## **Electronic supplementary information (ESI) for:**

# An inorganic starch-iodine analog: The inorganic-organic hybrid compound $\{(C_4H_{12}N_2)_2[Cu^II_4](I_2)\}_n$

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#### Instrumentation for characterization:

IR-ATR spectra were obtained on a Nicolet Magna-IR 760 (E.S.P.) spectrometer in a range from 4000 to 50  $\text{cm}^{-1}$ .

Raman-FT measurements were carried out on a Bruker Vertex 40 Raman/IR spectrometer in a range from 4000 to  $50 \text{ cm}^{-1}$ .

Powder X-ray diffraction patterns were measured at ambient temperature using a STOE STADI-P with Debye-Scherrer geometry, Mo-K $\alpha$  radiation ( $\lambda = 0.7093$  Å), a Ge(111) monochromator and the samples in glass capillaries on a rotating probe head. Simulated powder patterns were based on single-crystal data and calculated using the STOE WinXPOW software package (STOE WinXPOW Version 1.10; STOE& Cie GmbH, Darmstadt, Germany, 2002).

Thermogravimetry TG/DTA measurements were done on an Netzsch STA (Simultaneous Thermal Analyzer) 409 C under nitrogen in the temperature range from 50 to 600 °C and a heating rate of 10 K/min.

ESR studies were carried out with a frequency of 9.1576 GHz, CF 330 mT, modulation 0.4 mT at room temperature and 60 °C (333.15 K).  $Mn^{2+}$  (I = 5/2) was used as a standard. Energy dispersive X-ray analysis/scanning electron microscopy (EDX/SEM) was done with a digital CAMECA SX 100 Electron Microprobe (EMP) with 15.0 kV and 4.0 nA.

## Synthetic details:

CuO (fine powder) (0.160 g, 2.00 mmol) and Cu<sup>0</sup> (fine powder) (0.127 g, 2.00 mmol) were suspended in 10 mL of water under air. To the resulting black suspension a solution of HI (57 wt%, 7.620 g, 4.48 mL, d = 1.70 g/mL, 60.00 mmol) and elementary iodine, I<sub>2</sub> (1.269 g, 5 mmol) were added under vigorous stirring. At last piperazine (1.292 g, 15 mmol) was added to the violet mixture. After 30 min of stirring at room temperature the suspension was transferred to the 23 mL Teflon tube of a stainless steel autoclave which was sealed and heated for 72 h at 180°C. After cooling to room temperature for 55 h at a rate of 2.8 °C/h dark-blue prismatic crystals (suitable for X-ray diffraction) were obtained after filtration and drying under argon (yield 1.37 g, 34 % based on copper).

It is important to keep the crystals under argon. Upon air and oxygen contact the dark-blue color will change to a brighter-violet in a short time.

Analysis under argon:

 $C_8H_{24}N_4CuI_6$  (1001.25 g mol<sup>-1</sup>), calcd. C 9.60, H 2.42, N 5.60, Cu 6.35, I 76.05; found C 9.72, H 2.33, N 5.38, Cu 6.4, I 75.98%.

IR (ATR, cm<sup>-1</sup>):  $v_{max} = 3044$  (s), 2916 (w), 2762 (s), 2339 (m), 1528 (vs), 1420 (vs), 1070 (s), 1035 (s), 990 (s), 907 (s), 855 (s), 550 (s), 514 (w), 260 (br); see Fig. S1 and S2

#### Details of elemental analysis:

Copper analysis (10 mg of 1 were dissolved in 10 mL of conc. HNO<sub>3</sub>) was carried on a Vario 6 atomic absorption spectrometer from Analytik Jena Instruments.

The total amount of iodine in 1 was determined by volumetric titration with sodium thiosulfate,  $Na_2S_2O_3$  after Leipert's method.



**Fig. S1** Infrared spectrum of **1** in the range  $400-4000 \text{ cm}^{-1}$ .



**Fig. S2** Infrared spectrum of **1** in the range  $50-600 \text{ cm}^{-1}$ .



**Fig. S3** Raman spectrum of **1** in the range  $0-4000 \text{ cm}^{-1}$ . Note the strong intensity of the polyiodide bands versus the organic fingerprint and C-H region.



**Fig. S4** Raman spectrum of **1** in the range 200-4000  $\text{cm}^{-1}$  in order to enlarge the organic fingerprint and C-H region.

