DOI: 10.1002/chem.200900743

Reversible Interconversion between Luminescent Isomeric Metal–Organic Frameworks of $[Cu_4I_4(DABCO)_2]$ (DABCO = 1,4-Diazabicyclo[2.2.2]octane)

Dario Braga,[a] Lucia Maini,*[a] Paolo P. Mazzeo,[a] and Barbara Ventura*[b]

Abstract: The metal–organic frameworks (MOF) of cluster $[Cu_4I_4(DABCO)_2]$ (DABCO = 1,4-diazabicyclo[2.2.2]octane) have been prepared and characterized as two different crystalline forms, **I** and **II**. Form **I** is obtained by reaction of DABCO and CuI in aqueous solution or by solvothermal reaction, while form **II** is obtained by reacting DABCO and CuI in acetonitrile. Their luminescence properties in the solid state have been analyzed at room temperature and at 77 K. MOF **II** has bright emission with a maximum at 556 nm that shifts bathochromically at low temperature in conjunction with a marked change in the colour of the emission. The emission of MOF **I** has a maximum at 580 nm and a less pronounced temperature dependence. The peculiar luminescence properties of the two isomers have been interpreted by utilising current knowledge on the excited states properties of Cu^I cubane clusters. The two isomers exhibit a high degree of porosity and can release the disordered solvent molecules trapped in the channels, whilst preserving the crystal structure. Isomer **I** can be converted into **II** on exposure to acetonitrile or methanol vapour, whereas **II** reverts to **I** when heated in a closed pan at 250 °C.

Keywords: copper · crystal engineering · functional materials · luminescence · nanoporous materials · metal–organic frameworks

Introduction

Copper(I) is a versatile metal in coordination chemistry and readily forms clusters and complexes.[1,2] Such complexes show an unusual wealth of geometries and stoichiometries because of the relatively small energy difference between the various isomers, depending on synthetic conditions.[2–4] Although copper(I) iodide and bidentate ligands have been employed in the preparation of metal–organic framework (MOF) compounds, those containing cubane-like clusters are less common.[5–15] Moreover, iodide clusters of Cu^I show unique luminescence properties that have been the subject of great interest over the last 40 years,[16–20] and have been associated with attractive Cu···Cu (cuprophilic) interactions.[21,22] We have long been interested in the preparation of metal–organic as well as hybrid organic–inorganic framework compounds[23–25] within the scope of our crystal engineering endeavours.[26,27]

In this paper we investigate the interconversion between two MOFs obtained from the combination of the inorganic cluster Cu_4I_4 with the organic bifunctional ligand 1,4-diazabicyclo[2.2.2]octane (DABCO). $[Cu_4I_4(DABCO)_2]$ form **I** is obtained by reaction of DABCO and CuI in aqueous solution or by solvothermal reaction as described by Bi et al,[7] while form **II** is obtained by reacting DABCO and CuI in acetonitrile. Both MOFs exhibit a high degree of porosity and large open channels, which are promising for gas storage.[28] Interestingly, the two MOFs show different luminescence properties: at room temperature they have different emission maxima and isomer **II** shows an important temperature-dependent emission feature. The solid-state characterization evidence reveals that **I** can be converted into **II** if the solid material is exposed to acetonitrile vapour, whereas **II** reverts to **I** when heated in a closed pan at 250 °C. This is not the first time that Cu^I isomer interconversion has been observed. Ford[29] reported that the conversion of the $[CuI(4\text{-picolinic})]_\infty$ step-like structure into $[CuI(4\text{-picolinic})]_4$ cubane-like structure was induced by toluene vapour. This conversion was reversed by exposure of the cubane-

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[a] Prof. D. Braga, Dr. L. Maini, P. P. Mazzeo
Dipartimento di Chimica "G.Ciamician"
Università di Bologna
Via selmi 2, 40126 Bologna (Italy)
Fax: (+39) 051-2099456
E-mail: l.maini@unibo.it

[b] Dr. B. Ventura
Istituto per la Sintesi Organica e la Fotoreattività (ISOF) – CNR
Via Gobetti 101, 40129 Bologna (Italy)
Fax: (+39) 051-6399844
E-mail: bventura@isof.cnr.it

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200900743.

