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Copper(II) Nanoballs as monomers for polyurethane coatings: synthesis, urethane derivatization and kinetic stability†

Markus Tonigold,[a] Julia Hitzbleck,[b] Stefan Bahnmüller,[b] Gerhard Langstein[b] and Dirk Volkmer*[a]

The self-assembly of copper(II) ions and 5-(2-hydroxyethoxy)benzene-1,3-dicarboxylate (**1**) leads to Nanoballs in which twelve dinuclear copper(II) paddle-wheel units are interconnected *via* 24 ligands. The structure of the spherical coordination compound decorated with 24 hydroxy groups has been determined by single crystal X-ray structure analysis. As a model for the integration of Nanoballs into bulk polyurethane polymers and coatings, its reaction with phenylisocyanate is investigated. The stability of Nanoballs against hydrolytic decomposition is studied under acidic conditions and compared to simple copper(II) complexes. Release of copper(II) ions from Nanoballs is much slower than from discrete copper(II) paddle-wheel complexes, suggesting the use of Nanoballs as monomers for polyurethane-based antifouling coatings.

Introduction

Among structurally diverse molecular containers,[1] metal-organic polygons[2] and polyhedra (also named Nanoballs, MOPs, Nanocontainers or Nanocages)[3,4] came to the foreground during recent years. These discrete and highly symmetric coordination compounds are built through the interconnection of metal ions or clusters with simple, polyfunctional organic ligands (so-called linkers), mostly containing aromatic nitrogen or carboxylate-based donor groups. Compared to classical organic multi-stage syntheses, coordination-driven self-assembly leads to nanometer-sized complexes with well-defined cavities in a single step and in high yields. Beside their aesthetically pleasing structures, these compounds can serve as nanoreactors[5] as well as for delivery, storage, and separation technology.[6]

One route to obtain Nanoballs in high yield is to interconnect copper paddle-wheel coordination units at 120° angles with bifunctional ligands such as benzene-1,3-dicarboxylate (bdc) or its derivatives.[3] By changing the substituent R in the 5-position of bdc, Nanoballs being highly soluble in solvents—ranging from polar (high solubility in alcohols for R = OH)[3b] to nonpolar (high solubility in toluene, dichloromethane and THF for R = $OC_{12}H_{25}$)[3f]—are obtained.

However, assembling copper(II) paddle-wheel units with functionalized bdc acids may not lead automatically and exclusively to Nanoballs. Alternatively, two- or three-dimensional networks might be obtained,[7] depending on many factors that can influence the self-assembly process. These include the formation of metastable products if the reaction proceeds under kinetic control, as well as several other effects (influence of solvent, concentration, pH, temperature, or the presence of sterically or electronically demanding groups).[8] Moreover, thermodynamic principles seem to favour structures with small or no cavities.[9] Due to these reasons, developing the synthesis for novel Nanoball derivatives is an ambitious task, since appropriate reaction conditions have to be developed for each novel linker.[3] For this particular reason we studied the possibility to obtain new Nanoballs *via* derivatization of existing ones as an alternative to the *de novo* synthesis of the corresponding Nanoballs *via* self-assembly. It was necessary to invent a Nanoball with an appropriate surface functionalization scheme based on the linker 5-(2-hydroxyethoxy)benzene-1,3-dicarboxylate **1**, since all existing Nanoballs[3] in our hands showed poor solubility in solvents that are suitable for urethane formation.

Nanoball modified polyurethane polymers are promising candidates for improved antifouling systems, since soluble copper compounds are known to act as bactericides, algaecides, fungicides, or molluscicides.[10] However, existing antifouling systems still bear a high potential of further improvements because of the currently poor control over leaching of the active biocide,[11] and, moreover, there is a steadily increasing demand for antifouling paints that exhibit minimal ecotoxicity, longterm durability and a controlled release rate of the biocide. A comparison between supramolecular metal complexes and structurally similar low molecular metal complexes indicates that copper(II) based Nanoballs could solve these technical issues, at least in part. In aqueous solution, binuclear copper(II) carboxylates tend to dissociate to a large extent,[12]‡ whereas dissociation is reduced in less polar solvents.[13]

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† Electronic supplementary information (ESI) available: Details of crystallographic data collection and analysis, SAXS, UV/vis, *in situ* IR measurements and analysis of conversion reactions. CCDC reference numbers 692012 for $[Cu_{24}(C_{10}H_{10}O_6)_{24}(DMSO)_{14}(H_2O)_2(MeOH)_8]\cdot 22DMSO\cdot 23MeOH$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811004b

‡ The equilibrium constants K_1 and K_2 of copper(II) acetate in water (l mole^{-1}) were determined to be

$$Cu(OAc)_2 \rightleftharpoons Cu(OAc)^+ + OAc^- \; K_1 = 0.114 \; (293 \; K)$$

$$Cu(OAc)^+ \rightleftharpoons Cu^{2+} + OAc^- \; K_2 = 0.003 \; (293 \; K)$$

by spectrophotometric measurements,[12a] further confirmed by conductivity data ($K_1 = 0.103$ and $K_2 = 0.003$ at 273 K)[12b] and e.m.f. measurements $K_1 = 0.125$ and $K_2 = 0.004$ at 303 K).[12c]

For hydroxylated Nanoballs (R = OH in the 5-position of bdc), however, spectroscopic studies suggest longterm stability of Nanoballs in methanol without any detectable dissociation,[14] showing increased thermodynamic stability, superior to that of simple binuclear copper(II) carboxylates. Additionally, studies on the disassembly kinetics of other supramolecular architectures such as helices[15] show a much lower dissociation rate of supramolecular assemblies if compared to structurally similar basic coordination units.

To elucidate the advantages of using copper based Nanoballs in antifouling systems, we here demonstrate their stability under polymerization conditions. Moreover, we address the important question as to how fast copper(II) ions are released from Nanoballs under mildly acidic conditions thus mimicking a biological environment.

