Very Important Paper



Application of Electron-Rich Covalent Organic Frameworks COF-JLU25 for Photocatalytic Aerobic Oxidative Hydroxylation of Arylboronic Acids to Phenols

Guangjun Xiao⁺,^[a, b, c] Wenqian Li⁺,^[a, b] Tao Chen,^[a, b] Wei-Bo Hu,^[a, b] Hui Yang,^[a, b, c] Yahu A. Liu,^[d] and Ke Wen^{*[a, b, c]}

Visible-light-driven organic reactions are environmentally friendly green chemical transformations among which photosynthetic oxidative hydroxylation of arylboronic acids to phenols has attracted increasing research interest during the very recent years. Given the efficiency and reusability of heterogeneous catalysts, COF-JLU25, an electron-rich COFbased photocatalyst constructed by integrating electron-donating blocks 1,3,6,8-tetrakis(4-aminophenyl)pyrene (PyTA) and 4-

Introduction

Visible-light-driven organic reactions are environmentally friendly alternatives to chemical transformations.^[1] Since phenols are important intermediates widely found in natural products and pharmaceutical drug candidates, recent years have seen increasing attention to mild and efficient photosynthetic methods for hydroxylation of arylboronic acids to phenols.^[2] In order to enhance catalytic activities, various porous organic-based photocatalysts (POPs)^[3] have been designed, including covalent organic frameworks (COFs),^[2c,4] metal-organic frameworks (MOFs),^[2g,i] porous coordination polymers (PCPs),^[5] conjugated microporous polymers (CMPs),^[6] and hyper-crosslinked polymers (HCPs).^[7] Among those photocatalysts, COFs are especially fascinating owing to properties such as large surface area, structural versatility, easy post-synthetic modification, and high chemical stability.^[8] Furthermore, COFbased photocatalysts display longer-wavelength absorption, good fluorescence properties, and efficient charge transmission, originated from their tunable band gaps, extended π -conju-

- [a] G. Xiao,⁺ W. Li,⁺ T. Chen, W.-B. Hu, Prof. Dr. H. Yang, Prof. Dr. K. Wen Shanghai Advanced Research Institute, Chinese Academy of Sciences Shanghai 201210, P. R. China E-mail: wenk@sari.ac.cn
- [b] G. Xiao,⁺ W. Li,⁺ T. Chen, W.-B. Hu, Prof. Dr. H. Yang, Prof. Dr. K. Wen University of Chinese Academy of Sciences Beijing 100049, P.R. China
- [C] G. Xiao,⁺ Prof. Dr. H. Yang, Prof. Dr. K. Wen School of Physical Science and Technology, ShanghaiTech University Shanghai 201210, P. R. China
- [d] Dr. Y. A. Liu Medicinal Chemistry, ChemBridge Research Laboratories, San Diego CA 92127, USA
- [⁺] Authors contributed equally to this work.
- Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202100173

[4-(4-formylmethyl)-2,5-dimethoxyphenyl] benzaldehyde (TpDA), was selected as a photocatalyst for the oxidative hydroxylation of arylboronic acids. In our studies, COF-JLU25 demonstrated excellent photocatalytic activity with high efficiency, robust reusability, and low catalyst loading, showcasing an application potential of previously underexplored COF-based photocatalyst composed solely of electron-rich units.

gated frameworks, and π - π stacking columns.^[9] When COFbased catalysts specially designed for oxidative hydroxylation reactions were irradiated under visible light, the electron generated could be transferred to O2, forming superoxide radical anion $O_2^{\bullet-.[2b,c]}$ As $O_2^{\bullet-}$ is a critical active propellant to drive the oxidative hydroxylation of arylboronic acids to phenols, the catalytic performance should be able to be improved by sufficient electrons generated by photocatalysts and smooth transfer of the electrons from COFs to O_2 . In searching for such electron-rich COFs, our attention was attracted by the recently reported COF-JLU25 (Scheme 1) owing to its catalytic activity in the C-3 formylation reaction of Nmethylindole.^[10] Application of electron-deficient COFs and donor-acceptor COFs as photocatalysts has been well documented, [2b,c,k] but COF-based photocatalysts comprised solely of electron-donating units have not been commonly seen. Given that COF-JLU25 was constructed from two electrondonating units, 1,3,6,8-tetrakis(4-aminophenyl)pyrene (PyTA) and 4-[4-(4-formylmethyl)-2,5-dimethoxyphenyl] benzaldehyde (TpDA), we envisioned that the electron-rich units in such an eclipsed stacking structure might be a source for abundant electrons to facilitate oxidative reactions. Therefore, we explored the application of COF-JLU25 in photocatalytic aerobic oxidative hydroxylation of arylboronic acids to phenols.