like structure to pentane vapour. Differently from the cases discussed herein, however, the crystal of [CuI(4-picolinic)]$_4$ cubane contains a toluene molecule after exposure to toluene.[29]

Results and Discussion

MOF **I** of [Cu_4I_4(DABCO)$_2$] was obtained by solvothermal reaction and structurally and photophysically characterized at room temperature by Bi et al.[7] We have found that **I** can also be conveniently prepared in aqueous solution, while if the reaction is carried out in acetonitrile as described in the literature,[30] a new isomer **II** is obtained. A cubane cluster of Cu^I atoms is also present in MOF **II** and, as seen in **I**, DABCO fills the first coordination sphere of copper by forming a super tetrahedral unit [Cu_4I_4(DABCO)$_2$] with edges of about 8 Å length (Figure 1, top left).

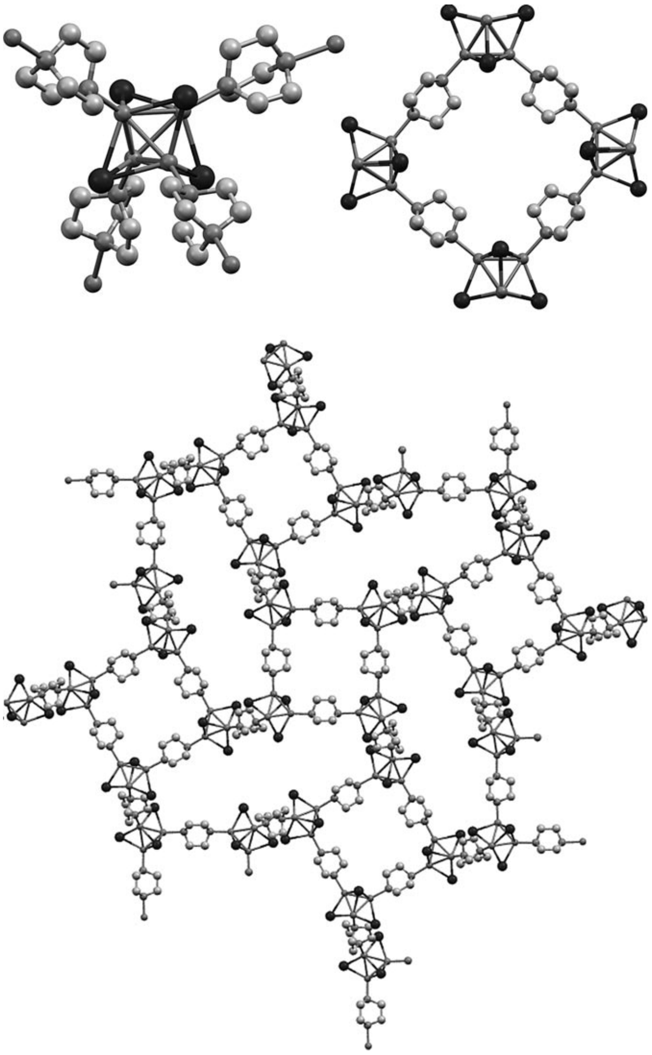


Figure 1. The CuI cubane cluster surrounded by the four DABCO ligands (top left), the four cubane clusters bridged by the ligands (top right) and the overall network formed (bottom).

It can be seen that four cubane clusters are bridged by the DABCO ligands to form a planar four-membered ring in the *ab* plane (Figure 1 b, top right) and each four-membered ring, in turn, connects to eight adjacent four-membered rings. These connections are also present in **I**, but the different rotation of the eight adjacent four-member rings in **I** and **II**, as shown in Figure 2, leads to two different packing arrangements.

