

Communications

One-Pot Fabrication of a Self-Assembled Organic–Inorganic Nanofiber Embedded Palladium Ion as a Catalyst

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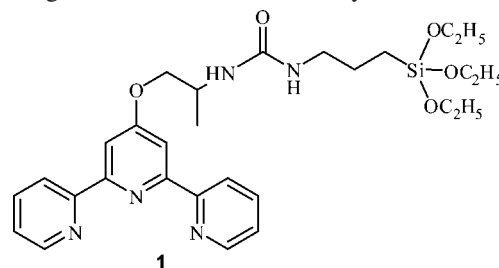
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The self-assembly of low molecular weight building blocks into meso- and nanoscale structures has recently attracted much attention.^{1–6} In particular, a large number of studies have focused on one-, two-, or three-dimensional self-assembly of organic molecules to form unique structures such as spheres, nanofibers, and tubes. Because self-assembled nanostructures are bound by noncovalent bonds such as hydrogen bonds and van der Waals and electrostatic interactions, they tend to be thermally unstable. Only a few studies, therefore, have reported useful reactions of such nanostructures that do not cause changes in the nanostructures.^{7,8} In one such report, the catalytic ability of a self-assembled peptide-based nanofiber in the hydrolysis of 2,4-dinitrophenylacetate was studied.^{7a} However, to our best knowledge,

the catalytic activity of a self-assembled supramolecular nanostructure in an organic reaction related to Sonogashira coupling or Heck reactions has never been developed.

The development of organic reagents immobilized onto silica gels with inorganic support used as catalysts in Sonogashira and Heck reactions has recently attracted attention because industry seeks more environment-friendly chemical manufacturing processes.^{9,10}

We recently reported on the fabrication of a terpyridine-based organic–inorganic hybrid nanofiber possessing a functional moiety that can bind to a metal ion.¹¹ This self-assembled nanofiber was quite stable in aqueous solution due to further sol–gel polymerization after gel formation. We therefore realized that this type of hybrid self-assembly might be suitable to prepare a functional nanomaterial for catalyzing organic reactions. Our new approach, described in this communication, was to design and synthesize a new nanostructure containing Pd²⁺. In this procedure, the terpyridine and triethoxysilane moieties of compound **1** were introduced as the binding site for palladium ion and as a precursor for sol–gel polymerization (Scheme S1, Supporting Information), respectively. In addition, the polymerized self-assembled **1** would act as an excellent supporting material with large surface area and thermal stability. These preparations are unique in that the hybrid nanofiber with palladium ion has been formed by one-pot reaction, that is, simply by heating of a mixture of **1** and Pd²⁺ without any solid support. We successfully used the complex as a catalyst in Sonogashira and Heck reactions. These reactions generated the corresponding cross-coupling products in excellent yields. Importantly, the self-assembled nanofiber **1**–Pd can be recovered and reused by a simple filtration of the reaction solution. We recycled the catalyst for 10 consecutive trials without significant loss of its reactivity.



