Nano- and Microstructures

DOI: 10.1002/ange.200601918

Ion Exchange as a Way of Controlling the Chemical Compositions of Nano- and Microparticles Made from Infinite Coordination Polymers**

*Moonhyun Oh and Chad A. Mirkin**

Micro- and nanosized particles play important roles in many different areas, including catalysis,[1] optics,[2] biosensing,[3] and data storage.[4] Recent advances in this field have made it possible to control many of the chemical and physical properties of these solid-state materials through control over their size, shape, and composition.[5] One important goal in this area is to be able to deliberately interconvert different particle compositions and structures through chemistry that occurs throughout the particle structure in addition to on its surface.[6] There are two ways to effect such transformations, either through a thermally or photochemically induced shape change[6a] or by chemical means that transform the particle from one chemical composition to another.[6b] Even though the latter approach, in principle, can provide a straightforward, economic, and potentially powerful way to access new classes of micro- and nanoparticle materials, very few such approaches have been developed and those that have been realized are quite limited in scope.[6b]

Typically, chemical transformations in the solid state require a high activation energy for the diffusion of small molecules or ions into the solid. Therefore, the reactions are usually slow and involve high temperature and/or pressure.[7] A beautiful demonstration of an exception to this rule is that CdSe can be converted to Ag_2Se in the context of nanosized particles at room temperature.[6b] In contrast, metal–organic coordination polymers are highly porous materials[8,9] that often allow small molecules to move freely within such structures. For this reason, they are typically used for gas storage[9] and catalysis.[8a] Recently, we, and others, have shown how such structures can be transformed into nano- and microparticle materials through controlled precipitation methods.[10,11] We hypothesized that because of the open framework of such structures, the small molecules and ions that comprise such structures should be highly accessible and, in certain cases, susceptible to ion-exchange reactions. Herein, we report a strategy that allows one to transform such particles into new compositions through selective cation-exchange reactions without significantly affecting the size or morphology of the particle (Scheme 1).

We previously reported a synthetic strategy for the preparation of infinite-coordination-polymer particles that consist of metalloligand (bis-metallo-tridentate Schiff base (BMSB)) building blocks and metal interconnecting nodes.[10] These structures form the basis for the studies described herein, and our starting reagents are Zn–BMSB–Zn (**1**) spherical particles suspended in methanol. The approach utilizes two different types of ions, those that are coordinated to the tridentate pockets of the BMSB ligands and those that link the BMSB ligands through the carboxylate groups to form the polymers. When Zn^{2+} is used as the metal ion, it can be readily displaced from the BMSB tridentate pockets but not from the carboxylate sites with a variety of metal ions.

In a typical reaction, we prepared a mixture of Zn–BMSB–Zn microparticles (**1**; average diameter $\approx 1.6\ \mu m$) and $Cu(OAc)_2 \cdot H_2O$ in methanol under ambient conditions. The mixture contained Cu^{2+} ions in a slight excess to ensure the replacement of all the Zn^{2+} ions coordinated to the tridentate Schiff base moieties within the particles. Zn–BMSB building blocks are highly fluorescent as are Zn–BMSB–Zn (**1**) particles; however, the product resulting from cation exchange, Cu–BMSB, is not.[10] Therefore, one can easily monitor the particle transformation by optical microscopy (OM) and fluorescence microscopy (FM, Figure 1 a–d, compare the OM and FM images). Within 5 min, most of the fluorescent Zn–BMSB–Zn (**1**) particles had been transformed into the Cu–BMSB–Zn (**2**) particles, and by 60 min the reaction was completed. This transformation could be followed by fluorescence or with the naked eye, as evidenced by a concomitant color change from orange (Zn–BMSB–Zn) to brown (Cu–BMSB–Zn, Figure 1 e).

