Functional Nanoparticles

DOI: 10.1002/ange.200705263

Valence-Tautomeric Metal–Organic Nanoparticles**

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Nano- and microparticles are involved in diverse applications ranging from data storage, catalysis, photonics, electronics, lithography, and microlenses to biosensors.[1] An important goal in this area is the fabrication of particles with novel compositions that can offer interesting properties for new applications. Coordination polymers are a class of solids created by the association of metal ions and multitopic organic ligands, and they have recently shown a wide range of promising properties in gas sorption, sensing, catalysis, ion exchange, magnetism, or optics.[2] Because of these properties and their synthetic flexibility, coordination polymers seem excellent candidates for the fabrication of functional nanoscale metal–organic particles (NMOPs).

Prior to this study, advances were made in fabricating NMOPs.[3] Thus far, the principal route has been the use of microemulsion techniques for the synthesis of Gd^{III} nanorods, which can be used as potential multimodal contrast-reformatting agents, and Prussian blue and triazole-based magnetic nanoparticles.[3–7] More recently, new NMOP obtained by precipitation processes have been reported.[8–13] Wang et al. and Mirkin et al. have proposed a promising strategy based on both coordination polymerization and precipitation in a poor solvent to produce cross-linked metal–organic spheres. For example, nano- and microspheres with interesting optical properties that show selective cation exchange have been obtained.[9,10] Inspired by this last approach, here we show how using the appropriate multitopic organic ligand makes it possible to structure well-known functional building blocks in the form of spherical particles. Polymerization of electroactive {Co(3,5-dbsq)(3,5-dbcat)} units,[14] where 3,5-dbsq$^-$ and 3,5-dbcat^{2-} are respectively the semiquinonate radical and catecholate forms of 3,5-di-*tert*-butyl-1,2-benzoquinone (dbq), with the ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) was chosen as the test case scenario. Complexes of general formula [Co^{III}(3,5-dbsq)(3,5-dbcat)(N–N)] interconvert reversibly between two valence tautomers—low-spin *ls*-[Co^{III}(3,5-dbsq)(3,5-dbcat)] and high-spin *hs*-[Co^{II}(3,5-dbsq)$_2$]—by reversible intramolecular transfer involving the metal ion and the redox-active ligand.[15,16] Since each electronic isomer has a different magnetic moment and optical properties, these complexes are candidates for use in future molecular electronic devices and switches,[17,18] and therefore serve as an excellent model system to create the first functional NMOPs that exhibit valence tautomerism.

In a typical experiment, an aqueous solution of $Co(CH_3COO)_2{\cdot}4H_2O$ was added to an ethanolic solution of 3,5-di-*tert*-butyl-1,2-catechol and bix with vigorous stirring at room temperature, and a very intense blue color developed. Blue nanoparticles were precipitated by fast addition of water to the mixture. The precipitate was then collected by centrifugation, washed several times with water, and finally redispersed in water.

Scanning (SEM) and transmission (TEM) electron microscopy images of the resulting blue colloid revealed the formation of spherical particles with an average diameter of 76 ± 9 nm (Figure 1 and Figure 2a). The average diameter was confirmed by dynamic light scattering (DLS) measurements, which showed a mean particle size of 75 ± 12 nm. Interestingly, the particle size could be controlled by regulating the rate of addition of water (poor solvent) to the reaction mixture. Figure 2 shows a series of colloidal spheres with average diameters of 76 ± 9, 110 ± 10, 140 ± 9, and 204 ± 13 nm that were systematically synthesized by decreasing the rate of water addition from 50 to 0.17, 0.1, and 0.07 mL s^{-1}, respectively. The particle sizes were determined by both SEM and DLS measurements.

X-ray powder diffraction data of the four batches showed that the particles are amorphous which prevents a detailed analysis of the structural connectivity. Nevertheless, additional characterization confirmed the polymerization of {Co^{III}(3,5-dbsq)(3,5-dbcat)} units through ditopic bix ligands, as shown in Figure 1a. The chemical composition of these particles was first determined by energy-dispersive X-ray spectroscopy, which confirmed that they contain cobalt, carbon, oxygen, and nitrogen. Furthermore, the elemental analysis of these particles is consistent with the proposed chain formation with formula [Co^{III}(bix)(3,5-dbsq)(3,5-dbcat)] (**1**). The infrared spectra show that the catechol and bridging bix ligands are coordinated to the cobalt ions, as

