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# Metal−Organic Hybrid Particles with Variable Sub-Stoichiometric Metal Contents

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Micro- and nanoscaled particles have received tremendous attention because of their critical role in many applications, including catalysis,[1] optics,[2] biosensing,[3] and data storage.[4] The most notable development in recent years is the emergence of structurally and compositionally divergent frameworks. In this regard, two types of particles deserve special attention. The first type of particle is constructed with pure organic molecules (organic molecule particles, OMPs), allowing the tuning of physical properties in a structure-dependent manner.[5] For example, the optical and electrical properties of OMPs could be easily regulated by controlling their size and shape.[6] The forces responsible for the OMP assembly could be donor−acceptor interactions, van der Waals interactions, and hydrogen bond.[7] The other type comprises organic molecules and metal ions (coordination polymer particles, CPPs),[8] offering tailorable particles through the choice of coordination force and environment. Compared with traditional particles, CPPs exhibit many advantages, such as reversible formation[8a] and composition modulation capabilities.[9] In addition, the interior sites of CPPs are readily accessible to external reagents, and in certain cases have led to the development of interesting properties (e.g., gas adsorption properties[10]). Overall, these two types of particles, by virtue of their distinctly different structures and compositions, hold great promise in their respective application areas.

We have initiated a research program aiming at the understanding of particle formation process and generation of novel types of particles. A major step forward would be the fabrication of particles with compositions intermediate between OMPs and CPPs. This intermediate-composition type of particles would enable the access of chemical and potentially functional space hitherto unachieved. Herein, we report on the synthesis of metal−organic hybrid particles (MOHPs) with variable substoichiometric metal contents. This initial investigation provides important insight into the inter-relationship between the seemingly disparate classes of particles.

It has been well-known that interactions between the constituent components (molecules, ions) dictate the final aggregation type[11] and could therefore affect the morphology and structure of the particles. Dynamic conversion of the morphology of particles has already been demonstrated through the change of external parameters (e.g., heat,[12] microenvironment[13]). We envisioned addition of metal ions into OMPs might induce the structural change by virtue of the weak nature of the forces behind the assembly of OMPs. We demonstrate that MOHPs can be fabricated with variable substoichiometric metal contents through the control of initial OMP precipitation process.

The proof-of-concept organic molecule we used is E-4,4′-di(N-(2-aminophenyl)amino)stilbene (**EDAPS**) (Scheme 1). The conjugated molecule framework (stilbene) imparts low solubility in water and most organic solvents. The selection of this model system also takes into consideration its coordination capability and fluorescence property. The coordination capability provides the basis for the transformation of initially formed OMPs with external metal ions. The fluorescence property enables the in situ monitoring of metal coordination and structural transformation process. An added advantage of using the aminophenyl group is its chemical reactivity toward many functional groups, enabling facile modification of the MOHP surface if desired.

Initial observations indicate that precipitation of **EDAPS** with water directly out of organic solution yielded micro- and nanoscaled structures that were stable for only a few

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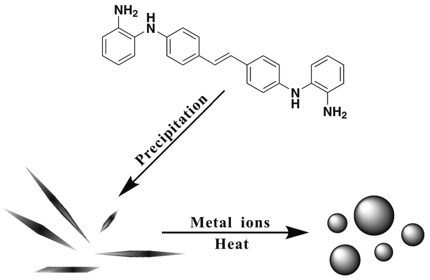
**Scheme 1. Fabrication of MOHPs with Variable Sub-Stoichiometric Metal Contents**



minutes. Coordination with metal ions stabilized these structures and caused a morphological transformation from shuttle-shaped OMPs to spherical MOHPs under heating. In a typical experiment (Scheme 1), a large excess of water was added to a DMSO solution of **EDAPS** (final volume ratio: water/DMSO = 30/1). This yielded a clear light yellow **EDAPS** suspension with plenty of **EDAPS** chunks (OMPs of **EDAPS**). To this suspension was further added $Cu^{2+}$ (starting molar ratio: metal ion/**EDAPS** = 1/1) and mixed thoroughly by a pipet. Reaction at an elevated temperature caused structural change with the concomitant color change from light yellow to grayish green or dark green. The color change eventually stopped, indicating the formation of stable MOHPs (Figure S14). Indeed, interaction of the metal ion with the organic molecule (Figure S15) constitutes the basis for the formation of MOHPs. Besides $Cu^{2+}$, other metal ions (e.g., $Fe^{3+}$) could also be employed to synthesize MOHPs (Figure S16). In addition, different from CPPs, initial molar ratio of **EDAPS** to $Cu^{2+}$ could be varied from 0.5 to 2 (Figure S17). One can control the size of MOHPs through the speed of addition of water and concentration of **EDAPS** (Table S1 and Figure S18).