Results and discussion

The linker 5-(2-hydroxyethoxy)benzene-1,3-dicarboxylic acid **1** (5-H_2hebdc) was synthesized from dimethyl-5-hydroxybenzene-1,3-dicarboxylate and ethylene chlorohydrin with an improved synthesis compared to literature methods (47% yield instead of 25–35%).[16] A precipitate forms immediately from an equimolar solution of **1** and $Cu(NO_3)_2$ in methanol after adding two equivalents of 2,6-dimethylpyridine. Recrystallization from dimethylsulfoxide (DMSO) and acetone afforded **2** as green crystals of formula $[Cu_{24}(C_{10}H_{10}O_6)_{24}(DMSO)_{14}(H_2O)_2(MeOH)_8]\cdot 22DMSO\cdot 23MeOH$ suitable for single crystal X-ray diffraction studies.

At room temperature **2** is highly soluble in various organic solvents (DMSO: 130 mg/mL; DMF: 210 mg/mL). Thermogravimetric analysis (TGA) shows distinct steps corresponding to a weight-loss of 8.4% in the temperature range from 30 to 106 °C (expected: 9.6% for complete loss of methanol and water from $[Cu_{24}(5\text{-hebdc})_{24}(CH_3OH)_8\ (DMSO)_{14}(H_2O)_2]\cdot 23CH_3OH\cdot 22DMSO$), and 16.9% in the temperature range from 106 to 230 °C (expected: 26.2% for complete loss of DMSO), respectively. Further weight-loss by 45% occurs from 230 to 400 °C, which is ascribed to the decomposition of the Nanoball **2**. These results indicate a thermodynamic stability against decomposition until at least 230 °C, comparable with structurally similar compounds.[3c]

In order to test if surface-derivatization of Nanoball **2** and its integration into polyurethane polymer networks is feasible without decomposition, the compound was dissolved in DMF, treated with a 300-fold excess of phenylisocyanate, precipitated and rinsed with methanol in order to produce derivate **3** ($[Cu_{24}(5\text{-pcebdc})_{24}(CH_3OH)_{24}]\cdot 12CH_3OH$, 5-pcebdc = 5-(2-phenylcarbamoyloxyethoxy)benzene-1,3-dicarboxylate). Unfortunately, we were not able to obtain single crystals of **3** suitable for single-crystal X-ray diffraction studies. Therefore, we evaluated the shape of **3** in solution by SAXS measurements, and the conversion from **2** to **3** by *in situ* IR measurements as well as by ^{1}H-NMR identification of the linker after acidic work up.§

§ Different equivalents of phenylisocyanate were added to solutions of 50 mg **2** in 1 mL DMF and reacted at 60 °C for 3 days. The solvent was evaporated, the residue treated with 1 M aqueous HCl followed by excessive extraction of the unreacted linker **1** and the derivatised linker **4** with 1-butanol. The conversion was analyzed by ^{1}H-NMR spectroscopy in DMSO-d_6 from the integrals of the ethoxy groups at $\delta = 4.11$–3.47 ppm for **2** and 4.45–4.38 ppm for **3**.

X-Ray structure analysis

To avoid rapid loss of occluded solvent molecules, crystals of **2** were directly covered with mineral oil after removing them from the mother liquor. Crystals of **2** were found to be completely stable if stored in the mother liquor. However, upon exposing them to air crystallinity is lost within minutes, leading to an uncertain number of occluded solvent molecules, which is common for such open framework structures.[3c,4g] Whereas problems of crystal aging could be minimized experimentally, some unavoidable problems in refining the structure of Cu-5-hebdc arose from the fact that the solvent molecules occluded in the crystal lattice as well as the 2-hydroxyethoxy substituent of the linker are largely disordered. These disordered groups had to be refined as rigid fragments using restraints with appropriate atomic coordinates taken from literature.[17] Due to the disorder we were not able to determine the exact amount and identity of all solvent molecules.†

2 has an outer dimension (as measured from the distance between opposite groups at the periphery) of 3.2 nm and consists of 12 Cu-paddle-wheel units interconnected *via* 24 linkers (Fig. 1a). The internal cavity has a diameter of 1.6 nm, neglecting coordinated solvent molecules pointing towards the centre, and the 12 paddle-wheel units form a cuboctahedron. The whole structure

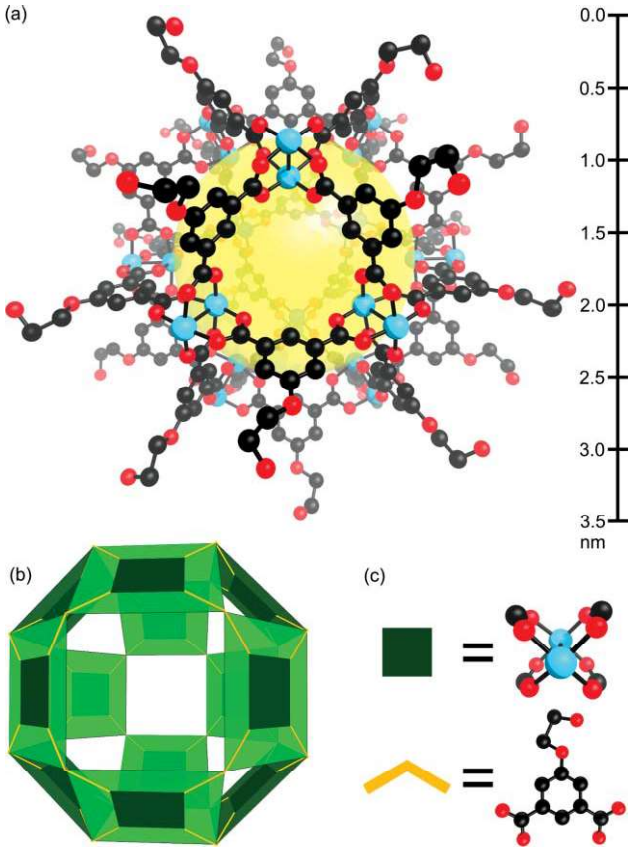

Fig. 1 (a) Ball-and-stick representation of the X-ray single-crystal structure of **2**. Cu, blue; O, red; C, black. Hydrogen atoms, coordinated and non-coordinated solvent molecules are omitted for clarity. The yellow sphere represents the internal cavity. (b) Schematic representation of **2** as a small rhombihexahedron comprised from (c) $Cu_2(CO_2)_4$ paddle-wheel (squares) linked at an 120° angle by 5-hebdc.

resembles to a small rhombihexahedron (Fig. 1b) composed of linked vertices of squares (Fig. 1c).