Further to these optical-property changes, energy-dispersive X-ray (EDX) spectra, inductively coupled plasma (ICP) analyses, and emission spectra that were measured before and after the cation-exchange reaction were consistent with the formation of the Cu–BMSB–Zn (**2**) product. The emission spectrum of the resulting particles reveals complete disappearance of fluorescence, indicating full exchange of two equivalents of Cu^{2+} for the two Zn^{2+} ions contained within the Zn–BMSB building blocks (Figure 1 f). A separate study of the Zn–BMSB monomer shows that one must remove both Zn ions within the Zn–BMSB to quench the fluorescence from this system. Furthermore, an EDX spectrum of the Cu–BMSB–Zn (**2**) particles measured after the cation exchange shows the expected Cu signal in addition to that of Zn (see the Supporting Information). Finally, ICP-analysis data are consistent with a change in the number of metal ions within the particles from three to one Zn^{2+} ion and from zero to two Cu^{2+} ions per repeating unit.[12]

Scanning electron microscopy (SEM) images of initial (Figure 2 a) and cation-exchanged (Figure 2 b) particles show that the size and shape of the particles are preserved after the

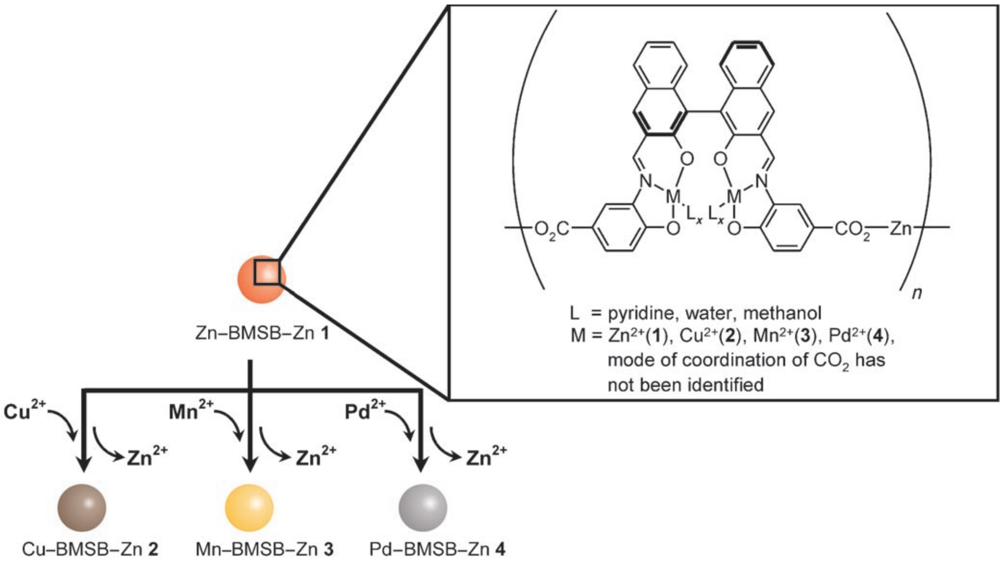
---

[*] Prof. Dr. C. A. Mirkin
Department of Chemistry
and International Institute for Nanotechnology
Northwestern University
2145 Sheridan Road, Evanston, IL, 60208-3113 (USA)
Fax: (+1) 847-467-5123
E-mail: chadnano@northwestern.edu
Prof. Dr. M. Oh
Department of Chemistry
Yonsei University
134 Shinchon-dong, Seodaemun-gu, Seoul 120-749 (Korea)

[**] C.A.M. acknowledges the ONR and NSF-NSEC program for supporting this research.

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

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1. Schematic representation of ion-exchange reactions.

