Electronic supplementary information for

Rate Enhancement for Hexose Sugar Oxidation on an Ethynylpyridine-Functionalized Pt/Al₂O₃ Catalyst with Induced Chirality

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**Experimental Section**

**General**

All reagents and solvents were commercially available and used without further purification. $^{13}$C cross-polarization (CP) magic-angle spinning (MAS) NMR measurements were respectively performed at 100.6 MHz at a sample spinning frequency of 8 kHz using a JEOL JNM-ECX-400 spectrometer with a 6 mm zirconia rotor. For the $^{13}$C CP MAS NMR measurements, the repetition delay was 1 s, the contact time was 5 ms, and the pulse width was 5.4 μs ($^1$H 90° pulse). IR spectra were collected on a JASCO FT-IR4200 spectrometer. UV/vis and CD spectra were obtained using JASCO V-670 and J-820 spectrometers using integrated spheres, respectively.

**Synthesis**

![Chemical structure](image)

2,6-Diethylidene-4-methoxymethoxy-pyridine (5): This compound was synthesized according to previous literature.\(^1\)

2,6-Bis(2-pyridylethylidene)-4-methoxymethoxy-pyridine (6): To a mixture solution of i-Pr$_2$NH (50 mL) and THF (50 mL) was added 5 (1.24 g, 6.6 mmol), 2-iodopyridine (2.7 g, 13.2 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (0.14 g, 0.13 mmol), (o-Tol)$_3$P (0.16 g, 0.53 mmol), Cul (0.05 g, 0.26 mmol). The mixture was stirred under N$_2$ at 343 K overnight. The resulting mixture was filtered to remove insoluble salt, and evaporated. The residue was purified by silica-gel column chromatography (eluent: AcOEt) to give 6 (1.22 g, 54%). IR (KBr): $\nu_{\text{max}}$ 2976, 2929, 2889, 2273, 1703, 1533, 1457 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 3.47 (3 H, s), 5.23 (2 H, s), 7.26-7.28 (2 H, m), 7.29 (2 H, m), 7.61 (2 H, $J = 1.2$, 7.8 Hz, dd), 7.69 (2 H, $J = 1.6$, 7.8 Hz, dt), 8.63 (2 H, $J = 0.8$, 4.8 Hz, td); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 20.1, 65.4, 90.0, 90.4, 95.3 112.6, 118.9, 122.4, 129.1, 134.1, 135.4, 140.2, 151.0. ESI-HRMS m/z calcd. for C$_{21}$H$_{14}$Na$_2$O$_2$ (M+Na)$^+$: 364.1062; found: 364.1056.

2,6-Bis(2-pyridylethylidene)-4-pyridone: To a CH$_2$Cl$_2$ (10 mL) solution of 6 (0.2 g, 0.59 mmol) was added CF$_3$COOH (1.5 g, 13.5 mmol). After stirring for 2 h at room temperature, the resulting mixture was quenched by adding aqueous NaHCO$_3$. The residue was extracted with CH$_2$Cl$_2$·H$_2$O. The organic layer was dried over MgSO$_4$, and concentrated to obtain 2,6-bis(2-pyridylethylidene)-4-pyridone. IR (KBr): $\nu_{\text{max}}$ 3079, 3047, 2992, 2961, 2916, 2831, 1758, 1553, 1463, 1153, 1135, 1014 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.22 (2 H, s), 7.29-7.33 (2 H, s), 7.58 (2 H, $J = 8.0$ Hz, d), 7.73 (2 H, $J = 4.0$, 8.0 Hz, d), 8.59 (2 H, $J = 4.0$ Hz, d); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 90.0, 90.3 113.8 119.1, 122.6, 129.6, 133.6, 133.7, 153.8. ESI-HRMS m/z calcd. for C$_{19}$H$_{12}$N$_2$O$_2$ (M+H)$^+$: 298.0982; found: 298.0992.
2,6-Bis(2-pyridylethynyl)-4-[(3-triethoxysilylpropyl)carbamoyloxypyridine (1): To a THF (10 mL) solution of 2,6-bis(2-pyridylethynyl)-4-pyridone was added 3-(triethoxysilyl)propyl isocyanate (0.22 g, 0.88 mmol). The resulting mixture was stirred at 60 °C for 15 h, and then concentrated by an evaporator. The mixture was added hexane, filtered to remove an insoluble matter and concentrated. The residue was purified by silica-gel column chromatography (eluent: AcOEt) to obtain 1 (0.17 g, 52% in 2 steps). IR (KBr): \( \nu_{\text{max}} = 3087, 2979, 2925, 2674, 2569, 2459, 2227, 1684, 1594, 1562, 1469, 1196, 1138 \text{ cm}^{-1} \); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta = 0.68 \) (2 H, \( J = 7.8 \) Hz, t), 1.22 (9 H, \( J = 7.0 \) Hz, t), 1.72 (2 H, \( J = 7.3 \) Hz, p), 3.28 (2 H, \( J = 6.8 \) Hz, q), 3.82 (6 H, \( J = 7.0 \) Hz, q), 5.82 (1 H, \( J = 5.8 \) Hz, t), 7.27 (2 H, \( J = 5.2 \) Hz, dd), 7.46 (2 H, s), 7.59 (2 H, 1.2, \( J = 8.0 \) Hz, d), 7.68 (2 H, \( J = 1.6 \), 7.7 Hz, dt), 8.61 (2 H, \( J = 4.4 \) Hz, d); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta = 7.8, 18.4, 22.9, 43.7, 58.7, 87.1, 88.5, 120.1, 123.7, 128.0, 136.4, 142.4, 144.3, 150.3, 152.1, 158.5 \text{ ES-I-HRMS m/z calcd. for C}_{25}H_{25}N_{6}O_{8}Si (M+H)^{+}: 489.1589; found: 489.1192. (Two ethoxy groups on silicon in 1 were hydrolyzed under the ionization condition during MS measurement.)

Attachment of EPy ligand on Pt/Al\(_2\)O\(_3\): To a toluene (40 mL) solution was added EPy ligand 1 (0.01 mmol, 5 mg) and Pt/Al\(_2\)O\(_3\) (1.0 g, Pt: 5 wt%), and stirred at 373 K for 24 h under N\(_2\). Followed by Sohxlet extraction with toluene for 24 h to remove the unreacted 1, EPy/Pt/Al\(_2\)O\(_3\) was obtained after drying under vacuum. The amounts of the binding EPy ligand (17 wt%) were measured by elemental analysis, assuming that the detected nitrogen was originated from the EPy ligand. EPy/Pt/Al\(_2\)O\(_3\) catalysts with different loading of 1 were prepared in a similar way.

UV/vis titration experiment for EPy/Pt/Al\(_2\)O\(_3\): A CH\(_2\)Cl\(_2\) (20 mL) dispersion of EPy/Pt/Al\(_2\)O\(_3\) (EPy: 17 wt%) (2 mg) was prepared. To this dispersion was added a CH\(_2\)Cl\(_2\) solution of octyl \( \beta \)-D-glucopyranoside (Oct-\( \beta \)-D-Glc) at the concentrations of 0.8, 1.6, 2.4, and \( 3.2 \times 10^{-3} \) M. UV/vis spectra of resulting dispersion were measured at a transmission mode by spectrometer attached with an integrating sphere unit at room temperature.

UV/vis titration experiment for MOM-protected ethynylpyridine 6: A CH\(_2\)Cl\(_2\) solution of 6 (1.0 \times 10^{-4} \text{ M}) was prepared in a quartz cell. Then, a CH\(_2\)Cl\(_2\) solution of Oct-\( \beta \)-D-Glc was added at the concentrations of 0.8, 1.6, 2.4, and \( 3.2 \times 10^{-3} \) M. UV/vis spectra of solution were measured at each concentrations of Oct-\( \beta \)-D-Glc.

CD measurement: A CH\(_2\)Cl\(_2\) dispersion (5 mL) of EPy/Pt/Al\(_2\)O\(_3\) (EPy: 17 wt%) (1.0 mg) was prepared in a quartz cell. Then, Oct-\( \beta \)-D-Glc or octyl \( \beta \)-L-glucopyranoside (58 mg, 0.02 mmol) was added to this dispersion. CD spectra of the dispersion with and without glucopyranoside were measured at a transmission mode by spectrometer attached with an integrating sphere unit at room temperature.

Catalytic reactions for the oxidation of hexose sugars: Catalyst (EPy/Pt/Al\(_2\)O\(_3\) (Pt: 5 wt%, EPy: 0.2 wt%) or Pt/Al\(_2\)O\(_3\) (Pt: 5 wt%)) (0.10 g), methyl \( \alpha \)-D-glucopyranoside (Me-\( \alpha \)-D-Glc) (or methyl-\( \alpha \)-D-galactopyranoside and methyl-\( \alpha \)-D-mannopyranoside) (1.0 mmol), and NaHCO\(_3\) (0.71 mmol, 0.06 g) was suspended in H\(_2\)O (3 mL) under oxygen atmosphere. Oxidation reactions were carried out at 353 K for 2, 5, and 9 h. After that, the resulting mixture was subjected with ion-exchange resin to adjust pH into acidity. Amount of reactant and product were analyzed by \(^{13}\)C NMR measurement. The molar ratio of them can be calculated from the average of the integrated intensities of the signals for the C2–C5 carbon atoms of each sugar in \(^{13}\)C NMR.
Catalytic reactions for the oxidation of cyclohexanemethanol: Catalyst (EPy/Pt/Al₂O₃ (Pt: 5 wt%, EPy: 0.2 wt%) or Pt/Al₂O₃ (Pt: 5 wt%)) (0.05 g) and NaHCO₃ (0.36 mmol, 0.031 g) was suspended in H₂O (1.5 mL) under oxygen atmosphere. Cyclohexanemethanol (0.5 mmol) was added and the mixture was stirred vigorously at 353 K for 1 h. After the system was cooled to room temperature, a few drops of conc. HCl aq. were added to acidify the pH of the solution. Then CH₂Cl₂ (1.5 mL) was added to the resulting mixture and the mixture was stirred vigorously for 10 min. to extract the organic compounds to CH₂Cl₂ phase. The amount of the reactant and product was monitored by GC (Shimadzu GC-14B, CHIRALDEX B-DM column), and the conversion of cyclohexanemethanol was determined by using a peak area ratio between the reactant and CH₂Cl₂. The extraction efficiencies of cyclohexanemethanol, cyclohexanealdehyde, and cyclohexanecarboxylic acid from aqueous phase to CH₂Cl₂ phase under the current catalytic condition were quantitative as determined by the GC peak areas of these compounds with respect to the peak area of CH₂Cl₂.

References for supporting information


Fig. S1 $^{13}$C liquid-state NMR spectrum of (a) 1 in CDCl$_3$, and $^{13}$C solid-state CP MAS NMR spectra of EPy/Pt/Al$_2$O$_3$ (EPy: (b) 0.2 wt%, (c) 1.7 wt%, and (d) 17 wt%).
Fig. S2 (A) TEM images of EPy/Pt/Al₂O₃ (EPy: 0.2 wt%, Pt: 5 wt%) and Pt/Al₂O₃ (Pt: 5 wt%). (B) Size distribution of Pt nanoparticles calculated by TEM images. The average diameters of the Pt particles on EPy/Pt/Al₂O₃ and Pt/Al₂O₃ were 3.3 ± 0.6 nm and 2.9 ± 0.7 nm, respectively.
**Fig. S3** $^{13}$C NMR spectra of Me-$\alpha$-D-Glc (▼) and methyl $\alpha$-D-glucuronic acid (○) during the oxidation reaction of Me-$\alpha$-D-Glc on EPy/Pt/Al$_2$O$_3$ (EPy: 0.2 wt%, Pt: 5 wt%) for (a) 0 h, (b) 2 h, (c) 5 h, and (d) 9 h.
Fig. S4 Conversion of the selective oxidation of Me-α-D-Glc on the EPy/Pt/Al₂O₃ (EPy: 0.2 wt%, Pt: 5 wt%) and Pt/Al₂O₃ (Pt: 5 wt%) catalysts. Error bars were estimated by the repetition of the oxidation reactions.

Fig. S5 ¹³C NMR spectra for the oxidation of D-glucose on (a) Pt/Al₂O₃ (Pt: 5 wt%) and (b) EPy/Pt/Al₂O₃ (Pt: 5 wt%) for 12 h. (a) D-Glucose was consumed, and several oxidized products were observed. (b) Unreacted D-glucose was mainly observed in the spectrum, and characteristic signals (○) were assigned to gluconic acid.
**Fig. S6** UV/vis absorption spectra of a CH$_2$Cl$_2$ suspension of EPy/Pt/Al$_2$O$_3$ (EPy: 17 wt%) before and after the filtration of the solid catalyst using a syringe filter (0.2 µm).

**Fig. S7** Changes in UV/vis spectra of 6 in CH$_2$Cl$_2$ upon titration with Oct-β-D-Glc (0 - 3.2 × 10$^{-3}$ M). Solid line: before titration.
**Fig. S8** The CD spectra of the suspension of EPy/Pt/Al₂O₃ (EPy: 1.7 wt%) (black) in CH₂Cl₂ and that after the addition of Oct-β-D-Glc (gray). There was no active CD signal observed.
\(^1\)H NMR spectrum for 2,6-bis(2-pyridylethynyl)-4-methoxymethoxypyridine (6)

\(^{13}\)C NMR spectrum for 2,6-bis(2-pyridylethynyl)-4-methoxymethoxypyridine (6)
$^1$H NMR spectrum for 2,6-bis(2-pyridylethynyl)-4-pyridone

$^{13}$C NMR spectrum for 2,6-bis(2-pyridylethynyl)-4-pyridone
$^1$H NMR spectrum for 2,6-bis(2-pyridylethynyl)-4-[(3-triethoxysilylpropyl)carbamoyl]oxy]pyridine (1)

$^{13}$C NMR spectrum for 2,6-bis(2-pyridylethynyl)-4-[(3-triethoxysilylpropyl)carbamoyl]oxy]pyridine (1)