

Electronic Supplementary Information for

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

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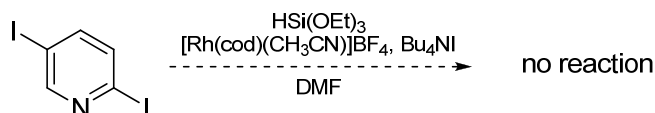
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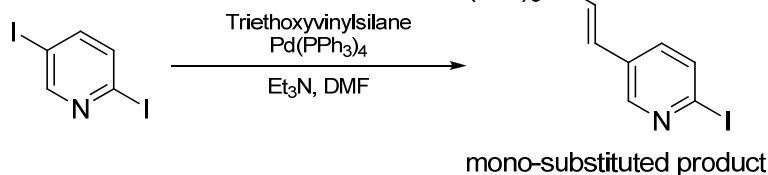
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Preliminary experiments

Rh-catalyzed silylation



Heck reaction



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

Experimental Section

General

All reagents and solvents were commercially available and used without further purification. ^1H 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 μs , respectively, for ^{29}Si DD MAS NMR. The repetition delay, contact time and pulse width were 5 s, 1.75 ms and 4.5 μs (^1H 90° 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 $\text{Cu-K}\alpha$ 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), PdCl₂(PPh₃)₂ (0.85 g, 1.21 mmol) and CuI (0.12 g, 0.60 mmol) in *i*Pr₂NH (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%). ¹H NMR (400 MHz, CDCl₃): δ 0.26 (9 H, s), 0.27 (9 H, s), 7.38 (1 H, d, *J* = 8.24 Hz), 7.68 (1 H, dd, 8.24 Hz), 8.62 (1 H, s); ¹³C NMR (100 MHz, CDCl₃): δ -0.1, 0.0, 97.3, 100.5, 101.4, 103.6, 119.8, 126.7, 139.0, 141.9, 152.9. The ¹H and ¹³C 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*-Bu₄NF (1.0 M THF solution, 60 mL, 60 mmol) and a few drops of H₂O subsequently. The reaction mixture was stirred for 4 h at room temperature, concentrated, and diluted with ether/H₂O. The separated ether layer was washed with brine, dried over MgSO₄, 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%). ¹H NMR (400 MHz, CDCl₃): δ 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); ¹³C NMR (100 MHz, CDCl₃): δ 79.1, 79.9, 82.3, 82.4, 119.0, 126.7, 139.2, 141.5, 152.9. The ¹H and ¹³C NMR data were identical to those reported in the literature.¹

2,5-Bis[(E)-2-(triethoxysilyl)vinyl]pyridine (1). To a CH₃CN (27 mL) solution of 2,5-diethynylpyridine (0.30 g, 2.36 mmol), [Rh(cod)Cl]₂ (23 mg, 0.047 mmol), PPh₃ (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 °C 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 °C/30 Pa to give **1** (0.47 g, 44%) as a yellow oil. IR (neat): ν_{\max} 2974, 2928, 2893, 1603, 1545, 1477, 1439, 1389, 1078, 960 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 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); ¹³C NMR (CDCl₃, 100 MHz): δ 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 C₂₁H₃₇NO₆Si₂ (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 °C 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 °C 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 × 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

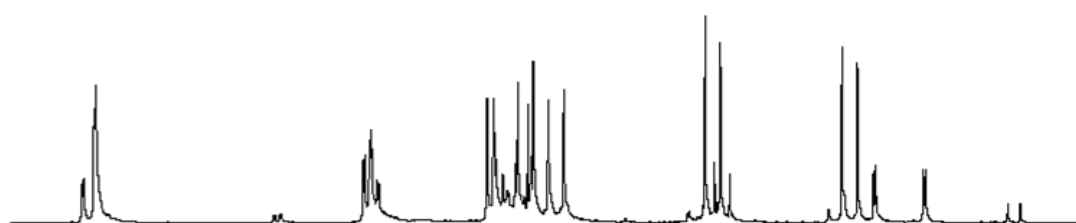
1. K. A. Bunten and A. K. Kakkar, *Macromolecules*, 1996, **29**, 2885–2893.
2. A. Sayari and W. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 12194–12195.

