Electronic Supplementary Information (ESI)

Synthesis of Cu, Zn and bimetallic Cu/Zn brass alloy nanoparticles from metal amidinate precursors in ionic liquid or propylene carbonate with relevance to methanol synthesis

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Content:

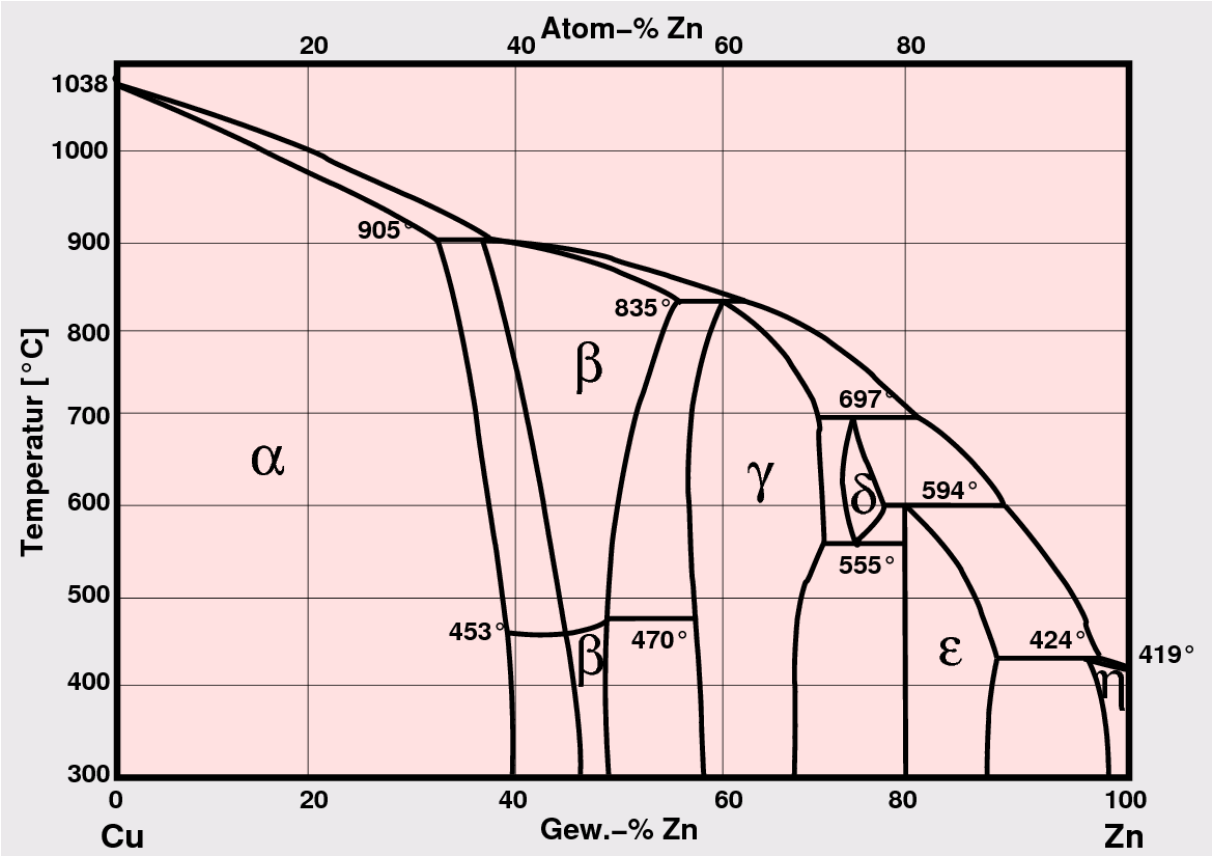


Fig. S1 Copper-Zinc binary alloy phase diagrams from ASM International Datebase, *ASM-253638-tlo3-CuZn*.

^{1}H NMR spectra:

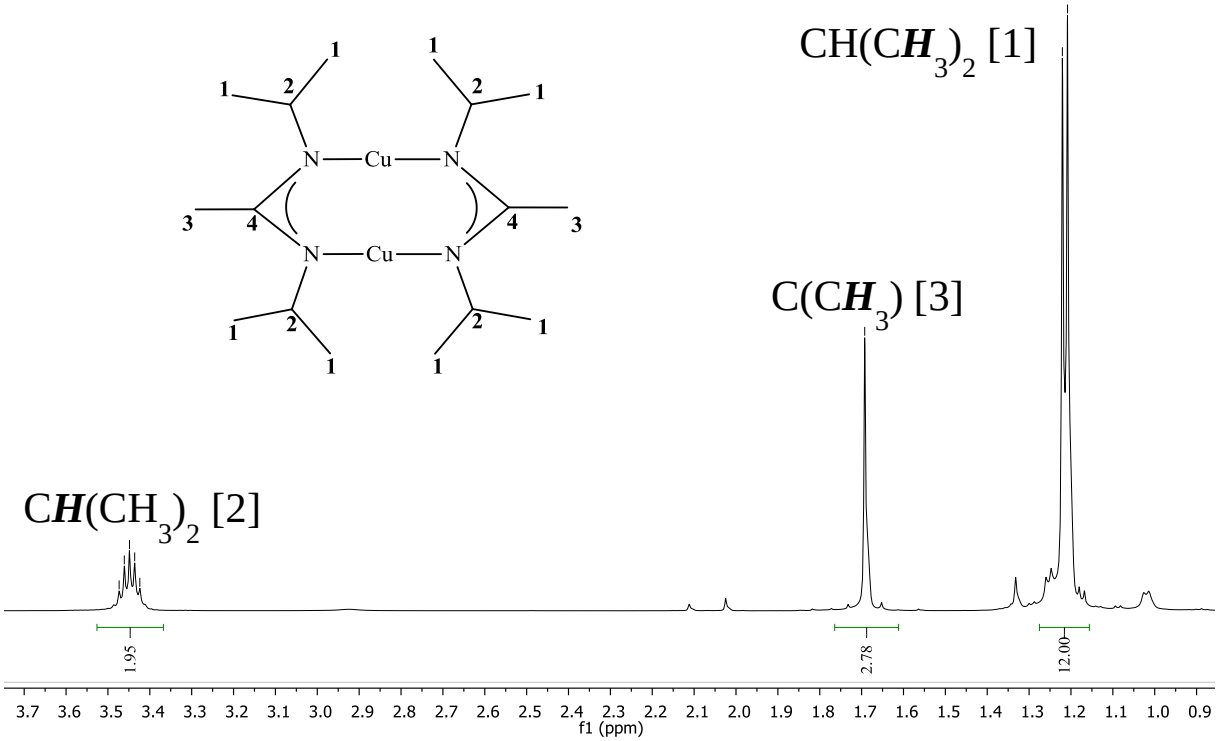


Fig. S2 ^{1}H NMR spectrum (C_6D_6, 500.131 MHz, 298 K) of {[Me(C(N^{i}Pr)$_2$]Cu}$_2$ (**1**).

Thermal stability of {[Me(C(N^{i}Pr)$_2$]Cu}$_2$ (**1**):

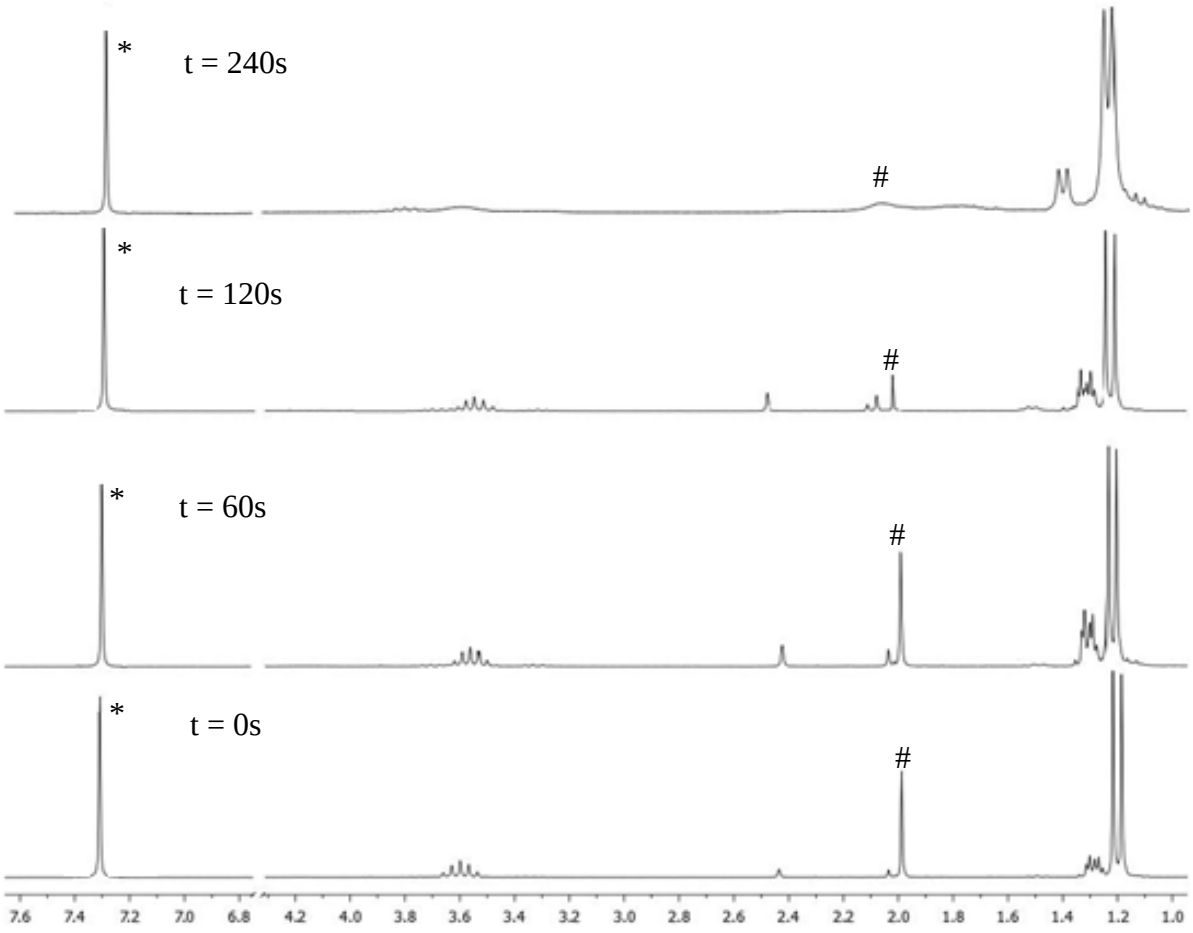


Fig. S3 Selected ^{1}H NMR spectra (C_6D_6, 200.771 MHz, 298 K) of a decomposition series of {[Me(C(N^{i}Pr)$_2$]Cu}$_2$ (**1**) at 220 °C in [BMIm][BF_4] upon 150 W microwave irradiation for the given time.
* residual proton solvent signal of C_6D_6
# signal of the N–C(CH_3)–N methyl group.
The {[Me(C(N^{i}Pr)$_2$]Cu}$_2$/[BMIm][BF_4] solution was sealed in microwave-tubes and heated up to 220 °C by microwave irradiation. The tubes were periodically removed from the microwave oven every 30 s and their ^{1}H NMR spectra were recorded by dissolving a 50 mg sample in 0.65 mL deuterated benzene. The intensity of the well separated peak with chemical shift δ = 1.91 ppm was recorded relative to the residual proton peak (δ = 7.3 ppm) in the C_6D_6 solvent.