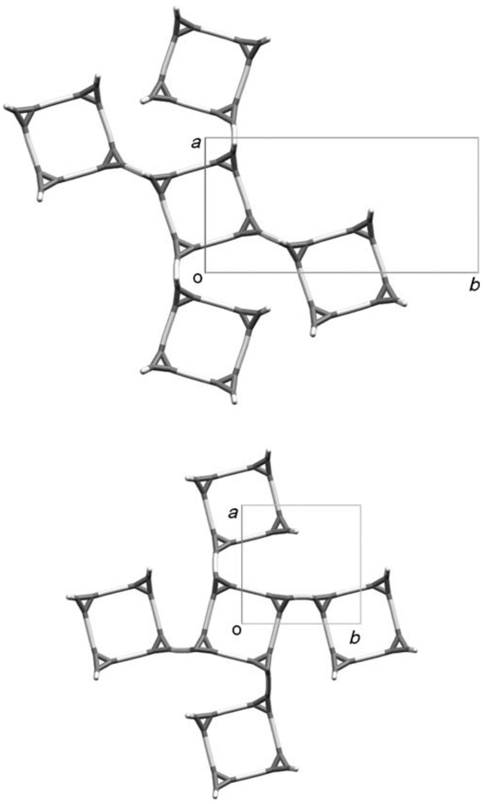


Figure 2. Comparison between the networks formed by MOF **I** (top) and MOF **II** (bottom). Iodine atoms are omitted and DABCO ligands represented as light gray sticks for sake of clarity.

Moreover MOF **II** is formed by two interpenetrating networks as shown in Figure 3, whereas **I** consists of a self-interpenetrating network.[7] It should be pointed out that diamond-related nets possessing tetrahedral four-connected nodes easily form interpenetrating structures.[31,32]

The two isomers show different channels along the [001] direction (Figure 4). In **I** the largest channel has a diameter of 7.068 Å (distance measured from diagonally opposite hydrogen atoms in the channel), whereas in **II** the channel centred on the origin has a diameter of 7.056 Å and the channel centred on $^1/_2$ a and $^1/_2$ b has a diameter of 7.066 Å (distance measured from diagonally opposite hydrogen atoms in the channel). However, the percentage of the total potential solvent accessible volume is equal to 20.5 % per unit cell in both structures.[33]

The crystal structure of **II** was determined from data collected at RT and at 80 K to investigate the presence of sol-

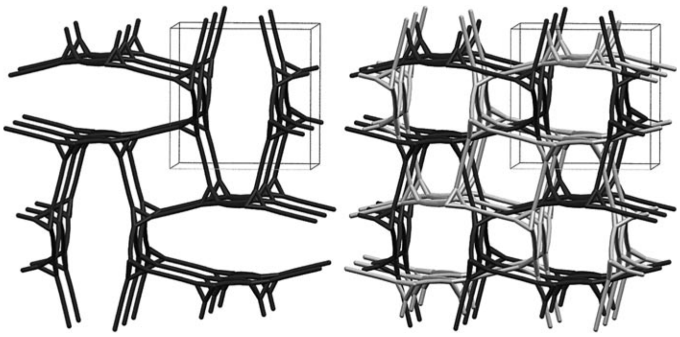


Figure 3. A single network of $[Cu_4I_4(DABCO)_2]$ (left) and the two interpenetrating networks (right). Only the tetrahedron formed by the four Cu atoms and the link between the metal atoms are shown.

