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Supramolecular Nanotubules as Catalytic Regulator for Pd Cation and Their Application in Selective Catalysis

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Abstract: Despite recent development of highly efficient and stable metal catalysts, conferral of regulatory characteristic to the catalytic reaction in heterogeneous system remains a challenge. Herein, novel supramolecular nanotubules were prepared by alternative stacking from trimeric macrocycles, which was found to be able to coordinate with Pd cations. The Pd complexes exhibited a high catalytic performance for C-C coupling reaction. Notably, the tubular catalyst was observed to be controlled by supramolecular reversible assembly and showed superior heterogeneous catalytic activity maintained for a number of recycles or reuse under aerobic environment. Furthermore, the supramolecular catalyst showed unprecedented selectivity for the multi-functional coupling reaction and was able to serve as a new construction of asymmetrical compounds.

Developing highly efficient and stable metal catalysts has attracted great attention in chemistry and material science because of both economic and environmental reasons.[1-4] In general, metal catalysts with small sizes are preferred due to their high surface area for efficient catalysis. However, the reversible reaction of catalysis can result in serious aggregation of metal species, causing the gradual decrease of the catalytic activity.[5-7] For this reason, the stabilizers such as surfactants,[8] polymers,[9-11] dendrimers,[12,13] silica,[14,15] and metal oxides[16-20] are actively investigated for preventing metal aggregation. Among them, sp^2-hybridized carbon materials are the most widespread supporting materials due to their low density, the high surface area and the ease to handle.[21-23] Introduction of a heteroatom such as nitrogen into conjugated carbon substrates would enhance electron capacity and thereby bind with metal atoms strongly.[24-26] Although ordered or disordered carbon-supported metal catalysts with remarkably enhanced activity have been successfully employed, they still have several deficiencies including lack of long-term stability, low dispersibility, deactivation or constant leaching, as well as low recyclability which limit their capacity and applications. Furthermore, the heterogeneous catalysts could not be controlled until the reaction is completed because of the difficult separation between the supporting materials and solvents during the reaction process, which is not suitable for multi- or selective catalysis.

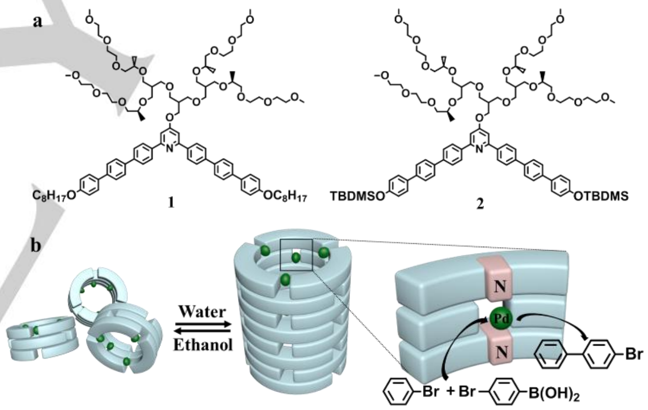

Figure 1. (a) Molecular structures of **1** and **2**; (b) Schematic representation of tubular regulator for catalytic reaction based on reversible stacking of macrocycles.

Aromatic rod amphiphiles consisted of conjugated carbon and hydrophilic coil segments as the sp^2-hybrid carbon family can aggregate into porous structure to enhance the diffusion of bulky aryl substrates and the transmission channels are well suitable as scaffolds for catalytic reaction in separated aromatic space.[27-32] Compared with the traditional supporting materials, the supramolecular substrates can be easily regulated by dynamic assembly through changing their environments because of their completely reversible formation.[33-36] For example, lateral attachment of hydrophilic oligoether segments into a linearly shaped aromatic rod leads the molecules to aggregate into toroidal nanostructures that are spontaneously connected with each other to form porous tubules in response to the aromatic guest.[37] The dynamic nature of the aggregates allows them to adapt the changes of pore surface to be more hydrophobic. As hinted from the adaptation by dynamic assembly, here we tried to

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align sandwich nanostructures with Pd ions as a catalytic core into hollow tubes to prepare the supramolecular porous catalyst. The supramolecular catalyst showed high efficiency for Suzuki-Miyaura (S-M) coupling reaction. Unlike conventional Pd catalysts, the catalyst could be used as the regulator for metal catalysis through dynamic assembly (Figure 1). Additionally, the catalyst recognized the size and type of starting materials and showed unprecedented selectivity for multi-functional S-M reaction, having potential to serve as a new concept for asymmetric catalysis.

