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Electronic Supplementary Information (ESI) for

Visible-light-responsive catalysis of a zinc-introduced lacunary disilicoicosatungstate for deoxygenation of pyridine *N*-oxides

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General: IR spectra were measured on JASCO FT/IR-4100 using KBr disks. Cold spray ionization mass (CSI MS) spectra were recorded on JEOL JMS-T100CS. NMR spectra were recorded on JEOL JNM ECA-500 spectrometer (¹H, 500.16 MHz; ²⁹Si, 99.37 MHz) by using 5 mm tubes. Chemical shifts (δ) were reported in ppm downfield from Si(CH₃)₄ (solvent, CDCl₃) for ¹H and upfield from Si(CH₃)₄ (solvent, CDCl₃) for ²⁹Si NMR spectra. UV/Vis spectra were measured on JASCO V-570 using 1 cm quartz cell. GC analysis was performed on Shimadzu GC-2014 with a flame ionization detector equipped with an Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a TC-1 capillary column (internal diameter = 0.32 mm, length = 30 m). GC mass spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV equipped with an InertCap 5MS/Sil. ICP-AES analysis was performed with Shimadzu ICPS-8100. TBA₄[γ -SiW₁₀O₃₂(H₂O)₂ $_2(\mu$ -O)₂] (I) was synthesized according to the reported procedure in our previous reports.⁸ Solvents and substrates were obtained from Wako Pure Chemical Industries, Kanto Chemical, and Tokyo Chemical Industry, and used after purification (if required).

Synthesis of TBA₇[{Zn(CH₃CN)}(γ-SiW₁₀O₃₄){γ-SiW₁₀O₃₂(CH₃CONH)}(µ-O)₂] (II): Compound I (699.9 mg, 0.12 mmol) was suspended in acetone (15 mL) at room temperature. Then, TBAOH·30H₂O (286 mg, 0.36 mmol) was added and the mixture was stirred for 5 min. After the reaction solution became clear, Zn(OAc)₂·2H₂O (21 mg, 0.1 mmol) was added portionwise. The reaction solution was stirred for 4 h at room temperature. After filtration, the solution was poured into diethyl ether (50 mL), and the resulting white precipitate was collected by filtration. The crude compound was purified by recrystallization from a mixed solvent of acetonitrile and diethyl ether to afford colorless crystals of II (0.22 g, 31% yield). Elemental analysis calcd (%) for TBA₇[{Zn(CH₃CN)}(γ-SiW₁₀O₃₄){γ-SiW₁₀O₃₂(CH₃CONH)}(µ-O)₂]; C, 20.85; H, 3.91; N, 1.89; Si, 0.84; W, 55.02; Zn, 0.98. Found: C, 20.44; H, 3.97; N, 1.67; Si, 0.83; W, 55.20; Zn, 0.99. IR (KBr pellet, cm⁻¹) v = 2958 (s), 2930 (m), 2871 (s), 1634 (m), 1482 (s), 1461 (sh), 1378 (m), 976 (m), 954 (s), 908 (s), 915 (sh), 880 (sh), 867 (s), 781 (sh), 678 (s), 550 (s). CSI mass (CH₃CN) *m/z* 3563 [TBA₉(ZnSi₂W₂₀O₆₈)(CH₃CONH)]²⁺, 6884 [TBA₈(ZnSi₂W₂₀O₆₈(CH₃CONH))]⁺. ²⁹Si NMR (CD₃CN) *δ* = -84.1, -85.6 ppm. ¹H NMR (CD₃CN) *δ* = 0.96 (t, *J* = 7.3 Hz), 1.39 (m), 1.62 (m), 3.15 (m), 2.39 (s) ppm.

X-ray crystallography: Diffraction measurements were made on a Rigaku MicroMax-007 Saturn 724 CCD detector with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at 123 K. Data were collected and processed using CrystalClear^{S1} and HKL2000.^{S2} Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. The structural analysis was performed using CrystalStructure^{S3} and Win-GX.^{S4} All structures were solved by SHELXS and refined by full-matrix least-squares methods using SHELXL.^{S5} The metal (Zn, Si, and W), oxygen, and nitrogen atoms in the POM frameworks were refined anisotropically. Solvents of crystallization and TBA cations were refined isotropically. CCDC- 1568655 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Bond valence sum (BVS) calculations: The BVS values were calculated by the expression for the variation of the length r_{ij} of a bond between two atoms *i* and *j* in observed crystal with valence V_i :

$$V_i = \sum_{j} \exp\left(\frac{r_0' - r_{ij}}{B}\right)$$

where B is constant equal to 0.37 Å, r'_0 is bond valence parameter for a given atom pair.^{S6}