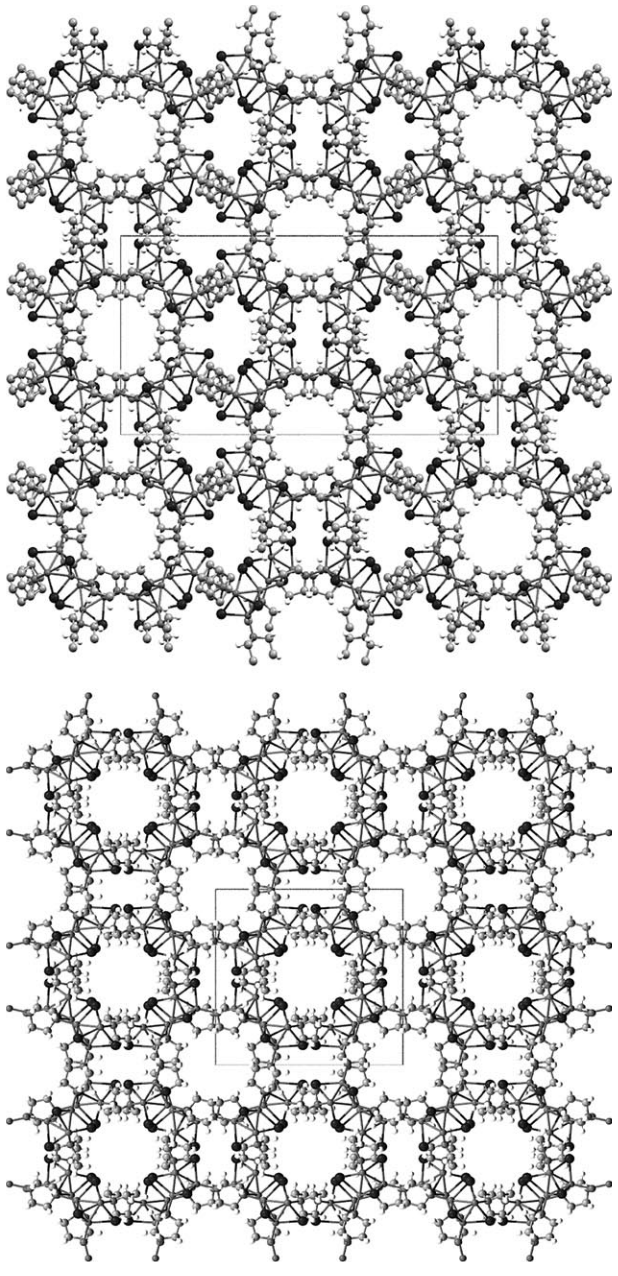


Figure 4. Comparison of the packing of MOF **I** (top) and MOF **II** (bottom).

vent molecules in the channel, albeit, without success. Residual electron density, which suggests the presence of solvent molecules in disordered positions, was observed at both temperatures.

TGA on MOF **II** shows a small loss of weight below 200 °C, which can be ascribed to the disorder solvent in the channel, while at higher temperatures the continuous loss of weight is due to the decomposition and release of the ligand. When TGA was performed on a sample of **II** that had been heated to 200 °C for 30 min, no weight loss below 200 °C was observed and a powder diffraction study confirmed that the crystal structure was retained. MOF **II** has been exposed to acetone, water, methanol and acetonitrile for three days to establish if an exchange of the molecules in the channel was possible. The powder diffraction measurements ascertained that no phase transition had occurred; TGA measurements showed that the weight loss below 200 °C was different, and IR spectroscopy of the volatile products of the TGA analysis was consistent with the solvent used in the vapour absorption experiments. MOF **I** was also exposed to the same solvents for three days: after exposure to acetone and water and also after the removal of the disordered solvent from the channels, the crystal structure was retained, while exposure to methanol and acetontirle afforded a conversion of MOF **I** into **II**.

Both isomers show photoluminescence at room temperature in the solid state associated with the presence of Cu···Cu distances shorter than 2.80 Å (see Tables 1 and 2). In isomer **I** two crystallographically independent Cu^I clusters are present (see Figure 5 and Table 1). No single crystal of **I** has been obtained by us, so we could not measure the Cu···Cu distances at low temperature.

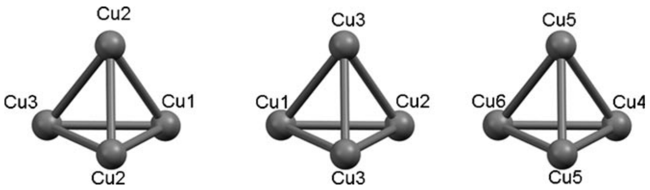


Figure 5. Labelling of MOFs **II** (left) and **I** (middle and right) with two crystallographic independent cubane clusters.

In isomer **II** the intermetallic distances significantly reduce on lowering the temperature (Table 2), which explains the bathochromic shift of the emission (see below).

Interconversion: The two isomers interconvert under different experimental conditions. When exposed to acetonitrile or methanol vapour **I** transforms quantitatively into **II** in three days, whereas **II** reverts into **I** when heated up to 250 °C in a closed pan.

Vapour digestion[34–36] in acetonitrile or methanol of $[Cu_4I_4(DABCO)_2]$ **I** may be mediated by a microsolution environment that induces formation of MOF **II**, probably due to a lower solubility of **II** in these solvents. Figure 6 com-

Table 1. Cu–Cu distances [Å] of MOF **I** (independent molecules 1 and 2) at room temperature.[7]

molecule 1	Cu1	Cu2	Cu3	molecule 2	Cu4	Cu5	Cu6
Cu1	–	2.605(4)	2.732(3)	Cu4	–	2.755(4)	2.608(4)
Cu2	2.605(4)	–	2.714(3)	Cu5	2.755(4)	2.653(4)	2.625(3)
Cu3	2.732(3)	2.714(3)	2.633(3)	Cu6	2.608(4)	2.625(3)	–

Table 2. Cu–Cu distances [Å] of MOF **II** at room temperature and 80 K.

