Soluble organic nanotubes for catalytic systems

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2016 Nanotechnology 27 115603
(http://iopscience.iop.org/0957-4484/27/11/115603)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 202.120.224.19
This content was downloaded on 19/05/2016 at 13:56

Please note that terms and conditions apply.
Soluble organic nanotubes for catalytic systems

Linfeng Xiong1, Kunran Yang1, Hui Zhang1, Xiaojuan Liao1 and Kun Huang1,2

1 School of Chemistry and Molecular Engineering, East China Normal University, 500 N, Dongchuan Road, Shanghai, 200241, People’s Republic of China
2 State Key Laboratory of Molecular Engineering of Polymers (Fudan University) Shanghai, People’s Republic of China

E-mail: xjliao@chem.ecnu.edu.cn and khuang@chem.ecnu.edu.cn

Received 10 October 2015, revised 18 December 2015
Accepted for publication 21 December 2015
Published 16 February 2016

Abstract
In this paper, we report a novel method for constructing a soluble organic nanotube supported catalyst system based on single-molecule templating of core–shell bottlebrush copolymers. Various organic or metal catalysts, such as sodium prop-2-yn-1-sulfonate (SPS), 1-(2-(prop-2-yn-1-yl)oxy)ethyl)-1H-imidazole (PEI) and Pd(OAc)2 were anchored onto the tube walls to functionalize the organic nanotubes via copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction. Depending on the ‘confined effect’ and the accessible cavity microenvironments of tubular structures, the organic nanotube catalysts showed high catalytic efficiency and site-isolation features. We believe that the soluble organic nanotubes will be very useful for the development of high performance catalyst systems due to their high stability of support, facile functionalization and attractive textural properties.

Keywords: soluble organic nanotubes, single-molecule templating, core–shell bottlebrush copolymers, organic or metal catalysts

(Some figures may appear in colour only in the online journal)

Introduction

Organic nanotubes are novel and attractive functional nanomaterials in terms of their controllable dimensions, functionalizable surfaces and walls, tailored composition and morphology [1–6]. Such materials possess a unique tubular structure and highly specific surface area, which can act as novel cylindrical nano-containers or adsorbents for drug carriers [7–9], substance separation [10–12] or sensors [13, 14]. In particular, the high surface area and porous structure allow small molecules to rapidly diffuse in and out of the nanotubes that render them amenable for catalytic supports. However, up to now, there have been relatively few reports on organic nanotubes as a support structure for a catalytic system. To date, only Komatsu et al have reported the synthesis and catalytic activity of human serum albumin nanotubes including gold nanoparticles as a layer wall component [15].

Molecular bottlebrushes are single graft copolymer molecules with a well-defined cylindrical shape which is a result of steric hindrance between the polymeric side chains forcing the backbone to adopt a nearly extended conformation [16–22]. The unique shape and easily controlled dimensions (from tens to hundreds of nanometers) of molecular bottlebrushes render them useful as single-molecule manipulators to create various nano-objects. Recently, we described a new strategy to produce organic nanotubes based on single-molecule templating core–shell bottlebrush copolymers [23–25]. The new method offers considerable advantages over the existing organic nanotube systems, such as excellent dimensional control (including length and pore diameter), tunable chemical compositions, an open-ended tubular structure and an accessible cavity for loading various target molecules. Therefore, we expect that the development of a soluble organic nanotube supported catalyst system on the basis of a
single-molecule soft-templating technique would open new vistas in the field of polymer supported catalysis.

Inspired by the pioneering work by Jean M J Fréchet et al using star polymers with ‘clickable’ cores as catalyst support [26], herein, we describe a novel synthesis of functionalized organic nanotubes with ‘clickable’ walls from bottlebrush copolymers with triblock terpolymer side chains. A highly efficient and tolerant copper(I) catalyzed alkyne-azide cycloaddition (CuAAC) reaction was used to incorporate a wide range of catalytic moieties into the resulting organic nanotubes. The ‘as-synthesized’ organic nanotube catalysts showed high catalytic efficiency and site-isolation features, which present a versatile platform for developing high performance catalyst systems by a unique combination of structural control and chemical versatility that is difficult to attain by other methods.

