

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. Farha^a and Joseph T. Hupp,^{a*}

^a*Department of Chemistry, Northwestern University 2145 Sheridan Road, Evanston, IL 60208-3113 (USA).*

^b*Department of Chemistry and Biochemistry, Graduate School of Engineering, Center for Molecular Systems (CMS), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395 (Japan).*

^c*X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439-4858 (USA).*

^d*Department of Chemistry, Stony Brook University, 100 Nichols Rd, Stony Brook, New York, 11794-3400*

^e*JST-PRESTO, Honcho 4-1-8, Kawaguchi, Saitama 332-0012 (Japan)*

Table of Contents

Section S1. **Characterization**

Section S2. **Difference envelope density analysis**

Section S3. **Photocatalytic reaction**

Section S1. Characterization

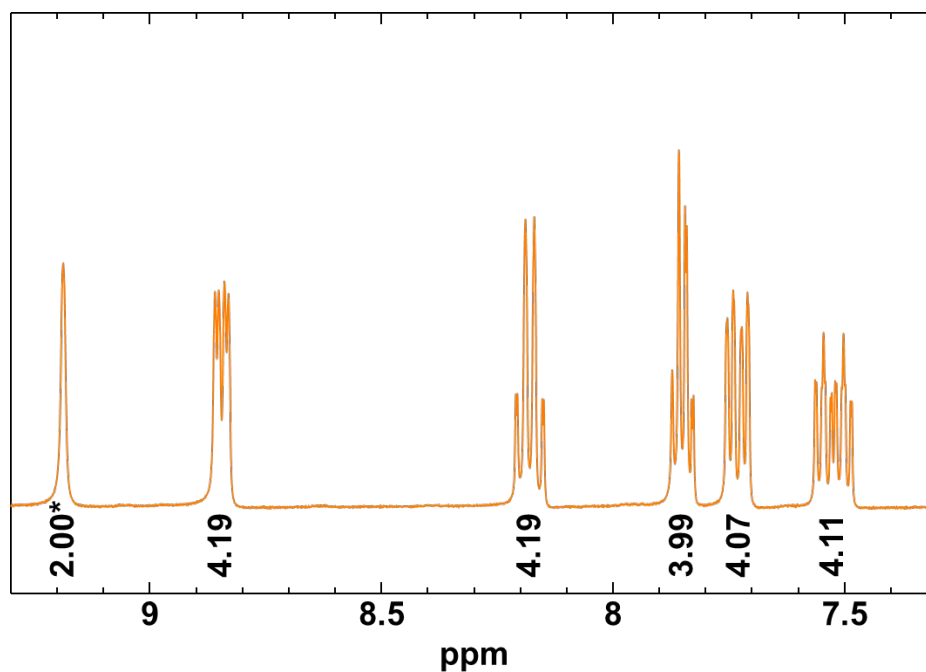


Figure S1. ^1H -NMR spectrum of $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{dcbpy})](\text{PF}_6)_2$ ($\text{RuC}_{32}\text{H}_{24}\text{N}_6\text{O}_4$) measured in d_6 -DMSO. Two protons of two carboxyl groups were not observed.