Adjacent paddle-wheel units in **2** are 1.0 nm apart from each other and represent the vertices of triangular and square apertures. These openings have widths of about 0.6 and 1.2 nm, respectively.[18] The dimensions of openings as well as the bonding distances and angles within the coordination framework of **2** are statistically identical to those observed in the structurally related Nanoballs reported previously.[3] Solvent molecules contained within the inner void of **2** are easily exchanged throughout these windows: Dissolving **2** in DMF followed by evaporation to dryness yields **2b** formulated as Cu_{24}(5-hebdc)$_{24}$(DMF)$_{33}$(H_2O)$_{10}$ according to elemental analysis. Thermogravimetric analysis (TGA) for **2b** shows a weight-loss of 18.4% in the temperature range from 30 to 225 °C (expected: 27.3% for complete loss of DMF and water).

Derivatization of the Nanoball

As a model for the integration of Nanoballs into bulk polyurethane polymers and coatings, its reaction with phenylisocyanate was investigated. We studied the process of urethane formation in detail by reacting **2** at 60 °C with different amounts of phenylisocyanate (as given in Fig. 2) in DMF for 3 days. The conversion of **2** into **3** was tracked *via* ^{1}H-NMR spectroscopy of the linkers after acidic work up.§ Fig. 2 shows that 4.5 equivalents of phenylisocyanate per hydroxy group of **2** are required for full conversion into **3**.

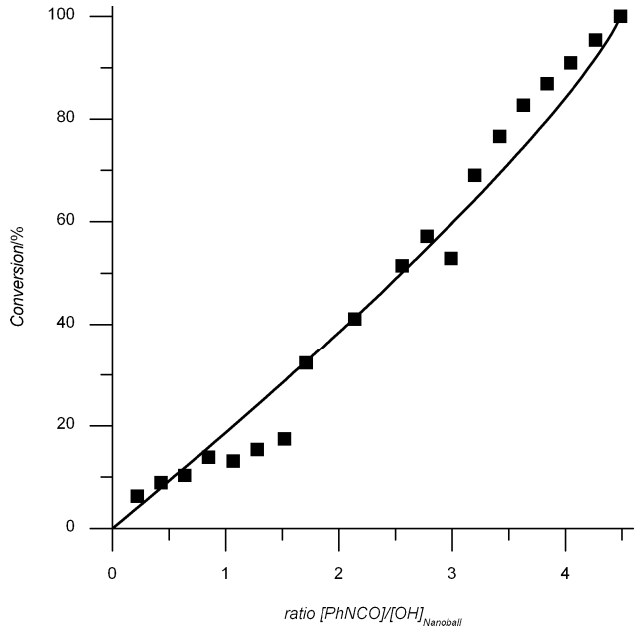

Fig. 2 Conversion of **2** into **3** depending on the ratio between phenylisocyanate (PhNCO) and the hydroxy groups of **2**. ($[OH]_{Nanoball} = 24 \times [\mathbf{2}]$).

A 3.5:1 ratio of phenylisocyanate in relation to surface hydroxy groups of **2** is required, since water and methanol molecules included in the voids of **2** do also react with phenylisocyanate. Further analysis of the conversion of **2** in concurrence to the side reaction of methanol (and water) reveals that the rate of urethane formation with phenylisocyanate is at the same order of magnitude for the hydroxy groups of **2** as for methanol.† Therefore, a covalent binding of the Nanoball **2** into polyurethane polymers seems feasible.

Since copper(II) coordination compounds in general show fast kinetic exchange of coordinated ligands, we investigated the stability of the Nanoball structures **2** and **3** in solution and under typical urethane formation conditions. The complex stability of **2** in DMF during the conversion into **3** under reaction conditions is confirmed by *in situ* FT-IR studies. The position of the COO asymmetric stretching band at 1646 cm^{-1},¶ typical for copper(II) paddle-wheel complexes and sensitive to changes of the chemical environment of the carboxylic group,[19] shows no shift during the reaction with phenylisocyanate.† Therefore, the copper(II) paddle-wheel units remain intact throughout the derivatisation of the Nanoball.

Small-angle X-ray scattering (SAXS)

SAXS measurements, which provide the shape and internal structure of particles in solutions,[20] were conducted to confirm that the structural features of **2** persist in solution. Additionally, we established the structure of the derivatization product **3** to prove that the Nanoball **2** can be chemically modified without loss of structural integrity of the rhombicuboctahedral complex. The logarithmic plot of SAXS intensity (*I*) *vs.* momentum transfer (*q*) for **2** and **3** is shown in Fig. 3 and 4, respectively, together with the numerical fit to the SAXS data evaluating the shape in solution. The representative reconstruction of the low resolution three-dimensional particle shape was provided by simulated annealing using the GNOM/DAMMIN software packages.[21,22]

