Supporting Information

Enhanced Catalytic Activity of Copper Complexes in Microgels for Aerobic Oxidation of Benzyl Alcohols

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Instruments and methods

NMR spectroscopy

NMR spectra were recorded at room temperature on a Bruker Avance II (400 MHz) or a Bruker Avance III (400 MHz). ^{1}H and ^{13}C NMR spectra are given relative to a deuterated solvent as an internal standard.

Dynamic light scattering (DLS)

Dynamic light scattering (DLS) measurements were performed to determine the hydrodynamic radius R_h of all synthesized microgels. The measurements were executed with an ALV/CGS-3 Compact Goniometer System from ALV-Laser Vertriebsgesellschaft mbH, employing a He-Ne laser with a wavelength of 632.8 nm as radiation source. For sample preparation, one drop of filtered (Chromafil®, PTFE filter, pore size 1.2 µm) aqueous microgel solution was filled into a DLS tube and diluted with filtered (Chromafil®, PTFE filter, pore size 0.2 µm) distilled water. The tube was placed in the measurement chamber in a toluene bath tempered at 25 °C. An angle-dependent measurement with angles ranging from 35° to 100° in steps of 5° was performed. The collected data were analyzed with a cumulant fit using the MathWorks®software MATLAB. The hydrodynamic radius R_h and the respective standard deviation were directly obtained from the fit.

Scanning electron microscopy (SEM)

Electron microscopy was used to picture the morphology of the synthesized microgels. The measurement was performed on a UHR- FE-SEM SU9000 from Hitachi. For SEM images the samples were prepared on silicon wafers.

Infrared spectroscopy (IR)

FT-IR spectra were recorded on a Shimadzu IRTracer 100 using a CsI beam splitter in combination with an ATR unit (Quest model from Specac utilizing a robust monolithic crystalline diamond) in a resolution of 2 cm^{-1}.

High resolution mass spectrometry (HRMS)

Electrospray ionization (ESI) mass spectrometry was performed on an LTQ Orbitrap XL of ThermoFisher Scientific with a source voltage of 4.49 kV, a capillary temperature of 299.54 °C and a tube lens voltage between 110 and 130 V.

Single crystal X-ray diffraction (XRD)

The single crystal diffraction data were collected on a Stadivari diffractometer of STOE with an Eulerian cradle and Dectris Pilatus3 R 200K hybrid-pixel detector with GeniX 3D high flux Mo radiation (λ = 0.71073 Å). The temperature was controlled by an Oxford Cryostream 800. Crystals were mounted with grease on glass fibers. Data were collected with X-Area Pilatus[1] and integrated with X-Area Integrate[2] and X-Area Recipe.[3] The absorption correction was performed by Gaussian integration with Stoe X-Red32, afterwards scaling of reflections with X-Area LANA.[4] The structure was solved by direct methods (XPREP[5], ShelXT[6]) and refined with ShelXle[7] against F^2 with the full-matrix least-square method (ShelXL[8]). Hydrogen atoms were derived from difference Fourier maps and

placed at idealized positions, riding on their parent C atoms, with isotropic displacement parameters Uiso(H) = 1.2Ueq(C) and 1.5Ueq(C methyl). All methyl groups were allowed to rotate but not to tip.

Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as CCDC – 1988615. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed to determine the copper concentration in the copper loaded microgels. The measurements were carried out on an 8800 ICP-MS Triple Quad (G3663A) from Agilent. Water was used as a matrix for the measurements and no internal standard was applied. The detection limit of the spectrometer for copper was 40.25 ppb with a background equivalent concentration of 591.8 ppb. For sample preparation, the microgel solutions were acidified with a 0.1 M hydrochloric acid solution. The acidified samples were measured by an external calibration. All measurements are five-time determinations.

Electron paramagnetic resonance spectroscopy (EPR)

EPR spectra were obtained at room temperature on a Miniscope MS 400 from Magnettech with a microwave frequency of 9.4 GHz. Microgel solutions (and copper complex and copper chloride solutions as references) with a concentration of 10 mM regarding the copper(II) chloride amount were measured. The B_0 field was adjusted to 308 mT with a range of 160 mT (228 – 388 mT) and a sweep time of 60 s. Other parameters were adjusted as follows: smooth = 0.1000 s, NOPs = 4096, gain mantissa = 5 and gain exponent = 1.

Gas chromatography

Gas chromatographic measurements were performed on a Shimadzu GC2010plus (FS-Supreme 5mS capillary column; 5% phenylmethylpolysiloxane, length: 30 m, diameter: 0.32 mm, film thickness: 0.25 µm, flame ionisation detector). To determine the conversion of the alcohols to the corresponding aldehydes 1,3-dimethoxybenzene was used as internal standard.

The relative response factors[9] f_P were calculated following equation $(S1)$, where A_P and A_{IS} are the areas of the product signal and the internal standard signal and [P] and [IS] are the concentrations of product and internal standard, respectively. With the response factor the concentration of product [P] within a sample can be calculated (equation $(S2)$).

$$f_{\mathrm{P}} = \frac{A_{\mathrm{P}} \cdot [\mathrm{IS}]}{A_{IS} \cdot [\mathrm{P}]} \qquad (S1)$$

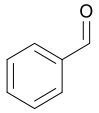
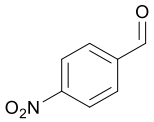
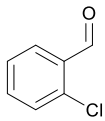
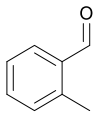
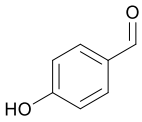
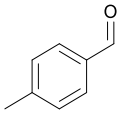
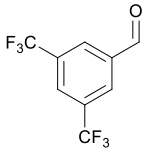
$$[\mathrm{P}] = \frac{A_{\mathrm{P}} \cdot [\mathrm{IS}]}{A_{\mathrm{IS}} \cdot f_{\mathrm{P}}} \qquad (S2)$$

For the determination of the response factors of each product five mixtures of the internal standard (40 µL) and a varying amount (20 mg, 40 mg, 60 mg, 80 mg, 100 mg) of product in 50 mL ethyl acetate were analyzed by GC to give area ratios. Each mixture was measured three times. The value of the response factors was obtained as an average over all measurements. The response factors are

summarized in Table S1. The quality of each response factor was determined by measuring the deviation on the conversion of a reference sample with known concentration of product and internal standard.

For the analysis of the product of the catalytic reactions the internal standard (25 µL) was added after the reaction was finished and the reaction mixture was stirred to let the internal standard be homogeneously distributed. Subsequently, a small amount of the reaction mixture (30 µL) was taken by a syringe and added to a mixture of NH_3 (0.3 mL) and Ethyl acetate (0.9 mL). Both phases were mixed heavily to remove residues of copper from the organic phase. The organic phase was dried by the addition of Na_2SO_4. The organic phase was analyzed via gas chromatography and the concentration of the product was calculated via equation $(S2$.

Table S1: Response factors f_P for the synthesized aldehydes and the corresponding deviation on the conversion.

