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# ZnO Nanoparticles From a Metal-Organic Framework Containing $Zn^{II}$ Metallacycles

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**Keywords:** Metallacycles / Tripodal ligands / Hydrogen bonds / Metal-organic frameworks / Nanoparticles

Nitrilotriacetic acid ($H_3NTA$) reacts in the solid phase with zinc hydroxide (1:1) to form a 3D ladder-like metal-organic framework that forms wurtzite ZnO nanoparticles when heated above 600 °C. Complex **1** contains a 1D zig-zag water chain. A mixed coordination network **2** is formed with excess $Zn^{II}$ hydroxide, which, on decomposition at about 500 °C, forms microwires of ZnO.

## Introduction

In the past decade, the design and synthesis of functional molecule analogues by the self-assembly of metal-connecting points and organic linkers under controlled reaction conditions has attracted a great deal of attention among the inorganic, materials, and supramolecular chemistry communities.[1] As a result of these concerted efforts, the studies on the syntheses of metal-organic frameworks (MOFs) have undergone tremendous development by virtue of their attractive topologies and potential application in areas such as magnetism, non-linear optics, electrical conductivity, host–guest chemistry, gas storage, nonlinear optics, ion-exchange, and catalysis.[2,3]

The development of metal complexes that assemble into predictable supramolecular structures in the crystal is of great interest because of their potential in designing new materials with desirable optical and magnetic properties.[4] Nitrilotriacetate ($H_3NTA$) is a multidentate $C_3$-symmetric tripodal ligand that has been attracting much attention.[5] The self-complementary character of this ligand controls its assembly into aggregates by intermolecular hydrogen bonds and its threefold symmetry is maintained upon complexation.

The physical properties such as electric conductivity and magnetic, optical, and mechanical characteristics of nanosized metal oxide particles are known to be substantially different from those of bulk materials. The preparation methods of metal oxide nanoparticles have been extensively studied to precisely control the morphology at the nanometer scale. ZnO is one of the most important oxide materials for such wide ranging industrial applications as transparent conductors, UV-protection films, and chemical sensors.[6] Synthetic routes that have been employed to prepare ZnO nanoparticles include a liquid-phase method, vapor deposition, and a precursor process.[7]

Here we report the solid-phase synthesis of $Zn^{II}$-containing metallacycles using simple yet versatile acid-base chemistry with the $C_3$-symmetric tripodal ligand nitrilotriacetic acid ($H_3NTA$) in a 1:1 ratio. The resulting complex **1** forms a ladder-like 3D polymeric metal-organic framework (MOF). The macrocyclic pores host a zig-zag 1D infinite chain of lattice water. Complex **1** forms wurtzite ZnO nanoparticles when heated above 600 °C. A mixed coordination network **2** is formed with excess $Zn^{II}$ hydroxide, which, on decomposition at around 500 °C, forms microwires of ZnO.

## Results and Discussion

### Synthesis and Characterization

Complex **1** was synthesized by a simple acid-base reaction in the solid phase. A mixture of nitrilotriacetic acid (1 mmol, 0.191 g) and anhydrous freshly prepared zinc hydroxide (1 mmol, 0.099 g) was ground thoroughly with a pestle in an open mortar at room temperature under air. The mixture was ground for 5 min until the mixture turned into a slurry. X-ray quality single crystals of Zn complex **1** were grown from water within a day at room temperature in quantitative yield. Complex **2** was synthesized following the same procedure as **1**, only the metal to ligand ratio was different (3:2).

### $[(HNTA)(H_2O)_3Zn^{II}]\cdot H_2O$ (1)

The molecular structure of complex **1** consists of a $Zn^{II}$ ion, partially deprotonated NTA, and water molecules (Fig-