Coordination geometry of the Zn1 atom in II: Kerton and Kozak proposed τ' parameter for the geometry and distortion in four-coordinated metal complexes.^{S7} In the ideal trigonal monopyramidal geometry, the largest angle is close to 120° and the smallest one is close to 90°. The τ' parameter is described by the following formula: $\tau' = (\{\beta + 90\} - \alpha) / 60$, where β is the largest angle obtained between a meridional donor atom, the metal and the apical donor atom, and α is the largest donor atom-metal-donor atom angle in the meridional plane. The ideal trigonal monopyramidal geometry gives $\tau' = 1.00$, while the ideal tetrahedral geometry gives $\tau' = 1.50$. The τ' parameter of the Zn1 atom in **II** (1.06) indicated that the coordination geometry of the Zn1 atom was close to trigonal monopyramidal. Several other geometric parameters for four-coordinated metal complexes, such as τ_4^{S8} and THC_{DA} , ^{S9} suggested that the coordination geometry of the Zn1 atom was close to trigonal monopyramidal (Table S4).

Electrochemistry: Cyclic voltammetric measurements were carried out with a Solartron SI 1287 Electrochemical Interface. A standard three-electrode arrangement was employed with a BAS glassy carbon disk electrode as the working electrode, a platinum wire as the counter electrode, and a silver wire electrode as the pseudoreference electrode. The voltage scan rate was set at 100 mV s⁻¹, and TBAClO₄ was used as the electrolyte. The potentials were measured using Ag/AgNO₃ reference electrode (10 mM AgNO₃, 100 mM TBAClO₄ in acetonitrile). Electrochemical reductions were carried out with an Electrochemical Analyzer ALS 600A using a BAS glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and a silver wire electrode as the pseudoreference electrode. Electrochemically four-electron-reduced II was prepared in acetonitrile (100 mM TBAClO₄) by constant potential electrolysis at -2.15 V vs. Ag/Ag⁺. The number of electrons stored within II was calculated by the electric current values and experimental times.

Photocatalytic deoxygenation of pyridine *N***-oxides:** A typical procedure for the deoxygenation of pyridine *N*-oxides is as follows: Into a Schlenk flask (volume: ca. 20 mL), **II** (5 µmol, 5 mol% with respect to pyridine *N*-oxides), pyridine *N*-oxides (0.1 mmol), acetone (1.0 mL), and a Teflon-coated magnetic stir bar were successively placed under Ar (1 atm). The reaction was initiated by irradiation with visible light ($\lambda > 400$ nm) with a Xe-lamp equipped with a 400 nm cut off filter (long-pass filter) at room temperature (*ca.* 30°C). The products were confirmed by comparison of their GC retention times and GC-MS spectra with those of authentic data. The yields of the products were periodically determined by GC analysis using an internal standard technique. After the reaction, the catalyst was retrieved as precipitate by addition of diethyl ether to the reaction solution. The retrieved catalyst was washed with diethyl ether, and then dried prior to being used for the reuse experiment. The CSI mass and IR spectra of the retrieved catalyst showed that the structure was preserved (Fig. S15, ESI[†]).

Compound data

Pyridine (2a): MS (EI) *m/z* (%): 79 (100), 78 (15).



2-Methylpyridine (2b): MS (EI) *m/z* (%): 94 (8), 93 (100), 92 (21), 79 (4), 78 (15), 67 (12), 66 (43), 65 (16), 64 (5), 63 (7), 53 (5), 52 (9), 51 (13), 50 (9).



3-Methylpyridine (2c): MS (EI) *m/z* (%): 94 (8), 93 (100), 92 (33), 78 (5), 67 (20), 66(42), 65(32), 64(6), 63(14), 62(7).



4-Methylpyridine (2d): MS (EI) *m/z* (%): 94 (8), 93 (100), 92 (27), 78 (5), 67 (18), 66 (43), 65 (28), 64 (5), 63 (11), 62 (5).