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- (1) (a) Shimizu, T.; Masuda, M.; Minamikawa, H. *Chem. Rev.* **2005**, *105*, 1401. (b) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133. (c) van Esch, J. H.; Feriga, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263. (d) Shinkai, S.; Murata, K. *J. Mater. Chem.* **1998**, *8*, 485.
- (2) (a) John, G.; Mason, M.; Ajayan, P. M.; Dordick, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 15012. (b) John, G.; Zhu, G.; Li, J.; Dordick, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4772. (c) Vemula, P. K.; Li, J.; John, G. *J. Am. Chem. Soc.* **2006**, *128*, 8932.
- (3) (a) Li, G.; Fudickar, W.; Skupin, M.; Klyszcz, A.; Draeger, C.; Latthias, M.; Fuhrhop, J.-H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1828. (b) Jonkheijm, R.; Hoeben, F. J. M.; Kleppinger, R.; Herrikhuizen, J. v.; Schenning, A. P. H.; Meijer, E. W. *J. Am. Chem. Soc.* **2003**, *125*, 15941.
- (4) (a) Moon, K.-S.; Kim, H.-J.; Lee, E.; Lee, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6807. (b) Lee, M.; Jang, C.-J.; Ryu, J.-H. *J. Am. Chem. Soc.* **2004**, *126*, 8082.
- (5) (a) Zubarev, E. R.; Pralle, M. U.; Sone, E. D.; Stupp, S. I. *J. Am. Chem. Soc.* **2001**, *123*, 4105. (b) Niece, K. L.; Hartgerink, J. D.; Donners, J. J. M.; Stupp, S. I. *J. Am. Chem. Soc.* **2003**, *125*, 7146. (c) Sone, E. D.; Zubarev, E. R.; Stupp, S. I. *Angew. Chem., Int. Ed.* **2002**, *41*, 1706.
- (6) (a) Kim, T. H.; Seo, J.; Lee, S. J.; Lee, S. S.; Kim, J.; Jung, J. H. *Chem. Mater.* **2007**, *19*, 5815. (b) Jung, J. H.; Rim, J. A.; Han, W. S.; Lee, S. J.; Lee, Y. J.; Cho, E. J.; Kim, J. S.; Ji, Q.; Shimizu, T. *Org. Biomol. Chem.* **2006**, *4*, 2033. (c) Lee, S. J.; Lee, S. S.; Kim, J. S.; Lee, J. Y.; Jung, J. H. *Chem. Mater.* **2005**, *17*, 6517. (d) Kameda, N.; Masuda, M.; Minamikawa, J.; Goutev, N. V.; Rim, J. A.; Jung, J. H.; Shimizu, T. *Adv. Mater.* **2005**, *17*, 2732.
- (7) (a) Guler, M.; Stupp, S. I. *J. Am. Chem. Soc.* **2007**, *129*, 12082. (b) Muraoka, T.; Cui, H.; Stupp, S. I. *J. Am. Chem. Soc.* **2008**, *130*, 1946.
- (8) Horike, S.; Dinča, M.; Tamaki, K.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 5854.

- (9) (a) Li, P.-H.; Wang, L. *Adv. Synth. Catal.* **2006**, *348*, 681. (b) Quignard, F.; Larbot, S.; Goutodier, S.; Choplin, A. *J. Chem. Soc., Dalton Trans.* **2002**, 1147. (c) Corma, A.; García, H.; Primo, A. *J. Catal.* **2006**, *241*, 123.
- (10) (a) Clark, J. H.; Macquarrie, D. J.; Mubofu, E. B. *Green Chem.* **2000**, *53*. (b) Choudary, B. M.; Nadhi, S.; Chowdari, N. S.; Kantam, M.; Sreedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127. (c) Ma, X.; Zhou, Y.; Zhang, J.; Zhu, A.; Jiang, T.; Han, B. *Green Chem.* **2008**, *10*, 59.
- (11) Cho, E. J.; Jeong, I. Y.; Lee, S. J.; Han, W. S.; Kang, J. K.; Jung, J. H. *Tetrahedron. Lett.* **2008**, *49*, 1076.

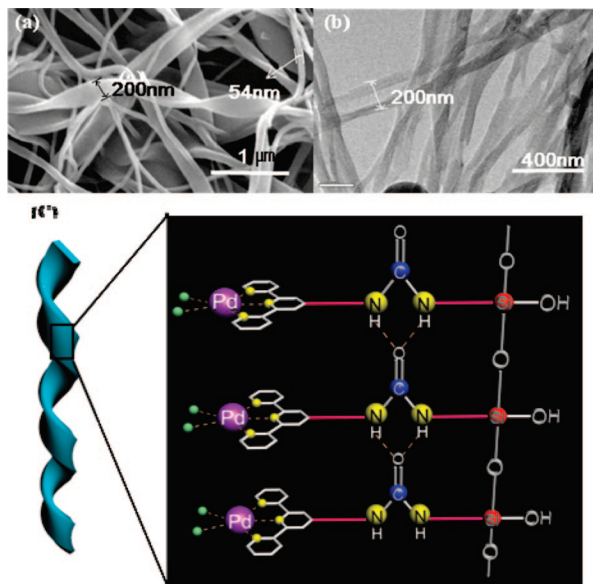


Figure 1. (a) SEM and (b) TEM images of the self-assembled nanofiber 1-Pd. (c) Proposed structure for the self-assembled 1 complex with Pd²⁺.