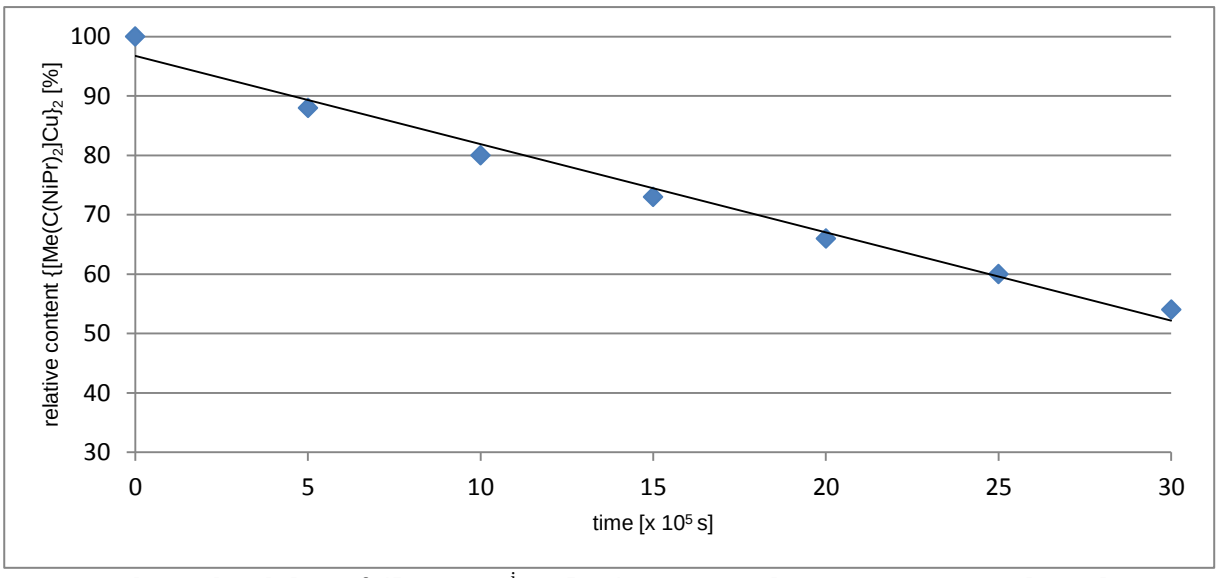


Fig. S4 Thermal stability of {[Me(C(N^{i}Pr)$_2$]Cu}$_2$ (**1**) according to Li, Barry und Gordon in an oven at 200°C (graphics prepared from data given in ref.[1]).

1 Z. Li, T. Barry and R. G. Gordon, *Inorg. Chem.*, 2005, **44**, 1728-1735.

Cu-NP dispersion in propylene carbonate (PC), 0.5 wt% Cu-NP/PC:

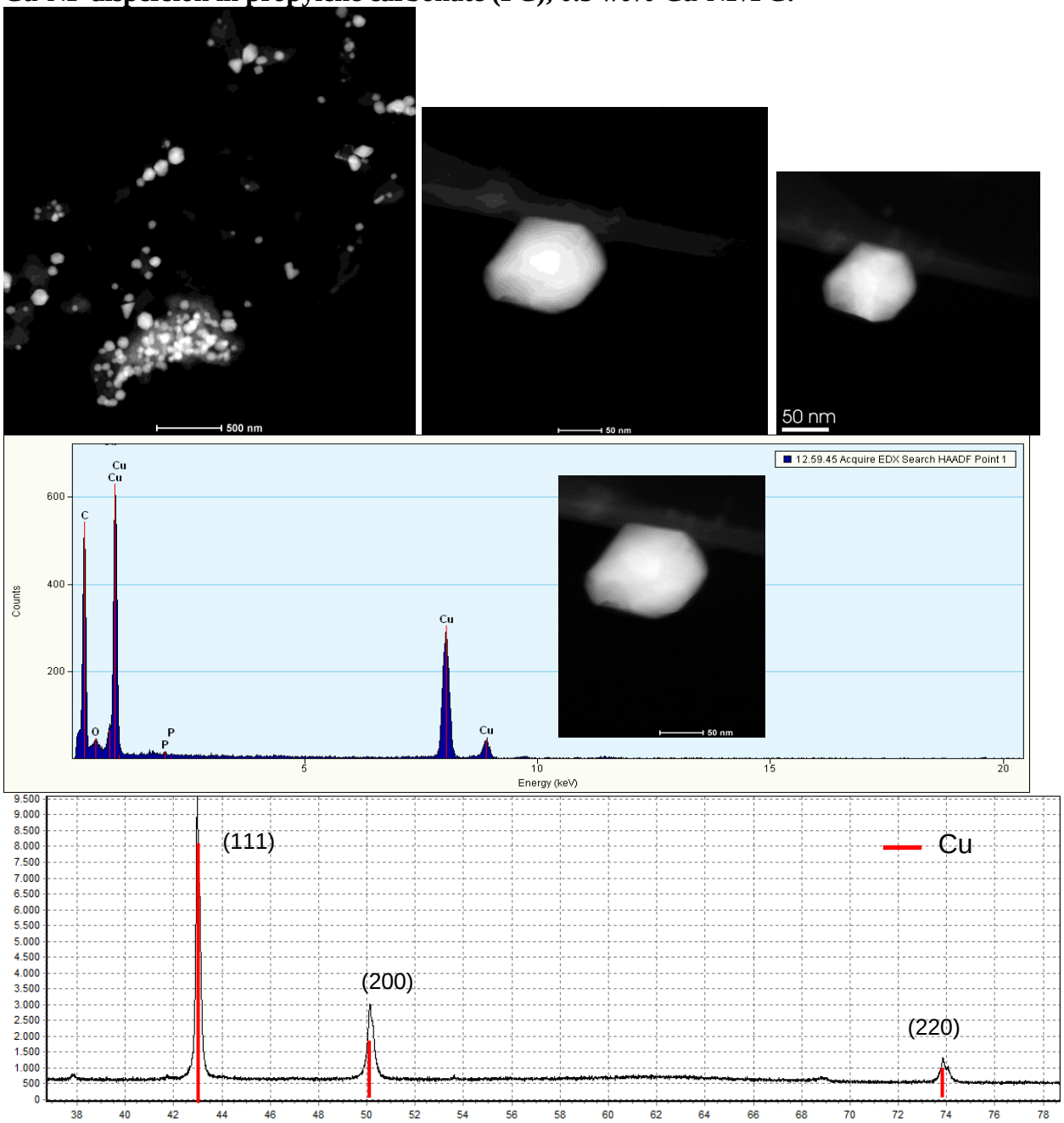


Fig. S5 HAADF-STEM (top), EDX (middle) and PXRD (bottom, Cu reference peaks in red from JCPDS data bank, No. 4-0836) of 0.5 wt% Cu-NPs in PC from $\{[Me(C(N^iPr)_2]Cu\}_2$ **1** (microwave irradiation for 10 min, 150 W, 220 °C). (STEM-EDX: FEI Technai f20, 200 or 136 kV, respectively; PXRD: 4 h, Cu-Kα, 35 kV).

Table S1 Cu-NP size and size distribution in 0.5 wt% Cu-NP dispersion. [a]

	TEM Ø (σ) [nm][b]	DLS Ø (σ) [nm][b]	PXRD Ø (σ) [nm][b,c]
dec. in $[BMIm][BF_4]$	9 (± 4)	13 (± 7)	7 (± 3)
dec. in propylene carbonate	85 (± 16)	102 (± 11)	55 (± 7)

[a] precursor $\{[Me(C(N^iPr)_2]Cu\}_2$ **1**, dispersions obtained by MWI with 50 W for 10 min at 220°C. BSc Thesis of Mrs. Christin Grunow, University of Düsseldorf, 2012, p. 32.

[b] Median diameter (Ø) and standard deviation (σ).

[c] from Scherrer equation $\varepsilon = \frac{K\lambda}{B\cos\theta_B}$ with ε = average diameter of nanocrystallites [Å], K = Scherrer factor (1); λ = X-ray wavelength (Cu-K_α =1.5406 Å), B = half-width of reflection (rad); θ_B = angle at peak-maximum [degree], with analysis here at the (111) reflection.

Zn-NP dispersion in [BMIm][BF_4], 0.5 wt% M-NP/IL:

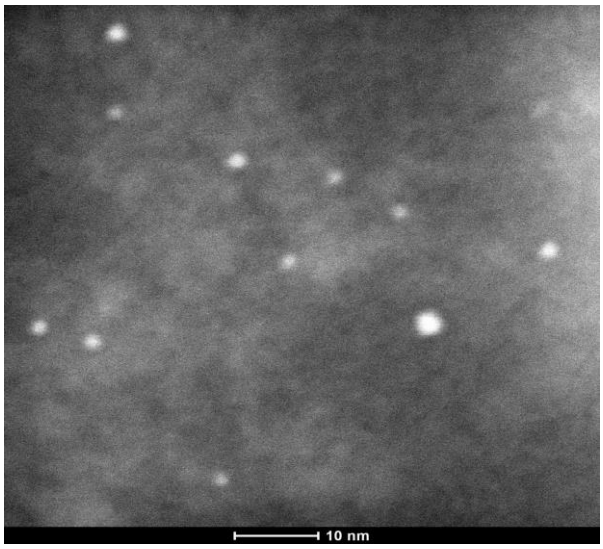


Fig. S6 HAADF-STEM of 0.5 wt% Zn-NPs in [BMIm][BF_4] from [Me(C(N^iPr)$_2$]$_2$Zn (**2**) (microwave irradiation for 10 min, 150 W, 220 °C). (TEM-EDX: FEI Technai f20, 200).