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ure 1). The X-ray structure determination shows that compound **1** contains hexacoordinate Zn$^{II}$ with a distorted octahedral geometry. The angular distortion around Zn from the octahedral geometry is significant. The N(1)–Zn–O angles deviate considerably from 90° and range between 78.22(7)° and 100.02(8)° while the N(1)–Zn–O(7) angle is only 162.19(11)°. The metal ion is bonded to two carboxylates from the ligand, each of which donates a single O atom. The third coordination site is occupied by the tertiary amine bridgehead N-atom of the ligand, while the remaining coordination sites of the octahedral geometry are occupied with water molecules. The resulting coordination polymer looks like an array of zinc-containing metallomacrocycles (see Supporting Information). The Zn–O(carboxylate) and Zn–N bond lengths are 2.068(3), 2.074(2), and 2.222(2) Å, respectively, in good agreement with other Zn$^{II}$ carboxylate complexes.[8] The Zn–O(water) bond lengths are 2.0671(17), 2.107(3), and 2.105(3) Å, and are also similar to other Zn–OH$_2$ bond lengths reported in the literature.[9] The bond lengths and bond angles are found to be within normal statistical errors.[8]

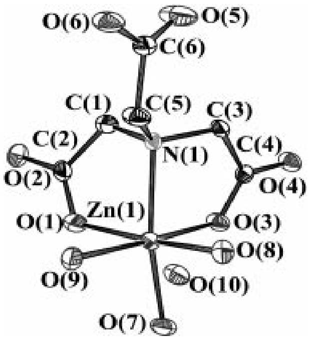

Figure 1. An ORTEP view of complex **1**.

Figure 2 shows an illustration of the 3D assembly of an infinite ladder framework. The rails of the ladder are made of almost linear, seven-atom units consisting of intermolecularly hydrogen bonded O(4)–C(4)–O(3)–Zn(1)–O(1)–C(2)–O(2) groups of NTA. The rungs of the ladder are made of an O atom of the axial water molecule. The distance between the rails of the ladder is 7.652 Å (distance between two adjacent Zn atoms forming the rail) and the two adjacent ladders are separated by 11.218 Å (distance between two Zn atoms of neighboring rails). However, the separation between the rungs of the ladder is 5.093 Å (forming the rail distance between two axial water oxygen atoms). Adjacent rails of the ladders are interconnected by intermolecular hydrogen bonds (Figure 2).

A crystal water molecule (O10) forms strong hydrogen bonds with neighboring metal-coordinated water molecules as well as with the coordinated O atom of the carboxylic acid group. Each of the crystal water molecules is hydrogen bonded to the four neighboring molecules in an almost tetrahedral arrangement (see Supporting Information). The hydrogen bonding between the crystal water molecules is comparatively weak in nature and forms a 1D zig-zag infinite water chain along the *b* axis (Figure 3), which is one of the probable proton wire structures found in biological systems.[10] A zig-zag motif of a water chain has also been reported for nonbiological system.[11]

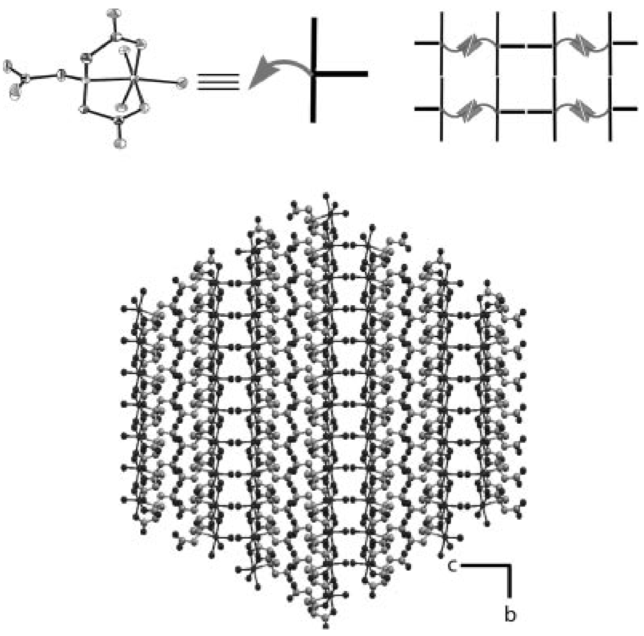

Figure 2. An infinite ladder framework along the *a* axis of **1**.

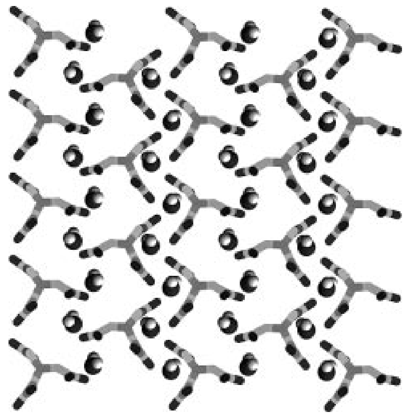

Figure 3. Perspective view of the zig-zag water chain in the crystal lattice of complex **1**.