The preparation of the self-assembled 1-Pd complex is as follows. Compound 1 (1.0 g) and Pd(OAc)₂ (608 mg, 1.5 equiv) were dispersed into water (200 mL) at temperatures above the melting point (T_m) of the hydrated sample. The Pd²⁺ ions bind to the nitrogen atoms of the terpyridine moiety of 1 by coordination bonds. In general, heating the mixture at 100 °C for 30 min was sufficient to obtain a homogeneous, transparent solution. The aqueous solution was then allowed to cool to room temperature to generate the self-assembled nanofiber 1-Pd complex. In this process, the sol-gel polymerization of three ethoxysilane moieties attached in 1 as the tail group proceeds into polymerized organic-inorganic hybrid nanofiber, which induces the stabilization of the self-assembled 1-Pd.^{11,12} In addition, the self-assembled nanofiber 1-Pd can be completely and reproducibly obtained by one-step reaction in aqueous solution.

To characterize the resultant morphology and size dimensions, we observed the individual self-assembled structures using energy-filtering transmission electron microscopy (EF-TEM) and field emission scanning electron microscopy (FE-SEM). In FE-SEM and EF-TEM images of 1-Pd revealed the formation of high-aspect-ratio nanostructures with diameters of 20–250 nm and lengths ranging from hundreds of nanometers to several micrometers (Figure 1).

Additionally, circular dichroism of 1-Pd at pH 7.0 revealed a broad peak ($n-\pi^*$ transition) between 195 and 230 nm (Figure S1, Supporting Information), which is a signature of the predominant presence of the intermolecular hydrogen bonds between amide groups. In addition, to obtain more detailed information about the nanostructure, FT-Raman was carried out. In the FT-Raman spectrum of 1-Pd, the characteristic peaks appeared at 1573, 1587, and 1601 cm⁻¹ (Figure S2a, Supporting Information). These peaks are assigned to $-C=N$ stretching vibrations of terpyridine,

Table 1. Catalytic Ability of the Self-Assembled Nanofiber 1-Pd for Sonogashira Reaction

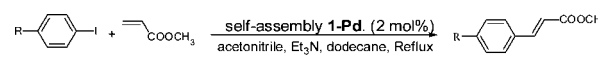
entry	aryl halide	yield (%)
1	R = -H	90.3
2	R = -CH ₃	98.8
3	R = -NO ₂	99.4
4	R = -OCH ₃	91.4
5	R = -COCH ₃	84.4
6	1-iodonaphthalene	81.0

attributable to the strong complexation between the terpyridine moiety and Pd²⁺. In aqueous solution, however, the stretching bands of the amide group for compound 1 appeared at 1616 cm⁻¹, indicating that the strong H-bonding networks formed in self-assembly are disentangled in the solution state (Figure S2b, Supporting Information). Furthermore, FT-IR spectroscopy showed new peaks for the self-assembled 1-Pd at around 3600 cm⁻¹ for $-\text{SiOH}$ and 1070 and 788 cm⁻¹ for $-\text{Si}-\text{O}-\text{Si}-$ (Figures S3 and 1c, Supporting Information). These findings support the view that 1-Pd was polymerized by hydrolysis and condensation that occurred in the self-assembly state. The self-assembled 1-Pd was not thermally reversible because the polycondensation reaction thermally stabilized its structure. We also confirmed the added amount of palladium by EDX (Figure S4, Supporting Information). The amount of palladium loaded on the surface of the self-assembled 1 was found to be 0.9 mmol g⁻¹, corresponding to about 20 wt % by weight.