Table S2 Zn-NP size and size distribution in 0.5 wt% Zn-NP dispersion. [a]

	TEM Ø (σ) [nm][b]	DLS Ø (σ) [nm][b]	PXRD Ø (σ) [nm][b,c]
dec. in [BMIm][BF_4]	3.5 (± 1.5)	6 (± 4)	2.9 (± 0.2)
dec. in propylene carbonate	5.5 (± 3.5)	11 (± 6)	----

[a] precursor [Me(C(N^iPr)$_2$]$_2$Zn (**2**), dispersions obtained by MWI with 50 W for 10 min at 220°C. BSc Thesis of Mrs. Christin Grunow, University of Düsseldorf, 2012, p. 35.
[b] Median diameter (Ø) and standard deviation (σ).
[c] from Scherrer equation $\varepsilon = \frac{K\lambda}{B\cos\theta_B}$ with ε = average diameter of nanocrystallites [Å], K = Scherrer factor (1); λ = X-ray wavelength (Cu-K_α =1.5406 Å), B = half-width of reflection (rad); θ_B = angle at peak-maximum [degree], with analysis here at the (111) reflection.

Bimetallic Cu/Zn nanoparticles

CuZn from PC (1.0 wt%)

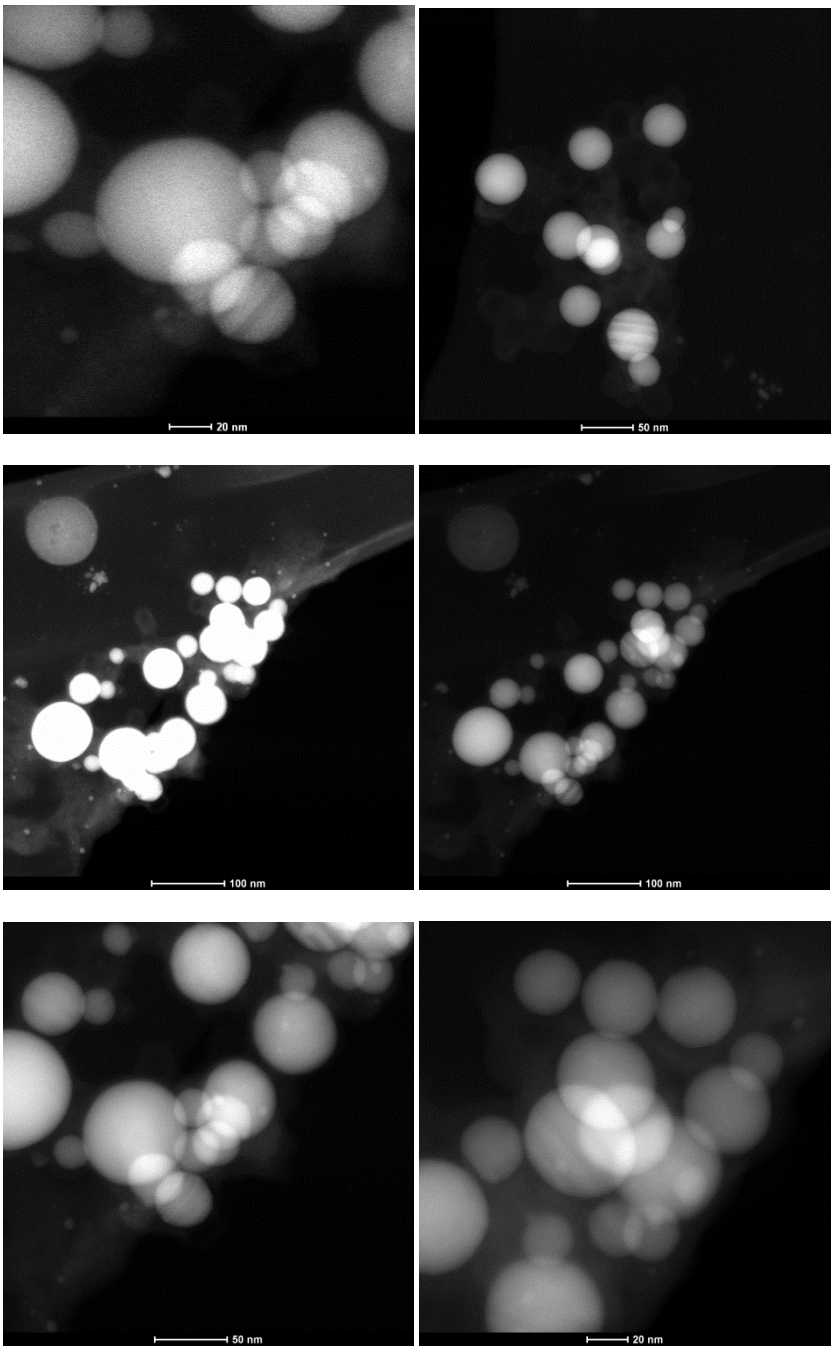


Fig. S7 HAADF-STEM for *β*-CuZn nanoparticles (1.0 wt% in PC).