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[**] This work was supported by projects MAT2006-13765. D.M. thanks the Ministerio de Ciencia y Tecnología for a RyC contract. The authors thank the Servei de Microscopia of the UAB, Serveis Científico-Tècnics of the UB, and the Laboratori de Nanotecnologia de MATGAS. I.I. thanks the ICN for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

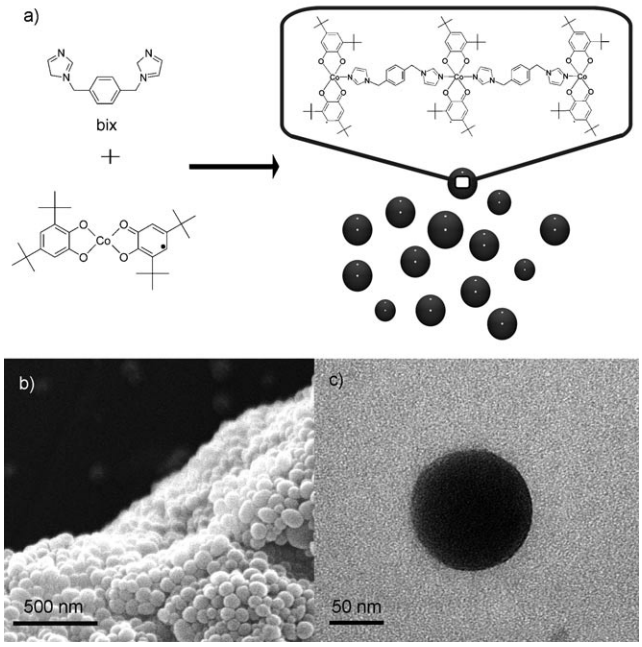

Figure 1. a) Coordination polymerization used to obtain valence-tautomeric NMOPs (schematic). b) SEM image of nanoparticles created by infinite coordination polymerization of {Co^{III}(3,5-dbsq)(3,5-dbcat)} units through bix ligands. c) High-resolution TEM image of one spherical nanoparticle.

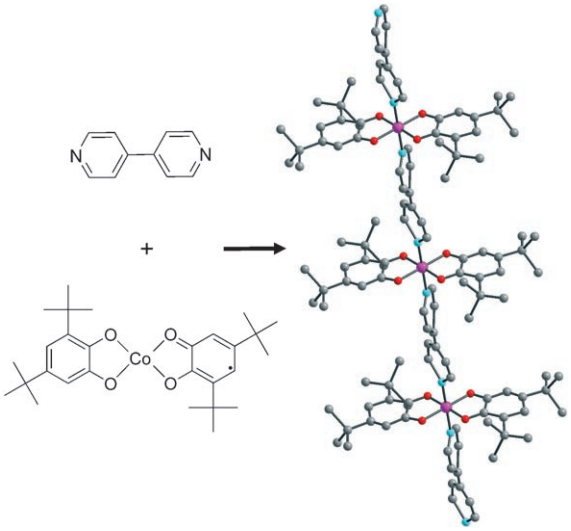

Figure 3. Synthesis and crystal structure of one-dimensional coordination polymer **2**. C gray, Co pink, N blue, O red, H not shown.

evidenced by the presence of characteristic C–O bands[19] at 1480 and 1446 cm^{-1} and two strong bands at 1649 and 1520 cm^{-1} typical of the bix ligand.[20] Finally, the MALDI-TOF mass spectrum indicates the presence of the bridging bix ligand at m/z 239.

To provide further evidence for formation of the one-dimensional coordination polymer in the particle-formation process, a model reaction was repeated with a different ditopic N,N′ ligand, 4,4′-bipyridyl (4,4′-bipy, Figure 3). In this case single crystals of a polymer with formula [Co^{III}(4,4′-bipy)(3,5-dbsq)(3,5-dbcat)] (**2**) that were suitable for X-ray diffraction studies were obtained by diffusion of an aqueous solution of $Co(CH_3COO)_2{\cdot}4H_2O$ into an ethanol solution of 3,5-di-*tert*-butyl-1,2-catechol and 4,4′-bipy. The crystal structure revealed the expected 1D polymer structure, in which metal ions are anchored by four oxygen atoms of the catechol ligands in equatorial positions and two nitrogen ligands of 4,4′-bipy in axial positions. This confirms the tendency for bridging N-aromatic N-donor ligands to form chains when they are associated with {Co^{III}(3,5-dbsq)(3,5-dbcat)} units, as previously described.[21–23]