Entry	Product	f_P	Deviation on the conversion
1		0.94	±2.0%
2		0.87	±1.0%
3		0.91	±0.5%
4		0.95	±4.0%
5		0.83	±4.5%
6		1.05	±0.5%
7		1.11	±6.0%

Column chromatography

Column chromatography was performed with silica gel 60 (40-63 µm) from Merck and with n-Hexane:Ethyl acetate (30:1) as eluent.

All analytical data for the used ligand and copper complex were deposited as original data in the repository Chemotion and are published under an Open Access model. The link to the original data is given in the analytical description.[10,11]

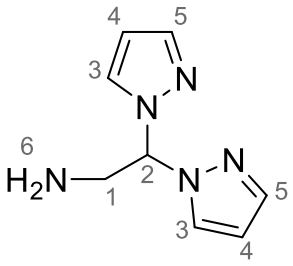
Synthetic procedures and analytics

Materials

N-Vinylcaprolactam (VCL, 98%, Sigma-Aldrich) was distilled under reduced pressure and subsequently recrystallized in n-hexane. Glycidyl methacrylate (GMA, 97%, Sigma-Aldrich) was purified by column chromatography using aluminium oxide (Honeywell Fluka, activated, alkaline, Brockmann I). Crosslinker N,N'- methylenebisacrylamide (BIS, 99%; Sigma-Aldrich) and initiator 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AMPA, 97%, Sigma-Aldrich) were used as received. For the ligand 2,2-dimethoxyethanamine (99%, Sigma-Aldrich), 1,8-Naphthalic anhydride (Sigma-Aldrich), Pyrazole (98%, Sigma-Aldrich), p-Toluenesulfonic acid (>98%, TCI) and Hydrazine monohydrate (>98%, TCI) were used as received. Copper(I) chloride (98%, Abcr) and copper(II) chloride (99%, Acros Organics) for the loading of the microgels were used as received.
The substrates for the catalytic reactions: Benzyl alcohol (99%, Alfa Aesar), 4-Nitrobenzyl alcohol (99%, Sigma-Aldrich), 2-Chloro benzyl alcohol (98+%, Alfa Aesar), 2-Methylbenzyl alcohol (98%, Alfa Aesar), 4-Hydroxy benzyl alcohol (99%, Sigma-Aldrich), 4-Methylbenzyl alcohol (>97%, TCI), 3,5-Bis(trifluoromethyl)benzyl alcohol (98%, Merck) and TEMPO (98+%, Alfa Aesar) as additive were also used as received. The following aldehydes which were used to determine the response factors were used as received from the following distributers: Benzaldehyde (99+%, Alfa Aesar), 4-Nitrobenzaldehyde (98%, Sigma-Aldrich), 2-Chloro benzaldehyde (97%, Abcr), 2-Methylbenzaldehyde (99%, Abcr), 4-Hydroxy benzaldehyde (98%, Alfa Aesar), 4-Methylbenzaldehyde (99+%, Acros Organics), 3,5-Bis(trifluoromethyl)benzaldehyde (98%, Abcr). The internal standard 1,3-dimethoxybenzene (97%, abcr) was used as received.
Corresponding solvents were analytical grade (Merck) and were used as received.

Synthesis of 2,2-di-pyrazol-1-yl-ethanamine[12]

The amine functionalized scorpionate ligand was synthesized following the procedure of Reger *et al.*[12] By a three-step synthesis starting from 1,8-naphthalic anhydride and 2,2-dimethoxyethanamine the product 2,2-di-pyrazol-1-yl-ethanamine was obtained as a hygroscopic brown solid. Yield: 96%.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, ^{3}J = 2.4 Hz, 2H, H-3), 7.57 (d, ^{3}J = 1.8 Hz, 2H, H-5), 6.40 (t, ^{3}J = 6.9 Hz, 1H, H-2), 6.29 (dd, ^{3}J = 2.3, 1.9 Hz, 2H, H-4), 3.78 (d, ^{3}J = 6.9 Hz, 2H, H-1), 1.97 (br s, 2H, H-6) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6 (2C, C-5), 129.2 (2C, C-3), 106.9 (2C, C-4), 77.2 (C-2), 45.0 (C-1) ppm.

IR $\tilde{\nu}$ [cm^{-1}]: 3375 (w), 3312 (vw), 3146 (w), 3122 (vw), 2914 (vw), 1705 (vw), 1641 (w), 1614 (w), 1513 (w), 1431 (m), 1391 (m), 1337 (w), 1298 (m), 1289 (m), 1263 (m), 1223 (w), 1206 (w), 1151 (vw), 1087 (s), 1043 (m), 966 (w), 931 (w), 915 (m), 896 (w), 852 (m), 809 (m), 755 (vs), 705 (s), 664 (w), 655 (m), 621 (vs), 611 (m), 505 (m).

HRMS-ESI^{+} (*m/z*): $[M + Na]^{+}$ calcd. for $C_8H_{11}N_5Na$, 200.09079; found, 200.09067.

Full analytic data have been deposited in the Chemotion repository. The full data set including original data files can be found free of charge under the following link: https://dx.doi.org/10.14272/PFBKJCSJBZOEJW-UHFFFAOYSA-N.1.

