

Communication

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Photosensitizing Metal-Organic Layers for Efficient Sunlight-Driven Carbon Dioxide Reduction

Guangxu Lan,^{1,†} Zhe Li,^{1,2,†} Samuel S. Veroneau,¹ Yuan-Yuan Zhu,¹ Ziwan Xu,¹ Cheng Wang,² and Wenbin Lin^{1,2,*}

¹Department of Chemistry, The University of Chicago, 929 E 57th Street, Chicago, Illinois 60637, United States

²College of Chemistry and Chemical Engineering, iCHEM, State Key Laboratory of Physical Chemistry of Solid Surface,

Xiamen University, Xiamen 361005, P.R. China

Supporting Information Placeholder

ABSTRACT: Metal-organic Layers (MOLs), a free-standing monolayer version of two-dimensional metal-organic frameworks (MOFs), have emerged as a new class of 2D materials for many potential applications. Here we report the design of a new photosensitizing MOL, Hf₁₂-Ru, based on Hf₁₂ secondary building units (SBUs) and $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) derived dicarboxylate ligands. After modifying the SBU surface of Hf12-Ru with $M(bpy)(CO)_3X$ (M = Re and X = Cl or M = Mn and X = Br) derived capping molecules through carboxylate exchange reactions, the resultant Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn MOLs possess both [Ru(bpy)₃]²⁺ photosensitizers and M(bpy)(CO)₃X catalysts for efficient photocatalytic CO₂ reduction. The proximity of the MOL skeleton to the capping ligands (1-2 nm) facilitates electron transfer from photoexcited $[Ru(bpy)_3]^{2+*}$ to $M^1(bpy)(CO)_3X$ (M = Re, Mn) catalytic centers, resulting in CO₂ reduction turnover numbers of 8,613 under artificial visible light and of 670 under sunlight. MOLs thus represent a novel platform to assemble multifunctional materials for studying artificial photosynthesis.

Metal-organic frameworks (MOFs) have recently provided a versatile material platform to study artificial photosynthesis and photocatalysis,¹⁻³ including proton reduction,⁴⁻⁷ CO₂ reduction,⁸⁻¹² water oxidation,¹³ and organic photocatalysis.¹⁴⁻¹⁷ Structural regularity and synthetic tunability of MOFs allow hierarchical integration of multiple functional moieties, including photosensitizers (PSs) and catalytic centers, to facilitate multi-electron or radical transfer in photoreactions.^{2, 18} However, due to intrinsically high absorptivity of most PSs, only superficial layers of MOFs are involved in photoreactions. Light scattering by MOF particles also reduces photon utilization. Furthermore, photocatalytic efficiency of MOFs is limited by restricted diffusion of radicals and other energetic intermediates through MOF channels. By reducing one dimension of MOFs to a single layer, metal-organic layers (MOLs) have recently emerged as a new class of functionalizable 2D materials for many applications.¹⁹⁻²² We believe that MOLs can overcome the aforementioned issues for MOFs due to their thinness and hold great promise for applications in artificial photosynthesis and photocatalysis.

Sunlight-driven CO₂ reduction to energy-rich compounds represents a promising approach to overcome the shortage of fossil fuels and to mitigate climate change.²³⁻³¹ Among many photocatalytic systems for CO₂ reduction, combinations of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) as a PS and Re^I(bpy)(CO)₃Cl as a CO₂ reduction catalyst have been most extensively studied due to their