II	Cu1	Cu2	Cu3	**II**	Cu1	Cu2	Cu3
RT				80 K			
Cu1	–	2.698(1)	2.593(2)	Cu1	–	2.6490(8)	2.5552(10)
Cu2	2.698 (1)	2.695(1)	2.733(1)	Cu2	2.6490(8)	2.6728(7)	2.6901(8)
Cu3	2.593 (2)	2.733(1)	–	Cu3	2.555(10)	2.6901(8)	–

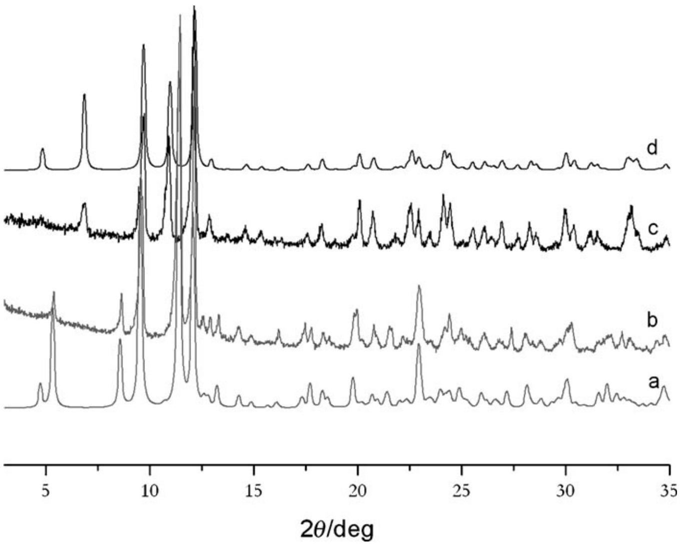


Figure 6. Conversion of MOF **I** into **II** upon exposure to acetonitrile vapour. a) The calculated powder pattern of **I**, b) X-ray diffraction pattern of **I** before exposure to the vapour, c) X-ray diffraction of the same sample transformed into **II** after exposure to the vapour of acetonitrile and d) calculated powder pattern of **II**.

pares the diffractograms; the diffraction pattern obtained after the vapour digestion does not exhibit peaks attributable to the starting material, MOF **I**, and matches the calculated one of MOF **II** well, which suggests a complete conversion to **II**.

The reverse process has also been studied. If MOF **II** is heated in a closed pan up to 250 °C, transformation into **I** takes place, while heating **II** in an open pan leads to decomposition. Interestingly, the transformation could be followed on a hot-stage microscope with the aid of an UV/Vis lamp. When **II** is heated at 250 °C in a capillary, a slow change in the colour of its emission under UV irradiation, from yellow to orange, could be appreciated by the naked eye. The powder recovered after 20 min showed a diffractogram corresponding to that of **I**. In this case the interconversion is not mediated by solution or melting; unfortunately, the DSC trace of **II** in closed pan only shows a broad endothermic phenomenon accompanied by an increase in the baseline. However, the thermal behaviour suggests that at high temperature MOF **I** is more stable than **II**.

Luminescence properties: The luminescence properties of the two isomers were investigated in the solid state, since the preparation of solutions was precluded by the insolubility of the compounds. Moreover, the dissolution in a solvent would result in a solution containing intact cubane clusters[16] but with a complete loss of the higher order packing, which is the main feature that differentiates the two isomers.

Isomers **I** and **II** show luminescence in the solid state at room temperature and at 77 K; the results are summarized in Table 3. The emission spectrum of **I** at room temperature, shown in Figure 7 (top), has a maximum at 580 nm, in agreement with a previous characterization.[7] At low temperature a bathochromic shift of 10 nm is observed (Figure 7 top and Table 3). The measured lifetimes are 8.0 µs at room temperature and 15.0 µs at 77 K (Table 3). Isomer **II** has a very intense room-temperature emission peaking at 556 nm with a lifetime of 13.4 µs (see Figure 7, bottom, and Table 3). At 77 K the emission spectrum red-shifts by 22 nm and narrows (Figure 7). This produces a modification in the emission colour from yellow to deep orange (see Figure 8) that can be quantified by the CIE (Commission International de L'Eclairage) 1931 chromaticity coordinates with values of ($x=0.46$, $y=0.51$) at room temperature and ($x=0.52$, $y=0.47$) at low temperature.