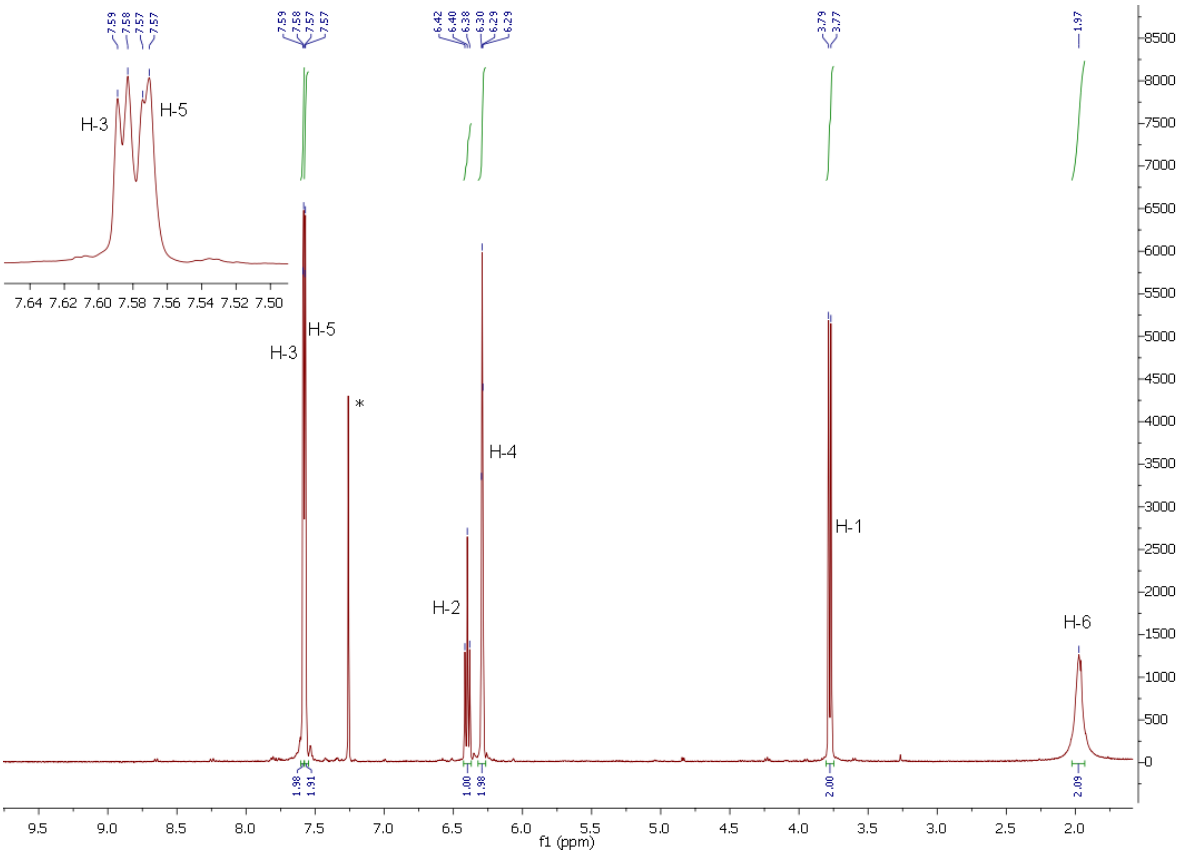


Figure S1: ^{1}H NMR spectra of the scorpionate ligand 2,2-di-pyrazol-1-yl-ethanamine (marks the solvent $CDCl_3$).*

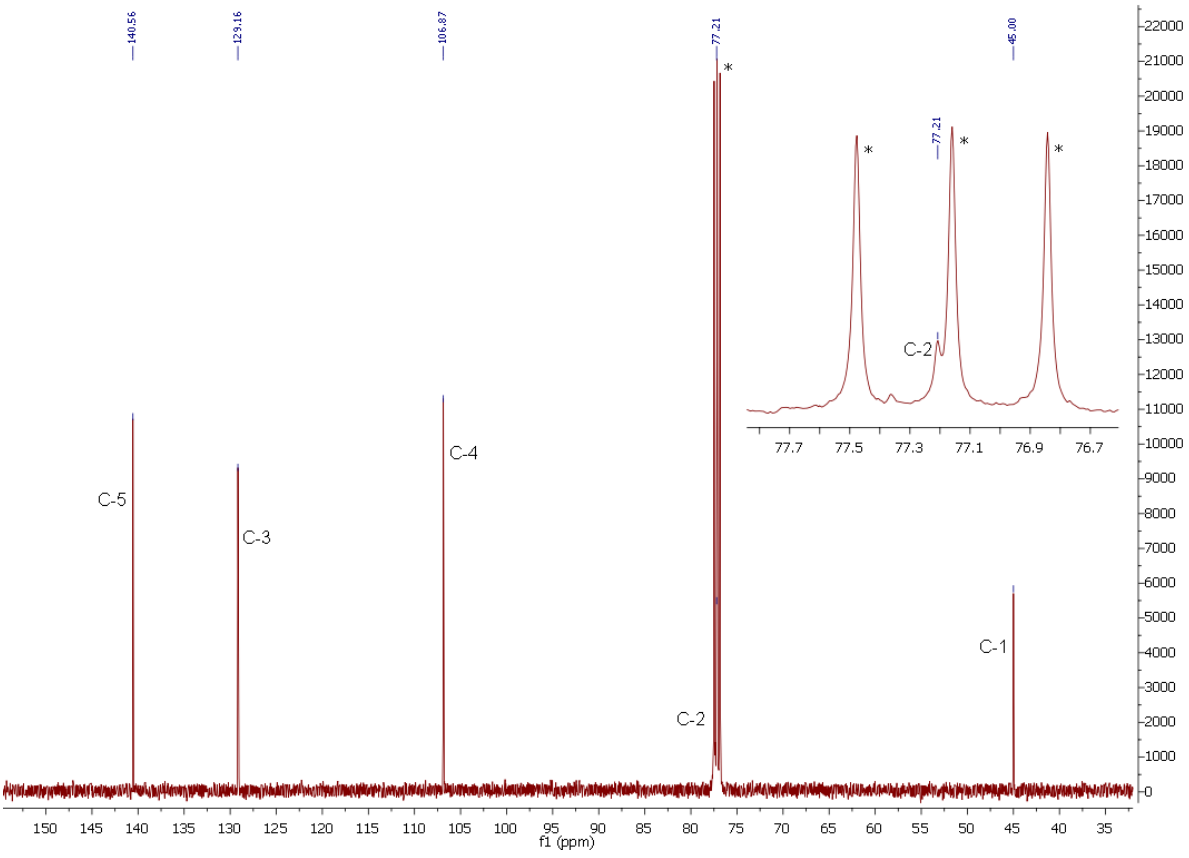


Figure S2: ^{13}C NMR spectra of the scorpionate ligand 2,2-di-pyrazol-1-yl-ethanamine (marks the solvent $CDCl_3$).*

Synthesis of pVCL-GMA microgel

The pVCL-GMA microgels were synthesized *via* free radical precipitation polymerization according to literature.[13] For synthesis of a 450mL-batch of the desired microgel, the reactants VCL (5.768 g, 87mol%), GMA (0.65 ml, 10mol%) and BIS (0.146 g, 2mol%) were dissolved in 449 mL of distilled, degased water in a round bottom flask with septum. For the start of the reaction the initiator AMPA (0.0771 g, 1mol%) dissolved in 1 mL of distilled water was rapidly added at 70 °C. The reaction was executed for 1.5 h under argon atmosphere giving pVCL-GMA microgels (88% yield). For purification, the microgel was dialyzed (pore size of dialysis membrane 12 000 Da to 14 000 Da) against distilled water and subsequently freeze-dried on a Christ Alpha 1-4 LDplus for analysis.

Functionalization of pVCL-GMA microgels

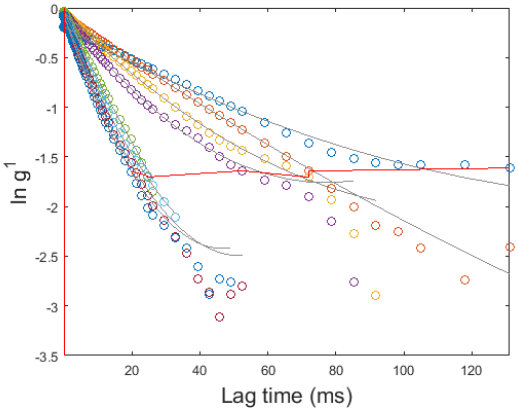
The pVCL-GMA microgel (2030 mg of which 10w% are GMA groups (determined by FTIR spectroscopy), 1.428 mmol related to the GMA content, 1 eq) was dispersed in distilled water (100 mL). 2,2-Di-pyrazol-1-yl-ethanamine (303.6 mg, 1.714 mmol, 1.2 eq) was added to the solution. The reaction mixture was stirred at room temperature for 16 hours. For purification, the functionalized pVCL-GMA-BPM microgel was dialyzed (pore size of dialysis membrane 12 000 Da to 14 000 Da) against distilled water and afterwards lyophilized.