The uncoordinated carboxylic acid group of NTA forms strong intramolecular hydrogen bonds with the neighboring O atom of the coordinated carboxylate group [O4···H4 1.793(5), O4–O6 2.604(7) Å and O6–H4–O4 170.23°]. O4 is acting as a H-bond acceptor and O6 as a H-bond donor and they act together like a clip (see Supporting Information), which eventually helps to form the 3D hydrogen-bonded MOF. Here, both water–MOF and water–water interactions are important for the stability of the overall polymeric structure.

The interaction between the MOF and the water chain is moderate, as thermogravimetric analysis of complex **1** under N$_2$ shows a 22.67% weight loss at around 100 °C, which corresponds to the loss of four water molecules (calculated 22.08%). Among the three carboxylic acid groups present in the ligand, two are coordinated to the metal ion as carboxylate. TG analysis shows the sequential removal of one $CO_2$ molecule from the uncoordinated carboxylic acid group and two $CO_2$ molecules from the two coordinated carboxylate groups in the ranges 260–330 °C (loss of 17.24%; calcd. 17.32%) and 330–420 °C (loss of 41.66%; calcd. 41.79%) respectively, which is in good agreement with the X-ray crystal structure. Complete decomposition is achieved at about 600 °C. The DSC plot shows an endothermic peak at 100 °C due to the loss of water molecules. It also shows two exothermic peaks at 310 and 370 °C due to the decomposition of the carboxylic acid groups.

The FT-IR spectrum of complex **1** shows a broad band centered at 3300 $cm^{-1}$ due to the presence of water molecules; this vanishes when the compound is heated under vacuum (0.1 mm) at 150 °C for 6 h. Two types of carboxylic acid groups are present in complex **1**: uncoordinated, unionized and coordinated, ionized. The FT-IR spectrum clearly shows the presence of uncoordinated, unionized COOH at 1740 $cm^{-1}$ and coordinated, ionized $COO^-$ at 1590 $cm^{-1}$; these values agree well with those in the literature (see Supporting Information).[12] The $^1H$ NMR spectrum shows a broad singlet in $D_2O$ at $\delta$ = 3.49 ppm ($NCH_2COOH$), which proves the dynamic complexation and decomplexation behavior of the third carboxylic acid group at room temperature in solution.

The powder X-ray diffraction patterns of **1** show significant changes in the peak positions as well as intensities before and after water removal (Figure 4), which match well with the simulated pattern.

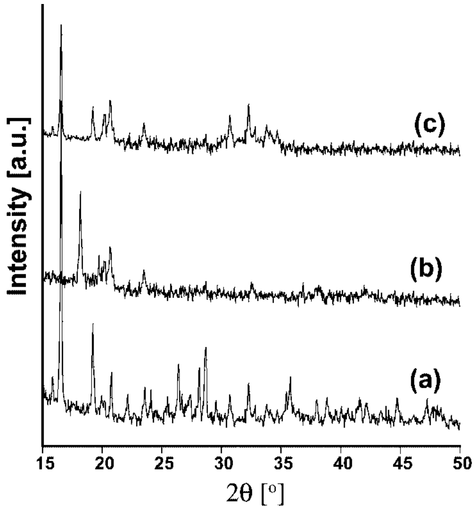

Figure 4. The powder XRD pattern of complex **1** before water removal (a), after water removal (b), and after re-hydration (c).

Thermal decomposition of complex **1** at 700 °C for 6 h in a muffle furnace forms wafers of ZnO with lengths ranging from 0.2 to 1.2 mm. The average size of these wafers remains unchanged with longer reaction time, up to 14 h. SEM images taken of several batches of samples showed that the entire wafer is formed from a uniform and densely packed array of ZnO nanoparticles (Figure 5). The nanoparticles' crystallinity was analyzed by powder X-ray diffraction techniques. The diffraction peaks (Figure 6) can be indexed as the wurtzite structure of ZnO (JCPDS 36-1451), thereby indicating that the zinc NTA complex has been thermally decomposed into ZnO.[13] The X-ray diffraction pattern shows an enhanced (101) peak resulting from the linear orientation of the nanoparticles. A typical synthesis yields particles with diameters ranging between 10 and 60 nm.