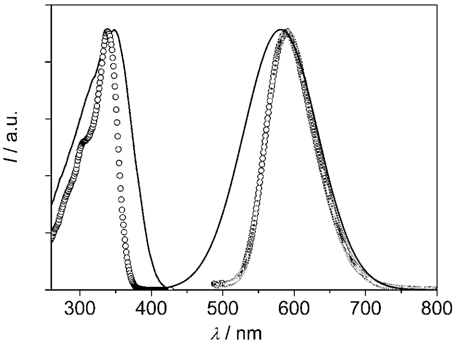
Table 3. Luminescence data of isomers **I** and **II** in the solid state at 295 and 77 K

	295 K		77 K	
	λ_{max} [nm][a]	τ [µs][b]	λ_{max} [nm][a]	τ [µs][b]
I	580	8.0	590	15.0
II	556	13.4	578	13.5

[a] Emission maxima, excitation at 350 nm. [b] Lifetimes, excitation at 331 nm.

The excitation spectra of the two isomers measured at both temperatures are characterized by an envelope of bands extending below 400 nm (Figure 7), with maxima at 349 and 339 nm for **I** and at 349 and 338 nm for **II** at room temperature and 77 K, respectively.

The luminescence of cubane $[Cu_4I_4(L)_4]$ clusters in which L is a saturated amine, as in the case of DABCO, is characterized by the emission of the so called "cluster-centred" (CC) excited states that exist only when the Cu···Cu distance in the cluster is lower than the sum of the orbital interaction radii (2.8 Å).[30] These states are of mixed iodide-to-copper charge transfer (XMCT) and d,s→p copper-centred (MC)



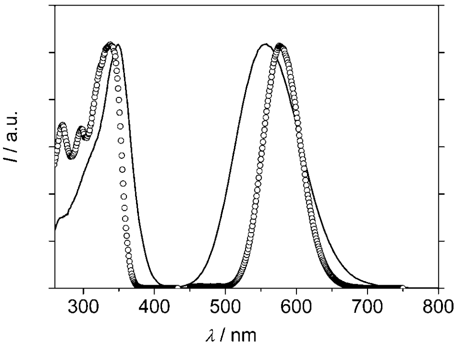


Figure 7. Top: Normalized emission spectra (420–800 nm, $\lambda_{exc}=350$ nm) and excitation spectra (260–420 nm, $\lambda_{em}=580$ and 590 nm for room temperature and 77 K, respectively) of solid **I** at room temperature (line) and at 77 K (circles). Bottom: Normalized emission spectra (430–800 nm, $\lambda_{exc}=350$ nm) and excitation spectra (260–430 nm, $\lambda_{em}=556$ and 578 nm for room temperature and 77 K, respectively) of solid **II** at room temperature (line) and at 77 K (circles).

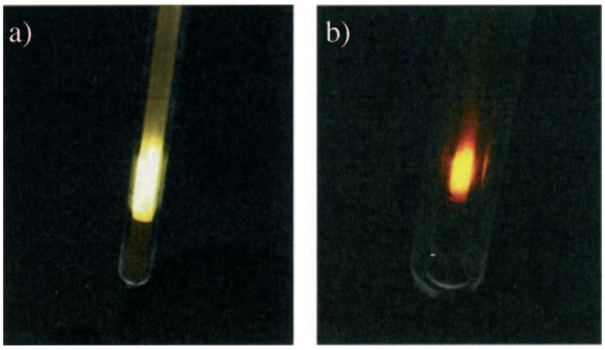


Figure 8. Emission of solid **II** excited at 350 nm a) at room temperature and b) at 77 K.