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 ($J = 19.20\text{--}19.68$ Hz) were assigned to protons of the trans-vinylene unit. The result indicates that trans- β addition selectively proceeded in the present procedure.

crude product



purified product

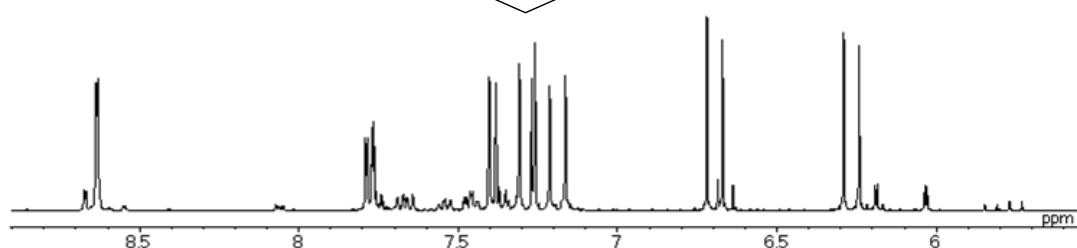


Fig. S1 ^1H NMR spectra (5.5–9.0 ppm) of the crude and purified products.

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.

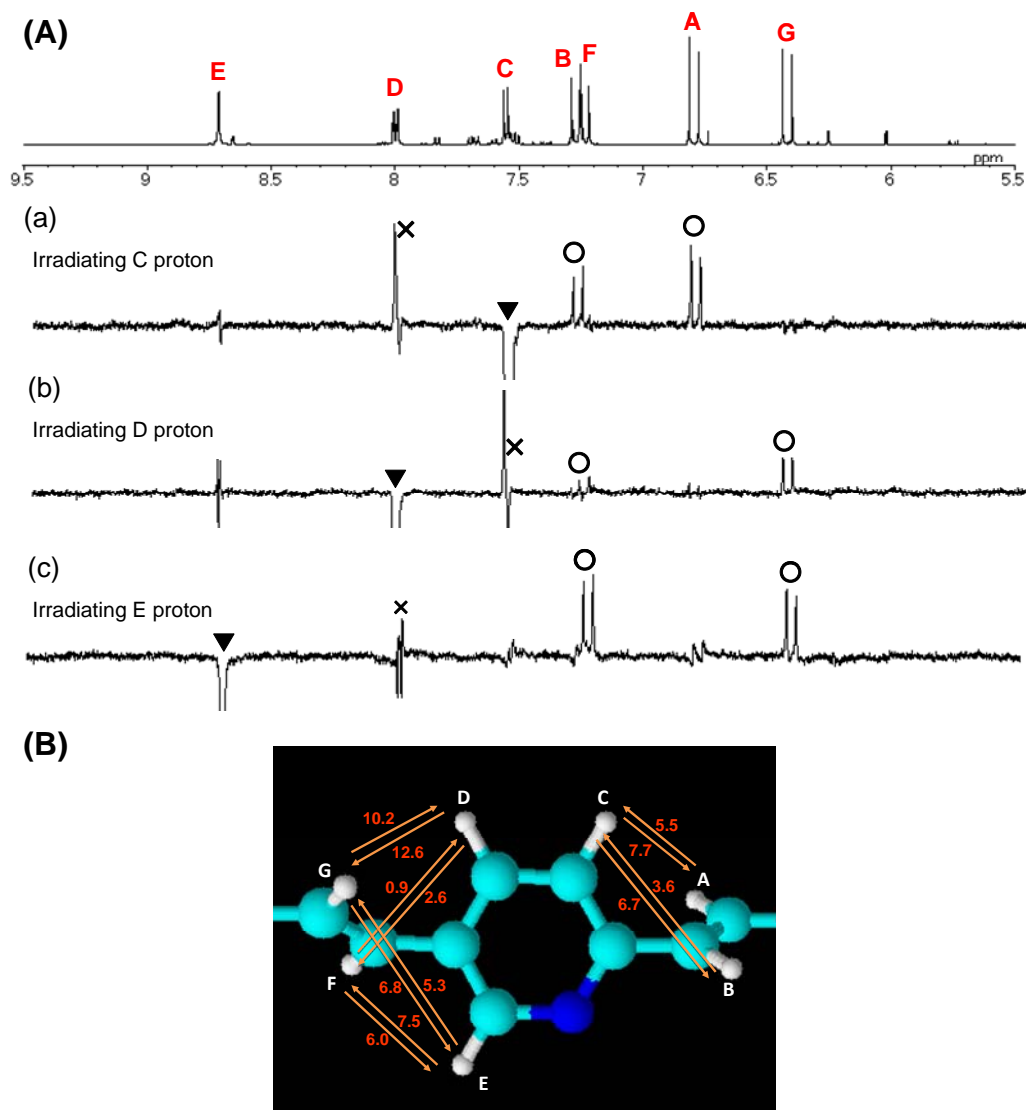