Results and Discussion

The COF-JLU25 synthesized by following a reported procedure (Scheme 1) was characterized by Fourier transform infrared (FT-IR) spectroscopy, solid-state ¹³C cross-polarization magic angle spinning (¹³C CP-MAS) NMR spectroscopy, powder X-ray diffraction (PXRD) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) surface area measurements, elemental analysis (EA)



and thermal gravimetric analysis (TGA). Fourier transform infrared (FTIR) spectrum of COF-JLU25 showed a typical stretching band of C=N at 1621 cm⁻¹ for COF-JLU25, but not for PyTA or TpDA, while the -HC=O band in TpDA (1691 cm⁻¹) and N-H₂ band in PyTA (3500~3300 cm⁻¹) were almost completely disappeared in COF-JLU25 (Figure S1), implying Shiff base formation from aldehyde and amino functionalities. The peak at 157 ppm in ¹³C CP-MAS NMR was also consistent with carbons of aldimines (Figure 1a).

The crystalline structure of the COFs was confirmed by powder X-ray diffraction (PXRD) measurement (Figure 1b). The

COF-JLU25 sample exhibited two intense XRD peaks at 2.70° and 5.39° which were assignable to (100) and (200) facets, respectively. Besides, three other peaks at 3.93° (110), 8.09° (300), and 10.80° (040) were also shown in the experimental PXRD pattern. The simulated PXRD patterns of an eclipsed AA stacking model could reproduce the PXRD results in terms of the peak position and intensity (R_{wp} of 4.87% and R_p of 3.35%). The unit cell was created with a P1 space group, and the Pawley refinement afforded cell parameters of a = b = 32.80 Å, c = 3.82 Å, and $\alpha = \beta = 90.00^\circ$ and $\gamma = 95.01^\circ$ (Figure S7 and S8). The SEM images of COF-JLU25 showed a root-like surface morphol-



Scheme 1. (a) Synthesis of COF-JLU25. (b) The structural model of COF-JLU25.



Figure 1. (a) Solid-state ¹³C CP-MAS NMR spectrum of COF-JLU25. (b) PXRD patterns of COF-JLU25. (c) TEM image of COF-JLU25 (scale bar = 50 nm). (d) N₂ adsorption isotherms of activated COF-JLU25 at 77 K. Insert: the derived pore size distribution.

ogy (Figure S2), while the TEM images revealed that COF-JLU25 has a stacked structure: clear lattice stripes corresponding to the ordered nanochannel (Figure 1c, Figure S3). Nitrogen adsorption-desorption experiments at 77 K featured a type-IV reversible isotherm which is characteristic for microporous structures (Figure 1d). The pore size distribution calculated by the nonlocal density functional (NLDFT) method suggested a narrow pore size distribution centered at 2.3 nm, which agreed well with the predicted pore diameter (2.5 nm) for eclipsed (AA) stacking geometries of the frameworks (Scheme S1). The value of the BET surface area in our case was measured to be 141.31 m²g⁻¹, smaller than the previously reported COF-JLU25.^[10] Usually, the difference in BET areas could be attributed to the different extent of structural twists and overlaps in COFs prepared under non-identical conditions. Another possible cause of a smaller BET surface area of COF-JLU25 obtained in our hands might be caused by unreacted monomers or oligomers trapped in the pores. TGA analysis indicated that COF-JLU25 retained more than 98% of its initial mass till 420 °C, and then started to decompose, with 72% of initial mass left as the temperature reached 800 °C (Figure S4). Besides, the structure of COF-JLU25 was retained after soaking in boiling water, NaHCO₃ (2 M), TFA, or NaOH (9 M) for 3 days (Figure S5). In addition, COF-JLU25 was stable under irradiation by a 20 W white light emitting diodes (LED) for 9 days, and in various organic solvents (Figure S6).