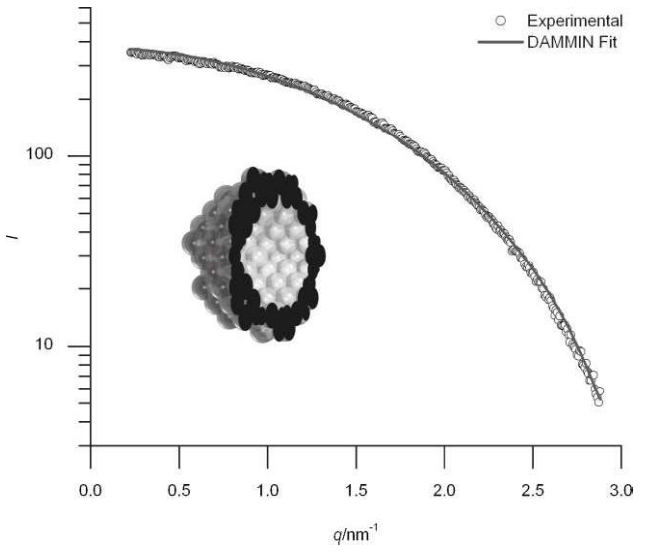

Fig. 3 Main plot: SAXS intensity (I) *vs* momentum transfer (q = 0.2–2.9 nm^{-1}) for a solution of **2** in DMF (c = 110 g/L). The symbols and the solid line correspond to the experimental data points and the numerical fit using GNOM/DAMMIN simulated annealing ($\chi = 5.217$), respectively. Inset: Bead model from low-resolution particle shape reconstruction for **2** obtained by the GNOM/DAMMIN fit, representing one half from a cross-sectional cut through the particle centre.

The radii of gyration (R_g) for these particles are 1.0 nm (for **2**) and 1.2 nm (for **3**). Both particle shapes derived from the SAXS measurements resemble to hollow spheres, in excellent agreement

¶ The COO asymmetric stretching band of the diacid **1** and its disodium salt are at 1692 cm^{-1} and 1567 cm^{-1}, respectively.

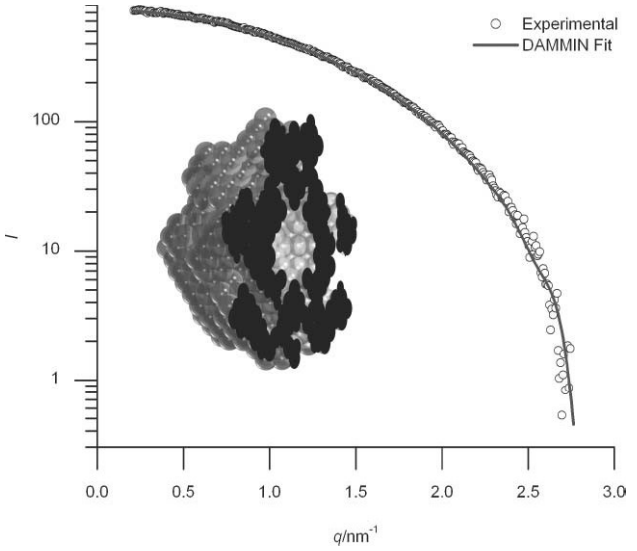

Fig. 4 Main plot: SAXS intensity (I) *vs* momentum transfer (q = 0.2–2.6 nm) for a solution of **3** in DMF ($c = 15.7$ g/L). The symbols and the solid line correspond to the experimental data points and the numerical fit using GNOM/DAMMIN simulated annealing ($\chi = 2.696$), respectively. Inset: Bead model from low-resolution particle shape reconstruction for **3** obtained by the GNOM/DAMMIN fit, representing one half from a cross-sectional cut through the particle centre.

with the expected shapes for **2** and **3**. Principally, bead models derived from experimental SAXS data show an effective spatial resolution of approximately 0.5 nm for molecules with radii of gyration below 1.5 nm.[23] Therefore, the dimensions of the hollow spheres derived from the DAMMIN calculations with inner and outer radii of approximately 0.4 and 1.3 nm for **2**, as well as 0.4 and 1.7 nm for **3**, are in good agreement with expected values (Fig. 5). The distances of the interior and exterior copper ions from the centre of the Nanoballs **2** and **3** are 0.8 and 1.1 nm, respectively. The maximal distance from the centre to the periphery is 1.6 nm for **2**.

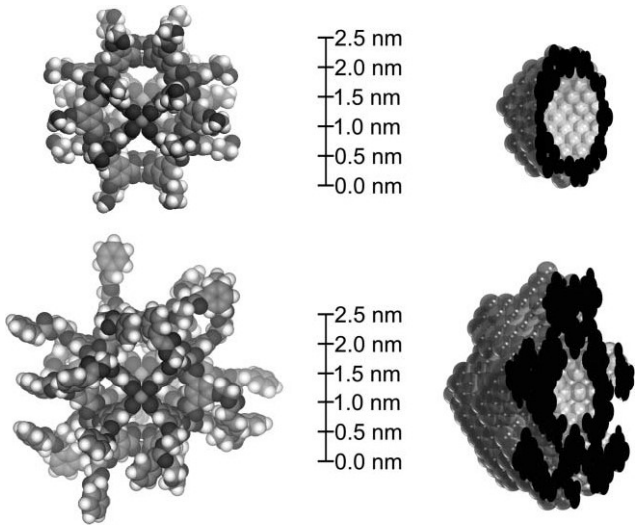

Fig. 5 Spacefilling models of **2** (upper left) and **3** (lower left) compared to bead models (one half from a cross-sectional cut through the centre) of **2** (upper right) and **3** (lower right) derived from GNOM/DAMMIN fits.

Table 1 Glass transition temperatures for polyurethanes consisting of **2**, 1,2-ethanediol and 2,4-toluene diisocyanate

Sample	wt% of **2** in polyurethane	T_g/°C	Sample	wt% of **2** in polyurethane	T_g/°C
5a	0	125	**5h**	1.7	20
5b	10^{-3}	115	**5i**	2.2	19
5c	10^{-2}	121	**5j**	2.6	2
5d	0.1	104	**5k**	3.0	17
5e	0.5	108	**5l**	3.3	37
5f	0.9	98	**5m**	4.8	35
5g	1.3	68	**5n**	6.2	40

The reconstructed shapes show less beads on their exteriors than it would be expected from their molecular models, which might be due to the high electron density of Cu^{II} centers on the one hand (increasing scattering intensities), and the disorder of the moieties in the 5-position of the organic linkers on the other hand (decreasing scattering intensities).