The catalyst is derived from the self-assembly of a bent-shaped aromatic amphiphile containing a coordinative unit of pyridine at the inner position with a alkyl segment at both ends as hydrophobic segments, which was decorated by hydrophilic oligoether dendron at its apex (Figure 1). To investigate the aggregation behavior of bent-shaped molecules, we have performed vapor pressure osmometry (VPO) experiments. The molecular weights of **1** based on an octyl-ended chain and **2** with a *tert*-butyldimethylsilyloxyl group were calculated 1713 and 1717 D, respectively. However, in the ethanol, the molecular weights of the primary aggregates were measured to be 5091 and 5212 D, respectively, which are three-folds as large as a single molecule (Figure S2), suggesting that both noncovalent macrocycles from **1** and **2** consist of three single molecules.[36] Subsequently, the addition of water into the ethanol solution would drive the trimeric macrocycles to stack on top of each other to form hollow tubules. Figure 2a and S3 show micrographs obtained from a 0.02 wt% mixed solution (EtOH:H_2O = 1:3) of **1** and **2** cast onto TEM grids. The TEM images of both samples show two parallel dark lines with a uniform distance of 4.0 nm. To further understand the aggregated nanosturctures, the scanning transmission electron microscope (STEM) experiment was implemented with a probe aberration corrector. STEM images show that the 1D objects were seperated by dark and white segments, indicative of the formation of hollow tubules with an external diameter of 4.0 nm and a hollow interior with a diameter of 2.3 nm (Figure 2b and S3). When the membranes of **1** and **2** were transferred onto carbon-coated copper grids and then negatively stained with uranyl acetate, both the external diameters of the tubules were observed as 5.8 nm (Figure 2e and S3c). The external diameters of the tubules are identical to those of trimeric macrocycles, suggesting that the tubules originated from the macrocyles stacking. To gain insight into the packing arrangements of the rod segments within the 1D aromatic domains, we performed optical experiments. Upon addition of water into ethanol, both the absorption spectra of **1** and **2** displayed a blue-shifted absorption maximum and reduced fluorescence intensity compared with those in ethanol solution, indicating the *H*-type aggregates were formed from the aromatic segments (Figure S4).[38] Circular dichroism (CD) spectra of the mixed solution of **1** showed a significant Cotton effect in the spectral range of the aromatic segments, indicating that the tubules adopt a one-handed helical structure (Figure 2f). To gain deeper insight into helical tubules, the atomic force microscopy (AFM) and two-dimensional X-ray diffraction (2D XRD) experiments were performed with thin membrane. Figure 3a shows two kinds of equidistant diffractions were observed at equator and meridian. The equidistant of 5.2 nm from equatorial diffractions corresponding to intercolumnar ordering, well matched with the external diameter determined from TEM experiments. Meanwhile, along the column axis several periodic reflections with equidistant of 2.8 nm were observed. Taking into account the structure and dimensions of trimeric macrocycles, this diffraction pattern is attributable to a pitch of helical tubules. Indeed, the AFM image of **1** revealed the formation of a right-handed helical structure with a pitch of 3.0 nm (Figure 2c), which is consistent with the CD and XRD results. These observations indicate that **1** self-assembles into the trimeric macrocycles, which, in turn, stack on top of each other with mutual rotation to form the right handed helical tubules.

We noticed that the tubular solution of **2** did not show CD signals within the area of aromatic absorption even though **2** contains chiral side groups (Figure 2f). For investigating the assembling geometries, we performed AFM measurements of the sample prepared by drop casting of the solution on a mica

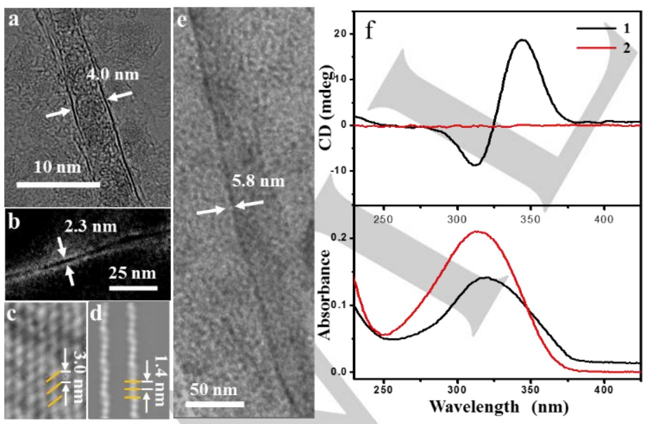

Figure 2. TEM, STEM, and AFM images and optical characterizations. TEM a), STEM b), and AFM c) images of **1** in ethanol-water mixture (1/3, v/v, 0.02 wt%). d) AFM image of **2** in ethanol-water mixture (1/3, v/v, 0.02 wt%). e) TEM image stained with uranyl acetate of **1** in ethanol-water mixture (1/3, v/v, 0.02 wt%). f) Absorption and CD spectra of **1** and **2** in ethanol-water mixture (1/3, v/v, 0.01 wt%).