Loading of the functionalized microgels with CuCl/$CuCl_2$ for analysis

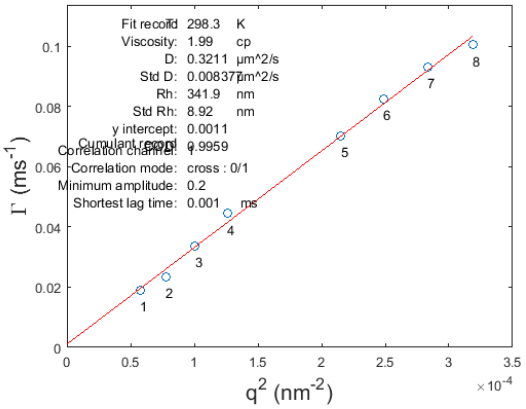
The functionalized pVCL-GMA-BPM microgel (21.3 mg of which 10w% are functionalized, 0.015 mmol related to a hypothetical complete functionalization, 1 eq) was dispersed in distilled water (4 mL). Copper(I) chloride (1.5 mg, 0.015 mmol, 1 eq) was added and the mixture was stirred for one hour at room temperature for complexation of the copper inside the microgel. Subsequently, the loaded microgel (Cu@pVCL-GMA-BPM) was dialyzed (pore size of dialysis membrane 12 000 Da to 14 000 Da) against distilled water and lyophilized. After onefold dialysis, ICP-MS and DLS samples were prepared by weighing in the loaded microgel and redispersing it in a defined amount of the respective solvent. Additionally, after twofold dialysis another ICP-MS sample was prepared.

For EPR analysis, the functionalized pVCL-GMA-BPM microgel (56.9 mg of which 10w% are functionalized, 0.04 mmol related to a hypothetical complete functionalization, 1 eq) was dispersed in distilled water (4 mL) and loaded with $CuCl_2$ (5.4 mg, 0.04 mmol, 1 eq). The reaction mixture was stirred for two hours at room temperature. EPR spectra of the microgel (in the following referred to as $CuCl_2$@pVCL-GMA-BPM) solution were recorded before and after onefold dialysis (pore size of dialysis membrane 12 000 Da to 14 000 Da) against distilled water. As references the spectra of copper(II) chloride and the free copper complex with the amine ligand [BPM$CuCl_2$] were recorded. Therefore, $CuCl_2$ (5.4 mg, 0.04 mmol, 1 eq) or $CuCl_2$ (5.4 mg, 0.04 mmol, 1 eq) and 2,2-di-pyrazol-1-yl-ethanamine (7.1 mg, 0.04 mmol, 1 eq) were dissolved in distilled water (4 mL) and stirred. Subsequently, EPR samples were prepared of both references.

DLS analysis

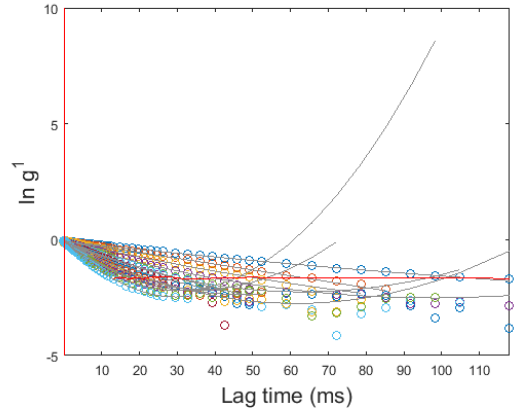


(a) Plot of ln g^1 *vs* τ.

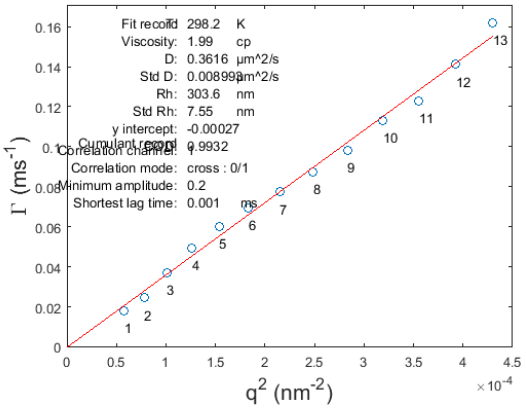


(b) Plot of Γ *vs* q^2.

Figure S3: DLS measurement of the pVCL-GMA microgel in DMSO.

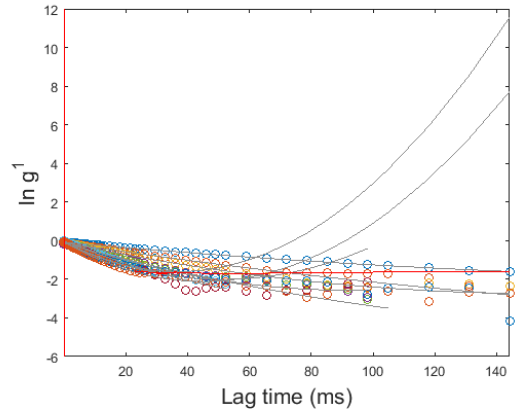


(a) Plot of ln g^1 *vs* τ.

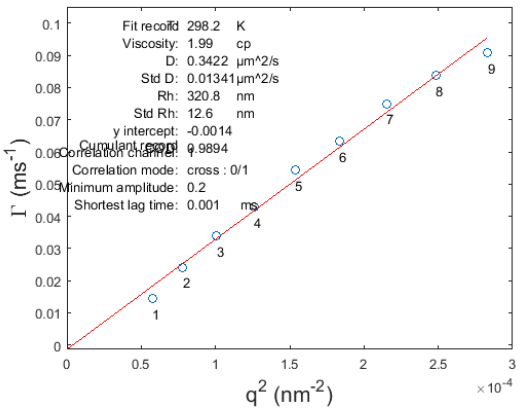


(b) Plot of Γ *vs* q^2.

Figure S4: DLS measurement of the functionalized pVCL-GMA-BPM microgel in DMSO.



(a) Plot of ln g^1 *vs* τ.



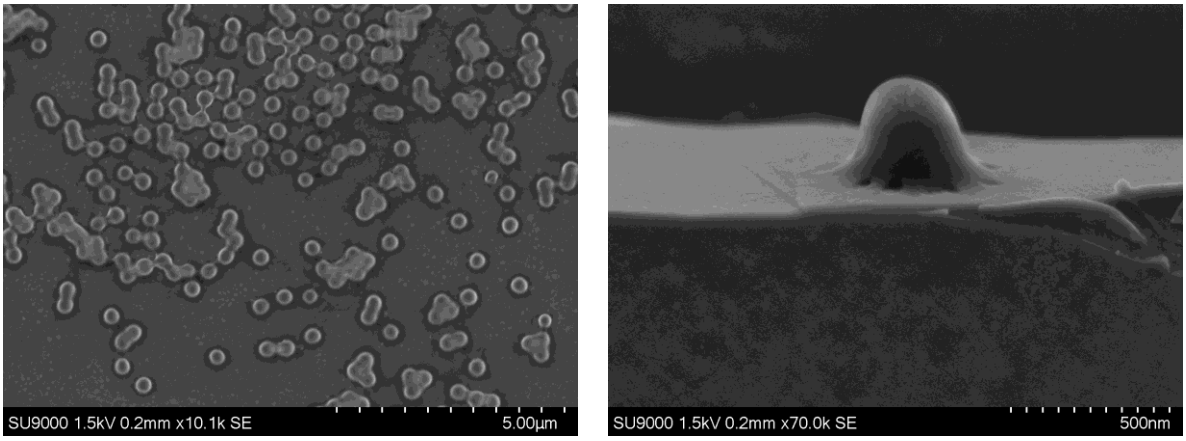
(b) Plot of Γ *vs* q^2.