Using the X-ray single-crystal structure data of **2**, we additionally calculated its hypothetical scattering intensities with the program CRYSOL,[24] which matches well with the observed experimental intensities.†

Polymerization of the Nanoball

Preliminary experiments were done to investigate whether **2** can be used as a monomer in polyurethanes. Hence, different amounts of **2** were reacted with 2,4-toluene diisocyanate and 1,2-ethanediol in DMF to obtain a series of polyurethanes (Table 1).

Since **2** has 24 surface functional groups per molecule, cross-linking is expected, leading to a rapid increase of viscosity (gel formation) and therefore the polymerisation should stop at low conversion fractions.[25] However, 3.5 molecules of methanol are present per hydroxy group in the structure of **2**. The Nanoballs therefore should form "star polymers" which are not cross-linked to each other. The additional linear polyurethane chains should decrease their length with increasing amount of **2** due to the remaining excess of methanol. Accordingly, the glass transition temperature (T_g) decreases with increasing amount of **2** in the polyurethanes (Table 1), since decreasing molecular weight of linear chains leads to a decreasing T_g[26] (whereas cross-linking due to the Nanoball **2** should principally increase the T_g[27]). For low contents of **2** (samples **5b-5e**), the polymerization stops before full conversion is achieved despite the excess of methanol, as shown by IR analysis since the isocyanate band at 2275 cm^{-1} remains.

Additionally, the polyurethanes which contain more than 4.8 wt% of **2** are soluble in DMF or DMSO, in contrast to all other samples including neat polyurethane (**5a**). The solubility provides additional evidence for the fact that cross-linking, which would lead to insoluble three-dimensional networks, is prevented. Altogether these results demonstrate that **2** can be used as monomer in polyurethane formation.

Hydrolytic stability of Nanoballs

To benefit from the antifouling properties of Cu^{II}, copper Nanoballs which are covalently attached to polyurethanes should exhibit slow and controlled release of the incorporated copper ions. The kinetic stability of the Nanoballs against acidic media (like human sweat)[28] was evaluated to investigate any influence of

the supramolecular structure on the stability of the copper paddle-wheel building units.

Upon treating DMF or DMSO solutions of **2** or **3** with weak acids, slow release of Cu^{II} ions is observed, in contrast to simple dinuclear paddlewheel complexes such as copper(II) acetate or benzoate, for which decomposition occurs spontaneously and very rapidly (within less than one second under the same conditions). The slow release is maintained when **2** is incorporated into polyurethanes. To keep the reaction rates sufficiently low for UV/vis spectroscopic investigations, soft acids with high pK_a which, however, are sufficiently strong to protonate isophthalic acids were chosen.[29]

Time dependent spectral changes of the UV/vis absorption characteristics of compounds **2**, **3** and **5n** (which is 6.2 wt% of **2** in polyurethane) were recorded for acidolysis in DMF and DMSO. During the course of reaction the typical band I of binuclear copper(II) complexes[30] (maximum absorption at 740 nm and 720 nm in DMF and DMSO, respectively) disappears to yield isolated and fully solvated copper(II) ions (maximum absorption at 830 nm and 800 nm in DMF and DMSO, respectively), without any detectable intermediates. Thus the corresponding global reaction, simplifying the Nanoballs as [CuL], is written:

$$[\mathrm{CuL}] + n\mathrm{H}^+ \rightarrow \mathrm{Cu}^{2+} + \mathrm{H}_n\mathrm{L}^{(2-n)-} \qquad (1)$$

Using at least tenfold excess of acid, the experimental data fit pseudo-first-order kinetics with respect to the complex in all cases. The kinetic data were processed as pseudo-first-order reaction according to eqn (2).

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{CuL}] = k_{\mathrm{obs}}[\mathrm{CuL}] \qquad (2)$$

Plots of the observed pseudo-first-order rate constants k_{obs} in DMF and DMSO as solvents *versus* H_3PO_4 concentrations are shown in Fig. 6 and 7. The observed rate constants k_{obs} display an

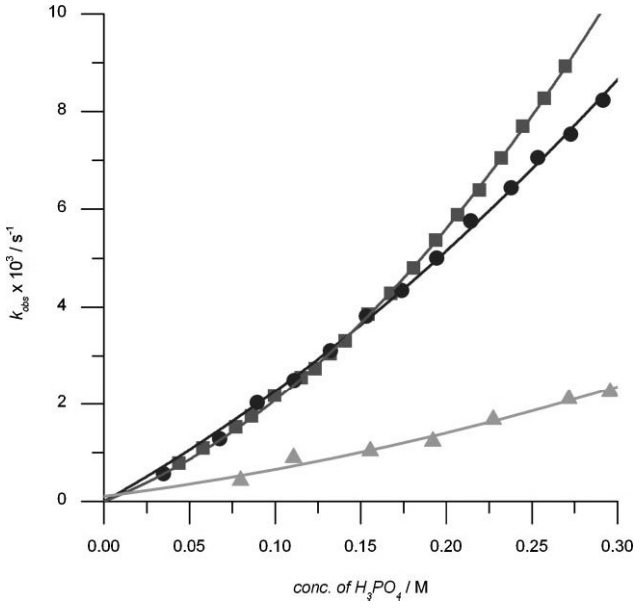

Fig. 6 Pseudo-first-order rate constants k_{obs} of **2** (■), **3** (●) and **5n** (6.2 wt% of **2** in polyurethane, ▲) as a function of [H_3PO_4]. Solvent, DMSO; $T = 25.0(2)$ °C.