ability to generate CO with high selectivity and efficiency.³²⁻³⁶ Previous studies have demonstrated an improvement of photocatalytic CO₂ reduction efficiency by linking $[Ru(bpy)_3]^{2+}$ and $Re^{I}(bpy)(CO)_3CI$ moieties in supramolecular systems.³⁷⁻³⁸ Herein we report the design of the first photosensitizing MOL, Hf₁₂-Ru, built from Hf_{12} secondary building units (SBUs) and $[Ru(bpy)_3]^2$ derived dicarboxylate ligands. SBU surface capping of Hf12-Ru with Re^I(bpy)(CO)₃Cl or Mn^I(bpy)(CO)₃Br derived monocarboxylic acids afforded multifunctional Hf12-Ru-Re and Hf12-Ru-Mn MOLs for efficient photocatalytic CO₂ reduction. The proximity of photosensitizing Hf12-Ru MOL skeleton to the capping monocarboxylate ligands (1-2 nm) facilitates multi-electron transfer from photoexcited $[Ru(bpy)_3]^{2+*}$ to $M^I(bpy)(CO)_3X$ (M = Re, Mn) catalytic centers, reaching 24-hour turnover numbers (TONs) of 3,849 and 1,347, respectively (Scheme 1). Remarkably, Hf₁₂-Ru-Re catalyzed sunlight-driven CO₂ reduction with a TON of 670 in 6 hours of daylight.

Scheme 1. Schematic showing the synthesis of Hf_{12} -Ru-M (M = Re or Mn) via monocarboxylic acid exchange of Hf_{12} -Ru and sunlight-driven CO₂ reduction.



 Hf_{12} -Ru MOLs were synthesized through a solvothermal reaction between $HfCl_4$ and $bis(2,2^{-}bipyridine)[5,5^{-}di(4-carboxyl$ $phenyl)-2,2^{-}bipyridine]ruthenium(II) dichloride (H₂L-Ru), in$ N,N-dimethylformamide (DMF) at 80 °C with trifluoroacetic acid $(TFA) and water as modulators (Figure S1, SI). <math>Hf_{12}$ -Ru is proposed as the first MOL constructed from Hf_{12} SBUs and laterally

connected linear **L**-Ru linkers to form an infinite 2D network of kagome dual (**kgd**) topology. Each Hf₁₂ SBU is also vertically capped by six TFA groups. Hf₁₂-Ru thus has a formula of Hf₁₂(μ_3 -O)₈(μ_3 -OH)₈(μ_2 -OH)₆(TFA)₆(L-Ru)₆. 2D Hf₁₂-Ru MOL forms in part due to stronger Hf-carboxylate bonds in the lateral direction than those in the vertical direction as we recently observed in Hf₁₂-based MOFs.³⁹



Figure 1. TEM (a) and HRTEM (b) of Hf_{12} -Ru. (c) PXRD pattern of Hf_{12} MOLs in comparison to the simulated pattern.⁴⁰ AFM topography (d) and height profile (e) of Hf_{12} -Ru. (f) Schematic showing a Hf_{12} cluster capped by TFA groups with an estimated height of ~1.7 nm.

Transmission electron microscopy (TEM) imaging showed Hf₁₂-Ru as flat nanoplates of \sim 100 nm in diameter (Figure 1a). The low contrast of the TEM images is consistent with the monolayer nature of Hf₁₂-Ru, which is confirmed by a nanoplate thickness of ~1.6 nm observed by atomic force microscopy (AFM, Figure 1d, e and Figure S4, SI). This thickness is consistent with the modeled height of Hf_{12} clusters capped with TFA groups (~1.7 nm, Figure 1f). High-resolution TEM (HRTEM) imaging confirmed the topological structure of Hf₁₂-Ru with lattice points corresponding to Hf₁₂ SBUs and fast Fourier transform (FFT) revealing a six-fold symmetry (Figure 1b) that is consistent with the projection of Hf₁₂-Ru structure along the vertical direction. The distance between adjacent lattice points in HRTEM images was measured to be 2.7 nm, matching the distance between adjacent Hf₁₂ SBUs. Moreover, the powder X-ray diffraction (PXRD) pattern of Hf12-Ru matched well with that simulated from the proposed Hf₁₂ MOL structure (Figure 1c).⁴⁰ All of these data support the proposed monolayer structure of Hf₁₂-Ru. Furthermore, the ¹H NMR spectrum of digested Hf₁₂-Ru showed all signals corresponding to H₂L-Ru without any other aromatic signals, which confirms the presence of only L-Ru ligands in Hf12-Ru

(Figure S3, SI). Finally, Hf_{12} -Ru showed similar absorption and emission spectra as H_2 L-Ru (Figure S5, SI), suggesting photosensitizing ability of Hf_{12} -Ru.