Figure S5: DLS measurement of the copper loaded functionalized microgel (Cu@pVCL-GMA-BPM) in DMSO.

Table S2: Hydrodynamic radii of the investigated microgels measured in DMSO.

Microgel	R_h [nm]
pVCL-GMA	341.9±8.9
pVCL-GMA-BPM	303.6±7.6
Cu@pVCL-GMA-BPM	320.8±12.6

SEM analysis



(a) Visualization of multiple microgels. *(b) Visualization of a single microgel.*

Figure S6: SEM images of the Cu@pVCL-GMA-BPM microgels.

Synthesis of Copper(II) 2,2-di-pyrazol-1-yl-ethanamine chloride [Cu{HC(Pz)$_2$CH$_2$NH$_2$}Cl$_2$]

To provide a first insight into the possible structure of the bis(pyrazolyl)methane copper complex in the interior of the microgels the complex was synthesized and crystals suitable for X-ray analysis should be grown. Since all attempts to obtain crystals with copper(I) chloride the corresponding copper(II) chloride complex was synthesized. Therefore, a solution of 2,2-di-pyrazol-1-yl-ethanamine (8.9 mg, 0.05 mmol, 1 eq) in DCM (1 mL) was added to a solution of copper(II) chloride (8.5 mg, 0.05 mmol, 1 eq) in MeOH (1 mL). Slow diffusion of diethyl ether into the complex solution leads to the formation of greenish blue crystals (9.5 mg, 0.031 mmol, 61%).

IR $\tilde{\nu}$ [cm^{-1}]: 3298 (w), 3238 (vw), 3113 (w), 2978 (w), 2163 (w), 1639 (w), 1513 (w), 1453 (w), 1403 (m), 1297 (m), 1264 (w), 1210 (w), 1158 (vw), 1091 (m), 1054 (m), 984 (vw), 938 (w), 919 (w), 903 (w), 846 (m), 783 (m), 767 (vs), 705 (m), 694 (m), 656 (vw), 628 (m), 608 (w), 576 (w).

HRMS-ESI$^+$ (*m/z*): calcd.: 274.99935 (100) [$C_8H_{11}N_5{}^{63}Cu^{35}Cl]^+$, 276.00270 (9) [$^{13}C_1{}^{12}C_7H_{11}N_5{}^{63}Cu^{35}Cl]^+$, 276.99754 (45) [$C_8H_{11}N_5{}^{65}Cu^{35}Cl]^+$, 278.00089 (4) [$^{13}C_1{}^{12}C_7H_{11}N_5{}^{65}Cu^{35}Cl]^+$, 278.99459 (14) [$C_8H_{11}N_5{}^{65}Cu^{37}Cl]^+$, 279.99794 (1) [$^{13}C_1{}^{12}C_7H_{11}N_5{}^{65}Cu^{37}Cl]^+$; found: 274.99945 (100), 276.00269 (8), 276.99686 (78), 278.00009 (6), 278.99423 (15), 279.99744 (1).

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-AMQWWHVPPZ-UHFFFADPSC-NUHFF-LUHFF-NUHFF-ZZZ

Additional analytical information on the copper complex including original data files is available via Chemotion repository: https://dx.doi.org/10.14272/AMQWWHVPPZUOKP-UHFFFAOYSA-L.1.

Crystal structure of Copper(II) 2,2-di-pyrazol-1-yl-ethanamine chloride $[Cu\{HC(Pz)_2CH_2NH_2\}Cl_2]$

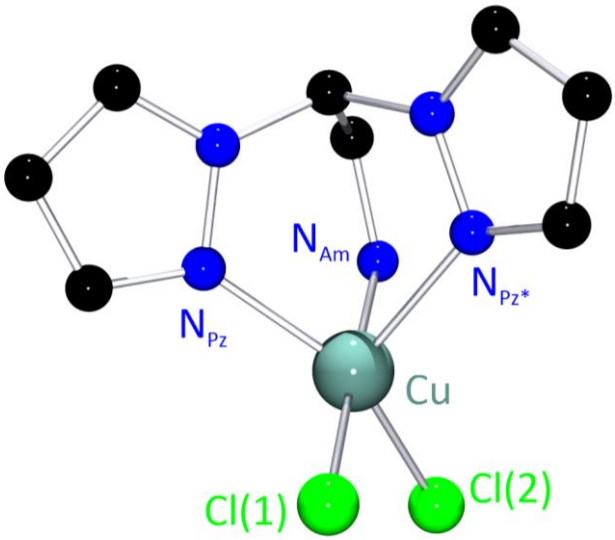


Figure S7: Molecular structure of the complex copper(II) 2,2-di-pyrazol-1-yl-ethanamine chloride $[Cu\{HC(Pz)_2CH_2NH_2\}Cl_2]$ in the solid state. Two complex molecules and one water molecule crystallize in the asymmetric unit. Hydrogen atoms, one independent complex molecule and the water molecule are omitted for clarity. N_{Am} = amine nitrogen donor atom, N_{Pz}/N_{Pz*} = pyrazolyl nitrogen donor atom.

Table S3: Selected bond lengths, angles and the τ_5 parameter of copper complex $[Cu\{HC(Pz)_2CH_2NH_2\}Cl_2]$.

	$[Cu\{HC(Pz)_2CH_2NH_2\}Cl_2]$	
	complex molecule 1	complex molecule 2
Bond length [Å]		
Cu-N_{Pz}	2.053(6)	2.052(5)
Cu-N_{Pz*}	2.205(6)	2.244(6)
Cu-N_{Am}	2.028(5)	2.022(5)
Cu-Cl(1)	2.289(2)	2.272(2)
Cu-Cl(2)	2.292(2)	2.274(2)
Bond angles [°]		
N_{Pz}-Cu-Cl(1)	159.6(2)	149.6(2)
N_{Am}-Cu-Cl(2)	172.3(2)	177.9(2)
τ_5[14]	0.21	0.47

Table S4: Crystallographic data and parameter of the copper complex.