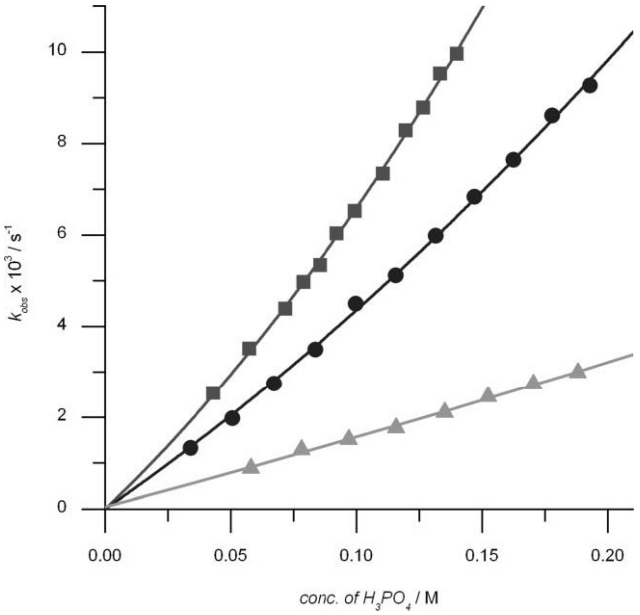

Fig. 7 Pseudo-first-order rate constants k_{obs} of **2** (■), **3** (●)and **5n** (6.2 wt% of **2** in polyurethane, ▲) as a function of [H_3PO_4]. Solvent, DMF; $T = 25.0(2)$ °C.

empirical second order dependence on the acid concentration as expressed with eqn (3).

$$k_{\mathrm{obs}} = k_1[\mathrm{H}^+] + k_2[\mathrm{H}^+]^2 \qquad (3)$$

In comparison with **2**, compound **3** shows slightly lower dissociation rates in DMSO for higher acid concentrations and clearly lower dissociation rates in DMF, indicating that the increased steric hindrance imposed by phenylisocyanate surface derivatization reduces the accessibility of the copper(II) centers (Fig. 6 and 7). The trend of lower dissociation rates due to enhanced steric hindrance is further continued when the Nanoball is incorporated into polymers. Nevertheless, the open framework structure of **2** and **3** facilitates access to the copper ions, making them less stable against hydrolytic decomposition when compared to macrocyclic Cu(II) complexes, which display half-lives ranging from 5.4 minutes to 6.7 months in 1 M perchloric acid.[31,32] The kinetic stability of the latter coordination compounds against Cu(II) release in acidic media results in part from their rigid structures[33] and, additionally, from the gain of (thermodynamic) complex stability due to the macrocyclic effect.[31,34]

With decreasing pK_a of the added acid (from chloroacetic acid over phosphoric acid to trifluoroacetic acid; $pK_a = 2.81$, 2.16 and 0.52, respectively), accelerated hydrolytic decomposition of the Nanoball occurs.† The observed influence of the acid strength hints at a mechanism where protonation of the interconnecting ligands occurs prior to dissociation. (Protonation of ligands that might be set free *via* a fast dissociation of the Nanoball in solution should lead to reaction rates independent from acid strength). The influence of the acid strength and the increased hydrolytic stability compared to simple binuclear copper(II) paddle-wheel complexes indicate that the Nanoballs show a cooperative behaviour, in which the fixed framework architecture makes it more difficult for the comprising subunits (copper ions or organic linkers) to leave the assembly.

Conclusions

We have presented the synthesis of a novel, highly soluble hydroxy-functionalized Nanoball which is based on the fundamental copper(II) Nanoball coordination unit previously reported by Zaworotko and co-workers.[3d] The hydroxy groups on the surface of our Nanoball can be easily and fully derivatized, since their reactivity is similar to simple alcohols, and the stability of the Nanoball under polymerization conditions is sufficiently high to retain its structural integrity. In this light we demonstrated that urethane-functionalized Nanoballs can be simply obtained *via* reaction of hydroxy-functionalized Nanoballs with phenylisocyanate. Compared to kinetically labile dinuclear copper(II) paddle-wheel complexes such as copper acetate or benzoate, Nanoballs are kinetically far more stable, which is presumably due to their more rigid interconnected framework structure. The increased stability compared to simple binuclear copper(II) complexes represents a promising perspective for using Nanoballs in polyurethane fibers or in antifouling coatings, since a slower and more controlled release rate of copper(II) ions is crucial for these applications.[11] An additional advantage above already existing systems[35] is the possibility to link Nanoballs into polymers, which is expected to increase the life-time of antifouling products and to give better release control of copper ions over time. Additional technological applications seem feasible, for instance controlled and slow release of encapsulated drugs which are hosted inside the Nanoballs' cavities. Cyclodextrins are already in use for storage and slow release of fragrances from clothings,[36] accordingly similar features could be added to Nanoball-functionalized fibers in future, such as slow drug release from these molecular depots due to the storage abilities of these compounds.[6]

Experimental

Materials and methods

Melting points (uncorrected): Büchi Melting Point B-540 apparatus. Infrared spectra: Bruker FTIR IFS 113v spectrometer; KBr pellets. UV/vis spectra: J & M TIDAS. NMR spectroscopy: Bruker DRX 400; data given as ppm; spectra referenced to the residual solvent peak. CI mass spectra: Finnigan MAT, SSQ 7000 mass spectrometer, single-stage-quadrupol system, intensities relative to base peak. TGA: Mettler Toledo TGA/SDTA 851, heating rate: 10 °C/min, nitrogen flow: 50 mL/min. SAXS: Bruker AXS Nano-STAR equipped with a HI-STAR area detector. Glass transition temperatures were monitored with a Perkin-Elmer DSC-7. Scan rates of 10 K/min were used in the differential scanning calorimetry (DSC) experiments with sample masses of 3–10 mg. Transition temperatures were taken from the second heating cycle.

All solvents were purified and dried according standard procedures where necessary.