Results and discussion

The bottlebrush copolymer precursor with triblock terpolymer side chains was synthesized by a combination of controlled radical and ring-opening polymerizations (scheme 1). First, core–shell bottlebrush copolymers with a polylactide (PLA) core and a poly(4-vinylbenzyl chloride-co-4-(3-butenyl)styrene) (PVBC/BS) shell were synthesized with the previously described method [24] from a poly(glycidyl methacrylate) PGM backbone with an average degree of polymerization of 200 and a polydispersity index of 1.09. In order to improve the solubility of the final organic nanotube catalysts, a third layer poly (N-isopropylacrylamide) (PNIPAAM) was introduced into the core–shell bottlebrush architecture of the precursor copolymers by reversible addition fragmentation chain transfer (RAFT) polymerization. As shown in scheme 1, the final bottlebrushes contain a degradable PLA core, a cross-linkable PVBC/BS middle layer with functional PVBC segments, and a PNIPAAM outer layer. Each branch was composed of a PLA block with an average of 24 repeat units and a PVBC/BS block with an average of 49 units, as well as a PNIPAAM block with an average of 300 repeat units, as measured by $^1$H NMR as shown in figure 1. All polymers, except for the final PNIPAAM grafted bottlebrush, had monomodal molecular weight distributions and low polydispersities (figure 2), which indicated efficient reinitiation and the formation of well-defined copolymers. It was difficult to reliably characterize the molecular weight distribution of P(GM-g-LA-g-VBC/BS-g-NIPAAM) bottlebrush copolymer due to its enormous size ($1.7 \times 10^7 \text{ g \cdot mol}^{-1}$), which made gel permeation chromatography (GPC) analysis impossible. Next, according to our previously reported method [24], the bottlebrushes with triblock terpolymer side chains were converted to organic nanotubes by intracross-linking of the PVBC/BS middle layer in the presence of Grubbs’ catalyst and subsequent removal of the polylactide core by acidic hydrolysis. Finally, benzyl chlorides in the functional PVBC
wall of organic nanotubes were further converted to azides by treatment with sodium azide, leading to azide-functionalized organic nanotubes. The complete removal of PLA and functionalization of the azide groups were confirmed by the disappearance of the characteristic PLA carbonyl stretch peak (1759 cm$^{-1}$) and the appearance of the characteristic azide band (2098 cm$^{-1}$) in the FTIR spectra, respectively (see figure S1, available in the supplementary data). The formation of azide-functionalized organic nanotubes was further characterized by transmission electron microscopy. Such cylindrical nanoparticles with an average length of $35 \pm 5$ nm include an azide-functionalized wall (figure 3), of which azide groups can serve as reactive anchor points for further reaction with alkyne-containing small molecule catalysts.

To determine whether the active catalysts could be ‘clicked’ into organic nanotube walls, several catalyst precursors or catalysts anchored to alkyne groups were reacted with the azide-functionalized nanotubes using a copper (I) catalyst (scheme 1). Reaction progress was monitored by the complete disappearance of the characteristic azide band (2098 cm$^{-1}$) in the IR spectrum of the synthesized azide band (2098 cm$^{-1}$) in the IR spectrum of the synthesized azide band catalysts (figure S1). The final nanotube catalysts were composed of a hydrophobic and cross-linked shell decorated with catalysts as well as hydrophilic corona, which shows an amphiphilic feature. In addition, the hollow porous structure of organic nanotubes will benefit the mass transformation, which will lead to enhanced reaction rates for catalytic reactions. Furthermore, the cross-linked shell layer and the outer PNIPAAM layer might also provide an external shielding against metal leaching or catalyst poisoning, even producing the site-isolation effect for one-pot cascade reaction. To demonstrate these hypotheses, we synthesized organic nanotube catalysts functionalized with acid, base, as well as Pd, and their catalytic properties also were studied in detail.