	$[Cu\{HC(Pz)_2CH_2NH_2\}Cl_2]_2 \times H_2O$
empirical formula	$C_{16}H_{24}Cl_4Cu_2N_{10}O$
formula mass [g mol^{-1}]	641.33
crystal size [mm]	0.120 x 0.090 x 0.080
T [K]	100
crystal system	triclinic
space group (No)	$P\bar{1}$ (2)
a [Å]	7.7357(15)
b [Å]	12.816(3)
c [Å]	13.522(3)
α [°]	110.78(3)
β [°]	103.66(3)
γ [°]	96.17(3)
V [Å^3]	1190.6(5)
Z	2
ρ_{calc} [g cm^{-3}]	1.789
μ [mm^{-1}]	2.268
λ [Å]	0.71073
F(000)	648
hkl range	-9/9; -15/15; -13/16
refIns collected	8358
independent refIns	4269
R_{int}	0.0584
No. parameters	322
R_1 [$I \geq 2\sigma(I)$]	0.0659
wR2 (all data)	0.1753
GoF	1.097
$\Delta\rho_{fin}$ max/min [e Å^{-3}]	0.706/-0.764

ICP-MS analysis

Copper concentrations are given in ppm $\left(\frac{mg(Cu)}{kg(water)}\right)$.

The expected copper concentration is calculated regarding the GMA groups in the microgel (one copper center per GMA monomer), e.g. calculated for the Cu@pVCL-GMA-BPM microgel after twofold dialysis:

$$c_{\text{Cu@pVCL-GMA-BPM}} = 6.0\ \frac{\text{mg(microgel)}}{\text{mL(water)}} \xrightarrow{\text{of that}} 0.60\ \frac{\text{mg(GMA)}}{\text{mL(water)}} \rightarrow \frac{n_{\text{GMA}} = 4.22 \cdot 10^{-6}\ \text{mol}}{\text{mL(water)}}$$

$$\xrightarrow{\text{of that}} c_{\text{Cu}} = 2.682 \cdot 10^{-4}\ \frac{\text{g(Cu)}}{\text{mL(water)}} \mathrel{\widehat{=}} 268.2\ \frac{\text{mg(Cu)}}{\text{kg(water)}}$$

Table S5: Results of the ICP-MS measurements for the determination of the copper concentration inside the microgels.

Sample	**MG-concentration** $\left[\frac{\text{mg(microgel)}}{\text{mL(water)}}\right]$	**Determined Cu-concentration** [ppm]	**Expected Cu-concentration** [ppm]	**Percentage**
Distilled water	---	0	0	---
pVCL-GMA	---	0.1	0	---
pVCL-GMA-BPM*	23.7	2.3	0	---
Cu@pVCL-GMA**	23.0	4.3	(1028.2)	(0.4%)
Cu@pVCL-GMA-BPM*	2.4	13.0	107.3	12.1%
Cu@pVCL-GMA-BPM**	6.0	12.5	268.2	4.7%

* ICP-MS measured after onefold dialysis.

** ICP-MS measured after twofold dialysis.

The unfunctionalized pVCL-GMA microgel and the used distilled water show no copper content as expected, whereas the functionalized pVCL-GMA-BPM microgel contains 2.3 ppm of copper. This may be due to small amounts of copper in the solvents used in the synthesis of the ligand. As a reference the copper concentration inside a “loaded” unfunctionalized pVCL-GMA microgel was determined after twofold dialysis. The low copper content of 4.3 ppm verifies that no permanent incorporation without the ligand functionalization occurs. The determined concentration only amounts to 0.4% of the theoretical maximal copper concentration regarding the used amount of copper chloride (values in brackets only calculated theoretically for comparison with the loaded microgels). The loaded Cu@pVCL-GMA-BPM microgels show a copper concentration of 13.0 ppm after onefold dialysis which equals 12.1% of the expected value. In another experiment the Cu@pVCL-GMA-BPM microgels were analyzed after twofold dialysis. Within this sample the copper content is further reduced to 4.7% of the expected amount (12.5 ppm). Thus, copper can be immobilized inside the ligand functionalized microgels which is not possible in the unfunctionalized microgels. However, the copper concentration in the Cu@pVCL-GMA-BPM microgels is much lower than expected. This is due to an incomplete functionalization of the pVCL-GMA microgels and the formation of tertiary amines as a result of the reaction between one amine ligand and two epoxide groups. Both reasons cause a lower ligand concentration inside the microgels and therefore a lower ability of the microgels to incorporate copper.

EPR analysis

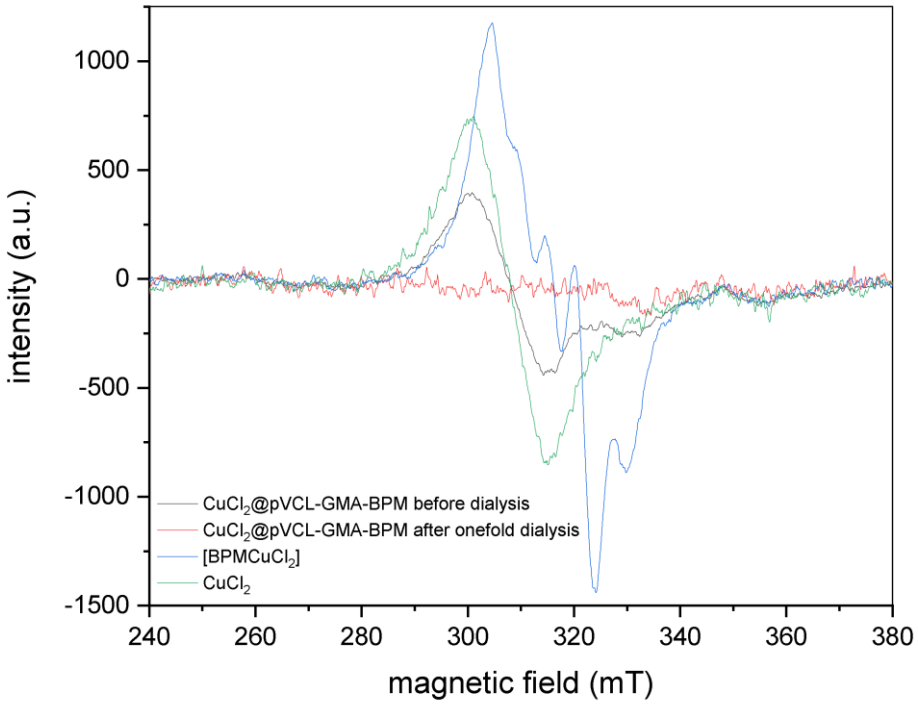


Figure S8: EPR spectra of $CuCl_2$@pVCL-GMA-BPM before and after dialysis. As references the spectra of $CuCl_2$ and the [BPM$CuCl_2$] complex are shown. The parameters were adjusted as follows: modulation = 0.2 and $MW_{atten.}$ = 6.0.