5-(2-Hydroxyethoxy)benzene-1,3-dicarboxylic acid (1)

Under argon, a suspension of 20 g (95.1 mmol) dimethyl-5-hydroxy-1,3-benzenedicarboxylic acid, 7.9 g (47.6 mmol) potassium iodide, 26.3 g (190 mmol) potassium carbonate and 18 mL (268 mmol) ethylene chlorohydrin in 290 mL cyclohexanone was refluxed for six days. The solvent was evaporated after filtration, and the remaining residue was treated with 20 g (357 mmol) potassium hydroxide in 130 mL ethanol:water (10:3) and refluxed for 7 hours. The solvent was evaporated and 1000 mL 1 M HCl were added to the residue. The aqueous phase was extracted four times with 200 mL ethyl acetate, and the combined organic phases were washed four times with 100 mL brine and dried over sodium sulfate. The solvent was evaporated, and the residue was washed with water and dichloromethane and recrystallized from 380 mL acetone to give **1** (10.2 g, 47%) as a white powder mp 210–211°C (from acetone) (lit.,[16] 200–203°C); (Found: C, 53.2; H, 4.4. Calc. for $C_{10}H_{10}O_6$: C, 53.1; H, 4.5%); ν_{max}(KBr)/cm^{-1} 3421, 2947, 1692, 1597, 1464, 1415, 1307, 1268, 1221, 1126, 1058, 981, 905, 758 and 680; δ_H (400 MHz; DMSO-d_6) 13.24 (2 H, br s, CO_2H), 8.07 (1 H, t, $J_{1,4}$ 1.4, Aryl), 7.66 (2H, d, $J_{1,4}$ 1.4, Aryl), 4.89 (1H,br s, OH), 4.11 (2 H, t, $J_{1,3}$ 4.8, CH_2CH_2) and 3.47 (2 H, t, $J_{1,3}$ 4.8, CH_2CH_2); δ_C(100 MHz; DMSO-d_6) 166.9, 159.4, 133.1, 122.7, 119.7, 70.7 and 59.9; *m/z* (CI) 227 (M + H$^+$, 22%) and 209 (100).

Tetracosakis(μ$_4$-5-(2-hydroxyethoxy)benzene-1,3-dicarboxylato)-diaqua-tetradecakis(dimethylsulfoxid)-octamethanol-tetracosa-copper(II) dimethylsulfoxide methanol solvate (2)

1 mL (8.6 mmol) 2,6-dimethylpyridine was added to a solution of 1.01 g (4.2 mmol) $Cu(NO_3)_2{\cdot}3H_2O$ and 0.95 g (4.2 mmol) **1** in 15 mL methanol within 1 minute under vigorous stirring. The immediately formed blue suspension was stirred for 30 minutes and filtered after adding 40 mL diethylether. The residue was washed two times with 20 mL methanol and 10 mL diethylether, dried over night in air and afterwards in vacuum at room temperature. Green single crystals of **2** were recrystallised by vapour diffusion of 75 mL acetone into a solution of the crude product in 50 mL DMSO (0.75 g, 40%), mounted in inert oil and transferred to the cold gas stream of the diffractometer (Found: C, 37.8; H, 4.8. Calc. for $C_{343}H_{536}Cu_{24}O_{213}S_{36}$: C, 38.3; H, 5.0%); ν_{max}(KBr)/cm^{-1} 3415, 3089, 2947, 2919, 2871, 1630, 1581, 1452, 1416, 1375, 1320, 1265, 1134, 1061, 1111, 1003, 985, 905, 861, 794, 780 and 731.

Tetracosakis(μ$_4$-5-(2-hydroxyethoxy)benzene-1,3-dicarboxylato)-tetracosa-copper(II) aqua N,N-dimethylformamide solvate (2b)

300 mg (28 μmol) **2** were dissolved in 10 mL DMF and evaporated to dryness in vacuum at 60 °C for three times to yield **2b** (250 mg, 94%) as a blue powder. (Found: C, 43.0; H, 4.8; N, 4.7. Calc. for $C_{339}H_{443}Cu_{24}N_{33}O_{187}$: C, 42.9; H, 4.7; N, 4.9%); ν_{max}(KBr)/cm^{-1} 3401, 2931, 1664, 1632, 1588, 1456, 1419, 1380, 1321, 1268, 1133, 1101, 1054, 1002, 898, 800, 775, 732, 665, 557 and 485.

Tetracosakis(μ$_4$-5-(2-phenylcarbamoyloxyethoxy)benzene-1,3-dicarboxylato)-tetracosamethanol-tetracosa-copper(II) methanol solvate, (3)

1.0 g (89 μmol) **2** and 3.0 mL (28 mmol) phenylisocyanate in 20 mL DMF were heated at 60 °C for two days. The solution was stirred for additional 12 hours after adding 20 mL methanol. The product precipitated after slow addition of another 150 mL methanol and was washed five times in 150 mL hot methanol, affording **3** (900 mg, 96%) as blue powder (Found: C, 49.0; H, 4.3; N, 3.3. Calc. for $C_{444}H_{456}Cu_{24}N_{24}O_{204}$: C, 48.8; H, 4.2; N, 3.1%); ν_{max}(KBr)/cm^{-1} 3386, 3332, 3081, 2964, 2927, 1733, 1636, 1591, 1538, 1452, 1381, 1318, 1218, 1062, 773 and 733.

5-(2-Phenylcarbamoyloxyethoxy)benzene-1,3-dicarboxylic acid (4)

200 mg (18.9 μmol) **3** were treated with 10 mL 1 M HCl for 30 minutes, extracted three times with 20 mL butanol and washed 6 times with 25 mL of water. The solvent was evaporated, and the crude product was recrystallized from acetone/chloroform to yield **4** (140 mg, 88%) as a white powder mp 202–204 °C (from acetone/$CHCl_3$); (Found: C, 58.3; H, 4.8; N, 4.0. Calc. for $C_{17}H_{15}NO_7 \cdot 0.25H_2O$: C, 58.4; H, 4.5; N, 4.0%); ν_{max}(KBr)/cm^{-1} 3330, 2934, 2569, 1713, 1599, 1543, 1446, 1409, 1315, 1281, 1239, 1067, 910, 757 and 692; δ_H (400 MHz; DMSO-d_6) 13.29 (2 H, br s, CO_2H), 9.76 (1H, br s, 1 NH), 8.10 (1 H, t, $J_{1,4}$ 1.5, Aryl), 7.68 (2 H, d, $J_{1,4}$ 1.5, Aryl), 7.47 (2 H, d, $J_{1,3}$ 8.1, Ph), 7.28 (2 H, dd, $J_{1,3}$ 7.3 and 8.1, Ph), 6.99 (1 H, t, $J_{1,3}$ 7.3, Ph), 4.45–4.38 (4 H, m, CH_2CH_2); δ_C(100 MHz; DMSO-d_6) 166.8, 158.5, 153.8, 139.5, 133.2, 129.2, 123.0, 122.9, 119.6, 118.7, 67.3 and 63.1; *m/z* (CI) 346 (M + H$^+$, 3%), 328 (5), 227 (3), 209 (5) and 120 (100).