Figure 2. (a) NMR spectrum of digested Hf_{12} -Ru-MBA. Yellow and green stars correspond to L-Ru ligands and MBA ligands, respectively. TEM (b), EXAFS fitting (c), AFM topography (d) and height profile (e) of Hf_{12} -Ru-Re.

Hf₁₂-Ru was modified with 2-(5'-methyl-[2,2'-bipyridin]-5yl)acetic acid (H-MBA) ligands on the surface to afford Hf₁₂-Ru-MBA by replacing weakly coordinating TFA groups on SBUs with MBA ligands. The ¹H NMR spectrum of digested Hf₁₂-Ru-MBA gave an MBA to L-Ru ratio of ~1:1 (Figure 2a and S8, SI), indicating complete replacement of TFA groups in Hf₁₂-Ru-MBA to give a formula of Hf₁₂(μ_3 -O)₈(μ_3 -OH)₈(μ_2 -OH)₆(MBA)₆(L-Ru)₆. Additionally, no signal corresponding to TFA was detected in the ¹⁹F NMR spectrum of digested Hf₁₂-Ru-MBA (Figure S9, SI). PXRD studies indicated that Hf₁₂-Ru-MBA exhibited the same structure as Hf₁₂-Ru (Figure 1c).

 Hf_{12} -Ru-MBA was then metalated with $Re(CO)_5Cl$ or $Mn(CO)_5Br$ to afford Hf_{12} -Ru-Re with the catalytic center $Re(MBA)(CO)_3Cl$ that is an analogue of $Re^l(bpy)(CO)_3Cl$ or Hf_{12} -Ru-Mn with the catalytic center $Mn(MBA)(CO)_3Br$ that is an analogue of $Mn^l(bpy)(CO)_3Br$. Hf_{12} -Ru-Re and Hf_{12} -Ru-Mn showed similar sizes and morphologies to Hf_{12} -Ru by TEM (Figure 2b and Figure S15, SI) and maintained the same structure as Hf_{12} -Ru as indicated by PXRD (Figure 1c). AFM studies showed that the thickness of Hf_{12} -Ru-Re and Hf_{12} -Ru-Mn increased to ~3.7 nm (Figure 2d, e, Figures S14, and S16, SI), which is consistent with the height of Hf_{12} clusters capped with MBA ligands (3.2-4.0 nm, Figure S19, SI). In Hf_{12} -Ru-Re and Hf_{12} -Ru-Mn, each catalytic center is adjacent to six L-Ru ligands, which enables multi-electron transfer from L-Ru to $Re(MBA)(CO)_3Cl$ or $Mn(MBA)(CO)_3Br$. Electron transfer was further facilitated by a

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short distance of 1.3 nm between each catalytic center and its nearest L-Ru ligand (Figure S20, SI).

Re and Mn coordination environments of Hf₁₂-Ru-Re, Hf₁₂-Ru-Mn, and Re(MeMBA)(CO)₃Cl and Mn(MeMBA)(CO)₃Br $\{MeMBA = methyl 2-(5'-methyl-[2,2'-bipyridin]-5-yl)acetate,$ Figure S10-13, SI} were determined by X-ray absorption spectroscopy. Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn showed similar extended X-ray absorption fine structure (EXAFS) profiles to Re(MeMBA)(CO)₃Cl and Mn(MeMBA)(CO)₃Br (Figure S22, SI), which were well fitted with their corresponding molecular models [Re(bpy)(CO)₃Cl for Hf₁₂-Ru-Re and Mn(bpy)(CO)₃Br for Hf₁₂-Ru-Mn, Figure 2c, S23-26, SI]. Moreover, Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn showed similar CO stretching vibrations and characteristic UV-Vis absorptions when compared to Re(MeMBA)(CO)₃Cl and Mn(MeMBA)(CO)₃Br, respectively (Figure S17-18, SI). These results indicate that Hf₁₂-Ru-Re and Hf12-Ru-Mn exhibit the same Re and Mn coordination environments as molecular photocatalytic CO2 reduction catalysts Re^l(bpy)(CO)₃Cl and Mn^l(bpy)(CO)₃Br, respectively.