Fig. S2 (A) NOE spectra of **1** measured in acetone- d_6 . (O) NOE signals, (x) scalar coupling signals, (▼) irradiation points (proton C (a), D (b), or E (c)). (B) NOE enhancement ratios (red number). Hydrogen, carbon and nitrogen atoms are shown in white, green and blue, respectively.

Structural properties

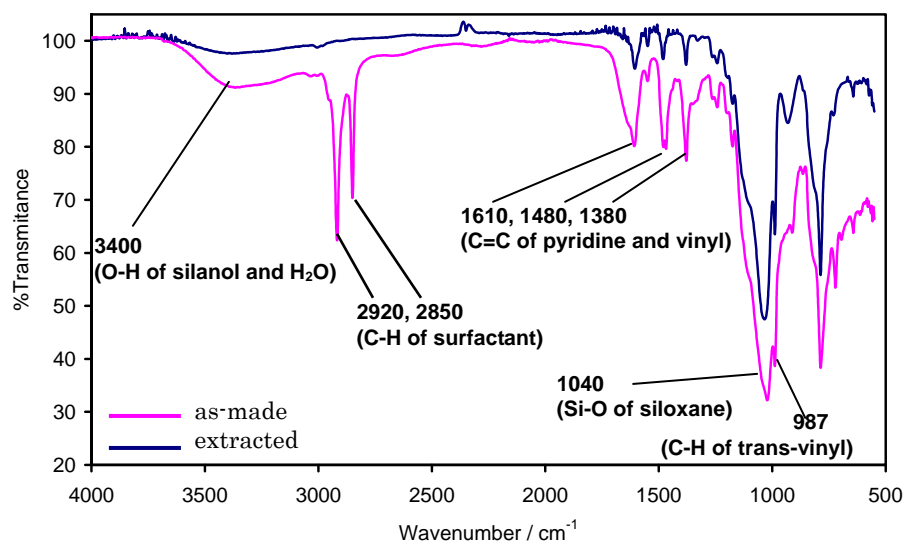


Fig. S3 IR spectra of v-Py-PMO before and after extraction of the surfactant.

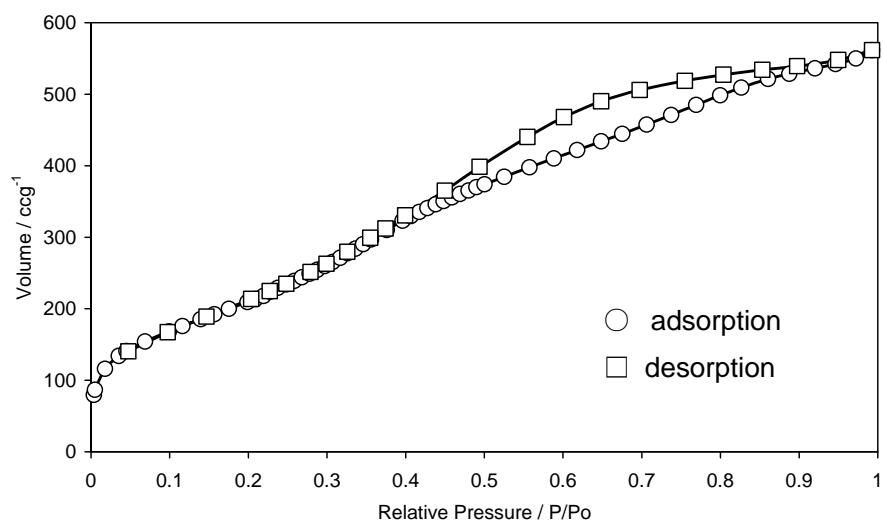


Fig. S4 Nitrogen adsorption/desorption isotherms of v-Py-PMO.