Polymerisation (5a–n)

In a typical experiment, 1.41 g (8.10 mmol) 2,4-toluene diisocyanate and 8.71 mg (0.8 μmol) **2** were heated in 2 mL DMF for 24 h. Afterwards, 500 mg (8.06 mmol) 1,2-ethanediol were added at −10 °C, the solution was heated for 5 d at 60 °C and the resulting product was dried for 12 h at 80 °C in vacuum. Polyurethanes containing other concentrations of **2** were prepared accordingly. (Found: C, 54.5; H, 5.7; N, 12.5. Calc. for $C_{11}H_{12}N_2O_4 \cdot 0.56C_3H_7NO$: C, 54.9; H, 5.8; N, 12.9%); ν_{max}(KBr)/cm^{-1} 3311, 2956, 2928, 1734, 1601, 1534, 1449, 1413, 1220, 1132, 1058, 997, 877, 814 and 763.

Crystal structure determination of 2

Intensity data for **2** were collected at 223 K on a STOE-IPDS image-plate diffractometer (graphite monochromator) using Mo-Kα radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects, no absorption correction was applied. Programs used: data collection: Bruker XSCANS,[37] data reduction: Bruker SHELXTL,[38] structure solution: SHELXS-97,[39] structure refinement: SHELXL-97,[40] molecular graphics: Diamond V3.1,[41] Mercury V1.5.[42] Structures were solved using direct methods and refined by full-matrix least squares on $|F|^2$. All disordered atoms and atoms with non-positive U_{eq} were calculated with isotropic, all others with anisotropic displacement parameters. An exact determination of the total amount and identity of the noncoordinated solvent molecules is not possible due to their strong disorder, Residual electron density maximums were refined as DMSO and methanol molecules where possible. The formula of the structure obtained this way is $[Cu_{24}(5\text{-hebdc})_{24}(CH_3OH)_8(DMSO)_{14}(H_2O)_2] \cdot 23CH_3OH \cdot 22DMSO$. Certain atom distances were specified as fixed due to problems caused by the diffuse electron density of the disordered solvent, guest molecules and 2-hydroxyethoxy groups. Hydrogen atoms were placed in geometrically calculated positions.

Crystal data for 2. Monoclinic, $P2_1/n$ (no. 14), $a = 26.220(5)$, $b = 39.060(8)$, $c = 26.643(5)$ Å, $\beta = 95.64(3)°$, $V = 27154(9)$ Å^3, $\rho_{calc} = 1.314$ g cm^{-3}, $\mu = 1.139$ mm^{-1}, $Z = 2$, $F(000) = 11140$, $\Theta_{max} = 24.09°$ ($-29 \le h \le 30$, $-43 \le k \le 44$, $-30 \le l \le 27$), 85619 data measured, 39811 unique ($R_{int} = 0.117$), Final residuals (for 2427 parameters) were $R_1 = 0.0993$ and $wR_2 = 0.1891$ for 12226 reflections with $I \ge \sigma(I)$, and $R_1 = 0.2441$, $wR_2 = 0.3008$, GOF = 0.853 for all 39811 data. Residual electron density was 2.00 and −0.90 e Å^{-3}.†

Hydrolytic decomposition of nanoballs in the presence of acids

The dissociation kinetics of the copper complexes in the presence of acids were investigated using spectrophotometry. The final copper(II) concentrations in all experiments were between 2.0–4.0 mmol/L. Acid concentrations in the range of 0.03–0.30 mol/L were prepared by adding an appropriate amount of acid stock solution with a micropipette followed by vigorous stirring for 5 s. An at least 15-fold excess of acid ensured pseudo-first-order conditions with respect to the copper complexes. Time resolved spectra were recorded on a diode array rapid scanning UV/vis spectrometer equipped with 1 cm quartz cuvettes at 25.0 (2) °C without further adjustment of ionic strength. Both the decrease of intensity at λ_{max} of the characteristic band I of copper(II) paddle-wheels[30] (740 nm for DMSO and 720 nm for DMF) as well as at the λ_{max} of the resulting copper(II) ions (830 nm for DMSO and 800 nm for DMF) were used to monitor the progress of decomposition. The absorbance *versus* time curves were recorded to calculate the pseudo first-order rate constants by linear regression using a spread-sheet calculation program.†

Small-angle X-ray scattering (SAXS)

Compound **2** was dissolved in DMF at a concentration of 110 g/L; compound **3** was dissolved in DMF at a concentration of 15.7 g/L. The solutions were filtered using 0.2 μm pore-size filters. The scattering experiments were done with a Bruker AXS Nano-STAR equipped with a HI-STAR area detector. The light source was a conventional X-ray tube operating at 35 mA and 40 kV (Cu $K\alpha$ = 0.154 nm). The blank-scattering contributions of the solvent, sample holder, and incoherent scattering were substracted prior to any calculations. The scattering data were transformed into pair-distance distribution functions (PDDF) *via* the program GNOM.[21] X-Ray solution scattering from the atomic coordinates of 2 was evaluated with the program CRYSOL.[24] The program DAMMIN[22] was used for *ab initio* shape determination from the PDDFs (by simulated annealing using a single phase dummy atom model).

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