Photoelectric Properties. The optical and photoelectric properties of COF-JLU25 were studied using ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS), photoluminescence (PL) spectroscopy, time-resolved photoluminescence (TRPL) spectroscopy, and ultraviolet photoelectron spectroscopy (UPS). The UV-Vis DRS of COF-JLU25 showed abroad absorption in the region from UV to visible regions (200-465 nm) (Figure 2a) and the PL spectrum showed a maximum emission intensity at 540 nm (Figure 2b). The TRPL spectrum revealed the PL decay kinetics from which the average lifetime excited at 360 nm was estimated to be 1.2 ns (Figure 2c). The optical band gap (Eq) of COF-JLU25 calculated by Kubelka-Munk function was 2.22 eV (Figure 2a). The energy of the valence band maximum ($E_{VB} = -5.77 \text{ eV}$) of the COFs relative to the vacuum level was obtained by subtracting the UPS width from the excitation energy (He I, 21.2 eV) (Figure 2d). Thus, the approximate conduction band potentials (E_{CB}) were calculated to be -3.55 eV, which was obviously higher than the potential of O₂/ $O_2^{\bullet-}$ (-4.16 eV) (Figure S9), allowing reduction of molecular O_2 to $O_2^{\bullet-}$ under appropriate light.

Photocatalysis Activity. In our initial exploration of aerobic hydroxylation of arylboronic acids to assess its photocatalytic activity of COF-JLU25, 4-(methoxycarbonyl) phenylboronic acid

Figure 2. (a) UV-vis diffuse reflectance spectrum of COF-JLU25. Inset: Band gaps determined by the Kubelka-Munk-transformed reflectance spectrum. (b) PL spectrum of COF-JLU25 (excitation at 360 nm). Insert: appearance of COF-JLU25. (c) TLPL spectrum of COF-JLU25 (excitation at 360 nm). (d) High-resolution valence band UPS of COF-JLU25.

Eur. J. Org. Chem. 2021, 1–7 www.eurjoc.org 3 These are not the final page numbers!

(1) was chosen as the substrate and *i*-Pr₂NEt as the sacrificial agent. The transformation of boronic acid **1a** to 4-(meth-oxycarbonyl) phenol (**2a**) was carried out in a mixed solvent of CH₃CN/D₂O under irradiation with a 20 W white light emitting diode (LED). As shown in Table 1, the reaction did not result in the desired product **2a** in the absence of COF-JLU25 (Table 1, entry 1). The transformation could not occur when the reaction was conducted in the dark, under N₂ atmosphere, or without a

Table 1. Control experiments for oxidative hydroxylation of 1 a. ^[a]								
HO _B OH HO _H HO _H HO HO HO H HO H								
								Entry
LIIUY	Thotocatalyst	visible light	All	DILA				
1	-	+	+	+	nd. ^[c]			
2	COF-JLU25	-	+	+	nd. ^[c]			
3	COF-JLU25	+	-	+	nd. ^[c]			
4	COF-JLU25	+	+	-	trace			
5	COF-JLU25	+	+	+	>99			
6	TpDA	+	+	+	nd. ^[c]			
7	PyTA	+	+	+	nd. ^[c]			

[a] Reaction conditions: **1a** (0.2 mmol), COF-JLU25 (5.0 mg), and *i*-Pr₂NEt (1.0 mmol) in CH₃CN/D₂O (3.0 mL, 4:1, v/v) under air and under irradiation of 20 W white LEDs for 20 h. [b] Determined by ¹H NMR of the crude mixture. [c] Not detected.

Figure 3. (a) The time-dependent conversions of **1 a**, **1 c**, **1 e**–**1 h** within 24 h. (b) The time-dependent conversions of **1 i**–**1 m** within 72 h.

sacrificial agent (Table 1, entries 2–4). The conversion **1a** could reach nearly 100% (Table 1, entry 5). On the contrary, when monomer (TpDA and PyTA) were used to replace COF-JLU25, no product was detected (Table 1, entries 6 and 7). In addition, we also performed a kinetic study by monitoring the time-dependent conversions using NMR analysis (Figure 3).

With the optimized reaction conditions, we explored the scope of arylboronic acid derivatives as substrates. We were delighted to find that the photocatalytic aerobic oxidative hydroxylation tolerated substrates with a broad variety of functional groups, such as ester, aldehyde, nitro, cyano, alkyl, and halide groups (Table 2 and Figure 3). Generally, phenylboronic acids with electron-withdrawing groups or heteroaromatic boronic acid (i.e. pyridinyl boronic acid) could be effectively converted into the corresponding phenols in high conversions (>90%, Table 2, entries 1-6) within 24 h. Larger conjugated π -electron systems showed good conversions (Table 2, entries 7 and 8). However, phenylboronic acids with no substituent (Table 2, entry 9), weak electron-donating substituent (Table 2, entry 10), or weak electron-withdrawing substituents (Table 2, entries 11-13) required prolonged reaction time to get a satisfactory conversion. This could be attributed to the reason that a boron atom connected to an electron-deficient conjugated π -electron system has a greater tendency to accept an electron from $O_2^{\bullet-}$ than a boron atom linked to an electronrich aromatic ring.