We first investigated the fluorescence and UV−vis absorption spectroscopy (Figure 1 and Figure S20 in the Supporting Information) of the MOHP generation process (Figures S21 and S22 in the Supporting Information). The enhanced fluorescence (462 nm) of **EDAPS** suspension compared with DMSO solution is most likely derived from aggregation, similar to the aggregation-induced emission (AIE) effect.[14] The fluorescnece enhancement in the aggregated state is caused by a restriction of the molecule rotation and more pronounced conjugation of the backbone as compared with free rotation and twisted conformation[15a] in the solution state. Reaction with $Cu^{2+}$ caused a fluorescence quenching, likely resulting from $Cu^{2+}$-coordination-induced disordered molecular arrangement of **EDAPS**. We propose that $Cu^{2+}$ continuously coordinates with **EDAPS** on the surface until saturation of $Cu^{2+}$ is reached. The intense absorption band located at about 400 nm can be assigned to electronic transitions delocalized throughout the whole molecule with a charge transfer character derived mainly from the HOMO (amino nitrogen directly connected with stilbene) to LUMO (stilbene) transition.[15b] During the reaction, we observed a slight red-shift (10 nm) of this band, which might be caused by intramolecular charge transfer (ICT) derived from $Cu^{2+}$ coordination.

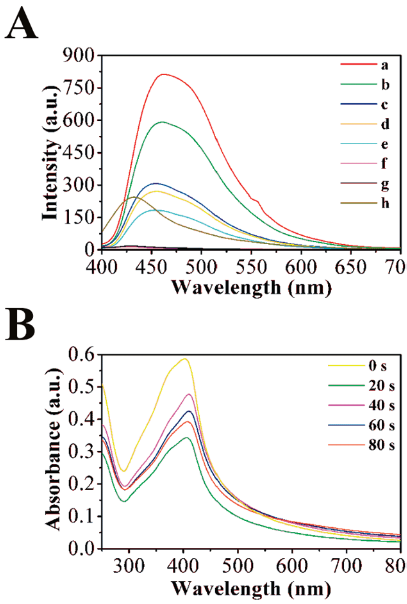


**Figure 1.** (A) Fluorescence and (B) UV−vis absorption spectra of MOHP preparation process. Excitation wavelength for fluorescence spectra: 374 nm. Samples a and b: **EDAPS** OMPs prepared by gradual injection of water (600 $\mu$L, 30 s for a and 2 s for b) into DMSO solution of **EDAPS** (20 $\mu$L, 0.04 M). Samples c−f: Intermediately evolved samples prepared by heating the mixture of $Cu(OAc)_2$ (aqueous solution, 4 $\mu$L, 0.2 M) and a at 50 °C for 10 s (c), 20 s (d), 40 s (e), and 80 s (f). Sample g: MOHPs derived from b. Sample h: DMSO solution (0.04 M) of **EDAPS**. For samples c−g, three centrifugation (15 000 rpm, 5 min)/washing (with water)/redispersion (water, 600 $\mu$L) cycles were used to remove excess $Cu^{2+}$. All samples were diluted to 1/9000 of the original concentration (a−g, water; h, DMSO) before fluorescence spectra were taken. UV−vis absorption spectra: The samples prepared by heating the mixture of $Cu(OAc)_2$ (aqueous solution, 4 $\mu$L, 0.2 M) and a at 50 °C for various amount of time. The samples were subject to identical centrifugation/washing/redispersion process. All samples for UV−vis absorption spectra were diluted to 1/60 of the original concentration by water (Supporting Information).

Then we carefully investigated the process by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure 2). Larger-sized MOHPs were selected for the initial imaging because of the ability to track the detailed structural transformation both on the surface and in the interior region. Addition of water to DMSO solution of **EDAPS** produced shuttle-like OMPs of **EDAPS** (Figure 2A and Figure S23 in the Supporting Information). At the early stage, spheres formed in situ from OMPs of **EDAPS** after the addition of $Cu^{2+}$ (Figure 2B). Smoothed surface was observed after heating at 50 °C for about 10 s (Figure 2C). Although smooth on the surface, the spheres are hollow in the interior (Figure 2D). Further heating caused a collapse of "wall" and led to the formation of irregular particles with "craters" (Figures 2E and 2F). Structural annealing of these particles afforded

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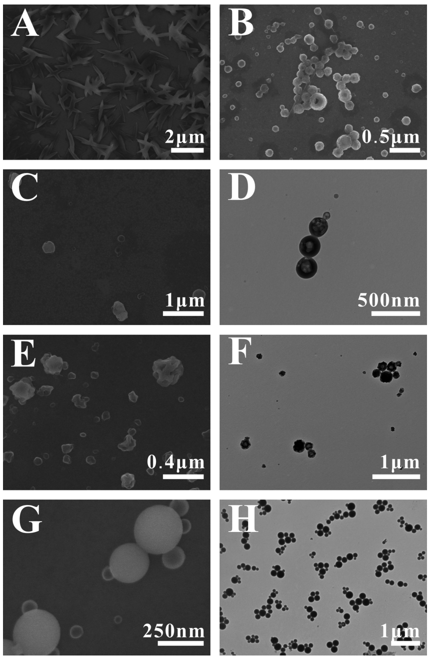