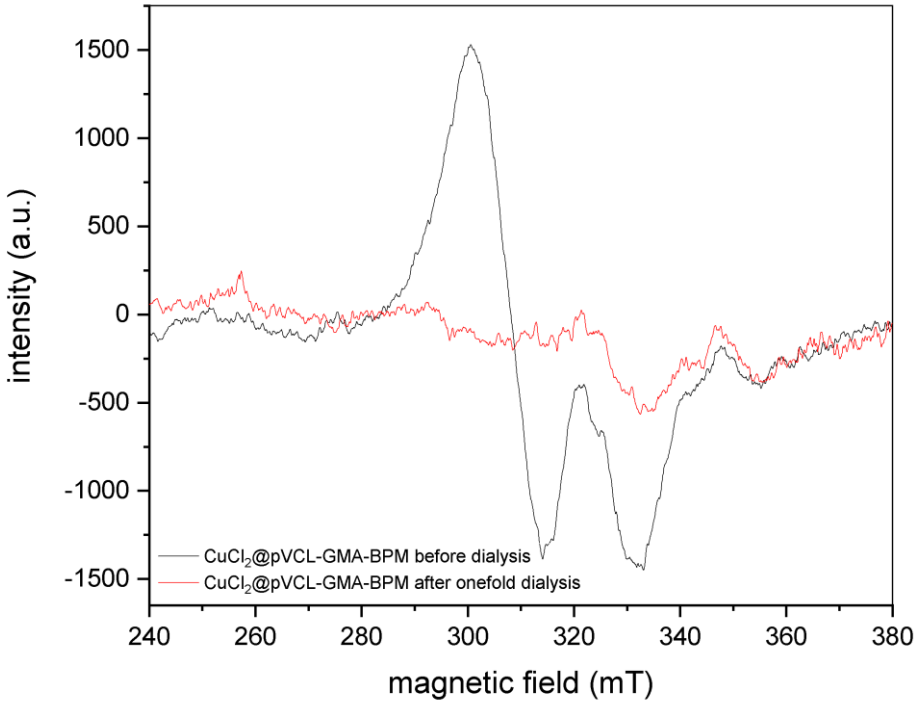


Figure S9: EPR spectra of $CuCl_2$@pVCL-GMA-BPM before and after dialysis. The parameters were adjusted as follows: modulation = 0.7 and $MW_{atten.}$ = 5.0.

EPR spectra were measured to analyze the binding of the copper centers inside the microgels before and after dialysis. For comparison the spectra of copper(II) chloride and the free copper complex with the amine ligand [BPMCuCl$_2$] were recorded. In Figure S8 all measurements are outlined. The [BPMCuCl$_2$] complex (blue line) shows a distinct fine structure so an orthorhombic coordination of the copper centers can be assumed. For CuCl$_2$ (green line) no fine structure is observable. The spectra of the CuCl$_2$@pVCL-GMA-BPM microgel before dialysis (black line) are similar to the spectra of CuCl$_2$. Regarding the results obtained by ICP-MS this similarity can be expected as only around one-twentieth of the copper inside the microgel is incorporated permanently. Thus, the majority of the copper ions within the sample are not bound and the EPR signal equals the signal of CuCl$_2$. This observation is further confirmed by the spectra of CuCl$_2$@pVCL-GMA-BPM after dialysis (red line) as the CuCl$_2$ signal is not observable anymore. The CuCl$_2$@pVCL-GMA-BPM microgels after dialysis were analyzed by ICP-MS showing a copper concentration of only 3% of the theoretically expected amount which is too low for EPR measurements.

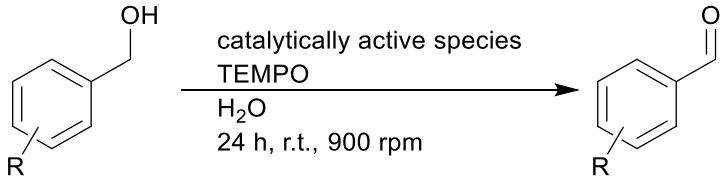
To compare the copper loaded microgels before and after dialysis more detailed EPR spectra of the samples were measured where the magnetic field modulation was increased (Figure S9). Adjusting the modulation leads to a better signal-to-noise ratio. For the CuCl$_2$@pVCL-GMA-BPM microgels before dialysis (black line) the signal of CuCl$_2$ is clearly visible at approximately 305 mT. Also, a signal at 330 mT is detected which can be observed in the CuCl$_2$@pVCL-GMA-BPM microgel after dialysis (red line) as well. This can be presumed as the signal of the copper which is permanently immobilized inside the microgel.

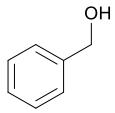
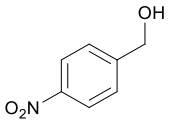
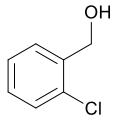
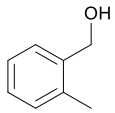
In conclusion, results obtained by ICP-MS and EPR analysis are consistent as both indicating the incorporation of only a small amount of copper centers inside the microgels and therefore the presence of unbound copper in the microgel solution before dialysis.

Catalytic reactions

For the first catalytic tests, the catalytically active species was formed *in situ* by dissolving or dispersing the precursors in water (4 mL). Different concentrations were tested because of optimization reasons. Therefore, either the functionalized microgel (92.8 mg of which 10w% are ligand, 10mol%) and copper chloride (5.7 mg, 0.057 mmol, 10mol%) or the amine ligand (10.2 mg, 0.057 mmol, 10mol%) and copper chloride (5.7 mg, 0.057 mmol, 10mol%) or only copper chloride (5.7 mg, 0.057 mmol, 10mol%) were used. The benzyl alcohol derivate (0.57 mmol, 1 eq) was added to the stirred solution and subsequently the reaction was started by adding TEMPO (9.0 mg, 0.057 mmol, 10mol%). The reaction mixture was stirred (900 rpm) at room temperature under air atmosphere for 24 hours. Afterwards, 1,3-dimethoxybenzene (25 µL) as an internal standard was added and a GC sample was prepared as described in the methods section. Therefore, a small amount of the reaction mixture (30 µL) was taken by a syringe, added to a mixture of NH_3 (0.3 mL) and ethyl acetate (0.9 mL), the phases were mixed to remove residues of copper from the organic phase and the organic phase was dried by the addition of Na_2SO_4. The conversion was determined via twofold gas chromatography measurement. All catalytic runs were performed twice. The averaged conversion of each product is displayed in Table S6.

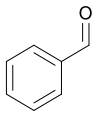
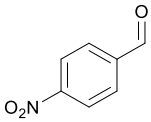
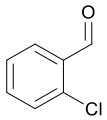
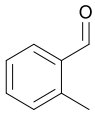
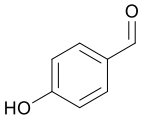
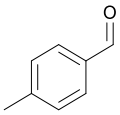
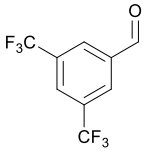
Table S6: Oxidation of primary alcohols to their corresponding aldehydes. The reaction was carried out in H_2O at room temperature and 10 mol% catalyst was used. Conversions were analyzed via gas chromatography.