character and originate from the strong interactions that occur between the atoms in the Cu_4I_4 core. Therefore, the spectra of isomers **I** and **II** can be interpreted in terms of CC emission. The large Stokes shift observed for both compounds (11400 cm^{-1} for **I** and 10700 cm^{-1} for **II** at room temperature) can be explained by the high distortion of the CC state with respect to the ground state. Theoretical studies demonstrate that in the excited state the cluster Cu···Cu distances decrease, while the Cu···I and I···I distances increase.[37,38] Since the LUMO of the transition is principally copper 4s in character and has a Cu–Cu bonding character,[16] the results obtained for isomers **I** and **II** can be interpreted as follows: a shorter Cu···Cu distance in the cluster might correspond to a higher Cu–Cu bonding character and, consequently, a stabilization of the CC excited state. In compound **I** two crystallographic independent cubane clusters are present and from Table 2 it is possible to derive a mean Cu···Cu distance of 2.688 and 2.670 Å for molecules 1 and 2, respectively, at room temperature. Both values are shorter than the mean Cu···Cu distance value obtained for isomer **II** at the same temperature: 2.692 Å (Table 1). The emission maximum of **I** is in fact red-shifted by 24 nm relative to **II** at room temperature, and the change in the colour of the emission from yellow to orange has been a useful tool to monitor the interconversion of **II** into **I** upon heating. At 77 K the emission spectra of both isomers present a bathochromic shift that is more pronounced for **II** (Figure 7 and Table 3). From Table 1 it is possible to derive for **II** an average intermetallic distance at 80 K of 2.651 Å, which is much shorter than in the room temperature case. In the absence of crystallographic data for **I** at low temperature, we can only assume, from the luminescence data, that in this isomer the Cu···Cu distances at low temperature are only slightly shortened relative to the room temperature case. It should be pointed out that for isomer **II** the phenomenon of a temperature-dependant emission colour should not be described in terms of luminescence thermochromism. This definition, coined by Hardt in the 1970s,[39] is generally attributed in the literature to copper iodide clusters only containing π-unsaturated ligands, in which the emission at low temperature is dominated by an iodine-to-ligand charge transfer (XLCT) band that appears at higher energy and has a shorter lifetime with respect to the CC band.[18,30] The luminescence lifetimes of isomers **I** and **II** are of the order of 10 μs in all examined conditions, in agreement with values obtained in solid for CC bands of other copper cubane clusters,[15,30] indicating a triplet character of the emitting state.[37] The excitation spectra of both compounds can be interpreted in terms of ^{1}CC transitions,[37] since ^{1}MLCT and ^{1}XLCT absorption bands cannot be present in these compounds in which the organic ligand is DABCO.

Conclusions

In this paper we have reported the synthesis of a new MOF **II** with high degree of porosity and the presence of large open channels, and studies are in progress to assess its potential for gas storage. We proved that mild synthetic conditions can also yield MOF **I**, which was obtained only from solvothermal synthesis. The two systems are isomers and show similarities in the crystal structures; namely the same super tetrahedral unit $[Cu_4I_4(DABCO)_2]$ and a potential solvent accessible volume of 20.5 % per unit cell. However the differences, though small, seem to play a significant role, since the different packing arrangement influences the Cu···Cu distances in the Cu_4I_4 cluster core and, consequently, the luminescence properties. The new isomer **II**, in particular, shows a bright luminescence both at room temperature and at 77 K, with lifetimes in the range of tenth of μs and an interesting bathochromic shift of the emission maximum when the temperature is lowered. This can open up to promising applications in the area of luminescent materials.

Additionally the two MOFs present an interesting reversible solid-to-solid transformation: MOF **I** can be converted into **II** if the solid material is exposed to acetonitrile or methanol vapour, whereas **II** reverts to **I** when heated in a closed pan at 250 °C.

Experimental Section

Synthesis of [$Cu_4I_4(DABCO)_2$] I: CuI (0.190 g, 1 mmol) was dissolved in the minimum amount of a saturated aqueous solution of KI (≈3 mL). While stirring, a solution of DABCO (0.134 g, 1.2 mmol) in water (15 mL) was added. The product precipitated instantly as a white powder that gave orange emission under UV/Vis radiation. The solid material was recovered by centrifugation and washed with water. The powder was characterized by X-ray powder diffraction.