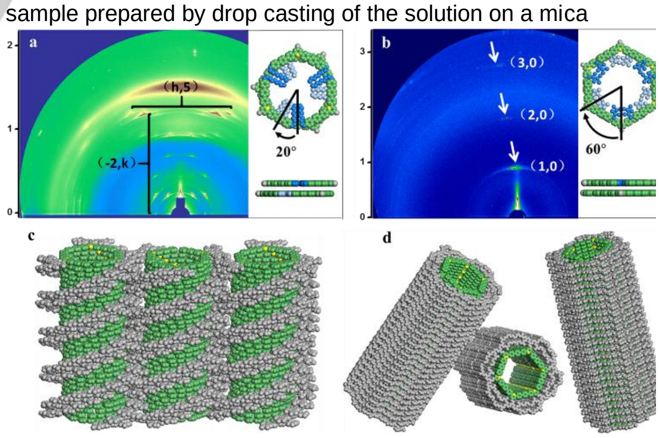

Figure 3. Stacked nanotubules from trimeric marcrocycles. 2D XRD patterns of **1** a) and **2** b) air-dried from mixed ethanol-water dispersions (1/3, v/v, 0.02 wt%). (Insert: top and front views of oriented neighboring macrocycles) Schematic representation of the tubules based on helically ordering of **1** c) and alternative stacking of **2** d). (The yellow balls represent nitrogen atoms, the blue and light blue chains represent the neighboring alkyl chains and the gray chains represent alkoxy chains. Alkyl chains in c) and d) are omitted for clarity) Details please see Figure S5 in supporting information.

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surface. The image clearly revealed that a periodically stacked 1D object with 6 nm diameter was formed (Figure 2d). The periodic structure was further analysized by 2D XRD. The 2D image of **2** based on bulky alkyl segments displays sharp spots in same direction that correspond to equidistant *q*-spacings which indexed as 0.9 nm (Figure 3b). Given the interdistance from macrocycle stacking (0.45 nm), the space of 0.9 nm is approximately twice larger than that between neighboring cycles, suggesting the formation of non-chiral tubules with an alternatively cyclical stacking (Figure 3d). In contrast to **1**, there is large steric hindrance in the inside of trimeric macrocycles prepared from **2**. So the neighboring macrocycles stacked on each other without overlay of the bulky hydrophobic segments to reduce the contact between aromatic segments and solvents.

Owing to the periodical location of pyridine at the inner surface of the tubules, it is facilitative for Pd cation to coordinate with pyridine resulting in the formation of the supramolecular catalyst. The dispersion of Pd within self-assembled tubules displayed enhanced stability than dissolved state due to the sandwich structure (Figure S6). In mixed solution with $PdCl_2$, the Pd cation was successfully coordinated to the pyridine ligand with the observation of the red-shifted absorption band and significantly suppressed emission intensity (Figure S7a and b). To take insight into the formation of supramolecular catalyst, X-ray photoelectron spectra (XPS) experiments were further performed. In the high-resolution spectra, a peak at 399.3 eV was observed and assigned to the pyridine nitrogen (1s).[39] However, the peak positively shifted to 400.1 eV in the supramolecular catalyst, confirming the existence of interaction between nitrogen and Pd (Figure S7c).[40] The amount of Pd in tubules was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), showing 92% of $PdCl_2$ formed the complexes on the inner pore of tubules. The molar ratio of nitrogen to palladium within the nanotubule was observed as 2.4 : 1 by semi-quantitative calculation from XPS experiments, which indicates Pd cation is coordinated by alternatively stacked pyridine (Figure 1).