Figure 3. Time-dependent CO generation TONs of Hf_{12} -Ru-Re (a) and Hf_{12} -Ru-Mn (b) along with their homogeneous controls H_2 L-Ru plus Re(MeMBA)(CO)₃Cl and H_2 L-Ru plus Mn(MeMBA)(CO)₃Br. N = 3. (c) PXRD patterns of Hf_{12} -Ru, Hf_{12} -Ru-Re, and Hf_{12} -Ru-Mn after photocatalysis. (d) Plots of CO generation TONs for Hf_{12} -Ru-Re in five consecutive runs (Section S4.2, SI).

Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn provide an excellent opportunity to test whether capping the surface of photosensitizing Hf₁₂-Ru with Re(MBA)(CO)₃Cl or Mn(MBA)(CO)₃Br catalyst could facilitate multi-electron transfer from photoexcited Hf12-Ru to catalytic Re or Mn centers to drive efficient CO₂ reduction (Scheme 1). The catalytic activities for visible-light driven ($\lambda > 400$ nm) CO₂ reduction of Hf₁₂-Ru-Re, Hf₁₂-Ru-Mn, and homogenous controls H₂L-Ru plus Re(MeMBA)(CO)₃Cl, or H₂L-Ru plus Mn(Me-MBA)(CO)₃Br) were studied in an oxygen-free CH₃CN solution with saturated CO₂, triethanolamine (TEOA), and 1-benzyl-1,4dihydronicotinamide (BNAH) or 1,3-dimethyl-2-phenyl-2,3dihydro-1H-benzo[d]imidazole (BIH) as sacrificial electron donor. The amount of generated CO was quantified by gas chromatography (GC) analysis of the headspace gas. The turnover number (TON) [defined as n(CO)] reached 3849 (BIH) or 2092 (BNAH) for Hf12-Ru-Re and 1367 (BIH) or 240 (BNAH) for Hf₁₂-Ru-Mn after 24 h irradiation (Figure 3a, b), which are superior to previously reported molecular systems (Table S6, SI). In comparison, H₂L-Ru plus Re(MeMBA)(CO)₃Cl and H₂L-Ru plus Mn(MeMBA)(CO)₃Br exhibited modest TONs of <54 under the same conditions. Greater than 70-fold increase in catalytic activity for Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn over their homogenous controls confirms the important role of hierarchical organization of PSs and Re or Mn catalytic centers in the MOLs in facilitating multielectron transfer processes to drive photocatalytic CO_2 reduction.

The CO₂ reduction product selectivity for Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn was examined by quantifying the amounts of HCOOH generated using high performance liquid chromatography (HPLC) (Figure S27 and Table S5, SI). Similar to previously reported molecular systems,^{38, 41} Hf₁₂-Ru-Re showed a ~98% selectivity for CO, while Hf₁₂-Ru-Mn generated more HCOOH with a 82% selectivity for CO.

To confirm the structural stability of the MOLs following 24hour CO₂ reduction, Hf₁₂-Ru, Hf₁₂-Ru-Re, and Hf₁₂-Ru-Mn were centrifuged from the reaction suspensions. The recovered MOLs showed the same PXRD patterns as freshly prepared MOLs (Figure 3c) with <1% leaching of Hf by inductively coupled plasma mass spectrometry. The recovered MOLs also showed similar CO stretching vibrations and characteristic UV-Vis absorptions to freshly prepared MOLs (Figure S28, 29, SI). To further confirm the photocatalytic durability of these MOLs, Hf₁₂-Ru-Re was used in 5 consecutive cycles of CO₂ reduction, showing consistent catalytic activity with a total TON of 8,613 (Figure 3d).