#### X-ray powder diffraction:



**Fig. S5** X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray of **1**. Black curve is measured on a sample of **1** with almost no grinding.

#### **ESR** spectrometry:



**Fig. S6** ESR spectrum of  $\{(C_4H_{12}N_2)_2[Cu^II_4](I_2)\}_n, \mathbf{1}$ .





Energy dispersive X-ray analysis/scanning electron microscopy (EDX/SEM):



**Fig. S8** EDX Spectrum of  $\{(C_4H_{12}N_2)_2[Cu^II_4](I_2)\}_n, \mathbf{1}$ 

A correct elemental analysis of Cu and iodine with EDX/SEM is not possible. The determined weight% values of Cu = 9.7 und I = 52.9 do not match because part of the iodine content of the sample evaporates when the electron beam is focused on the crystal surface.

### The iodine-starch reaction:

The *iodine test* is used to test for the presence of starch. Iodine,  $I_2$  (0.02 g; 0.078 mmol) was dissolved in an aqueous solution 2 mL of potassium iodide (0.04 g; 0.24 mmol). From this solution  $30\mu$ L reacts with a starch water solution (0.250 mg starch in 50 mL H<sub>2</sub>O) producing a deep blue-black color whose intensity depends on the polyiodide concentration/dilution with water (Fig. S9).



Fig. S9 Different starch-polyiodine concentrations in water

This reaction is the result of the formation of polyiodide chains from the reaction of starch and iodine. The amylose, or straight chain portion of starch, forms helices where iodine molecules assemble, forming a dark blue/black color. Starch is often used in chemistry as an indicator for iodometric redox titrations. The indicator is does not turn blue by the presence of iodide ( $\Gamma$ ) alone.

In the presence of an agent which oxidizes  $\Gamma$  to  $I_2$  the solution turns blue. In the presence of a reducing agent which turn  $I_2$  into  $\Gamma$ , the blue color disappears because triiodide  $(I_3^-)$  or pentaiodide  $(I_5^-)$  ions break up into individual iodide ions, disassembling the complex. Thus, bubbling of air (oxgen) through the  $I_2/\Gamma$  solution gives colourless starch solution after 4 h (Fig. S10).



Fig. S10 Bubbling of air through the starch-iodine/iodide solution for 4 h.

The decolorizing oxidation process of starch- $I_2/\Gamma$  with air was followed by UV/VIS spectroscopy on a J&M *TIDAS* UV/VIS Spectrometer in the range between 300 and 800 nm (Fig. S11).



**Fig. S11** UV/Vis absorption spectra of the blue starch- $I_2/\Gamma$  solution (Fig. S10) after bubbling air through the blue solution for 0, 1, 2, 3 and 4 h.

# The linear $I_4^{2-}$ versus the linear $I_5^-$ anion

A linear  ${I_4}^{2-}$  was found in the compound  $(C_5H_7N_2Se)_2I_3\cdot {}^1\!/_2I_4$ 

(F. Bigoli, F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, V. Lippolis, M. L. Mercuri, M. A. Pellinghelli and E. F. Trogu, *Inorg. Chem.*, 1996, **35**, 3194-3201, see Table 8 and Fig. 4).

However, the literature reported Raman spectrum for linear  $I_4^{2-}$  does not fully match with our Raman-spectrum.

The characteristic Raman band of linear  $I_4^{2-}$  is said to be a strong band at 155 cm<sup>-1</sup> (see Fig. 4 in the above reference). This band should be of comparable intensity as the band for the concomitant  $I_3^-$  in the same compound at 112 cm<sup>-1</sup>.

On the other hand, the possible distances from our disorder model of the polyiodide chain match better for  $I_4^{2-}$  than for  $I_5^-$ : I $\cdots$ I–I $\cdots$ I]<sup>2-</sup> with ~3.4 – 2.8 – 3.4 Å which matches with the possible sequence 3.39 – 2.76 – 3.39 Å from our model

 $[I-I\cdots I-I]^-$  with ~2.8 – 3.2 – 3.2 – 2.8 Å which is difficult to fully match with our model, where it is not possible, taken the I atoms on their final refined positions, to have 4 consecutive distances of 2.75 – 3.07 or 3.39 – 3.07 or 3.39 – 2.75.