To probe the viability of these soluble organic nanotubes for catalyst support, N-(2-hydroxyethyl)-imidazole (HEIZ)
small molecules and imidazole-containing organic nanotubes (base-nanotube) were used as the water-soluble catalyst and support for the hydrophobic or water-incompatible catalyst, respectively. Additionally, an imidazole-containing diblock copolymer with similar composition was also prepared by a combination of RAFT polymerization and click reaction and their catalysis properties were also evaluated as a control experiment (scheme S1). The Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate in water was used as a model reaction to evaluate the catalytic activity. The catalysis results showed that the imidazole-containing nanotube catalyst demonstrated activity superior to that of water soluble HEIZ, or the imidazole-containing diblock copolymer (scheme 2). As expected, no product formed for the water soluble HEIZ as catalyst, indicating that the hydrophilic HEIZ remained in the water phase instead of interacting with the hydrophobic reactant. However, the imidazole-containing diblock copolymer showed a slightly higher catalytic activity, which may be related to their micellar structure in aqueous environments. The micellar structure evidenced by the DLS measurement (see figure S2 in the supplementary data) might act as a microreactor for the hydrophobic reactant. Surprisingly, in the same catalyst loading and reaction condition, the Knoevenagel condensation reaction could be finished completely when the imidazole-containing organic nanotubes were used as catalyst. We reasoned that the superior catalytic activity of nanotube catalysts is due to the placement of catalytic imidazole moieties within the hydrophobic environment of the nanotube wall. Meanwhile, the open-end tubular structure of nanotubes will also accelerate the mass transfer and reaction process, leading to the high catalytic efficiency of nanotube catalysts.

As previously mentioned, the organic nanotubes with a cross-linked tube wall and the outer PNIPAAM layer might produce site-isolated effects for one-pot cascade reactions due to the external shielding effect. In order to prove this assumption, a pair of incompatible acid and base groups (sodium prop-2-yn-1-sulfonate (SPS) and 1-(2-(prop-2-yn-1-yloxy)ethyl)-1H-imidazole (PEI)) were anchored onto the wall of the nanotube to obtain the acid- and base-organic nanotube catalysts, respectively (figure S3). An acid-catalyzed acetal hydrolysis and the subsequent base-catalyzed Knoevenagel condensation were carried out as model reactions to evaluate the utility of these new materials for site-isolation application. Reactions with either free acid or base, and with base-nanotube or acid-nanotube catalysts were also performed as control experiments. The results showed that tandem deacetalization-Knoevenagel reactions completed perfectly for the combination of acid-nanotube catalyst with base-nanotube catalyst. However, no cascade product C was observed (table 1) when the sequence was carried out only in the presence of small-molecular catalysts HEIZ or p-toluenesulfonic acid (PTSA) with acid-nanotube or base-nanotube catalysts, respectively. As predicted, these small-molecular catalysts could freely diffuse into the wall of the nanotube catalysts and deactivate the acidic and basic groups through acid-base neutralization reactions. Therefore, the deactivated nanotube catalysts could no longer catalyze the reaction cascade. This acid-base neutralization-induced deactivation was also confirmed by mixing both HEIZ and PTSA in the reaction solution (entry 4). These results are in agreement with our assumption that the organic nanotubes provide effective site isolation, preventing mutual deactivation of incompatible wall-bound catalytic groups.

To examine whether this method could be generalized, we further functionalized the azide-nanotubes with 2-ethynylpyridine to produce the pyridine-functionalized nanotubes via Huisgen reaction (scheme 1). The pyridine-functionalized nanotubes can be further reacted with Pd (OAc)$_2$ to provide the desired Pd-nanotube catalysts. The Pd content was determined by inductively coupled plasma mass spectrometry (ICP-MS) to be 6.2%, which corresponds to a 98% metalation yield. To further investigate the coordination state of the catalysts, UV–vis, TEM and energy-dispersive x-ray spectroscopy (EDX) characterizations were performed. From the UV–vis spectra (figure S4), it was found that the palladium functionalized nanotube showed mainly one peak around 293 nm, which was probably assigned to the ligand to metal charge transfer transition (LMCT) [27, 28]. EDX data also shows an intense palladium peak at 2.85 keV, indicating that Pd(II) were supported on organic nanotubes (figure S5). Figure 1 shows a typical TEM image of a fresh Pd-containing nanotube catalyst, from which it can be seen that the black dots with sizes in the range of 3–6 nm are highly dispersed on the nanotube support. The black dots are attributed to the Pd (0) nanoparticles formed upon the electron-beam induced reduction of the original Pd(II) species during the TEM measurements. This phenomenon has previously been noticed and explained by other groups [29, 30]. However, the organic nanotubes cannot be observed clearly in the TEM image because of their poor contrast compared to the Pd nanoparticles. To check the catalysts performance of the synthesized Pd-nanotubes, we choose the Suzuki–Miyaura reaction of arylhalide with phenylboronic acid as a model reaction. The reaction was conducted in EtOH and H$_2$O at 50 °C and K$_2$CO$_3$ as the base for 24 h (scheme 3). The result revealed that the Pd-nanotubes displayed a high catalytic reactivity in the Suzuki–Miyaura reaction and a high yield (97%) can be obtained according to GC-MS measurement. An important merit of Pd-nanotube catalysts is that they can be conveniently recycled and reused by easy precipitation from the crude reaction mixture into ether. The Pd-nanotube catalyst could be used repetitively at least five times without significant decrease in the yield of 4-methoxy-1,1'-biphenyl. On the other hand, the TEM image revealed that the Pd-nanotube preserved its original morphology well after being reused five times, showing excellent stability against both catalyst aggregation or structural damage (figure S6).