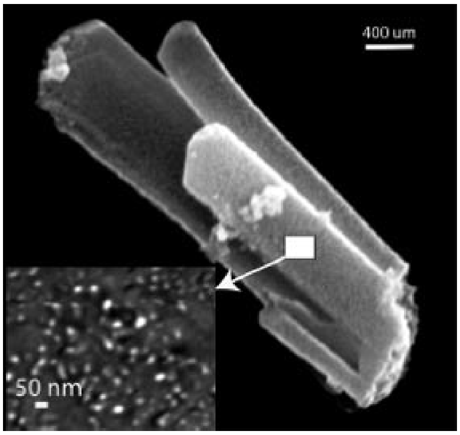

Figure 5. SEM micrographs of microwafers made of ZnO nanoparticles.

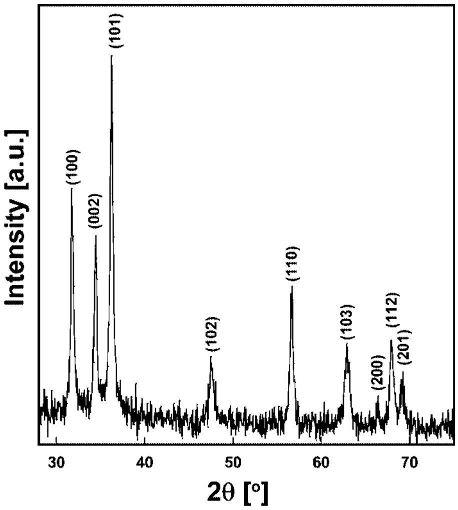

Figure 6. Powder XRD pattern of ZnO (wurtzite) nanoparticles.

### $[(H_2O)_6Zn][(NTA)_2Zn_2]\cdot 2H_2O$ (2)

The dimeric Zn nitrilotriacetato complex **2** is formed in the presence of an excess of zinc hydroxide. The asymmetric unit contains the hexaaquazinc(II) cation, the dimeric Zn-NTA complex anion, and crystal water. There are three symmetry-independent Zn sites in the structure. The first two of them (Zn1 and Zn2) are distorted octahedral with five carboxyl oxygens and one amine nitrogen making up the coordination environment. The other zinc cation, Zn3, is coordinated to six water molecules. Zn1 and Zn2 are bridged together by the carboxylic O3, O4, O11, and O12 atoms to form an infinite metal-organic framework. Among these four oxygen atoms, O3 and O11 form very rare μ-oxo carboxylato type bridges where each carboxylate ligand is bonded to three metal centers. Atom O3 forms a stronger bond with Zn2 [Zn(1)–O(3) 2.365(2), Zn(2)–O(3) 1.947(2) Å] while O11 forms a stronger bond with Zn1 [Zn(1)–O(11) 1.948(2) and Zn(2)–O(11) 2.351(2) Å]. Atom O3 occupies the axial position of Zn1 but the equatorial position of Zn2, whereas O11 occupies the axial position of Zn2 and the equatorial position of Zn1. The remaining four carboxylic oxygen atoms (O2, O6, O8, and O10) are not coordinated to the metal cation but form strong hydrogen bonds with the water molecules coordinated to the Zn3 cation. The carboxylic acid of one arm of each NTA unit is coordinated to the three zinc centers simultaneously along the crystallographic *ab* plane, which results in the formation of a complicated 3D polymeric rectangular network (Figures 7 and 8). The other two arms of each NTA unit form extensive hydrogen bonds with water molecules along the crystallographic *bc* plane. The overall 3D network is built up with the help of water of hydration (O19 and O20). The crystal water molecule O19 acts as a double hydrogen-bond donor as well as acceptor, while O20 acts as a single hydrogen-bond donor and acceptor. Both of these water molecules are strongly hydrogen bonded to the carboxylate as well as another coordinated water molecule. Unlike the mononuclear Zn-NTA complex **1**, there is no direct hydrogen bond between two crystal water molecules, which, in turn, prevents the formation of any water network in the solid-state structure. Two of the alternate rectangular void spaces in the 2D rectangular network are filled with these water molecules. Alternating Zn-aqua and Zn-NTA moieties form this 2D network.