Synthesis of [$Cu_4I_4(DABCO)_2$] II: DABCO (0134 g, 1.2 mmol) was dissolved in acetonitrile (15 mL) at 70 °C and was added, under stirring, to a solution of CuI (0.190 g, 1 mmol) acetonitrile in (15 mL) at 70 °C. The product precipitated as a fine white powder, that gave yellow emission under UV/Vis radiation; it was left stirring in solution under reflux at 70 °C for about 3 h. The solid material was recovered by centrifugation and washed with water and acetone. The powder was characterized by X-ray powder diffraction. Single crystals were obtained by a three-layer crystallization: the lower layer was CuI dissolved in saturated aqueous solution of KI; the middle layer was pure solvent (acetonitrile or toluene); and the top layer was a solution of DABCO in acetone. Crystals appeared after 5–7 days and were chosen with the help of UV lamp.

Interconversion: MOF **II** was heated in sealed capillary up to 250 °C for 20 min and the powder pattern was measured on a capillary stage to ascertain the full conversion.

Vapour digestion was attained by placing a glass sample holder, containing the powder sample of starting MOF **I**, in a cylindrical weighing bottle containing the solvent—acetonitrile, acetone, water, or methanol—(5 mL): in this way the powder and the solution were not in contact; the reaction took place in a closed system.

Photophysics: Powder samples placed inside two quartz slides were used for room-temperature determinations, while for 77 K measurements the powder was placed in a capillary quartz tube immersed in liquid nitrogen contained in a home-made quartz dewar. Emission and excitation spectra were recorded in front face mode, using a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Uncorrected emission spectra are reported, the uncertainty on the band maxima is 2 nm. The CIE 1931 coordinates were evaluated from the area of the luminescence spectra and corrected for the photomultiplier response by using the three colour matching functions.[40] Luminescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting device, by using pulsed NanoLED excitation sources at 331 nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer, with an estimated error on the lifetimes of 10 %.

DSC measurements: Calorimetric measurements were performed using a Perkin–Elmer Diamond equipped with a model ULSP90 intracooler. Temperature and enthalpy calibrations were performed by using high purity standards (*n*-decane, benzene and indium). The samples (3–5 mg) were placed in aluminium closed pans. Heating was carried out at 5 °C min^{-1} in the temperature range from 25 to 300 °C.

TGA: TGA measurements were performed using a Perkin–Elmer TGA7 in the temperature range 35–335 °C under N_2 gas flow and heating was carried out at 5 °C min^{-1}; and using a Netzsch STA 409 PC/PG coupled with a FTIR in the temperature range 25–590 °C under N_2 gas flow and heating was carried at 10 °C min^{-1}.

X-ray powder diffraction: X-ray powder diffractograms were collected on a Panalytical X′Pert PRO automated diffractometer with $Cu_{K\alpha}$ radiation and X′Celerator detector without a monochromator. When required, powder data were collected with a spinner capillary stage. The program PowderCell[41] was used for calculation of X-ray powder patterns.

Crystal structure determination: Crystal data for **II** were collected on a Oxford Xcalibur S with $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, monochromator graphite and equipped with a liquid nitrogen Oxford-Cryostream device. Crystal data and details of measurements are summarized in Table 4. SHELX97[42] was used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were added in calculated positions. Mercury[43] was used for the graphical representation of the results. The program PLATON[33] was used to calculate the solvent accessible void. CCDC-723349 and 723350 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data and details of measurements for MOF **II**.

formula	$C_{12}H_{24}Cu_4I_4N_4$	$C_{12}H_{24}Cu_4I_4N_4$
M_r	986.11	986.11
T [K]	293(2)	80(2)
system	tetragonal	tetragonal
space group	*P*4/*mcc*	*P*4/*mcc*
a [Å]	18.2095(14)	17.9914(2)
b [Å]	18.2095(14)	17.9914(2)
c [Å]	16.0985(17)	15.9344(3)
V [Å^3]	5338.0(8)	5157.81(13)
Z	8	8
F(000)	3616	3616
θ range [°]	2.5–29	2.5–28.8
μ(MoKα) [mm^{-1}]	7.774	8.045
measured reflns	55 530	15 432
unique reflns	3545	3224
parameters	122	122
GOF on F^2	1.018	1.088
$R1$ (on F, [$I > 2\sigma(I)$])	0.0394	0.0278
$wR2$ (F^2, all data)	0.0975	0.0574

Acknowledgements

We thank Katia Rubini for DSC and TGA measurements and Dr. Nicola Armaroli for helpful discussion. Funding from CNR of Italy (PM.P04.010, Project MACOL) and University of Bologna are gratefully acknowledged.

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Received: September 15, 2009