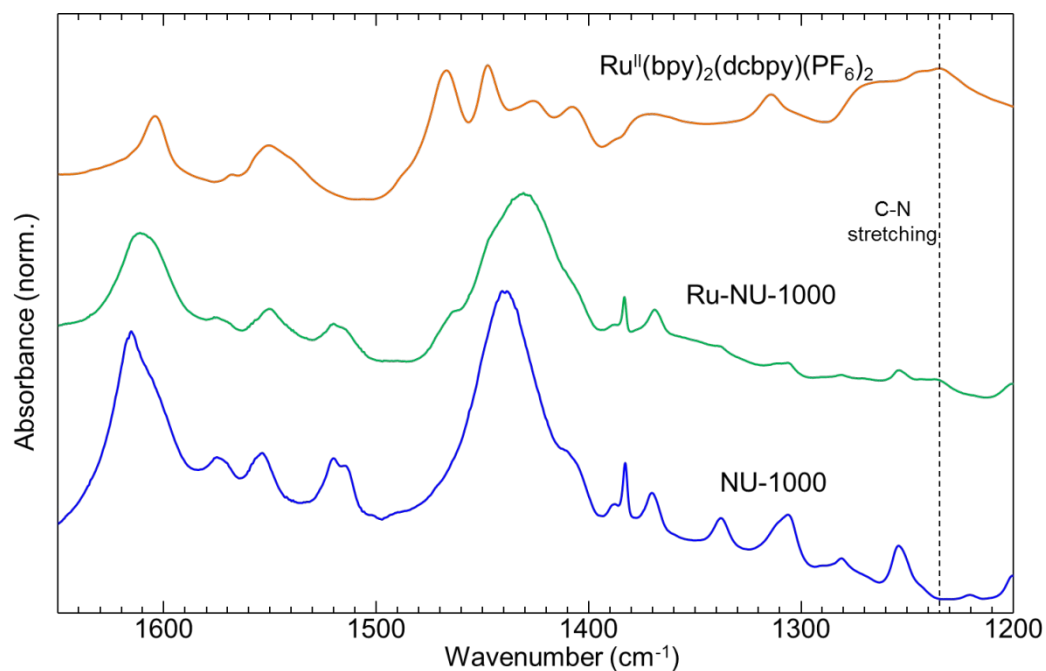


Figure S2. DRIFTS spectra of $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{dcbpy})](\text{PF}_6)_2$ (orange), Ru-NU-1000 (green), NU-1000 (blue) at room temperature. The peak at 1234 cm^{-1} due to C-N stretching in Ru complex was also observed in Ru-NU-1000.

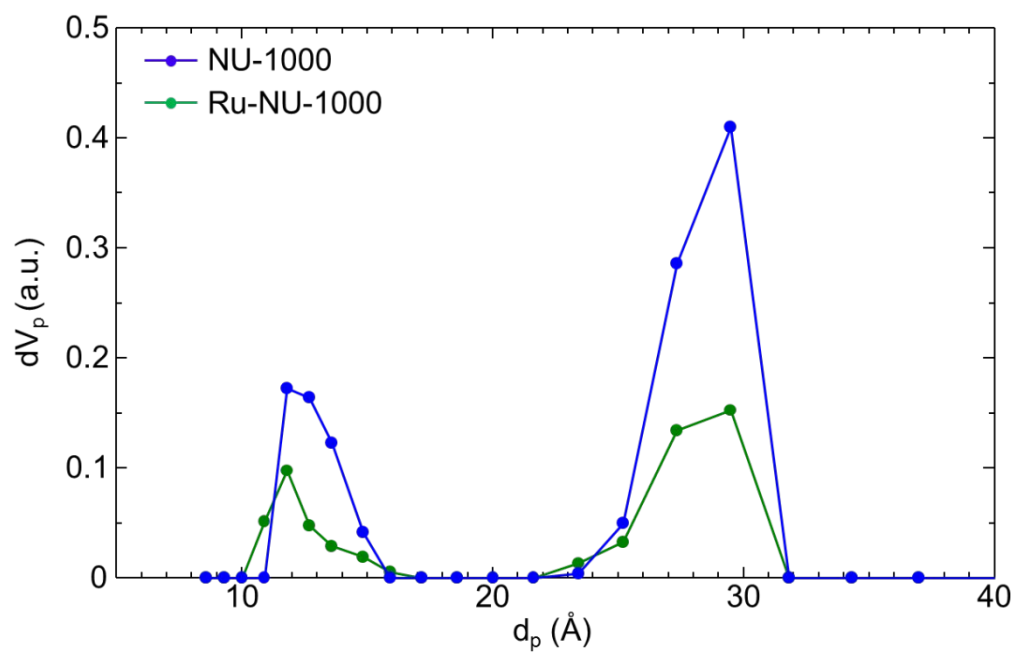


Figure S3. Pore diameter distribution of NU-1000 (blue) and Ru-NU-1000 (green).

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 $>1.7\sigma$ 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 Zr₆ 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 O₂ 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 deuteriochloroform for ¹H-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 = $2 \times \text{Product} / (\text{Substrate} + 2 \times \text{Product})$) (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(dcbpy)](PF₆)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

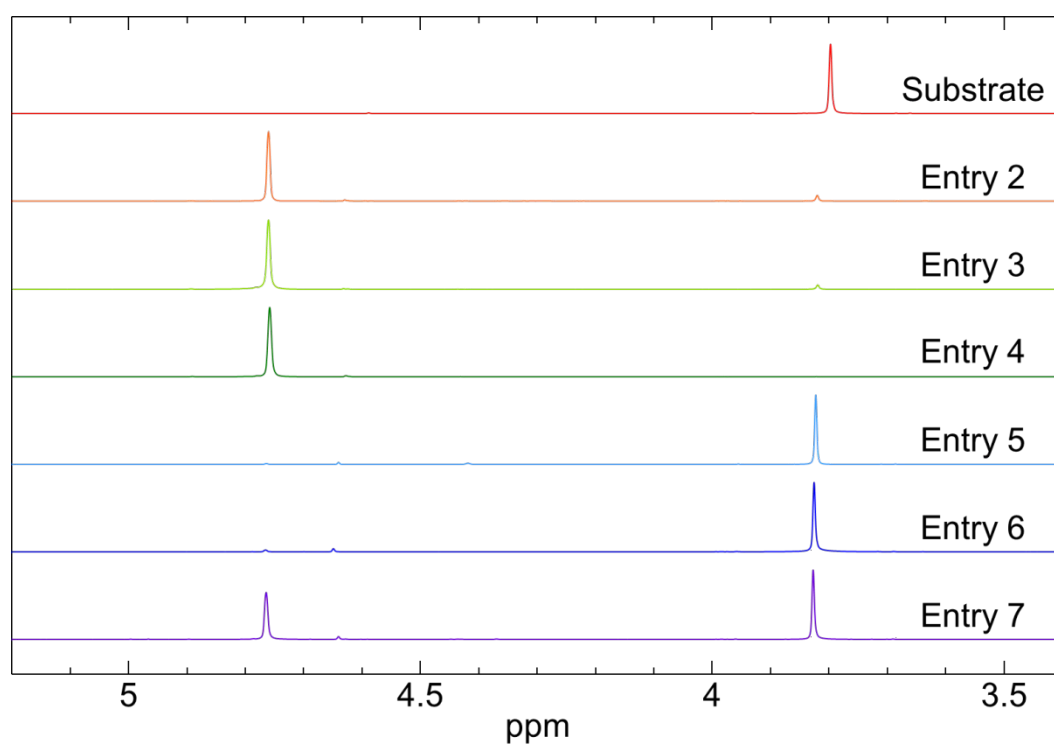


Figure S4. ^1H -NMR spectra of each photocatalysis condition. The peaks around 3.8 ppm and 4.76 ppm were assigned to substrate and product, respectively.

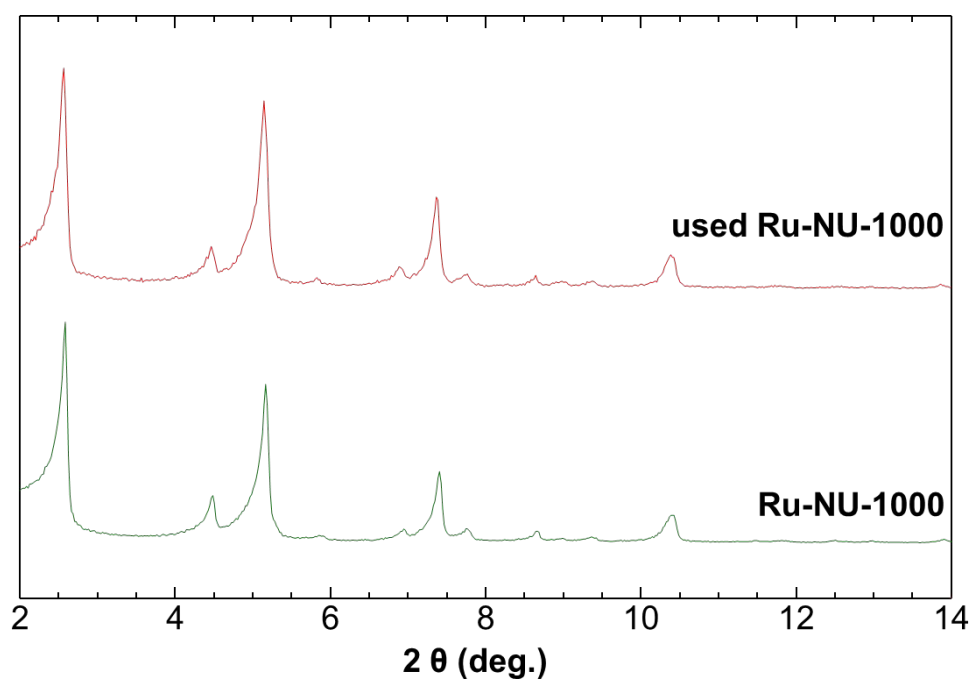


Figure S5. PXRD patterns of Ru-NU-1000 once used for photocatalysis (red) and unused Ru-NU-1000 (green)