The CO₂ reduction mechanism was investigated by photophysical and electrochemical studies. The phosphorescence spectra of Hf₁₂-Ru were measured with the addition of different equivalence of BIH or Re(MeMBA)(CO)₃Cl. As shown in the Figure S30, the phosphorescence of Hf₁₂-Ru was efficiently quenched by BIH but not by Re(MeMBA)(CO)₃Cl, indicating that the excited Hf₁₂-Ru was reductively quenched by BIH to generate [Hf₁₂-Ru]⁻ (Figure S30, SI). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies demonstrated that Hf₁₂-Ru had similar reduction potential to H₂L-Ru (E^{red}_{1/2} = -0.89 V vs SCE, corresponding to Hf₁₂-Ru to [Hf₁₂-Ru]⁻), which is negative enough to reduce Re(MeMBA)(CO)₃Cl (E^{red}_{1/2} = -0.34 V vs SCE, Figure S31 and Table S7, SI). Moreover, we showed that the photocatalytic efficacy of Hf₁₂-Ru-Re system is sensitive to the distance between L-Ru photosensitizing center and the capping Re catalytic center (Figure S32-34 and Table S8, SI).



Figure 4. Sunlight-driven CO_2 reduction TONs of Hf_{12} -Ru-Re in 6 hours.

We next examined Hf_{12} -Ru-Re catalyzed CO_2 reduction upon sunlight irradiation. The Hf_{12} -Ru-Re reaction suspension was prepared as above, and placed near a window inside a chemistry laboratory at the University of Chicago. This suspension was stirred from 11:00 am to 5:00 pm on Jun. 18th to Jun. 24th in 2018 (Figure S35, SI). Remarkably, Hf_{12} -Ru-Re catalyzed CO_2 reduction under sunlight irradiation with unprecedented efficiency, reaching a TON of 670 in 6 h (Figure 4). The effectiveness of Hf_{12} -Ru-Re catalyzed sunlight-driven CO_2 reduction was understandably weather dependent, with the highest TON of 670 achieved on sunny Jun. 18th, 2018 and the lowest TON of 138 observed on rainy Jun. 22^{nd} , 2018. To the best of our knowledge, this work presents the first study of sunlight-driven CO₂ reduction using a combination of [Ru(bpy)₃]²⁺ as a PS and Re^I(bpy)(CO)₃Cl as a CO₂ reduction catalyst.

In summary, we have synthesized the first MOL based on readily functionalizable linear dicarboxylate ligands. The postsynthetic functionalization of photosensitizing Hf₁₂-Ru MOL with $M(bpy)(CO)_3X$ (M = Re or Mn) moieties via carboxylate exchange reactions afforded Hf₁₂-Ru-Re and Hf₁₂-Ru-Mn MOLs that possess both [Ru(bpy)₃]²⁺ photosensitizers (PSs) and $M(bpy)(CO)_3X$ catalysts for efficient photocatalytic CO₂ reduction. We showed that multi-electron transfer from photoexcited [Ru(bpy)₃]^{2+*} to $M^1(bpy)(CO)_3X$ (M = Re, Mn) catalytic centers is greatly facilitated by the proximity of the photosensitizing MOL skeleton to the capping CO₂ reduction turnover numbers (TONs) of 8,613 under artificial visible light and of 670 under sunlight. This work thus provides a versatile synthetic strategy to multifunctional MOLs for studying artificial photosynthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <u>http://pubs.acs.org</u>. Synthesis and characterization of MOLs, X-ray absorption spectroscopy, and photocatalytic CO₂ reduction procedures.

AUTHOR INFORMATION

Corresponding Author

*wenbinlin@uchicago.edu

Author Contributions

[†]These authors contributed equally.