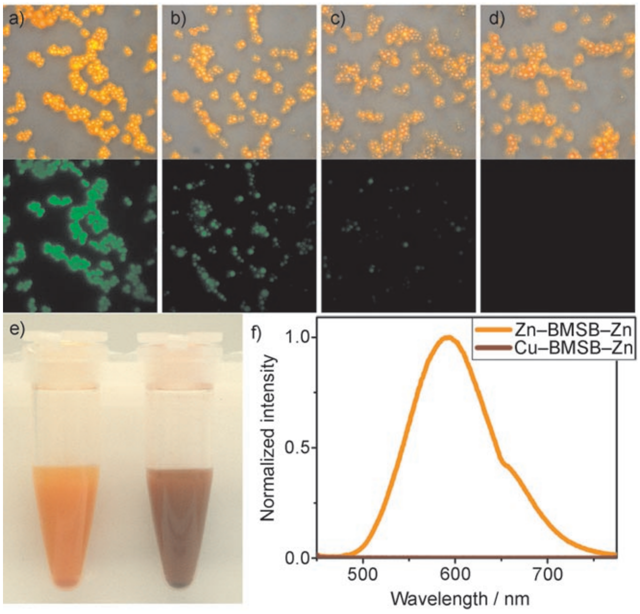


Figure 1. Chemical-transformation reactions from Zn–BMSB–Zn (**1**) to Cu–BMSB–Zn (**2**) microparticles through cation exchange: a–d) time related OM (top) and FM (bottom) images. t = a) 0 min, b) 1 min, c) 5 min, and d) 60 min. e) A photograph showing the color changes (left: **1**, right: **2**) and f) emission spectra obtained by exciting at 420 nm.

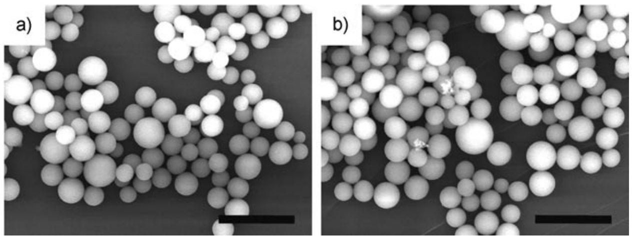


Figure 2. SEM images of spherical microparticles: a) initial Zn–BMSB–Zn (**1**) and b) chemically transformed Cu–BMSB–Zn (**2**). Scale bars = 5 µm.

reaction. From these data, we can conclude that the Cu^{2+} ions only exchange with the Zn^{2+} coordinated to the tridentate Schiff base and not the Zn^{2+} ions that form the interconnecting nodes. When excess Cu^{2+} ions are used in the exchange reaction, the reaction occurs at a faster rate, but results in the same product, Cu–BMSB–Zn (**2**). Under the conditions studied, there is no evidence for the formation of the Cu–BMSB–Cu product, which is a reflection of the difference in binding strength of the two coordination sites.

The cation-exchange reaction rate is size dependent. Indeed, ≈200-nm particles prepared by literature methods[10] undergo a Cu^{2+}-exchange reaction in a few minutes as compared to the hour required to effect it with the micron-scale particles. Again, FM and OM images clearly show the transformation (Figure 3 b), with minimal change seen in

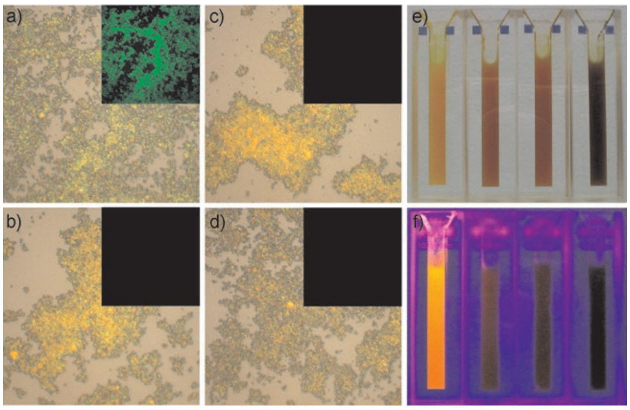


Figure 3. OM and FM (inset) images of spherical nanoparticles: a) initial fluorescent Zn–BMSB–Zn (**1**) and cation-exchanged nonfluorescent products b) Cu–BMSB–Zn (**2**), c) Mn–BMSB–Zn (**3**), and d) Pd–BMSB–Zn (**4**). Digital photographs of a series of nanoparticles (left to right: **1**, **2**, **3**, and **4**): e) without and f) with UV irradiation. The latter shows the starting nanoparticle composition is fluorescent whereas the products are not.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

particle size; the average particle sizes measured before (212 nm) and after the cation-exchange reaction (215 nm) by dynamic light scattering (DLS) are nearly identical (see the Supporting Information for size distribution).