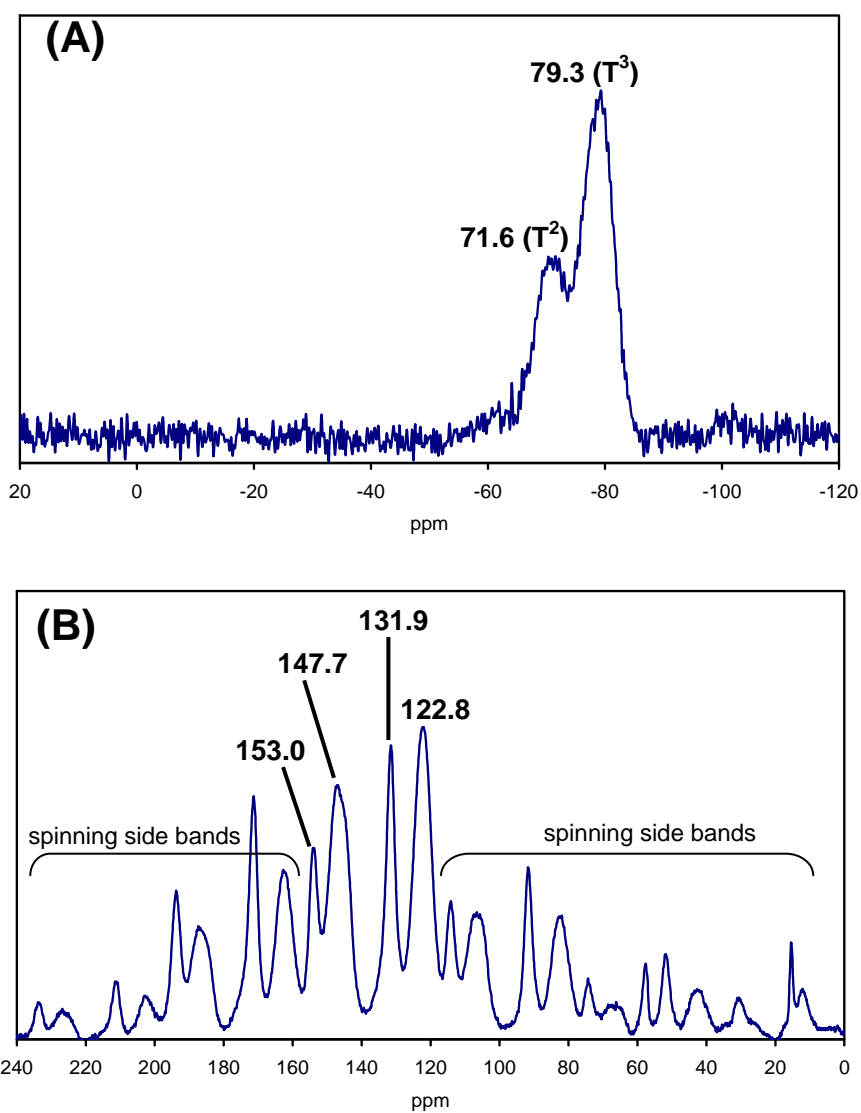


Fig. S5 (A) ^{29}Si MAS and (B) ^{13}C CP-MAS NMR spectra of v-Py-PMO.