Notes

The authors declare no competing financial interests.

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REFERENCES

- 1. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. Science **2013**, *341* (6149), 1230444.
- 47 2013, 341 (6149), 1230444.
 48 2. Zhang, T.; Lin, W. Chem. Soc. Rev. 2014, 43 (16), 5982-5993.
 - 3. Cook, T. R.; Zheng, Y.-R.; Stang, P. J. Chem. Rev. 2012, 113 (1), 734-777.
- 4. Lan, G.; Zhu, Y.-Y.; Veroneau, S. S.; Xu, Z.; Micheroni, D.; Lin, W. J.
 Am. Chem. Soc. 2018, 140 (16), 5326-5329.
- *Am. Chem. Soc.* 2018, 140 (16), 5326-5329.
 5. Fateeva, A.; Chater, P. A.; Ireland, C. P.; Tahir, A. A.; Khimyak, Y. Z.; Wiper, P. V.; Darwent, J. R.; Rosseinsky, M. J. Angew. Chem. Int. Ed.
 2012, 51 (30), 7440-7444.
- 54 6. Wang, C.; DeKrafft, K. E.; Lin, W. J. Am. Chem. Soc. 2012, 134 (17), 7211-7214.
- 55 7211-7214. 7. Yuan, S.; Qin, J.-S.; Xu, H.-Q.; Su, J.; Rossi, D.; Chen, Y.; Zhang, L.;
- Lollar, C.; Wang, Q.; Jiang, H.-L. ACS Cent. Sci. 2017, 4 (1), 105-111.