Conclusion

We have constructed a new class of catalyst system using soluble organic nanotubes as a support structure via single-molecule templating core–shell bottlebrush copolymers. The catalysis results demonstrate that the soluble organic
nanotube catalysts system not only offers high active catalysis but also displays unusual site-isolation effects. Moreover, the high stability of support resulted in outstanding recycling properties of the system. By preparing the organic nanotubes with rationally designed surfaces and walls for objective functional materials, we believe that the novel soluble organic nanotubes can be applied in various catalytic fields in the future.

**Experimental section**

**Materials**

All reagents were used as received from commercial suppliers unless stated otherwise. Glycidyl methacrylate (GM, Acros 97%) was distilled before use. Dichloromethane (DCM) and N,N-dimethylformamide (DMF) were distilled from calcium hydride. 2,2-Azoisobutyronitrile (AIBN) and N-isopropylacrylamide (NIPAAM) were purified by recrystallization from methanol and hexane, respectively. S-1-Dodecyl-S′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (TC) [31], 2-cyanoprop-2-yl-4-cyanodithiobenzoate (CPD) [32], 4-(3-butenyl)styrene (BS) [33], sodium prop-2-ynylsulfonate (SPS) [34], 1-(2-(prop-2-yn-1-yl oxy)ethyl)-1H-imidazole (PEI) [35] were synthesized according to literature procedures.

**Measurements**

All 1H NMR spectra were recorded on a Bruker AVANCE III™ 500 spectrometer (500 MHz) using CDCl3 or DMSO-d6 as a solvent. GPC data was obtained from a Waters GPC system equipped with a Waters 2414 refractive index detector, a 1515 isocratic HPLC pump, and two Waters HPLC columns. THF (HPLC grade) was used as the solvent for polymers and eluent for GPC with a flow rate of 1 ml min⁻¹ at 30 °C. UV/vis spectra were obtained using UV2400 and FTIR analyses were carried out using a Thermo NICOLET is50. TEM images were obtained using a JEM-2100F TEM instrument. Samples were prepared by dip-coating a 400 mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. GC/MS analyses were recorded on an Agilent 5973 Mass Selective Detector (70 eV) using a HP-5MS fused silica capillary column and argon as a carrier gas (1 ml min⁻¹). The split ratio was 1:50. The injector temperature was 270 °C and the detector was 280 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid catalyst</th>
<th>Base catalyst</th>
<th>Conversion of A(%)</th>
<th>Yield of C(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>acid-nanotube</td>
<td>base-nanotube</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>acid-nanotube</td>
<td>HEIZ</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>PTSA</td>
<td>base-nanotube</td>
<td>10%</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>PTSA</td>
<td>HEIZ</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Reaction conditions: 10 mol% acid and base catalysts were used. The reaction mixtures were stirring for 12 h at 50 °C in DMF/H2O (v/v) = (40:1), n(A):n(D) = 1:4, [A] = 60 mM.

Yields are based on GC-MS measurements.

**Scheme 3.** Catalytic activity and recycle test of Pd-nanotubes in the Suzuki–Miyaura cross-coupling reaction of 1-iodo-4-methoxybenzene with phenylboronic acid. Reaction conditions: 1 mol% Pd organic nanotube catalyst was used. The reaction mixtures were stirred for 24 h at 50 °C in EtOH/H2O (v/v) = 10:1, n(A):n(B):n(K2CO3) = 1:1.5:3, [A] = 40 mM. Yields are based on GC-MS measurements.