2,6-dimethyl pyridine (2e): MS (EI) *m/z* (%): 108 (8), 107 (100), 106 (38), 92 (18), 79 (12), 77 (8), 67 (4), 66 (34), 65 (21), 64 (4), 63 (8).



4-Phenylpyridine (2f): MS (EI) *m/z* (%): 156 (13), 155 (100), 154 (35), 140 (6), 128 (17), 127 (19), 126 (7), 115 (13), 102 (14), 78 (4), 77 (10), 76 (8), 75 (6), 64 (6), 63 (8), 51 (15), 50 (8).



4-Vinylpyridine (2g): MS (EI) *m/z* (%): 107 (8), 106 (16), 105 (100), 104 (44), 79 (14), 78 (40), 77 (18), 65 (8), 63 (5), 52 (24), 51 (28), 50 (18).



4-Chloropyridine (2h): MS (EI) *m/z* (%): 115 (32), 114 (7), 113 (100), 86 (6), 79 (5), 78 (84), 76 (7), 52 (6), 51 (52), 50 (39).



4-Pyridiencarboxaldehyde (2i): MS (EI) *m/z* (%): 108 (8), 107 (100), 106 (37), 79 (7), 78 (48), 53 (5), 52 (32), 51 (47), 50 (25).



4-Cyanopyridine (2j): MS (EI) *m/z* (%): 105 (8), 104 (100), 103 (5), 78 (6), 77 (64), 76 (22), 75 (11), 64 (15), 53 (5), 52 (8), 51 (18), 50 (27).

Formula	$C_{128}N_{15}O_{69}Si_2ZnW_{20}\\$
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	18.2388(1)
<i>b</i> (Å)	51.6192(4)
<i>c</i> (Å)	20.9479(2)
β (deg)	102.4143(3)
$V(\text{\AA}^3)$	19260.8(3)
Ζ	4
$\mu (\mathrm{mm}^{-1})$	12.097
$R_1(I > 2\sigma(I))$	0.0777
wR_2	0.1910
GOF	1.200

 Table S1. Crystallographic data for II.

	Bond length (Å)		Bond angle (°)
Zn1–N1	2.092	∠O1–Zn1–O3	126.52
Zn1–O1	1.943	∠O2–Zn1–O3	127.34
Zn1–O2	1.940	∠O1–Zn1–O2	97.85
Zn1–O3	1.974	∠O1–Zn1–N1	100.44
		∠O2–Zn1–N1	100.98
		∠O3–Zn1–N1	97.45

 Table S2. Selected bond lengths and angles of II.

Zn1	1.95	W110	6.18
Si1	3.91	W201	6.00
Si2	3.91	W202	5.99
W101	6.07	W203	6.20
W102	6.00	W204	6.24
W103	6.31	W205	6.06
W104	6.16	W206	6.16
W105	6.00	W207	6.21
W106	6.29	W208	6.07
W107	6.14	W209	6.15
W108	6.12	W210	6.12
W109	6.04		

Table S3. BVS values of zinc, tungsten, and silicon atoms of II.

	τ'	$ au_4$	THC _{DA}
П	1.06	0.75	0.15
Tetrahedral	1.5	1.00	1.00
Trigonal monopyramidal	1.00	0.85	0.00

Table S4. Various geometric parameters calculated for the Zn1 atom in II.



Fig. S1 CSI mass spectrum of **II** in acetonitrile. The sets of signals at m/z 3563 and 6884 were assignable to $[TBA_9(ZnSi_2W_{20}O_{68})(CH_3CONH)]^{2+}$ and $[TBA_8(ZnSi_2W_{20}O_{68})(CH_3CONH)]^{+}$, respectively.



Fig. S2 a) ¹H NMR and b) ²⁹Si NMR spectra of **II** in CD₃CN.



Fig. S3 Cyclic voltammogram of a) I (0.2 mM), b) I' (0.2 mM), and c) II (0.2 mM) in acetonitrile.



Fig. S4 Reaction profiles for the deoxygenation of 1a in the presence of II and I'. Reaction conditions: Catalyst (5.0 mol%), 1a (0.1 mmol), 4-methoxybenzyl alcohol (0.5 mmol), acetonitrile (1.0 mL), photo-irradiation ($\lambda > 400$ nm).



Fig. S5 UV/Vis spectra of **II** (0.2 mM) in the absence (black line) and presence (red line) of 4-methoxybenzyl alcohol (100 mM) in acetonitrile.