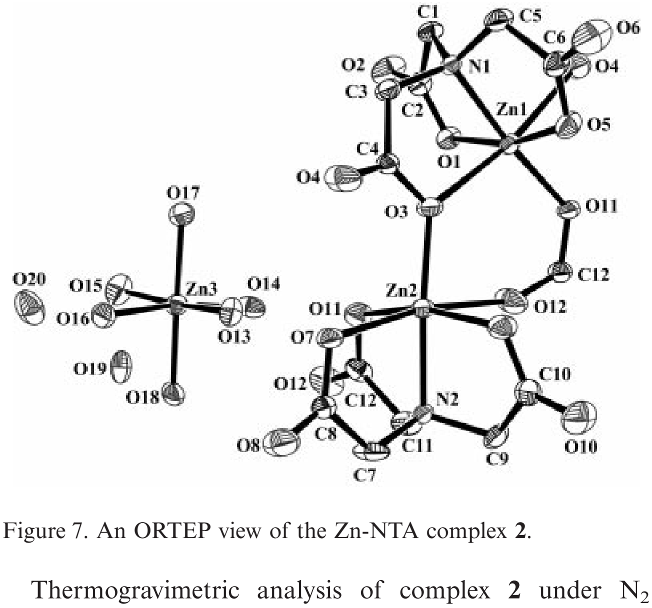

Figure 7. An ORTEP view of the Zn-NTA complex **2**.

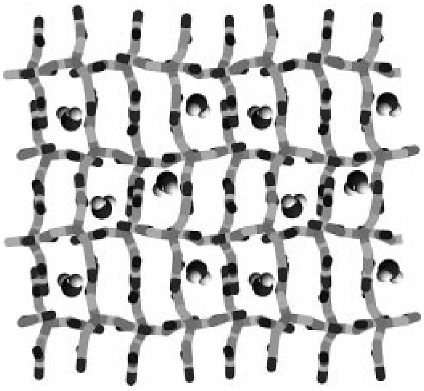

Figure 8. An infinite rectangular network along the *ab* plane of **2**.

Thermogravimetric analysis of complex **2** under $N_2$ shows a 21.08% weight loss between 30 and 100 °C corresponding to the loss of eight water molecules (calcd. 20.09%). All six coordinated carboxylic acid groups are removed between 100 and 240 °C with a weight loss of 47.08% (calcd. 46.11%), which is in good agreement with the X-ray crystal structure. Complete decomposition is achieved at about 480 °C and shows the formation of ZnO as the decomposed product. The DSC plot shows an endothermic peak at 75 °C due to the loss of water molecules. It also shows two exothermic peaks at 200 and 340 °C due to the decarboxylation and complete decomposition, respectively.

The FT-IR spectrum of complex **2** shows a broad band centered at 3500 $cm^{-1}$ due to the presence of water molecules, which also vanishes when heated, as for complex **1**. Unlike complex **1**, however, it contains only coordinated, ionized types of carboxylic acid groups, which absorb at 1620 $cm^{-1}$.[12]

Complex **2** decomposes above 500 °C to form microwires of ZnO with lengths ranging from 200 nm to 8 μm. The average size and shape of these fibers does not change with temperature and reaction time. The powder X-ray diffraction pattern of these microwires also confirms the presence of the wurtzite structure of ZnO (Figure 9).

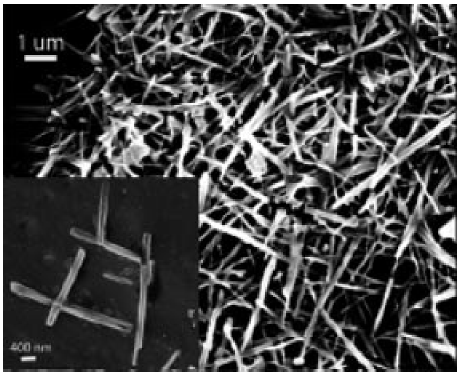

Figure 9. SEM micrographs of ZnO microwires.