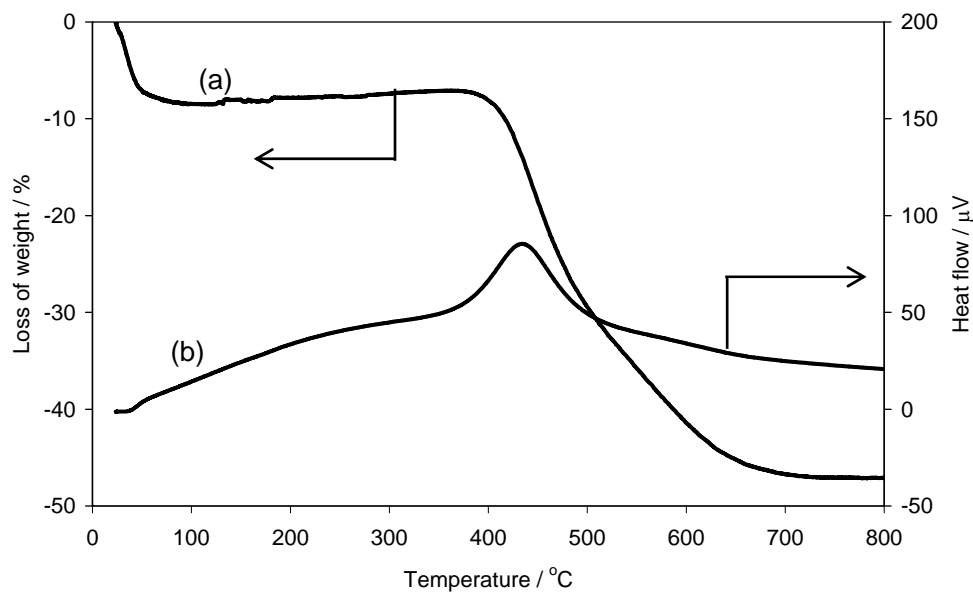


Fig. S6 (a) Thermogravimetric analysis (TGA) and (b) differential thermal analysis (DTA) curves of v-Py-PMO in air.

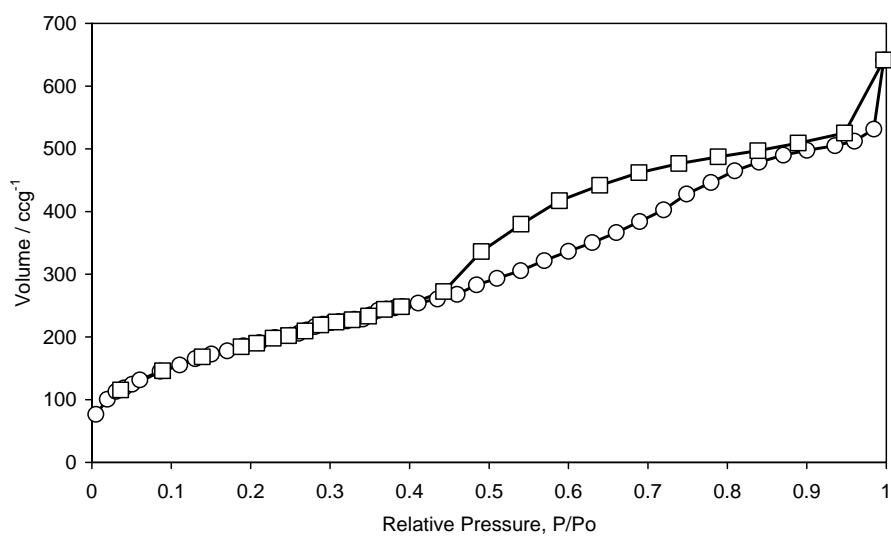


Fig. S7 Nitrogen adsorption/desorption isotherms of v-Py-PMO after exposure to TFA and NH₃ vapor. The Brunauer-Emmett-Teller surface area and pore volume were 718.42 m²g⁻¹ and 0.630 cm³g⁻¹, respectively.

Adsorption behavior of Cu²⁺

UV/vis absorption measurements were carried out for Cu(BF₄)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 Cu²⁺ in the solution, indicating a high adsorption capacity for Cu²⁺. 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 Cu²⁺ appeared around 750 nm after the treatment. The former behavior was similar to that of the precursor **1** after coordination of Cu²⁺ in a solution (Fig. S10), suggesting that Cu²⁺ adsorption in v-Py-PMO is attributable to coordination to the pyridine rings in the framework.

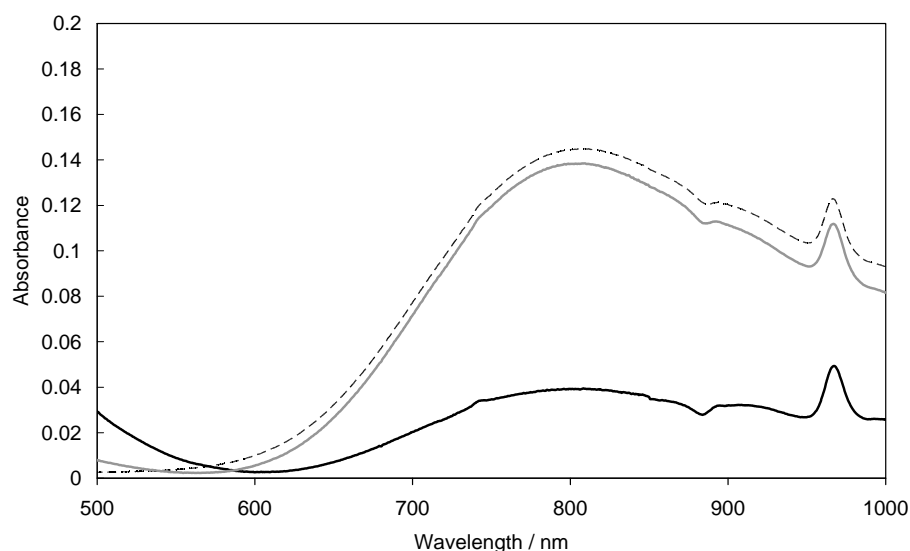


Fig. S8 UV-vis spectra of Cu(BF₄)₂ solutions before (dashed) and after the adsorption procedure with v-Py-PMO (black solid) or v-Ph-PMO (grey solid). The initial Cu²⁺ concentration was 8.9 × 10⁻³ M.

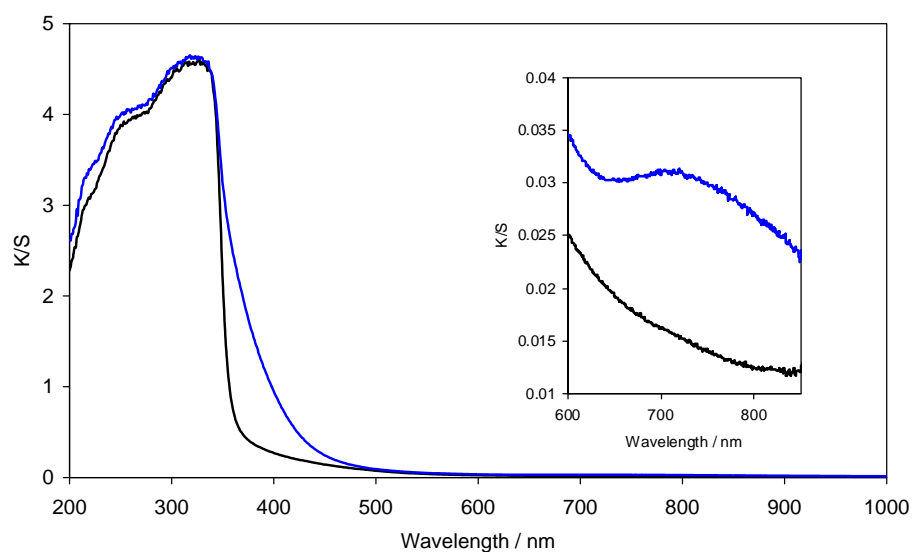


Fig. S9. UV/vis diffuse reflectance spectra of v-Py-PMO before (black) and after (blue) adsorption of Cu^{2+} .

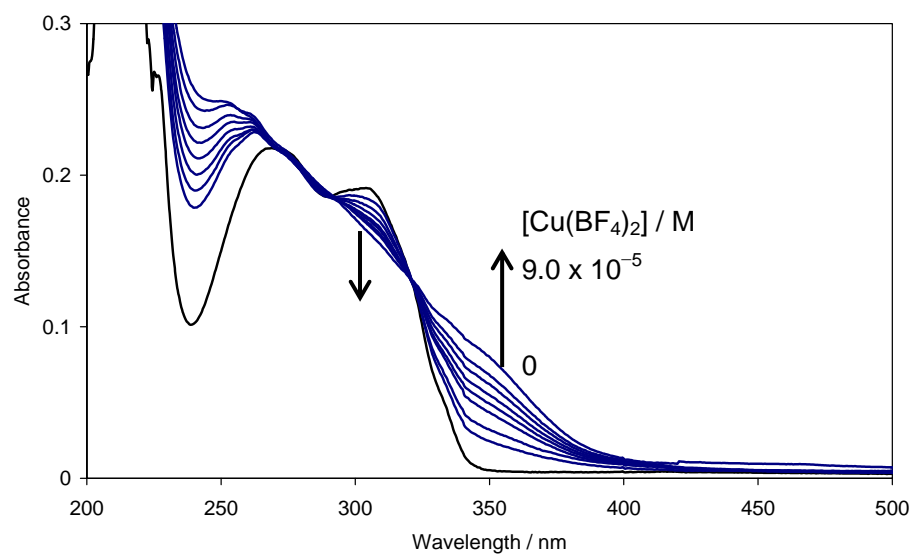


Fig. S10. UV/vis spectral change of **1** with titration of a $\text{Cu}(\text{BF}_4)_2$ solution. Conditions: $[\mathbf{1}] = 1.4 \times 10^{-5}$ M, $[\text{Cu}(\text{BF}_4)_2] = 0-9.0 \times 10^{-5}$ M, CH_2Cl_2 , light path length = 10 mm.

Desorption behavior of Cu²⁺

The amount of Cu²⁺ in Cu²⁺-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 Cu²⁺ 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 Cu²⁺, which was confirmed by nitrogen adsorption/desorption isotherms after the washing (Fig. S12).

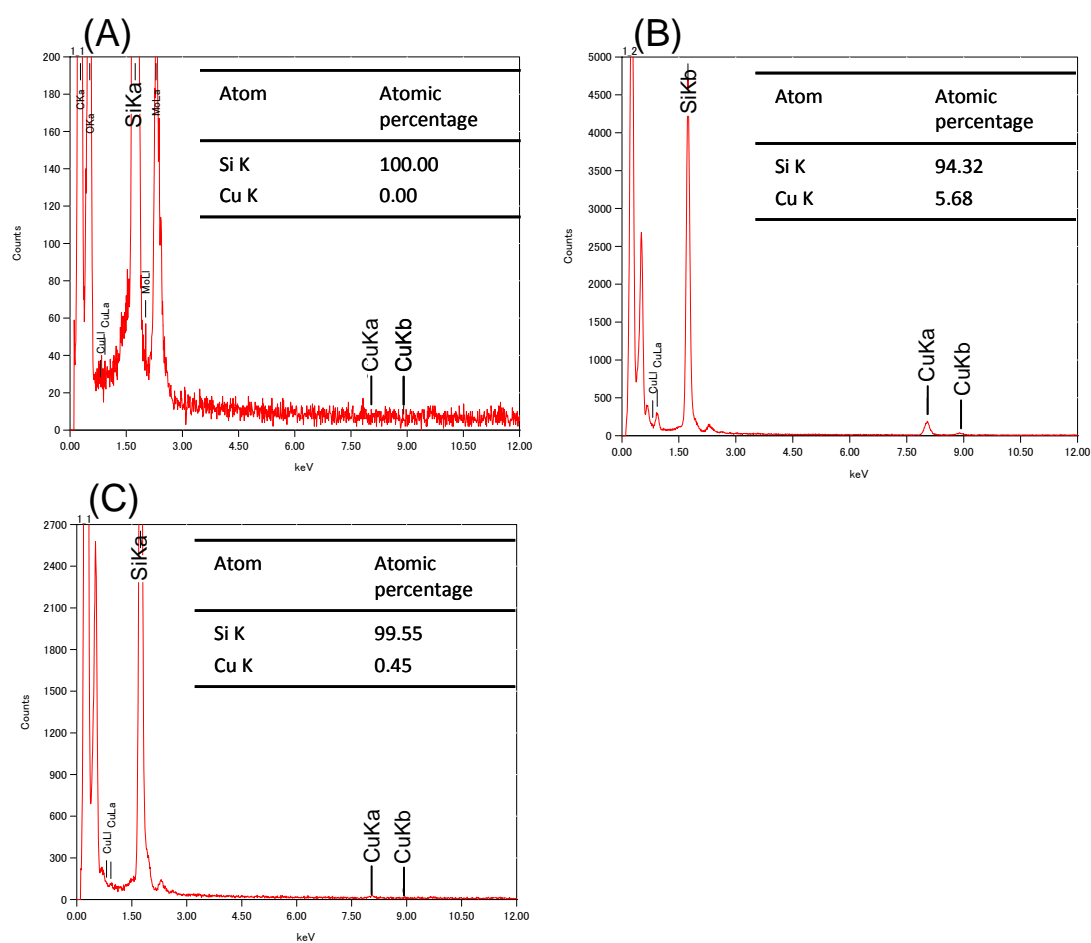


Fig. S11 EDS spectra of pristine v-Py-PMO (A) and Cu²⁺-adsorbed v-Py-PMO before (B) and after (C) washing with water.

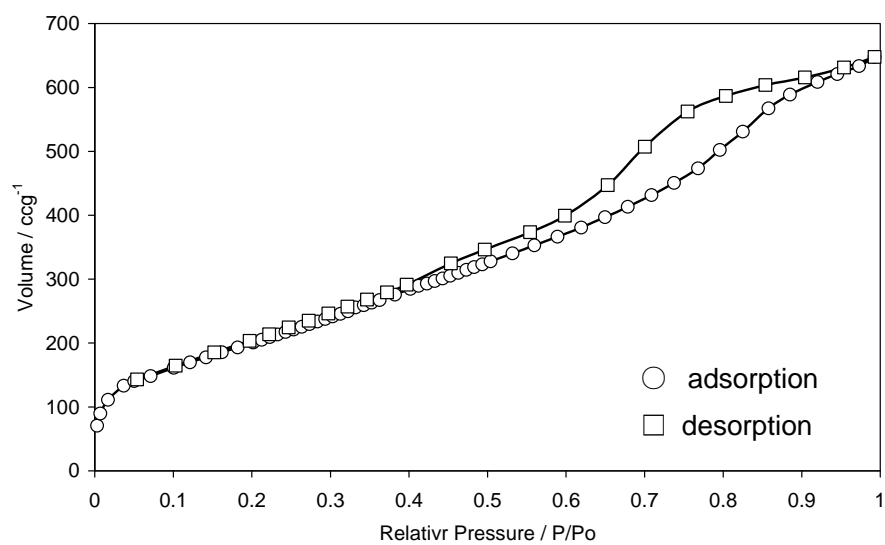
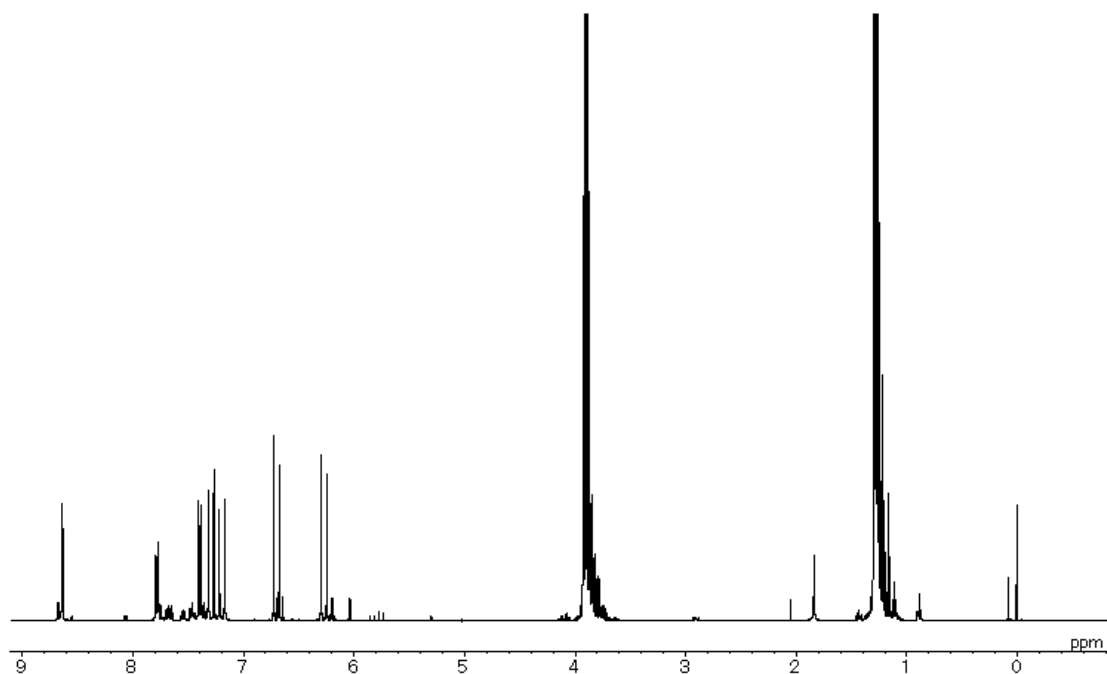


Fig. S12 Nitrogen adsorption/desorption isotherms of Cu²⁺-adsorbed v-Py-PMO after washing with water. The Brunauer-Emmett-Teller surface area and pore volume were 757 m²g⁻¹ and 0.685 cm³g⁻¹, respectively.

^1H and ^{13}C NMR spectra of 2,5-bis[(E)-2-(triethoxysilyl)vinyl]pyridine (1)

^1H NMR spectrum



^{13}C NMR spectrum