A principal characteristic of valence-tautomeric systems is the variation of the magnetic moment on interconversion from the low-spin to the high-spin isomer. This is not only important for their possible integration into molecular electronic devices, but also for characterization of the interconversion process. Figure 4 shows the temperature dependence of $\chi_M T$ of the metal–organic nanoparticles and a crystalline sample of **2** in the temperature range of 5–350 K under an external applied magnetic field of 0.1 T. An abrupt valence-tautomeric transition is observed for crystalline complex **2**. At low temperatures the observed $\chi_M T$ value is 0.4 emu K mol^{-1}, which is in agreement with dominance of the low-spin isomer *ls*-[Co^{III}(3,5-dbsq)(3,5-dbcat)] bearing one unpaired electron. Increasing the temperature induces a gradual increase of the magnetic moment up to a $\chi_M T =$ 0.6 emu K mol^{-1} at 275 K. Then, a further increase of the temperature induces an abrupt transition over a narrow temperature range of 40–50 K up to a maximum value of $\chi_M T = 2.6$ emu K mol^{-1} at 340 K. Such a $\chi_M T$ value is in

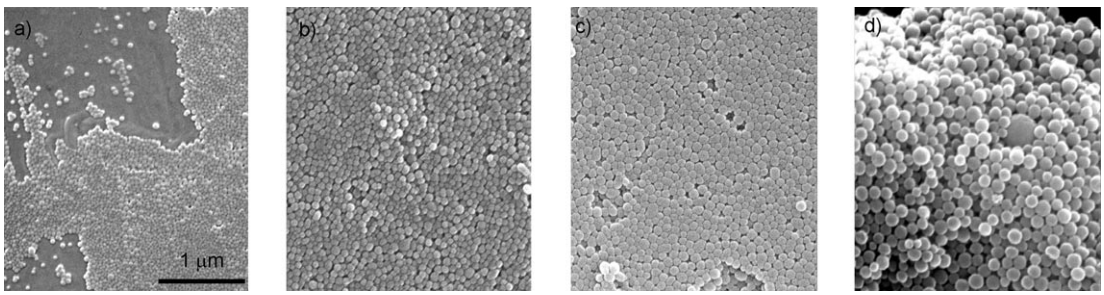

Figure 2. SEM images of colloidal spheres of **1** with average diameters of a) 76 ± 9, b) 110 ± 10, c) 140 ± 9, and d) 204 ± 13 nm, as determined by SEM and DLS. The 1-μm scale bar is the same for all SEM images.

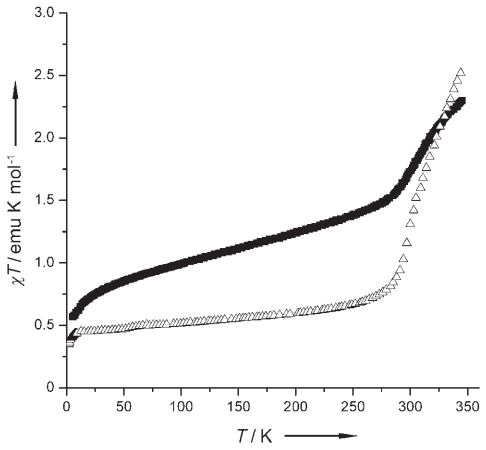

Figure 4. χT values as a function of temperature for the amorphous metal–organic nanospheres of **1** (■) and crystalline coordination polymer **2** (△).

agreement with conversion to the high-spin isomer *hs*-[Co^{II}-(3,5-dbsq)$_2$] bearing one $S = 3/2$ (catechol) and two $S = 1/2$ (semiquinone) independent units.[15]

The magnetic properties of the nanoparticles were directly measured on an aqueous colloidal suspension (76 ± 9 nm in diameter) located in a sealed tube to ensure that the magnetic properties correspond to the behavior of dispersed nanoparticles (Figure 4). The stability of the nanospheres during the magnetic measurements was confirmed by SEM before and after the measurements. Even though the transition is not complete, the $\chi_M T$ value of 2.2 emu K mol^{-1} at 340 K is close to the expected value for the *hs*-[Co^{II}(3,5-dbsq)$_2$] isomer. On cooling, we observed an abrupt decrease of $\chi_M T$ to 1.4 emu K mol^{-1} at 270 K that is associated with a valence-tautomeric interconversion from the *hs*-[Co^{II}(3,5-dbsq)$_2$] to the *ls*-[Co^{III}(3,5-dbsq)(3,5-dbcat)] isomer of a fraction of molecules. Below 270 K, the $\chi_M T$ value monotonically decreases to a value of 0.6 emu K mol^{-1} at 5 K that is in agreement with gradual conversion of the remaining molecules in the high-spin state. Such a gradual decrease is common for noncrystalline phases and has been previously observed for tautomeric coordination polymers.[24] The magnetic properties of nanoparticles of different sizes all exhibited similar dependence on temperature. Therefore, the variation of the slope mostly likely can be correlated with the presence of two different relaxation mechanisms associated with different network environments and/or the presence of an additional structural transition, as recently reported by Dei et al.[25,26]