We also evaluated the utility of this method for producing additional particle compositions with other metal ions such as Mn^{2+} and Pd^{2+}. We prepared a mixture of Zn–BMSB–Zn (**1**) nanoparticles and $Mn(OAc)_2$ or $Pd(OAc)_2$ in methanol under ambient conditions. In contrast to the process involving Cu^{2+} exchange, excess Mn^{2+} or Pd^{2+} (> 20 equiv) must be used to observe significant conversion as measured by fluorescence. The transformations could be followed by fluorescence or with the naked eye (Figure 3). In addition, these nanoparticles, like their Cu^{2+} counterparts, have been characterized by EDX, DLS, and emission spectroscopy (see the Supporting Information).

In conclusion, we have demonstrated that selective cation exchange within the context of nano- and microparticles made from infinite coordination polymers can be used to transform one particle composition into several new ones in a very efficient process. The fast rates of these processes under ambient conditions, which are derived from the porosity of the structures and the labile nature of the Zn-coordination interactions, are unusual (especially when compared to their solid-state counterparts) but extremely useful. These rates provide a way of creating one precursor set of particles that can be deliberately and controllably transformed into a new set of compositions with properties that are derived from the metallated BMSB building blocks.

Received: May 15, 2006
Published online: July 21, 2006

Keywords: chemical transformation · coordination polymers · ion exchange · metalloligands · nanostructures

---

[1] a) A. T. Bell, *Science* **2003**, *299*, 1688–1691; b) S.-W. Kim, M. Kim, W. Y. Lee, T. Hyeon, *J. Am. Chem. Soc.* **2002**, *124*, 7642–7643.
[2] a) J. Wang, M. S. Gudiksen, M. X. Duan, Y. Cui, C. M. Lieber, *Science* **2001**, *293*, 1455–1457; b) F. Fleischhaker, A. C. Arsenault, V. Kitaev, F. C. Peiris, G. Freymann, I. Manners, R. Zentel, G. A. Ozin, *J. Am. Chem. Soc.* **2005**, *127*, 9318–9319.
[3] Y. C. Cao, R. Jin, C. A. Mirkin, *Science* **2002**, *297*, 1536–1540.
[4] S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* **2000**, *287*, 1989–1992.
[5] a) X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59–61; b) D. Horn, J. Rieger, *Angew. Chem.* **2001**, *113*, 4460–4492; *Angew. Chem. Int. Ed.* **2001**, *40*, 4330–4361; c) J. Chen, T. Herricks, Y. Xia, *Angew. Chem.* **2005**, *117*, 2645–2648; *Angew. Chem. Int. Ed.* **2005**, *44*, 2589–2592.
[6] a) R. Jin, Y. Cao, C. M. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **2001**, *294*, 1901–1903; b) D. H. Son, S. M. Hughes, Y. Yin, A. P. Alivisatos, *Science* **2004**, *306*, 1009–1012.
[7] a) S. Feng, R. Xu, *Acc. Chem. Res.* **2001**, *34*, 239–247; b) R. E. Schaak, T. E. Mallouk, *Chem. Mater.* **2002**, *14*, 1455–1471.
[8] a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; b) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522; c) M. Oh, G. B. Carpenter, D. A. Sweigart, *Acc. Chem. Res.* **2004**, *37*, 1–11; d) F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2001**, *123*, 7740–7741; e) B. Moulton, J. Lu, M. J. Zaworotko, *J. Am. Chem. Soc.* **2001**, *123*, 9224–9225; f) S.-I. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, M. Yamashita, *J. Am. Chem. Soc.* **2002**, *124*, 2568–2583.
[9] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; b) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012–1015.
[10] M. Oh, C. A. Mirkin, *Nature* **2005**, *438*, 651–654.
[11] X. Sun, S. Dong, E. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 13102–13103.
[12] There are inherent difficulties in formulating the exact number of methanol and other guest molecules in the particles. ICP analysis of the starting materials and products from the **1** to **2** conversion (≈210-nm diameter average particle size) shows a decrease in Zn content (from 21.59 to 8.13%) and an increase in Cu content (from 0 to 15.31%) after the cation-exchange reaction.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim