Supporting Information for

Regioselective Functionalization of the Mesoporous Metal-Organic Framework, NU-1000, with Photo-active tris-(2,2'-Bipyridine)ruthenium(II)

Hisanori Nagatomi,a,b Leighanne C. Gallington,c Subhadip Goswami,a Jiaxin Duan,a Karena W. Chapman,d Nobuhiro Yanai,b,e Nobuo Kimizuka,b Omar K. Farhaa and Joseph T. Hupp,aa

aDepartment of Chemistry, Northwestern University 2145 Sheridan Road, Evanston, IL 60208-3113 (USA).
bDepartment of Chemistry and Biochemistry, Graduate School of Engineering, Center for Molecular Systems (CMS), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395 (Japan).
cX-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439-4858 (USA).
dDepartment of Chemistry, Stony Brook University, 100 Nichols Rd, Stony Brook, New York, 11794-3400

eJST-PRESTO, Honcho 4-1-8, Kawaguchi, Saitama 332-0012 (Japan)
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Section S1. Characterization

**Figure S1.** $^1$H-NMR spectrum of [Ru$^{II}$(bpy)$_2$(dcbpy)](PF$_6$)$_2$ (RuC$_{32}$H$_{24}$N$_6$O$_4$) measured in d$_6$-DMSO. Two protons of two carboxyl groups were not observed.

**Figure S2.** DRIFTS spectra of [Ru$^{II}$(bpy)$_2$(dcbpy)](PF$_6$)$_2$ (orange), Ru-NU-1000 (green), NU-1000 (blue) at room temperature. The peak at 1234 cm$^{-1}$ due to C-N stretching in Ru complex was also observed in Ru-NU-1000.
**Figure S3.** Pore diameter distribution of NU-1000 (blue) and Ru-NU-1000 (green).
Section S2. Difference envelope density (DED) analysis

Ambient temperature powder diffraction data were collected at beamline 17-BM-B at the Advanced Photon Source using 17.04 keV (0.72768 Å) x-rays. Capillaries were loaded with powdered samples, then placed into a sample changer cassette. Diffraction patterns were collected using an amorphous silicon area detector. Calibration and data reduction to one-dimensional patterns were performed using GSAS-II. \[1\] Lattice parameters were extracted from powder diffraction patterns via Le Bail whole pattern fitting.\[2,3\] A previously published crystal structure for NU-1000 (P6/mmm) was used as a starting model for these analyses.\[4\] Hexagonal lattice and pseudo-Voigt profile parameters were refined. Structure envelopes were generated from the extracted intensities of 24 reflections (out to \{6 -1 0\}) using previously described methods.\[3,5–7\] Difference envelope densities were then calculated via subtraction of the structure envelope of NU-1000 from that of Ru-NU-1000 to approximate the location of electron density associated with Ru.\[8\] Surfaces were drawn at >1.7σ level to preferentially show contributions from Ru.

Section S3. Photocatalytic reaction\[9,10\]

To demonstrate the photocatalytic ability of Ru-NU-1000, an amino oxidative coupling was performed. 3 mg of Ru-NU-1000 (the amount of Ru complex was calculated based on the ratio of Zr\(_6\) node and Ru complex in Ru-NU-1000 by ICP-OES) were dispersed in 1 ml toluene and 100 mol equivalent 4-methylbenzylamine against Ru complex were also added as a substrate. Then, the dispersion was sealed in a microwave glass tube, and the dispersion was purged with O\(_2\) for 1 minute. Then, the dispersion was irradiated with Blue LED (450 nm). After irradiation, the dispersion was filtered to remove insoluble contents. The filtrate was dried once under reduced pressure and re-dissolved in deuterochloroform for \(^1\)H-NMR measurement. The conversion yield for amine oxidative coupling of 4-methylbenzylamine was calculated by comparing integration ratio between the peak of substrate and product (Conversion yield = 2*Product / (Substrate + 2*Product)) (Fig. S4).

For the reuse experiment, once used Ru-NU-1000 was washed with acetonitrile several times and then used for a new photocatalytic reaction. Furthermore, the structure preservation of once used Ru-NU-1000 was confirmed PXRD measurement (Fig. S5).

As control experiments, the photocatalytic reaction was carried out with 1 mol% [Ru(bpy)\(_2\)(decbpy)](PF\(_6\))\(_2\) in acetonitrile and bare NU-1000 in toluene under the same condition. The amount of NU-1000 was calculated by subtracting the amount of Ru complex from 3 mg of Ru-NU-1000.
Figure S4. $^1$H-NMR spectra of each photocatalysis condition. The peaks around 3.8 ppm and 4.76 ppm were assigned to substrate and product, respectively.

Figure S5. PXRD patterns of Ru-NU-1000 once used for photocatalysis (red) and unused Ru-NU-1000 (green)
Figure S6. The diffuse reflectance UV spectra (left) and steady state emission spectra of NU-1000 and Ru-NU-1000.

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