CuZn from [BMIm][BF_4] (1.0 wt%)

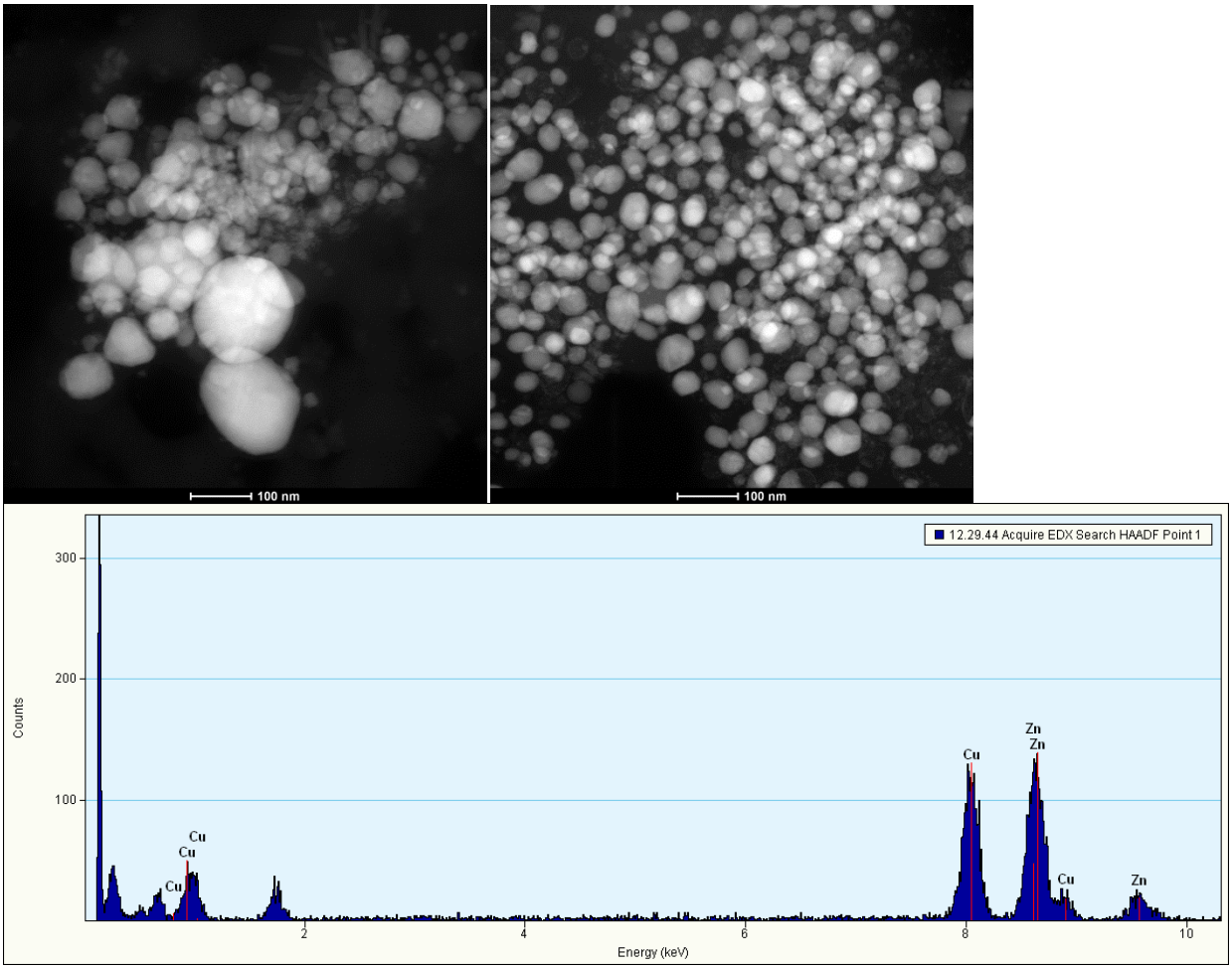


Fig. S8 HAADF-STEM (top) and EDX (bottom, averaged over 10-15 particles) of *β*-CuZn nanoparticles in IL.

Cu_3Zn from [BMIm][BF_4] (1.0 wt%)