<table>
<thead>
<tr>
<th>run</th>
<th>first</th>
<th>second</th>
<th>third</th>
<th>fourth</th>
<th>fifth</th>
</tr>
</thead>
<tbody>
<tr>
<td>yield (%)</td>
<td>97</td>
<td>94</td>
<td>95</td>
<td>96</td>
<td>93</td>
</tr>
</tbody>
</table>
column temperature was kept at 60 °C for 3 min, increased to 280 °C at a rate of 25 °C min⁻¹, and then held at 280 °C for 5 min. The Pd content in the material was analyzed by the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method (IRIS INTREPID II XPS, Thermo Electron, USA). Micelle size distribution of the obtained imidazole-containing diblock copolymer in aqueous solution was measured with a Zetasizer Nano ZS (Malvern Instruments, UK).

**Acid-nanotube, base-nanotube and Pd-nanotube synthesis**

**Synthesis of PGM backbone.** GM (2 mL), CPD (18 mg), AIBN (2.4 mg) and benzene (2 mL) were mixed in a reaction vessel and degassed by three freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 15 h. The mixture was diluted with DCM, precipitated into methanol three times and dried under vacuum at room temperature for 24 h. Yield = 1.6 g (76%). GPC (PS standards): \[ M_n = 1.90 \times 10^5 \text{ g mol}^{-1}, \frac{M_w}{M_n} = 1.09. \] \[ \text{DP}_{NMR} = 200. \]

**Hydrolysis of PGM.** PGM (1.0 g), THF (20 mL) and acetic acid (40 mL) were mixed in a 250 mL round-bottom flask. The reaction mixture was stirred and placed in an oil bath at 60 °C, followed by the slow addition of 61.5 mL water over the course of 2 h. After stirring for 24 h at 60 °C, the solvent was removed on a rotary evaporator. The isolated polymer was precipitated from MeOH into diethyl ether three times and dried under vacuum at 25 °C for 24 h. Yield = 0.93 g (82%). \[ ^1H \text{NMR}: \text{conversion} = 95\%. \]

**Synthesis of poly(GM-g-LA).** Hydrolyzed PGM (500 mg) was dissolved in 50 mL dry DMF in a 250 mL round-bottom flask. D,L-lactide (11.7 g) was added into the mixture and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.35 mL) was followed. The reaction was continued for 1.5 h at room temperature and the reaction was quenched by 2.44 g benzoic acid. The resulting polymer was precipitated from THF into methanol/water (v:v = 1:1) three times and dried at 25 °C under vacuum for 24 h. Yield = 9.3 g (75%). GPC (PS standards): \[ M_n = 1.47 \times 10^5 \text{ g mol}^{-1}, \frac{M_w}{M_n} = 1.10. \] \[ ^1H \text{NMR}: n (PLA) = 24. \]

**Synthesis of P(GM-g-LA-g-VBC/BS).** Hydroxyl end groups of the PLA polymer were then modified to install trithiocarbonate functionalities, as described in [36]. The RAFT modified polymer (200 mg) was mixed with 4-vinylbenzyl chloride (VBC) (3.9 mL), BS (4.7 mL), AIBN (1.6 mg) and toluene (2 mL) in a reaction vessel and degassed by three freeze-pump-thaw cycles. The reaction was conducted at 65 °C for 24 h and stopped by opening the flask to air. The resulting reaction mixture was then precipitated into MeOH and precipitated from DCM into MeOH two more times. The yellow solid was dried under vacuum at 25 °C for 24 h. Yield = 580 mg (4.7%). GPC (PS standards): \[ M_n = 2.73 \times 10^5 \text{ g mol}^{-1}, \frac{M_w}{M_n} = 1.26. \] \[ ^1H \text{NMR}: n (VBC) = 30, n(PS) = 19. \]

