Electronic Supplementary Information for

Crystal-like periodic mesoporous organosilica bearing pyridine units within the framework

Minoru Waki, a,b Norihiro Mizoshita, a,b Tetsu Ohsuna, a,b Takao Tani a,b and Shinji Inagaki *a,b

aToyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan.
bCore Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan.

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**Preliminary experiments**

**Rh-catalyzed silylation**

\[
\begin{align*}
\text{I} & \quad \text{I} \\
\text{N} & \quad \text{N} \\
\text{I} & \quad \text{I}
\end{align*}
\]

\[
\text{HSi(OEt)}_3 + [\text{Rh} \cdot \text{cod} \cdot (\text{CH}_2\text{CN})] \cdot \text{BF}_4^- \cdot \text{Et}_3\text{Ni} \rightarrow \quad \text{no reaction}
\]

**Heck reaction**

\[
\begin{align*}
\text{I} & \quad \text{I} \\
\text{N} & \quad \text{N} \\
\text{I} & \quad \text{I}
\end{align*}
\]

\[
\text{Triethoxyvinylsilane} \quad \text{Pd} \cdot (\text{Ph}_3) \_4 \quad \text{Et}_3\text{N}, \text{DMF}
\]

\[
\begin{align*}
\text{(EtO)}_2\text{Si} & \quad \text{mono-substituted product}
\end{align*}
\]

**Scheme S1.** Preliminary experiments for Rh-catalyzed silylation and Heck reaction of 2,5-diiodopyridine with alkoxysilanes.

**Experimental Section**

**General**

All reagents and solvents were commercially available and used without further purification. \(^1\)H and \(^{13}\)C NMR spectra were measured using a Jeol ECX-400 spectrometer operating at 400 and 100 MHz, respectively. Nuclear Overhauser effect (NOE) measurements were carried out using a Jeol Lambda-500 model spectrometer operating at 500 MHz. \(^{29}\)Si dipolar decoupling (DD) and \(^{13}\)C cross-polarization (CP) magic angle spinning (MAS) NMR measurements were carried out at 79.49 and 100.6 MHz, respectively, using a Bruker ADVANCE 400 spectrometer with a 7 mm zirconia rotor at a sample spinning frequency of 4 kHz. The repetition delay and pulse width were 80 s and 4.5 \(\mu s\), respectively, for \(^{29}\)Si DD MAS NMR. The repetition delay, contact time and pulse width were 5 s, 1.75 ms and 4.5 \(\mu s\) (\(^1\)H 90º pulse), respectively, for \(^{13}\)C CP MAS NMR. Chemical shifts were referenced to tetramethylsilane and glycine for \(^{29}\)Si and \(^{13}\)C NMR, respectively. X-ray diffraction (XRD) profiles were recorded on a Rigaku RINT-TTR diffractometer using Cu-K\(\alpha\) radiation (50 kV, 300 mV). Nitrogen adsorption and desorption isotherms were measured using a Yuasa Nova3000e sorptometer. BET surface areas were calculated from the linear sections of the BET plots (P/P\(_0\) = 0.1 – 0.2). Pore-size distributions were determined using the density functional theory (DFT) method (the DFT kernel: N\(_2\) at 77 K on silica, cylindrical pore, nonlinear density functional theory (NLDFT) equilibrium model). Pore volumes were estimated by the t-plot method. TEM observation was performed using a Jeol JEM-EX2000 operating at 200 kV. IR spectra were collected on a Thermo Fisher Scientific Nicolet AVATAR-360 FT-IR spectrometer using an attenuated total reflection (ATR) attachment. UV/vis absorption and fluorescence emission spectra were obtained using Jasco V-670 and FP-6500 spectrometers, respectively.
Synthesis

2,5-Bis(trimethylsilylethynyl)pyridine.\(^1\) A suspension of 2,5-diiodopyridine (10 g, 30.2 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (0.85 g, 1.21 mmol) and CuI (0.12 g, 0.60 mmol) in iPr\(_2\)NH (120 ml) and THF (40 ml) was cooled with an ice bath, and then to this suspension was added trimethylsilylacetylene (11.8 g, 121 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 16 h. The resulting mixture was filtered to remove insoluble matter, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/AcOEt = 10:1) to give 2,5-bis(trimethylsilylethynyl)pyridine (7.4 g, 90%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.26 (9 H, s), 0.27 (9 H, s), 7.38 (1 H, d, \(J = 8.24\) Hz), 7.68 (1 H, dd, \(J = 8.24\) Hz), 8.62 (1 H, s); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) –0.1, 0.0, 97.3, 100.5, 101.4, 103.6, 119.8, 126.7, 139.0, 141.9, 152.9. The \(^1\)H and \(^13\)C NMR data were identical to those reported in the literature.\(^1\)