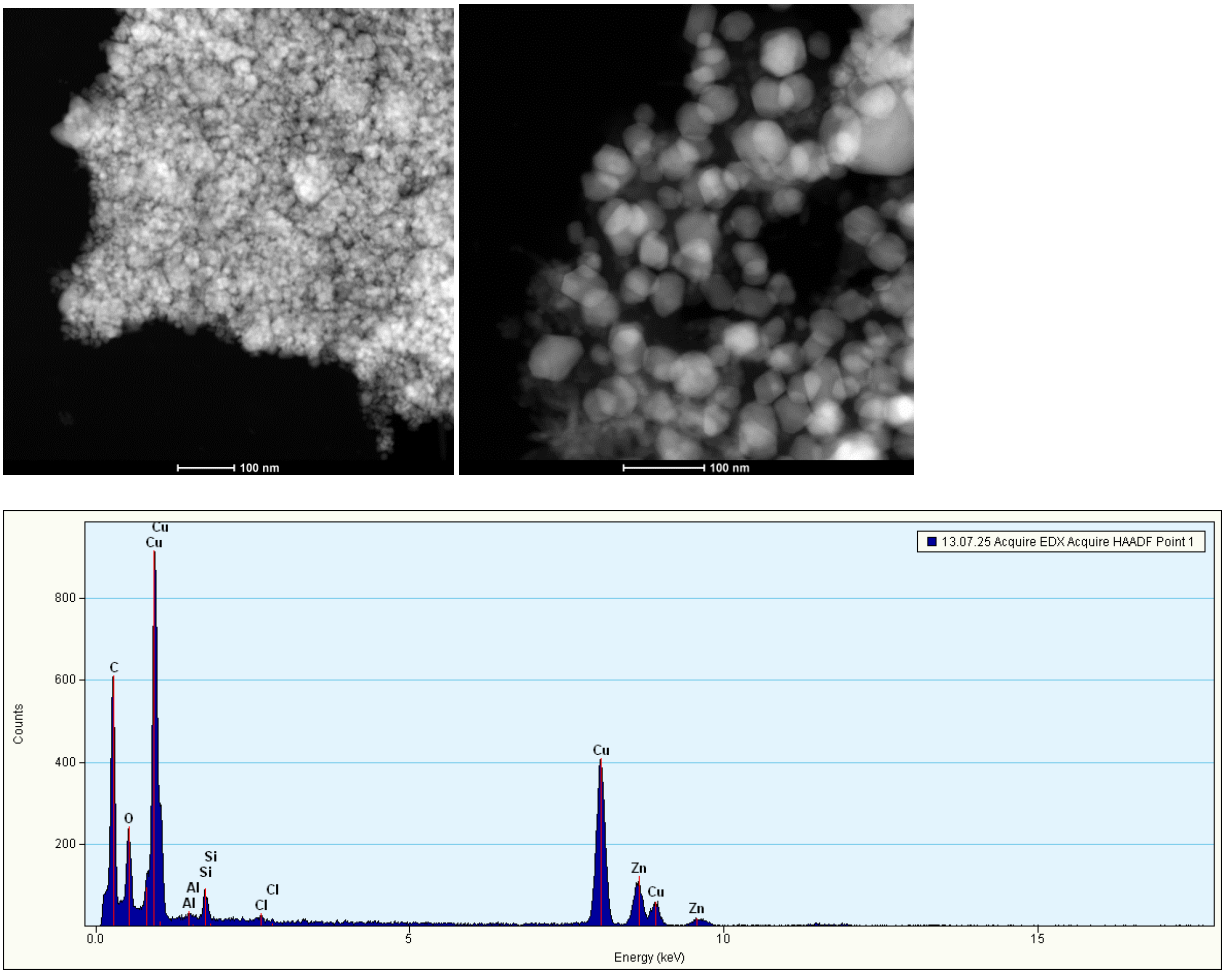
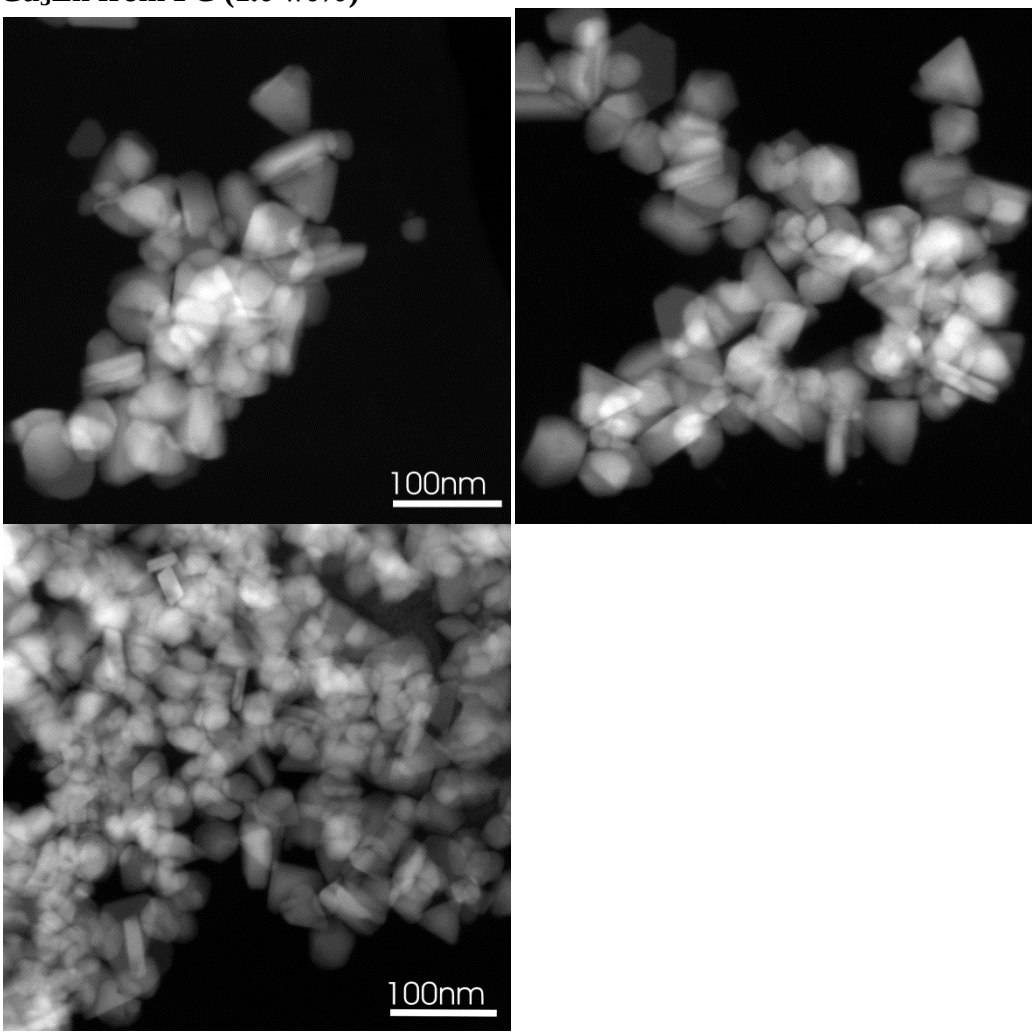


Fig. S9 HAADF-STEM (top) and EDX (bottom, averaged over 10-15 particles) of γ-Cu_3Zn nanoparticles in [BMIm][BF_4].

