reagents and solvents used were of analytical grade. IR spectra were recorded on a Perkin–Elmer 100 FTIR spectrophotometer as ATR between 4000 and 650 $cm^{-1}$. The elemental analyses (C, H, and N contents) were determined with a LECO CHNS-932 instrument. TG and DTA curves were obtained using a Seiko Exstar 6200 TG/DTA thermal analyzer under a dynamic air atmosphere. A sample size of 3–5 mg and a heating rate of 10 °C $min^{-1}$ in the temperature range of 30–1000 °C were used. X-ray diffraction data collection for single crystals was carried out on a Stoe IPDS2/Bruker Quest D8 diffractometer. Room temperature magnetic susceptibility measurement was carried out using a Sherwood Scientific MKI model Gouy magnetic balance. The Brauner–Emmett–Teller (BET) specific surface area and $N_2$ adsorption–desorption-isotherms were measured using a Quantochrome NOVA 4200e instrument at 77 K. Fluorescence spectra of solid samples at room temperature were run on Molecular Devices Spectra M5 fluorescence spectrophotometer with emission slits of 4 nm, respectively.

### 2.2. Preparation of $\{[Cu^{I}I][Cu^{II}(pdc)(H_2O)]\cdot 1.5MeCN\cdot H_2O\}_n$ (**1**)

#### 2.2.1. Single crystals

5 mL of acetonitrile solution of CuI (0.0475 g, 0.25 mmol) was mixed with 5 mL of DMF solution of $H_2pdc$ (0.0418 g, 0.25 mmol) at r.t. and mixed for 30 s with an ultrasonic bath in a glass vial as a stock mixture. Then 0.1 mL formic acid was added to the 1 mL stock mixture and kept in an oven at 120 °C. Single crystals suitable for X-ray diffraction analysis were collected after three weeks.

**Table 1**
Basic X-ray data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Formula | $C_7H_5Cu_2INO_5$ | $C_{46}H_{66}Cu_7I_2N_9O_{36}$ |
| Formula weight | 437.10 | 2019.66 |
| *T* (K) | 300(2) | 100(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| Crystal system | tetragonal | Tetragonal |
| Space group | *P*4/*nmm* | *I*4/**mmm** |
| *a* (Å) | 19.210 (5) | 18.129 (4) |
| *c* (Å) | 10.994 (3) | 21.841 (5) |
| $\alpha\ \beta\ \gamma$ (°) | 90 | 90 |
| *V* ($Å^3$) | 4057.1 (19) | 7178 (3) |
| *Z* | 8 | 4 |
| $\mu$ ($mm^{-1}$) | 3.62 | 2.99 |
| *F*(000) | 1640 | 4008 |
| Crystal size (mm) | 0.18 × 0.17 × 0.14 | 0.26 × 0.23 × 0.09 |
| $\theta$ range (°) | 1.50–24.99 | 2.25–24.99 |
| Refections: total/unique | 12128/1997 | 27366/1818 |
| $R_{int}$ | 0.060 | 0.038 |
| Absorption coefficient | numerical | numerical |
| Minimum, maximum transmission factors | 0.604, 0.747 | 0.446, 0.686 |
| Data/restraints/parameters | 1997/0/82 | 1818/0/98 |
| Goodness-of-fit (GOF) on $F^2$ | 1.02 | 1.02 |
| $R_1$ [$I > 2\sigma(I)$] | 0.032 | 0.055 |
| $wR_2$ (all data) | 0.083 | 0.180 |
| Maximum, minimum $\Delta\rho_{elect}$ (e $Å^{-3}$) | 1.20, −0.45 | 1.34, −2.74 |

#### 2.2.2. Bulk production

5 mL of acetonitrile solution of CuI (0.0475 g, 0.25 mmol) was mixed with 5 mL of DMF solution of $H_2pdc$ (0.0418 g, 0.25 mmol)