2,5-Diethynylpyridine.\(^1\) To a THF (160 mL) solution of 2,5-bis(trimethylsilylethynyl)pyridine (7.4 g, 27.1 mmol) was added \(n\)-Bu\(_4\)NF (1.0 M THF solution, 60 mL, 60 mmol) and a few drops of H\(_2\)O subsequently. The reaction mixture was stirred for 4 h at room temperature, concentrated, and diluted with ether/H\(_2\)O. The separated ether layer was washed with brine, dried over MgSO\(_4\), and then the solvent was completely evaporated. The residue was chromatographed on silica gel (hexane/AcOEt = 3:1) to give 2,5-diethynylpyridine (3.0 g, 88%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 3.26 (1 H, s), 3.31 (1 H, s), 7.45 (1 H, dd, \(J = 7.32\) Hz), 7.75 (1 H, dd, \(J = 10.52\) Hz), 8.68-8.69 (1 H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 79.1, 79.9, 82.3, 82.4, 119.0, 126.7, 139.2, 141.5, 152.9. The \(^1\)H and \(^13\)C NMR data were identical to those reported in the literature.\(^1\)

2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine (1). To a CH\(_3\)CN (27 mL) solution of 2,5-diethynylpyridine (0.30 g, 2.36 mmol), [Rh(cod)Cl]\(_2\) (23 mg, 0.047 mmol), PPh\(_3\) (50 mg, 0.19 mmol) was added triethoxysilane (1.55 g, 9.44 mmol) under an argon atmosphere. The reaction mixture was stirred at 100 ºC for 24 h. After cooling to room temperature, the reaction mixture was filtered through charcoal and Celite bed, and then the solvent was completely evaporated. The residue was purified by Kugelrohr distillation at 190–200 ºC/30 Pa to give 1 (0.47 g, 44%) as a yellow oil. IR (neat): \(\nu_{\text{max}}\) 2974, 2928, 2893, 1603, 1545, 1477, 1439, 1389, 1078, 960 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 1.25–1.29 (18 H, m), 3.86–3.92 (12 H, m), 6.27 (1 H, d, \(J = 19.68\) Hz), 6.70 (1 H, d, \(J = 19.68\) Hz), 7.19 (1 H, d, \(J = 19.68\) Hz), 7.28 (1 H, d, \(J = 19.20\) Hz), 7.40 (1 H, d, \(J = 8.24\) Hz) 7.77–7.79 (1 H, m), 8.64 (1 H, d, \(J = 2.28\) Hz); \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 18.2, 58.7, 120.9, 121.7, 123.3, 132.4, 133.5, 145.0, 147.9, 148.9, 155.1; APCI-HRMS m/z calcd. for C\(_{21}\)H\(_{37}\)NO\(_6\)Si\(_2\) (MH\(^+\)): 456.2237; found: 456.2243.

Divinylpyridine-bridged (v-Py)-PMO. To a mixture of octadecyltrimethylammonium chloride (surfactant: 0.94 g), a 6 N sodium hydroxide aqueous solution (1.25 mL), and distilled water (55
mL) was added the precursor 1 (1.0 g, 2.19 mmol) under vigorous stirring at room temperature. The suspension was stirred for another 24 h. The suspension was heated at 96 ºC for 24 h under a static condition. Then, the resulting precipitate was filtered and washed with distilled water, affording as-made v-Py-PMO. The surfactant was removed by washing the as-made materials (0.65) in EtOH (94 mL) with concentrated HCl (3 g) at 60 ºC for 16 h.

**Protonation and deprotonation of v-Py-PMO**
Protonation of v-Py-PMO was performed by exposure to trifluoroacetic acid vapor for 10 min. The resulting powder was dried under vacuum. For deprotonation, the protonated v-Py-PMO was exposed to ammonia vapor for 10 min, and dried under vacuum.

**Adsorption of Cu²⁺ to v-Py-PMO**
To a CH₂Cl₂/MeOH (10:1) solution of Cu(BF₄)₂·6H₂O (0–1.8 x 10⁻² M) was added v-Py-PMO (20 mg) or divinylbenzene (v-Ph)-PMO (20 mg) prepared according to the literature.² The suspension was stirred for 20 h at room temperature. After filtration with a membrane filter (0.2 μm), the amount of the non-adsorbed Cu²⁺ in the filtrate was measured by UV/vis spectrometer. The adsorbed amounts of Cu²⁺ were calculated from the decrease of the absorbance due to Cu²⁺ at 800 nm.

**References**
Confirmation of trans-β addition for hydrosilylation of 2,5-diethynylpyridine

**1H NMR measurement**

The 1H NMR spectrum of the crude product obtained by hydrosilylation of 2,5-diethynylpyridine shows a formation of mainly one isomer. The product purified by Kugelrohr distillation was identified as a trans-β adduct 1 because the signals at 6.27, 6.70, 7.19, and 7.28 ppm with large coupling constants ($J = 19.20–19.68$ Hz) were assigned to protons of the trans-vinylene unit. The result indicates that trans-β addition selectively proceeded in the present procedure.