- 8. Blake, A. J.; Champness, N. R.; Easun, T. L.; Allan, D. R.; Nowell, H.; George, M. W.; Jia, J.; Sun, X.-Z. Nat. Chem. **2010**, *2* (8), 688.
- 9. Fu, Y.; Sun, D.; Chen, Y.; Huang, R.; Ding, Z.; Fu, X.; Li, Z. Angew.
- Chem. Int. Ed. 2012, 51 (14), 3364-3367.
- 10. Wang, C.; Xie, Z.; deKrafft, K. E.; Lin, W. J. Am. Chem. Soc. 2011, 133 (34), 13445-13454.
- 11. Xu, H.-Q.; Hu, J.; Wang, D.; Li, Z.; Zhang, Q.; Luo, Y.; Yu, S.-H.; Jiang, H.-L. J. Am. Chem. Soc. **2015**, *137* (42), 13440-13443.
- 12. Fei, H.; Sampson, M. D.; Lee, Y.; Kubiak, C. P.; Cohen, S. M. *Inorg. Chem.* **2015**, *54* (14), 6821-6828.
- 13. Paille, G. g.; Gomez-Mingot, M.; Roch-Marchal, C.; Lassalle-Kaiser, B.; Mialane, P.; Fontecave, M.; Mellot-Draznieks, C.; Dolbecq, A. J. Am. Chem. Soc. **2018**, *140* (10), 3613-3618.
- 14. Zhang, Y.; Guo, J.; Shi, L.; Zhu, Y.; Hou, K.; Zheng, Y.; Tang, Z. Sci. Adv. 2017, 3 (8), e1701162.
- 15. Yu, X.; Cohen, S. M. J. Am. Chem. Soc. 2016, 138 (38), 12320-12323.
- 16. Liu, Y.; Howarth, A. J.; Hupp, J. T.; Farha, O. K. Angew. Chem. 2015, 127 (31), 9129-9133.
- 17. Johnson, J. A.; Zhang, X.; Reeson, T. C.; Chen, Y.-S.; Zhang, J. J. Am. Chem. Soc. **2014**, *136* (45), 15881-15884.
- 18. Cui, Y.; Yue, Y.; Qian, G.; Chen, B. Chem. Rev. 2011, 112 (2), 1126-1162.
- 19. Cao, L.; Lin, Z.; Peng, F.; Wang, W.; Huang, R.; Wang, C.; Yan, J.; Liang, J.; Zhang, Z.; Zhang, T. *Angew. Chem. Int. Ed.* **2016**, *55* (16), 4962-4966.
- 20. Lan, G.; Ni, K.; Xu, R.; Lu, K.; Lin, Z.; Chan, C.; Lin, W. Angew. Chem. 2017, 129 (40), 12270-12274.
- 21. Lin, Z.; Thacker, N. C.; Sawano, T.; Drake, T.; Ji, P.; Lan, G.; Cao, L.; Liu, S.; Wang, C.; Lin, W. *Chem. Sci.* **2018**, *9* (1), 143-151.
- 22. Zhao, M.; Wang, Y.; Ma, Q.; Huang, Y.; Zhang, X.; Ping, J.; Zhang, Z.; Lu, Q.; Yu, Y.; Xu, H. *Adv. Mater.* **2015**, *27* (45), 7372-7378.
- 23. Berardi, S.; Drouet, S.; Francas, L.; Gimbert-Suriñach, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. *Chem. Soc. Rev.* **2014**, *43* (22), 7501-7519.
- 24. Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. *Chem. Rev.* **2013**, *113* (8), 6621-6658.
- 25. Roy, S. C.; Varghese, O. K.; Paulose, M.; Grimes, C. A. Acs Nano 2010, 4 (3), 1259-1278.
- 26. Sakimoto, K. K.; Wong, A. B.; Yang, P. Science 2016, 351 (6268), 74-77.
- 27. Yu, J.; Low, J.; Xiao, W.; Zhou, P.; Jaroniec, M. J. Am. Chem. Soc. 2014, 136 (25), 8839-8842.
- 28. Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. *Annu. Rev. Phys. Chem.* **2012**, *63*, 541-569.
- 29. Diercks, C. S.; Liu, Y.; Cordova, K. E.; Yaghi, O. M. Nat. Mater. 2018, 1.
- 30. McDaniel, N. D.; Bernhard, S. Dalton Trans. 2010, 39 (42), 10021-10030.
- 31. Hou, J.; Cao, S.; Wu, Y.; Liang, F.; Ye, L.; Lin, Z.; Sun, L. Nano Energy **2016**, *30*, 59-68.
- 32. Hawecker, J.; Lehn, J.-M.; Ziessel, R. J. Chem. Soc., Chem. Commun. 1983, (9), 536-538.
- 33. Morris, A. J.; Meyer, G. J.; Fujita, E. Acc. Chem. Res. 2009, 42 (12), 1983-1994.
- 34. Takeda, H.; Ishitani, O. Coord. Chem. Rev. 2010, 254 (3-4), 346-354.
- 35. Windle, C. D.; Perutz, R. N. Coord. Chem. Rev. 2012, 256 (21-22), 2562-2570
- 36. Won, D.-I.; Lee, J.-S.; Ji, J.-M.; Jung, W.-J.; Son, H.-J.; Pac, C.; Kang, S. O. J. Am. Chem. Soc. **2015**, *137* (42), 13679-13690.
- 37. Gholamkhass, B.; Mametsuka, H.; Koike, K.; Tanabe, T.; Furue, M.;
- Ishitani, O. *Inorg. Chem.* **2005**, *44* (7), 2326-2336. 38. Tamaki, Y.; Ishitani, O. *ACS Catal.* **2017**, *7* (5), 3394-3409.
- 39. Dai, R.; Peng, F.; Ji, P.; Lu, K.; Wang, C.; Sun, J.; Lin, W. Inorg.
- *Chem.* **2017**, *56* (14), 8128-8134.
- 40. PXRD pattern was simulated by complete integrating method in real space.
- 41. Grills, D. C.; Ertem, M. Z.; McKinnon, M.; Ngo, K. T.; Rochford, J. Coord. Chem. Rev. 2018, 374, 173-217.

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58 59 60

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