**Synthesis of P(GM-g-LA-g-VBC/BS-g-NIPAAM).** Poly (GM-g-LA-g-VBC/BS) (150 mg), NIPAAM (2.65 g), AIBN (0.36 mg) and 1,4-dioxane (7.6 mL) were mixed in a reaction vessel and degassed by three freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 5 h. The resulting mixture was precipitated from THF into ethyl ether three times and dried under vacuum at room temperature for 24 h. Yield = 490 mg (13%). \[ ^1H \text{NMR}: n \text{ (NIPAAM)} = 300. \]

**Intramolecular shell-cross-linking.** Bottlebrush copolymers of P(GM-g-LA-g-VBC/BS-g-NIPAAM) (450 mg) were dissolved in 150 mL of DCM under nitrogen. Grubbs’ first generation catalyst (30 mg) was added into the reaction solution and stirred at room temperature under nitrogen for 16 h. At the end of the reaction, 0.1 mL of ethyl vinyl ether was injected to the solution to quench the catalyst. Then most of the solvent was evaporated and shell-cross-linked polymers were precipitated into ethyl ether and precipitated from THF into ethyl ether two more times.

**Core etching.** Cross-linked bottlebrush copolymers (400 mg) were dissolved in 20 mL THF/MeOH (v:v = 10:1), 0.2 mL 5 M KOH was added at room temperature. The solvent was evaporated and precipitated into ethyl ether after being reacted for 10 h. The product was precipitated from THF into ethyl ether two more times.

The azidation of organic nanotubes. 299 mg NaN₃ (4.6 mmol) was added to a solution of core-etched organic nanotubes (360 mg) in dry DMF (40 mL). The mixture was stirred at 50 °C for 40 h. After being cooled to room temperature, the mixture was then dialyzed against nanopure water for three days to remove residuals.

**Synthesis of organic nanotube supported sulfonic acid catalyst (acid-nanotube).** A mixture of CuSO₄ · 5H₂O (10 mg, 0.04 mmol), sodium ascorbate (39.6 mg, 0.2 mmol), sodium prop-2-yn-1-sulfonate (SPS) (6 mg, 0.04 mmol), azided organic nanotube (50 mg), 2 mL H₂O and 2 mL DMF were placed in a reaction flask. The mixture was stirred at 60 °C for 24 h under N₂. After being cooled to room temperature, the mixture was acidified by H₂SO₄ and then dialyzed against nanopure water for three days to remove residuals.

**Synthesis of organic nanotube supported imidazole catalyst (base-nanotube).** A mixture of CuSO₄ · 5H₂O (30 mg, 0.12 mmol), sodium ascorbate (120 mg, 0.6 mmol), 1-(2-(prop-2-yn-1-yl oxy)ethyl)-1H-imidazole(PEI) (18 mg, 0.12 mmol), azided organic nanotube (150 mg), 0.5 mL H₂O and 5 mL DMF were placed in a reaction flask. The mixture was stirred at 60 °C for 24 h under N₂. After being cooled to room
temperature, the mixture was then dialyzed against nanopure water for three days to remove residuals.

**Synthesis of organic nanotube supported Pd catalyst (Pd-nanotube).** A mixture of CuSO4·5H2O (10 mg, 0.04 mmol), sodium ascorbate (39.6 mg, 0.2 mmol), 2-ethylpyridine (6 mg, 0.06 mmol), azidized organic nanotube (50 mg), 0.5 ml H2O and 5 ml DMF were placed in a reaction flask. The mixture was stirred at 60 °C for 24 h under N2. After being cooled to room temperature, the mixture was then dialyzed against nanopure water for three days to remove residuals. After removal of most of the water under vacuum, the pyridine modified organic nanotube (pyridine-nanotube) and palladium acetate (5.4 mg, 0.024 mmol) was dissolved in 2 ml DMF and stirred at room temperature for 48 h. After most of the solvent was removed, the solution was precipitated into ethyl ether and repeated two more times. The content of Pd in the organic nanotube determined by ICP AES was 0.58 mmol g⁻¹.

**Conditions for the model Knoevenagel condensation reaction**

Reaction catalyzed by organic nanotube supported imidazole. 1 mg of base-nanotube (~3.6 × 10⁻⁴ mmol imidazole groups, 0.01 eq) was dissolved in 0.5 ml of deionized water. Benzaldehyde (3.8 mg, 3.6 × 10⁻² mmol, 1.0 eq) and ethyl 2-cyanoacetate (16.3 mg, 14.4 × 10⁻² mmol, 4.0 eq) was added, and the reaction was stirred vigorously for 16 h at room temperature. When the stirring was stopped, no phase separation occurred in the reaction mixture. About 10 ul mixture was taken from the reaction, diluted by 1 ml MeOH and analyzed by GC-MS after being dried by anhydrous MgSO₄. The conversion was 95%.