Cu_3Zn from PC (1.0 wt%)



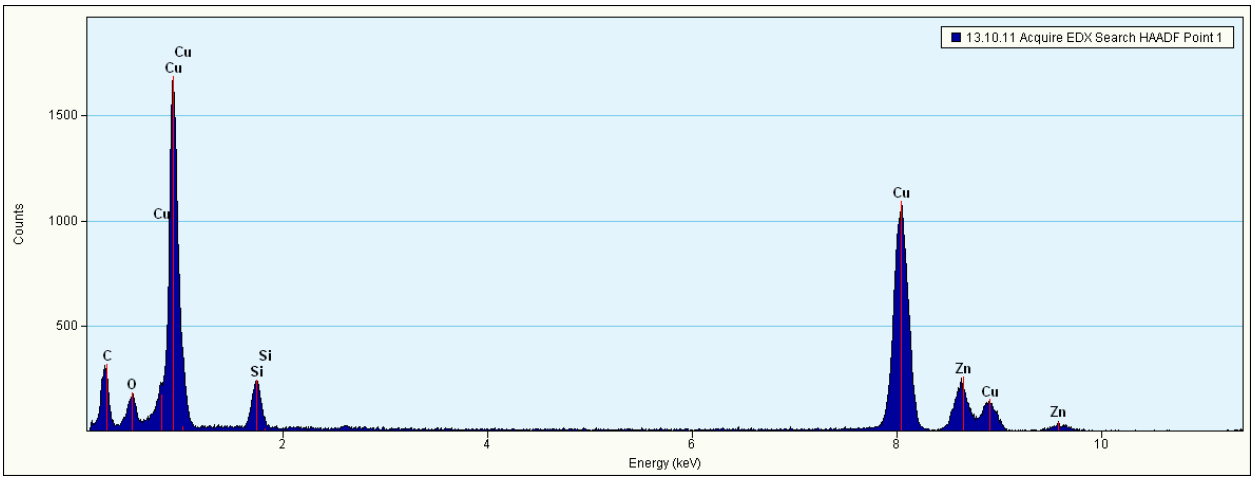


Fig. S10 HAADF-STEM (top) and EDX (bottom, averaged over 10-15 particles) of γ-Cu_3Zn nanoparticles in PC.

Catalytic MeOH synthesis

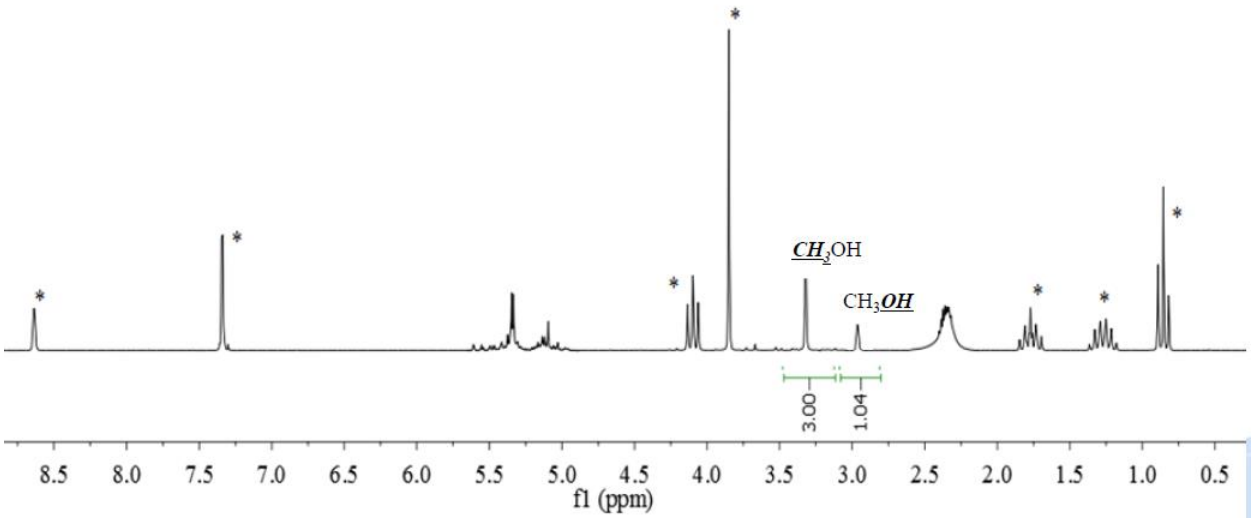


Fig. S7 ^{1}H NMR Spectrum ($CDCl_3$, 500.13 MHz, 265 K) of the reaction solution from the catalytic methanol synthesis with β-CuZn-NP/IL dispersion (1.0 wt% CuZn in *[BMIm][BF_4] at 220 °C and 30 bar after 3 h).

Calibration XPS

Spectra have been recorded, using Al K_{alpha} X-rays, from clean samples of copper, silver and gold, at 20 eV and 10 eV pass energies and compared with reference values. The results are shown below.

20 eV Pass Energy

	Reference	Experiment	Difference
Au 4f7/2	83.98 ± 0.02	84.00	+ 0.02
Ag 3d5/2	368.26 ± 0.02	368.25	- 0.01
Cu 2p3/2	932.67 ± 0.02	932.71	+ 0.04

10 eV Pass Energy

	Reference	Experiment	Difference
Au 4f7/2	83.98 ± 0.02	84.00	+ 0.02
Ag 3d5/2	368.26 ± 0.02	368.24	- 0.02
Cu 2p3/2	932.67 ± 0.02	932.67	0.0