**Figure 2.** SEM (A, B, C, E, and G) and TEM (D, F, and H) images of MOHP preparation process. The samples are listed as follows: **EDAPS** suspension prepared by gradual injection of water (600 $\mu$L in 30 s) to DMSO solution of **EDAPS** (20 $\mu$L, 0.04 M) (A). Samples after heating the mixture of $Cu(OAc)_2$ (aqueous solution, 4 $\mu$L, 0.2 M) and A at 50 °C for 5 s (B), 10 s (C, D), 40 s (E, F). Samples after heating the mixture of $Cu(OAc)_2$ (aqueous solution, 4 $\mu$L, 0.2 M) and A at 50 °C for 80 s and at 95 °C for an additional 15 s (G, H).

final smooth, spherical-shaped MOHPs (Figures 2G and 2H). In the case of smaller-sized MOHPs, no apparent hollowing and associated collapse process were observed (see Figure S23 in the Supporting Information). The OMP-to-MOHP structural transformation process is believed to derive from coordination-induced twisting of molecular conformation[16] and weakening of the intermolecular interactions, leading to the heat-assisted reorganization of constituent components. And similar to CPPs, spherical-shaped MOHPs formed in order to minimize the interfacial free energy between the particles and surroundings.[8c]

Through this method, we can obtain MOHPs that range from 20 to 400 nm (see Figure S18 in the Supporting Information). The observation is smaller-sized MOHPs would form if one precipitates **EDAPS** out of DMSO solution in a shorter period of time. This agrees with the proposed mechanism that MOHPs form through the transformation of OMPs, the width of which is related to the precipitation speed. Addition of water at an ultralow speed (e.g., 600 $\mu$L of water in more than 60 s) would cause an immediate yet irreversible precipitation of **EDAPS**. In contrast, preparation at an ultrahigh speed (e.g., 600 $\mu$L of water in no more than 1 s) may produce MOHPs too small (<20 nm) to be concentrated by centrifugation. The substoichiometric metal contents of MOHPs are inversely related to the particle diameters (see Table S2 in the Supporting Information). The molar ratio of **EDAPS** to Cu can be varied from 16.9 to 7.8 as the particle diameter changes from ~200 nm to ~50 nm. This likely reflects the fact that a substantial portion of the metal ions reside on the MOHP surface, the area of which is dictated by the particle diameter. Indeed, the charge repulsion between particles in the solution is responsible for the stabilization of MOHPs. **EDAPS** suspension exhibits a zeta potential of approximately +29.9 and +21.8 mV for large and small OMPs of **EDAPS**, respectively. This positive value is indicative of the presence of associated $H^+$ on the surface. After heating at 50 °C for 10 s, 20 s, 40 s, and 2 min, the zeta potential of a reaction mixture of **EDAPS** suspension (larger-sized OMPs) and $Cu^{2+}$ (starting molar ratio: **EDAPS**/Cu = 1/1) changed to approximately +36.1 mV, +38.7 mV, +45.2 mV, and eventually reached approximately +54.0 mV (see Table S3 in the Supporting Information). The increase in zeta potential is caused by the extensive coordination of $Cu^{2+}$.

The surface of MOHPs could be modified with different functional groups. Further coordination of **EDAPS** with $Cu^{2+}$ on the MOHP surface would afford amino group-capped MOHPs. Molecules with other functional groups could be incorporated onto the MOHP surface through EDC-NHS coupling with amino groups. For example, coupling with 3-mercaptopropionic acid (MPA) allows the generation of mercapto group-capped MOHPs. This kind of MOHPs could bind with 2-mercaptoethanol covered Au nanoparticles (see Figures S24 and S25 in the Supporting Information). Initially, amino-group-modified MOHPs displayed positive charge (approximately +23.1 mV; see Table S3 in the Supporting Information). After EDC-NHS coupling with MPA, substantial surface amino groups were changed to mercapto groups. These groups were neutral in water. A decrease in zeta potential was therefore observed (approximately +19.1 mV).

In conclusion, we have developed a method for the fabrication of MOHPs with variable substoichiometric metal contents and particle diameters. The synthesis process involves the coordination-induced, heat-assisted structural transformation of OMPs. The surface of MOHPs could be further functionalized with other molecules. This novel type of particles could serve as the critical linking node bridging currently extensively explored OMPs and CPPs and is likely to offer unique functional properties that are otherwise impossible to obtain because of the compositional and structural tunability.

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**Supporting Information Available:** Experimental procedures, characterization data for all the compounds, and particle formation process (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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