Fig. S6 CSI mass spectrum of the mixture of **II** and of 4-methoxybenzyl alcohol (500 equivalents with respect to **II**) in acetone. The sets of signals at m/z 3671 and 7101 were assignable to $[TBA_9H(ZnSi_2W_{20}O_{68})(C_8H_9O_2)_2]^{2+}$ and $[TBA_8H(ZnSi_2W_{20}O_{68})(C_8H_9O_2)_2]^{+}$, respectively.



Fig. S7 a) UV/Vis spectra of I' (0.2 mM) before (black line) and after (blue line) irradiation with visible light ($\lambda > 400$ nm) for 100 min in the presence of 4-methoxybenzyl alcohol (100 mM) in acetonitrile under Ar (1 atm), and the four-electron-reduced I' (0.2 mM, gray broken line) upon electrochemical reduction at -2.15 V (vs Ag/Ag⁺; four-electron reduction) in the presence of 4-methoxybenzyl alcohol (100 mM). b) UV/Vis spectra of the photo-reduced I' (0.2 mM) before (blue line) and after (black broken line) addition of 1a (100 equivalents with respect to I') in acetonitrile under Ar (1 atm).



Fig. S8 Reaction profiles of the deoxygenation of 1a in the presence of (a) II and (b) I'. Reaction conditions: Catalyst (5.0 mol%), 1a (0.1 mmol), 4-methoxybenzyl alcohol (0.5 mmol), acetonitrile (1.0 mL), photo-irradiation ($\lambda > 400$ nm). The initial reaction rates of II and I' were 2.0 and 1.6 mM min⁻¹, respectively.



Fig. S9 Reaction profiles of the deoxygenation of 1a in the presence of (a) II and (b) I'. k_{obs} vs. [4-methoxybenzyl alcohol] plots of the deoxygenation of 1a with (c) II and (d) I'. Reaction conditions: Catalyst (5.0 mol%), 1a (0.1 mmol), 4-methoxybenzyl alcohol (0.25 mmol, 0.5 mmol, 0.75 mmol), acetonitrile (1.0 mL), photo-irradiation ($\lambda > 400$ nm).



Fig. S10 Cyclic voltammogram of 1a (10 mM) in acetonitrile.



Fig. S11 a) Cyclic voltammogram of **II** (0.2 mM) before (black line) and after (red line) addition of **1a** (100 equivalents with respect to **II**) in acetonitrile, and b) **I'** (0.2 mM) before (black line) and after (red line) addition of **1a** (100 equivalents with respect to **I'**) in acetonitrile.



Fig. S12 CSI mass spectrum of the mixture of **II** and **1a** (20 equivalents with respect to **II**) in acetone. The signal at m/z 6938 was assignable to $[TBA_8H\{ZnSi_2W_{20}O_{69}(C_5H_5NO)\}]^+$.



Fig. S13 CSI mass spectrum of **II'** in acetonitrile. The sets of signals at m/z 3914 and 7585 were assignable to $[TBA_{12}(ZnSi_2W_{20}O_{70})]^{2+}$ and $[TBA_{11}(ZnSi_2W_{20}O_{70})]^+$, respectively.



Fig. S14 UV/Vis spectra of the two-electron-reduced **II**' (0.2 mM) before (blue line) and after (black line) addition of **1a** (200 equivalents with respect to **II**') in acetonitrile under Ar (1 atm).



Fig. S15 a) IR spectra of **II** (black line) and the retrieved **II** after the photocatalytic deoxygenation of pyridine *N*-oxide (red line). b) CSI mass spectrum of the retrieved **II** after the photocatalytic deoxygenation of pyridine *N*-oxide. The sets of signals at m/z 3563 and 6884 were assignable to $[TBA_9(ZnSi_2W_{20}O_{68})(CH_3CONH)]^{2+}$ and $[TBA_8(ZnSi_2W_{20}O_{68})(CH_3CONH)]^{+}$, respectively.



Fig. S16 CSI mass spectrum of **II** in acetone. The sets of signals at m/z 3543 and 6843, assignable to $[TBA_9H(ZnSi_2W_{20}O_{69})]^{2+}$ and $[TBA_8H(ZnSi_2W_{20}O_{69})]^+$, respectively.

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