Owing to the highly ordered porous structure and the significant stability for Pd cation at the porous walls, the Pd-coordinated tubule of **2** can be used as supramolecular catalysts with high active capacity for the S-M reaction with phenylboronic acid at ambient temperature. The tubular catalyst of **2** gave high catalytic conversions for all benzene halide (Table S1, entries 1-3). With bulky substrates, however, the catalyst did not work as biphenyl substrates (Table S1, entry 4). The results showed that biphenyl halide in this reaction was larger than the aperture of the tubules and the reaction could only occur for small benzene substrate. Notably, the tubular catalyst exhibited the switching behavior according to reversible self-assembly, hence this supramolecular catalyst has served as the regulator for metal catalyst. As a result of poor diffusion of the reagents in molecularly dissolved state, the reaction could be halted immediately after the addition of ethanol to the reaction mixture leading to the deaggregation of the tubules, which induces the loss of catalytic activity. Thus, the conversion could also be monitored freely after the reaction was quenched. Figure S8 shows the conversion in real time, demonstrating the catalytic reaction undergoes within 10 min with high conversion. Furthermore, the supramolecular catalyst exhibited high reusability under the reaction conditions with an aryl halide/molecule **2** molar ratio of 50:1. After completion of the reaction, the dissolved macrocycles were readily recovered by centrifugation. The catalyst was reformed after the addition of water and reused upon new reactants were added. After recycling procedures, we removed the catalyst and analyzed the reaction mixture by ICP-AES. No leaching Pd was detected during the disassembly and assembly processes, and the initial activity was completely maintained during five cycles of the reaction (Figure S9). AFM and TEM studies clearly revealed that the reassembled tubules of **2** remains with same size and morphology even after exposure to the coupling reaction. Based on these results, we conclude that the tubular catalyst of **2** exhibits superior heterogeneous catalytic activity in terms of stability, recyclability, and reusability in C-C coupling reaction. In contrast to general Pd nanoparticles on solid supports, the catalyst additionally shows regulatory characteristic in heterogeneous reaction by supramolecular assembly and dis-assembly process.[5,10]

The special regulation with uniform porous surface motivated us to explore the selectivity of the S-M reaction using multi-functional substrate to develop new asymmetric coupling reaction Thus, the reaction with bi-reactive sites was investigated with 4-bromophenylboronic acid and bromobenzene. It is known that the general Pd catalysts usually give aryl polymers or multiple products (Table S1, entry 5). Remarkably, when the reaction was carried out by using tubular catalyst of **2**, the product of 4-bromobiphenyl was obtained reaching up to 90 % within 30 min (Table S1, entry 6). The probable reason for the high selectivity can be explained by spatial effect of tubular pores. As mentioned above, the aperture of tubular substrate is suitable for small benzene bromide, thus resulting in the enhanced activity for monocoupling reaction.

In summary, we have demonstrated that stimuli-responsive supramolecular tubules through the self-assembly of trimeric-macrocycles with alternative stacking can be used as catalytic regulator in heterogeneous system. The porous tubules from the self-assembly of *N*-substituted aromatic macrocycles provide a unique property to stabilize Pd cation on the inner surface against metal agglomeration, and provide high catalytic activities during a number of recycles owing to its special sandwich construction for the stable formation of coordinated bond with Pd cation. Notably, the heterogeneous catalyst based on the self-assembled tubular substrate could be suspended and restarted conveniently through the supramolecular reversible assembly. Furthermore, the catalyst was endued with unprecedented selectivity within aryl polymerization due to the spatial effect of tubular aperture. The special regulation with unprecedented selectivity for C-C reaction presented here would provide a useful way to construct asymmetrical compounds with high catalytic activity.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Supramolecular chemistry • Nanostructures • Self-assembly • Heterogeneous catalysis • Supported catalysts

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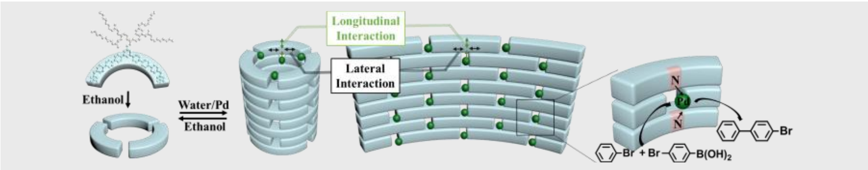

Nanotubules as catalytic regulator: A novel supramolecular catalyst was prepared by alignment of sandwich nanostructures with metal catalytic core. The catalyst could be used as the regulator for metal catalysis through reversible assembly (see picture).

Supramolecular Catalytic Regulator

S. Wu, Y. Li, S. Xie, C. Ma, J. Lim, J. Zhao, D. S. Kim, M. Yang, D. K. Yoon, M. Lee, S. O. Kim, Z. Huang**

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