![Fig. S1 1H NMR spectra (5.5–9.0 ppm) of the crude and purified products.](image)

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NOE measurement

NOE measurements were carried out for 1. Positive NOE signals were observed at proton A and B of the vinylene unit at 2-position of the pyridine ring upon irradiation to proton C. Likewise, positive NOE signals were observed at proton F and G of the vinylene unit at 5-position of the pyridine ring upon irradiation to proton D or E. These results indicated a trans-β form of the product.

Fig. S2 (A) NOE spectra of 1 measured in acetone-d$_6$. (O) NOE signals, (x) scalar coupling signals, (▼) irradiation points (proton C (a), D (b), or E (c)). (B) NOE enhancement ratios (red number). Hydrogen, carbon and nitrogen atoms are shown in white, green and blue, respectively.
Structural properties

Fig. S3 IR spectra of v-Py-PMO before and after extraction of the surfactant.

Fig. S4 Nitrogen adsorption/desorption isotherms of v-Py-PMO.
Fig. S5 (A) $^{29}$Si MAS and (B) $^{13}$C CP-MAS NMR spectra of v-Py-PMO.
Fig. S6 (a) Thermogravimetric analysis (TGA) and (b) differential thermal analysis (DTA) curves of v-Py-PMO in air.

Fig. S7 Nitrogen adsorption/desorption isotherms of v-Py-PMO after exposure to TFA and NH$_3$ vapor. The Brunauer-Emmett-Teller surface area and pore volume were 718.42 m$^2$g$^{-1}$ and 0.630 cm$^3$g$^{-1}$, respectively.
**Adsorption behavior of Cu$^{2+}$**

UV/vis absorption measurements were carried out for Cu(BF$_4$)$_2$ solutions before and after the adsorption procedure with v-Py-PMO or v-Ph-PMO (Fig. S8). The treatment with v-Py-PMO significantly decreased the concentration of Cu$^{2+}$ in the solution, indicating a high adsorption capacity for Cu$^{2+}$. UV/vis diffuse reflectance spectra of v-Py-PMO were also measured before and after the treatment (Fig. S9). The absorption edge of v-Py-PMO at 350 nm was red-shifted and the band due to Cu$^{2+}$ appeared around 750 nm after the treatment. The former behavior was similar to that of the precursor I after coordination of Cu$^{2+}$ in a solution (Fig. S10), suggesting that Cu$^{2+}$ adsorption in v-Py-PMO is attributable to coordination to the pyridine rings in the framework.

![Graph showing UV-vis spectra](image_url)

Fig. S8 UV-vis spectra of Cu(BF$_4$)$_2$ solutions before (dashed) and after the adsorption procedure with v-Py-PMO (black solid) or v-Ph-PMO (grey solid). The initial Cu$^{2+}$ concentration was 8.9 x 10$^{-3}$ M.
Fig. S9. UV/vis diffuse reflectance spectra of v-Py-PMO before (black) and after (blue) adsorption of Cu$^{2+}$.

Fig. S10. UV/vis spectral change of I with titration of a Cu(BF$_4$)$_2$ solution. Conditions: [I] = 1.4 x 10$^{-5}$ M, [Cu(BF$_4$)$_2$] = 0–9.0 x 10$^{-5}$ M, CH$_2$Cl$_2$, light path length = 10 mm.
**Desorption behavior of Cu^{2+}**

The amount of Cu^{2+} in Cu^{2+}-adsorbed v-Py-PMO before and after washing with water was evaluated by energy dispersive X-ray spectroscopy (EDS) (Fig. S11). The signals due to Cu species mostly disappeared after the washing, suggesting that Cu^{2+} adsorbed in v-Py-PMO was almost completely removed by the washing. The mesoporous structure of v-Py-PMO was preserved during the adsorption/desorption processes of Cu^{2+}, which was confirmed by nitrogen adsorption/desorption isotherms after the washing (Fig. S12).

![Fig. S11 EDS spectra of pristine v-Py-PMO (A) and Cu^{2+}-adsorbed v-Py-PMO before (B) and after (C) washing with water.](image_url)
Fig. S12 Nitrogen adsorption/desorption isotherms of Cu$^{2+}$-adsorbed v-Py-PMO after washing with water. The Brunauer-Emmett-Teller surface area and pore volume were 757 m$^2$ g$^{-1}$ and 0.685 cm$^3$ g$^{-1}$, respectively.
$^1$H and $^{13}$C NMR spectra of 2,5-bis[(E)-2-(triethoxysilyl)vinyl]pyridine (1)

$^1$H NMR spectrum

$^{13}$C NMR spectrum