Control reactions (catalyzed by N-(2-hydroxyethyl)-imidazole (HEIZ) and imidazole-containing diblock copolymer) have been performed using the same method as the reactions catalyzed by the base-nanotube. The loading of catalysts and the starting materials was as follows. Reaction catalyzed by HEIZ: benzaldehyde (3.8 mg, 3.6 × 10⁻² mmol, 1 eq), ethyl 2-cyanoacetate (16.3 mg, 14.4 × 10⁻² mmol, 4 eq), HEIZ (0.04 mg, 3.6 × 10⁻⁴ mmol, 0.01 eq) in 0.5 ml water; reaction catalyzed imidazole-containing diblock copolymer: benzaldehyde (3.8 mg, 3.6 × 10⁻² mmol, 1 eq), ethyl 2-cyanoacetate (16.3 mg, 14.4 × 10⁻² mmol, 4 eq), imidazole-containing diblock copolymer (0.52 mg, 3.6 × 10⁻⁴ mmol, 0.01 eq) in 0.5 ml water. The two reaction mixtures were stirred vigorously at room temperature for 16 h. For the reaction catalyzed by HEIZ, phase separation occurred after stirring stopped. The reaction catalyzed by imidazole-containing diblock copolymer had the same atmosphere as the reaction catalyzed by the base-nanotube. No condensation product was detected in the HEIZ catalyzed reaction, and the reaction catalyzed by imidazole-containing diblock copolymer reached 30% conversion.

**General procedure for the one-pot cascade catalytic experiment**

To a solution of acid-nanotube (10 mg, ~7.0 × 10⁻³ mmol sulfonic acid groups, 0.1 eq) and base-nanotube (11 mg, ~7.0 × 10⁻³ mmol imidazole groups, 0.1 eq) in 0.6 ml DMF, H₂O (15 ul, 0.83 mmol), (dimethoxymethyl)-benzene (10.6 mg, 7.0 × 10⁻² mmol) and ethyl 2-cyanoacetate (31.4 mg, 28.0 × 10⁻² mmol) were added in a reaction flask. The mixture was heated to 50 °C for 12 h. About 10 ul mixture was taken from the reaction, diluted by 1 ml MeOH and analyzed by GC-MS after being dried by anhydrous MgSO₄.

**General procedure for the the Suzuki–Miyaura catalytic experiment**

Pd-nanotube catalyst (10 mg, 4.8 × 10⁻³ mmol, 0.01 eq), K₂CO₃ (20 mg, 14.4 × 10⁻² mmol, 3.0 eq), borophenolic acid (9 mg, 7.2 × 10⁻² mmol, 1.5 eq), 4-idoanisole (12 mg, 4.8 × 10⁻² mmol, 1.0 eq), ethanol (1 ml) and H₂O (0.1 ml) were added in a reaction vessel and degassed by three freeze-pump-thaw cycles. The mixture was heated to 50 °C for 24 h. About 10 ul mixture was taken from the reaction, diluted by 1 ml MeOH, and analyzed by GC-MS after being dried by anhydrous MgSO₄. After being cooled to room temperature, the mixture was precipitated into ethyl ether after most of the solvent had been removed. The solid was again dissolved in ethanol and ethyl ether was removed after centrifugation. The catalyst was recycled five times.

Other detailed experimental descriptions can be found in the supplementary data.

**Acknowledgments**

This work is supported by the National Natural Science Foundation of China grants 51273066, 21574042 and 21204022; the Shanghai Pujiang Program grant 13PJ1402300; the Research Fund for the Doctoral Program of Higher Education of China 20120076120005; and the Fundamental Research Funds for the Central Universities.

**References**


[27] Schweinfurth D, Pattacini R, Strobel S and Sarkar B 2009 New 1,2,3-triazole ligands through click reactions and their palladium and platinum complexes *Dalton T.* **9291–7