In summary, we have demonstrated that precipitation/coordination polymerization is a suitable approach for the fabrication of pre-synthesized units into functional metal–organic nanoparticles. Size-tunable nanoparticles that exhibit valence tautomerism have been obtained by using electroactive [Co^{III}(3,5-dbsq)(3,5-dbcat)] units and the appropriate bridging ligand. Such a bridging ligand or polymerizing agent was previously shown by others to be crucial to the formation of nanoparticles. Whereas the bix ligand yields amorphous nanoparticles, the 4,4′-bipyridine ligand yields a crystalline material. The high flexibility of this strategy and its scalability to several different functional molecular materials will certainly expand the synthesis of NMOPs with novel properties by simple polymerization of functional units/clusters and metal ions with the appropriate bridging ligands.

Experimental Section

All reagents were purchased from Aldrich Chemical Co. and used as received. 1,4-Bis(imidazol-1-ylmethyl)benzene was synthesized according to literature procedures.[27]

1,4-Bis(imidazol-1-ylmethyl)benzene (121 mg, 0.5 mmol) and 3,5-diterbutylcatechol (110 mg, 0.5 mmol) were first dissolved in 10 mL of ethanol. The addition of an aqueous solution of $Co(CH_3COO)_2{\cdot}4H_2O$ (120 mg, 0.5 mmol in 2 mL H_2O) led to a color change to dark blue. A blue precipitate consisting of valence-tautomeric nanoparticles was obtained by fast addition of 50 mL H_2O. C,H,N analysis (%) calcd for $C_{56}H_{74}O_6CoN_4$: C 70.19, H 7.78, N 5.85; found: C 69.80, H 7.93, N 5.25; IR (KBr pellet): $\tilde{\nu} = 2980$ (s), 1663 (s), 1581 (s) 1519 (s), 1479 (s), 1446 (s), 1245 (m), 1108 (m), 657 cm^{-1} (m).

Crystals of **2** were obtained by diffusion in a test tube over three weeks of an aqueous solution of $Co(CH_3COO)_2{\cdot}4H_2O$ (124 mg, 0.5 mmol) into an ethanol solution of 3,5-di-*tert*-butyl-1,2-catechol (111 mg, 0.5 mmol) and 4,4′-bipyridyl (78 mg, 0.5 mmol). C,H,N analysis (%) calcd for $C_{38}H_{48}O_4CoN_2$: C 69.6, H 7.38, N 4.27; found: C 69.35, H 7.59, N 4.21; IR (KBr pellet): $\tilde{\nu} = 3436.3$ (s) 2961 (s), 1608.7 (s), 1586 (s), 1484 (m), 1414 (m), 806 cm^{-1} (m).

Crystal data of **2**: $C_{38}H_{48}O_4CoN_2$, $M_r = 656$ g mol^{-1}, monoclinic, $C2/c$ (no. 15); $a = 10.560(5)$, $b = 32.544(10)$, $c = 10.979(5)$ Å, $\beta = 99.57(5)°$, $V = 4923.1(3)$ Å^3; $Z = 4$, $\rho = 1.067$ g cm^{-3}, $\mu = 1.488$ mm^{-1}, final $R_1 = 0.098$, $wR_2 = 0.165$ for $I > 4\sigma(I)$; 5087 reflections, 1737 unique reflections (753 observed) X-ray diffraction data were recorded under synchrotron irradiation ($\lambda = 0.977$ Å) at the BM16 Spanish beamline of ESRF with a CCD detector at 150 K. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 with SHELX-97.[28] Crystal adsorption was corrected by Scalepack.[29] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were generated geometrically and refined isotropically. CCDC-670425 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic susceptibilities of both samples were measured in the temperature range 5–350 K with a Quantum Design MPMS XL SQUID magnetometer operating at a magnetic field strength of 0.1 T. The susceptibility of dispersed particles was corrected for the contribution of a sealed tube filled with the same amount of water as used for preparing the dispersion and for the diamagnetism of the sample estimated from Pascal's constants.

Received: November 15, 2007
Published online: January 28, 2008

Keywords: cobalt · coordination polymers · magnetic properties · nanostructures · tautomerism

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