To understand the coordination behavior between compound 1 and palladium ion, we measured the NMR spectra of 1 upon the addition of the palladium to obtain the stoichiometric ratio between 1 and Pd²⁺. As shown in Figure S5 (Supporting Information), five peaks from the aromatic moiety of 1 appeared at 8.76–7.53 ppm. Upon the addition of Pd²⁺, new peaks appeared gradually at 8.91, 8.73, 8.50, 8.36, and 7.92 ppm. With increasing Pd²⁺ concentration, the intensities of these new peaks increased whereas the intensities of the original peaks at 8.76–7.53 ppm gradually decreased until a mole ratio of 1 was obtained. The coexistence of the separated signals of the complex 1 and uncomplex 1 species demonstrated that the chemical exchange is slow compared with the NMR time scale. Above a mole ratio of 1, the original peaks completely disappeared, indicating that 1 is converted into a new species upon addition of the palladium ion in a 1:1 formation (see Table of Contents graphic).

The activity of the catalyst for the self-assembled nanofiber 1-Pd was examined in the Sonogashira coupling reaction of iodobenzene and phenylacetylene in the presence of 2 mol % of the self-assembled 1-Pd and 2 equiv of K₂CO₃ in ethanol under ligand-, copper-, and amine-free conditions at reflux temperature. The reaction generated the corresponding cross-coupling product in 90.3% yield (Table 1). Encouraged by this result, we examined the Sonogashira coupling reaction using other substituted iodobenzene derivatives containing electron withdrawing or electron donating groups under the same conditions for the comparison. For both electron withdrawing and donating groups, 81.0–98.8% yield

(12) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216.

Table 2. Catalytic Ability of the Self-Assembled Nanofiber 1-Pd for Heck Reaction


entry	aryl halide	yield (%)
1	R = -H	94.3
2	R = -CH ₃	57.9
3	R = -NO ₂	77.2
4	1-iodonaphthalene	45.7

was obtained in short reaction times (Table 1), which is comparable to the yields obtained for SiO₂-supported palladium catalysts.⁹ These results indicate that the self-assembled 1-Pd is useful as a new catalyst for the Sonogashira coupling reaction.

The recyclability of the self-assembled nanofiber 1-Pd was also surveyed. After carrying out the reaction, the reaction solution was filtered using a sintered glass funnel and the residue washed with CH₂Cl₂ (5 mL), Et₂O (5 mL), C₂H₅OH (5 mL), and hexane (5 mL), respectively. After being dried at room temperature, the catalyst was reused directly without further purification. The self-assembled nanofiber 1-Pd can be recovered, recycled, and used for 10 consecutive trials without loss of activity, suggesting that the self-assembled 1-Pd is useful as a new recyclable heterogeneous catalyst in organic reaction.

Similarly, the self-assembled 1-Pd was used as a catalyst in the Heck reaction (Table 2). The reaction conditions were

optimized using iodobenzene and methyl acrylate as the model reaction. Using acetonitrile as a solvent and triethylamine as a base, the materials showed effective catalytic activity and led to various disubstituted alkenes in 45.7–94.3% yield (Table 2). The reaction of iodobenzene with methyl acrylate was successfully achieved, showing that the self-assembled 1-Pd is also useful as a new catalyst for the Heck reaction.

In conclusion, we have demonstrated that the self-assembled, terpyridine-based organic–inorganic hybrid **1** with Pd²⁺ forms a nanofiber supramolecular structure, in which the amount of Pd²⁺ on the surface of **1** was 0.9 mmol g⁻¹. The nanofiber complex 1-Pd acted as a novel and efficient catalyst for the Sonogashira and Heck reactions. The observations offer a new design concept for supramolecular catalysts, suggesting that nanofibers of high aspect ratio and internal order are potentially interesting catalytic devices.

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Supporting Information Available: Synthesis of compound **1**, FT-IR spectra of 1-Pd in the solid and solution states, EDX, CD, and NMR spectra of compound **1** with addition of Pd(II). This material is available free of charge via the Internet at <http://pubs.acs.org>. CM803026C