## Conclusions

We have been able to synthesize two different metal-organic frameworks in the solid state by changing the metal to ligand ratio. An infinite array of metallacycles forms an interesting ladder and rectangular net like structures. The mononuclear complex **1** contains a 1D zig-zag infinite water chain. The stability of the water chain is derived from strong H-bonding interactions with the carboxylate group and the metal-bound water molecules. The binuclear complex **2** contains a very rare μ-oxo carboxylato bridge, where one carboxylate ligand binds to three metal centers simultaneously. Several other combinations of metal and ligand to synthesize MOFs of interest in solvent-free methods are currently under investigation in our laboratory. We have also demonstrated a precursor synthesis of ZnO nanoparticles and microwires with a wurtzite structure. The crystal lattice deposition temperatures for ZnO are very high because of the formation of extensive coordination networks of these supramolecular complexes. The technique demonstrated here can be extended to the synthesis of a wide range of nanomaterials having similar structures. These studies are currently underway in our laboratory.

## Experimental Section

**Materials and Methods:** Reagents were purchased from commercial sources and, unless otherwise stated, were used as received. Nitrilotriacetic acid was purchased from Sigma–Aldrich Co. and used without further purification. The IR spectra were recorded with a Perkin–Elmer Spectrum One FT-IR Spectrometer as KBr disks in the range 4000–400 $\mathrm{cm^{-1}}$. The thermogravimetric analyses (TGA) of the compounds were performed with an SDTA 851e TGA thermal analyzer (Mettler Toledo) with a heating rate of 2 $^{\circ}\mathrm{C\,min^{-1}}$ under $N_2$ with 5–10 mg of sample per run. Scanning electron micrograph (SEM) images were obtained with a LEO-1430 VP electron microscope on samples glued onto an aluminum stub and gold sputtered. Powder XRD data were recorded with a Seifert powder X-ray diffractometer (XRD, 3003TT) with Cu-$K_{\alpha}$ source ($\lambda$ = 1.54 Å) on a glass surface for an air-dried sample.

**X-ray Crystallography:** Colorless single crystals of **1** and **2** were grown by slow evaporation of an aqueous solution of the complexes at room temperature. The X-ray diffraction data were collected at room temp. with a Bruker three-circle diffractometer (Bruker Nonius SMART APEX-II) equipped with CCD area detectors, and using graphite-monochromated Mo-$K_{\alpha}$ radiation ($\lambda$ = 0.71073 Å) from a 60-W microfocus Siemens Microsource with glass polycapillary optics. The SMART[14] software was used for data acquisition and the SAINT[14] software for data extraction. The structures were solved by direct methods and refined by full-matrix least-squares against $F^2$. Absorption corrections were done using SADABS. Structures were solved and refined using SHELX 97.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined.

**Compound 1:** $C_6H_{15}NO_{10}Zn$, $M$ = 326.58, orthorhombic, $a$ = 12.2958(10), $b$ = 6.6129(10), $c$ = 27.846(2) Å, $V$ = 2262.4(4) Å$^3$, space group *Pbca*, $Z$ = 8, $T$ = 298(2) K, $\mu$ (Mo-$K_{\alpha}$) = 2.288 $\mathrm{mm^{-1}}$, $F(000)$ = 1170, GOF = 1.103; final $R$ indices: $R_1$ = 0.0213 [$I > 2\sigma(I)$], $wR_2$ = 0.0610; $R$ indices (all data): $R_1$ = 0.0224, $wR_2$ = 0.0604.

**Compound 2:** $C_{12}H_{28}N_2O_{20}Zn_3$, $M$ = 716.53, orthorhombic, $a$ = 12.7369(10), $b$ = 11.3290(10), $c$ = 16.4424(14) Å, $V$ = 2372.6(3) Å$^3$, space group $Pna2_1$, $Z$ = 4, $T$ = 298(2) K, $\mu$ (Mo-$K_{\alpha}$) = 3.120 $\mathrm{mm^{-1}}$, $F(000)$ = 1272, GOF = 0.931; final $R$ indices: $R_1$ = 0.0282 [$I > 2\sigma(I)$], $wR_2$ = 0.0980; $R$ indices (all data): $R_1$ = 0.0291, $wR_2$ = 0.0997.

CCDC-280983 (for **1**) and -612885 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): The TGA-DSC curves, FT-IR spectra, powder XRD patterns, and selected figures.

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