Entry	Substrate	CuCl Conversion [%]	[BPMCuCl] Conversion [%]	Cu@pVCL-GMA-BPM Conversion [%]
1		20.7	20.3	11.0
2		23.9	10.9	3.5
3		21.4	25.2	2.7
4		20.9	35.0	5.0

For the catalytic oxidation reactions under optimized conditions the catalytically active species was formed *in situ* by dissolving or dispersing the precursors in DMSO (4 mL). Therefore, the functionalized microgel (21.3 mg of which 10w% are functionalized, 0.015 mmol related to a hypothetical complete functionalization, 5mol%) and copper chloride (1.5 mg, 0.015 mmol, 5mol%) or the amine ligand (2.7 mg, 0.015 mmol, 5mol%) and copper chloride (1.5 mg, 0.015 mmol, 5mol%) or only copper chloride (1.5 mg, 0.015 mmol, 5mol%) were used. The benzyl alcohol derivate (0.30 mmol, 1 eq) was added to the stirred solution and subsequently the reaction was started by adding TEMPO (2.3 mg, 0.015 mmol, 5mol%). The reaction mixture was stirred (900 rpm) at room temperature under air atmosphere for 24 hours. Afterwards, 1,3-Dimethoxybenzene (25 µL) as an internal standard was added, GC samples were prepared as described above and the conversion was determined via twofold gas chromatography measurement. All catalytic runs were performed twice. The conversion of each product and run is displayed in Table S7.

Table S7: Conversion of the catalytic aerobic oxidation reaction of the benzyl alcohols to their corresponding aldehydes. All catalytic runs were performed using 5mol% catalyst.

Entry	Product	Conversion to aldehyde* [%]					
		CuCl		[BPMCuCl]		CuCl@pVCL-GMA-BPM	
1		42.6	42.6	79.6	54.2	100.0	98.8
2		40.8	40.3	71.6	76.2	52.3	53.2
3		56.0	55.6	49.6	68.2	91.9	74.0
4		45.4	45.6	42.4	55.0	92.1	92.0
5		63.7	63.8	36.7	26.7	67.6	67.3
6		40.5	40.6	91.0	92.9	97.5	97.1
7		51.6	51.3	48.2	42.5	77.2	77.8

* Every value is the average of a twofold determination.

As a reference we tested the catalytic activity using only 1, 2 and 3mol% of CuCl (Table S8) and BPMCuCl (Table S9) for the oxidation of benzyl alcohol as we showed with the ICP-MS analysis that our catalytic system has less catalytic centers. The results show that the conversion decreases when using less CuCl or copper complex. This is also in accordance with the literature as most catalytic systems based on copper/TEMPO use 5 mol% as concentration for the catalyst and show less activity with less catalyst.[15,16,17]

In addition, we tested the unfunctionalized microgels (pVCL-GMA) with CuCl under optimized reaction conditions (5mol% catalyst) (Table S10). The results show that there is no enhancement in catalytic activity in comparison to the reaction with CuCl due to any coordination of the Cu^{+} ions inside the microgel.

Both reference experiments show the importance of the copper complex inside the protective environment of the microgel for the catalytic activity of our system. The copper complex in combination with the microgel is essential to reach high conversions which are not possible with only CuCl or BPMCuCl as catalyst. Even with lower concentration of catalytically active centers we reach in nearly all cases higher conversions in comparison to all systems analyzed in this paper.

Table S8: Conversion of the catalytic aerobic oxidation reaction of the benzyl alcohol to the corresponding aldehyde using 1, 2 and 3mol% CuCl as catalyst.

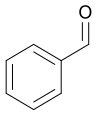
		Conversion to aldehyde* [%]					
Entry	**Product**	**1% CuCl**		**2% CuCl**		**3% CuCl**	
1		33.1	33.1	37.0	37.0	39.3	39.4

Table S9: Conversion of the catalytic aerobic oxidation reaction of the benzyl alcohol to the corresponding aldehyde using 1, 2 and 3mol% BPMCuCl as catalyst.

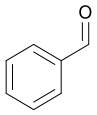
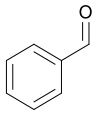
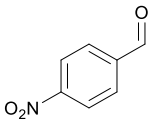
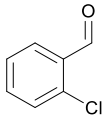
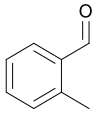
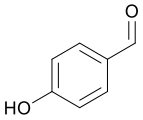
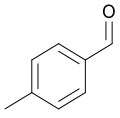
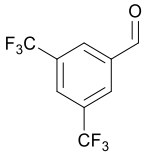
		Conversion to aldehyde* [%]					
Entry	**Product**	**1% BPMCuCl**		**2% BPMCuCl**		**3% BPMCuCl**	
1		40.6	40.0	47.4	47.3	47.2	47.2

Table S10: Results of the reference experiments to determine the influence of the ligand for catalytic activity. 5 mol% copper was used for the reaction corresponding to the optimized reaction conditions.

		Conversion to aldehyde* [%]	
Entry	**Product**	**CuCl@pVCL-GMA**	
1		47.2	45.7
2		43.6	42.0
3		42.0	41.4
4		44.6	44.5
5		5.9	5.9
6		47.7	47.3
7		32.4	32.3

Recycling

In this case a recycling of the catalytically active microgel was not possible under these reaction conditions. Removing the microgel via centrifugation still left residues of the microgel in the reaction mixture and the microgel that was recovered (about 80%, gravimetrical analysis) showed no activity in the oxidation reaction. Precipitation with bases like NaOH (2wt%) or triethyl amine leads to a coagulation of the microgel and a redispersion was not possible. The extraction of the reaction mixture with n-heptane or methyl cyclohexane leads to an accumulation of the microgel at the phase boundary. Removal of the microgel and subsequent redispersion was only partly successful but also showed no catalytic activity.

Benzaldehyde

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 7.93 – 7.86 (m, 2H), 7.68 – 7.60 (m, 1H), 7.58 – 7.46 (m, 2H) ppm.

4-Nitrobenzaldehyde

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.16 (s, 1H), 8.40 (d, *J*=8.7, 2H), 8.08 (d, *J*=8.8, 1H) ppm.

2-Chlorobenzaldehyde

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.50 (d, *J*=0.8, 1H), 7.93 (dd, *J*=7.7, 1.8, 1H), 7.54 (ddd, *J*=8.0, 7.2, 1.7, 1H), 7.46 (dd, *J*=8.1, 1.3, 1H), 7.40 (t, *J*=7.5, 1H) ppm.

o-Tolualdehyde (2-Methylbenzaldehyde)

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 10.28 (s, 1H), 7.80 (dd, *J*=7.6, 1.5, 1H), 7.48 (td, *J*=7.5, 1.5, 1H), 7.37 (td, *J*=7.7, 1.3, 1H), 7.27 (d, *J*=8.2, 1H), 2.68 (s, 3H) ppm.

4-Hydroxybenzaldehyde

^{1}H NMR (400 MHz, Chloroform-d) δ = 9.87 (s, 1H), 9.85 (s, 0H), 8.05 – 7.59 (m, 2H), 7.08 – 6.66 (m, 2H) ppm.

p-Tolualdehyde (4-Methylbenzaldehyde)

^{1}H NMR (400 MHz, Chloroform-d) δ = 9.97 (s, 1H), 7.82 – 7.74 (m, 2H), 7.37 – 7.23 (m, 2H), 2.44 (s, 3H) ppm.

3,5-Bis(trifluoromethyl)benzaldehyde

^{1}H NMR (400 MHz, Chloroform-d) δ = 10.13 (s, 1H), 8.35 (s, 2H), 8.14 (s, 1H) ppm.

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