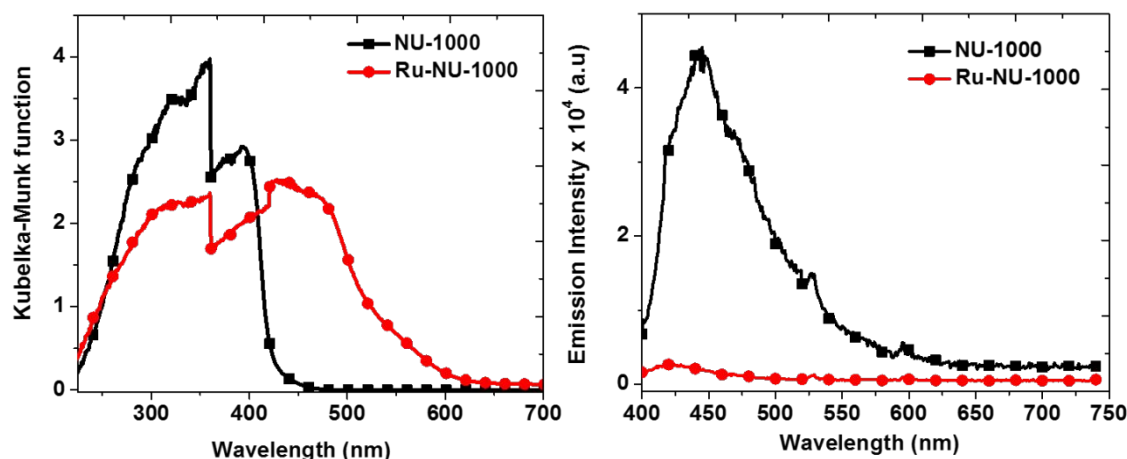


Figure S6. The diffuse reflectance UV spectra (left) and steady state emission spectra of NU-1000 and Ru-NU-1000.

References

- [1] B. H. Toby, R. B. Von Dreele, GSAS-II: the genesis of a modern open-source all-purpose crystallography software package. *J. Appl. Crystallogr.* **2013**, *46*, 544–549.
- [2] A. Le Bail, H. Duroy, J. L. Fourquet, Ab-initio Structure Determination of LiSbW₈ by X-ray Powder Diffraction. *Mater. Res. Bull.* **1988**, *23*, 447–452.
- [3] V. Petříček, M. Dušek, L. Palatinus, Crystallographic Computing System JANA2006: General features. *Zeitschrift für Krist. - Cryst. Mater.* **2014**, *229*, 345.
- [4] J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. DeMarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, Farha, O.K, Hupp, J.T., Vapor-Phase Metalation by Atomic Layer Deposition in a Metal–Organic Framework. *J. Am. Chem. Soc.* **2013**, *135*, 10294–10297.
- [5] A. A. Yakovenko, J. H. Reibenspies, N. Bhuvanesh, H.-C. Zhou, Generation and Applications of Structure Envelopes for Porous Metal–organic Frameworks *J. Appl. Crystallogr.* **2013**, *46*, 346–353.
- [6] L. B. McCusker, C. Baerlocher, R. Grosse-Kunstleve, S. Brenner, T. Wessels, Solving Complex Zeolite Structures from Powder Diffraction Data. *Chim. Int. J. Chem.* **2001**, *55*, 497–504.
- [7] L. B. McCusker, C. Baerlocher, Using Electron Microscopy to Complement X-ray Powder Diffraction Data to Solve Complex Crystal Structures. *Chem. Commun.* **2009**, 1439–1451.
- [8] A. A. Yakovenko, Z. Wei, M. Wriedt, J.-R. Li, G. J. Halder, H.-C. Zhou, Study of Guest Molecules in Metal–Organic Frameworks by Powder X-ray Diffraction: Analysis of Difference Envelope Density. *Cryst. Growth Des.* **2014**, *14*, 5397–5407.
- [9] J. H. Ko, N. Kang, N. Park, H.-W. Shin, S. Kang, S. M. Lee, H. J. Kim, T. K. Ahn, S. U. Son, Hollow Microporous Organic Networks Bearing Triphenylamines and Anthraquinones: Diffusion Pathway Effect in Visible Light-Driven Oxidative Coupling of Benzylamines *ACS Macro Lett.* **2015**, *4*, 669–672.
- [10] C. Wang, Z. Xie, K. E. Dekrafft, W. Lin, Doping Metal–Organic Frameworks for Water

Oxidation, Carbon Dioxide Reduction, and Organic Photocatalysis *J. Am. Chem. Soc.* **2011**, *133*, 13445–13454.