This photocatalyst could be easily separated from the reaction solution by centrifugation and directly used in the next catalytic run without any extra treatment or reactivation. In the reusability test, the conversion rate of this photocatalyst was not significantly reduced for seven successive cycles of reuse, as evidenced by NMR analysis (Figure S10 and S11). The crystal-

Table 2. Substrate scope of COF-JLU25-catalyzed oxidative hydroxylation of 1 to $2^{[a]}$								
air visible light COF-JLU25 DIEA (5 equiv) Ar-B(OH)₂ 1 rt 2								
Entry	1	Ar-	Time [h]	Conversion [%] ^[b]				
1 2 3 4 5 6 7 8 9 10 11 12 13	1a 1b 1c 1d 1e 1f 1h 1i 1j 1k 1l 1m	$\begin{array}{l} 4\text{-}CH_3O_2CC_6H_4\\ 4\text{-}NO_2C_6H_4\\ 3\text{-}CHOC_6H_4\\ 3\text{-}CHOC_6H_4\\ 4\text{-}NCC_6H_4\\ \text{pyridine-4-yl}\\ 4\text{-}CC_6H_5COC_6H_4\\ \text{quinolin-6-yl}\\ C_6H_5^{(c)}\\ 4\text{-}CH_3C_6H_4^{(c)}\\ 4\text{-}CIC_6H_4^{(c)}\\ 4\text{-}CIC_6H_4^{(c)}\\ 4\text{-}CIC_6H_4^{(c)}\\ \text{-}CH_5C_{c}H_4^{(c)}\\ \text{-}CH_5C_{c}H_5C_{c$	12 24/56 18 12 18 16 18 24 24/72 24/72 24/72 24/72 24/72 24/72	99 90/99 99 99 99 99 99 91 35/99 25/99 43/99 40/99 38/99				

[a] Reaction conditions: 1 (0.2 mmol), COF-JLU25 (5.0 mg), and *i*-Pr₂NEt (1.0 mmol) in CH₃CN/D₂O (3.0 mL, 4:1, v/v) under air and under irradiation of 20 W white LEDs. [b] Determined by ¹H NMR of the crude mixture. [c] DIEA (2.5 equiv.) was added at 24 h and 48 h.

linity of COF-JLU25 was well preserved even after seven cycles, as shown by the PXRD analysis (Figure S12).

The excellent photocatalytic activity, robust reusability, and low catalyst loading made COF-JLU25, possibly other electronrich COFs, as candidates of photocatalysts for oxidative hydroxylation of arylboronic acids. Nonetheless, it is not feasible to make a direct comparison of catalytical activities among COFs with different electronic structures, such as electrondeficient, donor-acceptor, and electron-rich COFs, owing to various combinations of diverse building units in three categories of COFs.

To gain preliminary insight into the mechanism of the oxidative hydroxylation reaction, the generation of $O_2^{\bullet-}$ was verified by electron paramagnetic resonance (EPR) spectrum (Figure S13). In the presence of superoxide radical scavenger 5,5-dimethyl-1-pyrroline N-oxide (DMPO), a typical signal of the adduct of DMPO and $O_2^{\bullet-}$ was detected by EPR spectrum of the air-saturated reaction mixture after being irradiated by visible light for over 60s. Based on the verified existence of $O_2^{\bullet-}$, a plausible photocatalytic mechanism was proposed.^[2b,c] A photogenerated electron reduces O_2 to $O_2^{\bullet-}$ which then attacks the empty *p*-orbital of boron atom to form peroxide radical **3**. One electron is deprived from the sacrificing agent DIEA by the photogenerated hole on the surface of the catalyst to form radical cation 5. One hydrogen radical is transferred from 5 to 3 to result in unstable peroxide anion 7 which rearranges into phenyl dihydrogen borate 8. The hydrolysis of borate 8 provides the final product phenol 2 (Figure 4).

Conclusion

In conclusion, electron-rich COF-based photocatalyst, COF-JLU25 was studied for its catalytical behavior in the aerobic photocatalytic transformation of arylboronic acids to phenols.

Figure 4. Proposed mechanism of the photocatalytic hydroxylation of arylboronic acids in the presence of COF-JLU25.

Eur. J. Org. Chem. 2021, 1-7

www.eurjoc.org

These are not the final page numbers! 77

The transformation catalyzed by COF-JLU25 features low catalyst loading, high efficiency, robust reusability, and compatiability with substrates bearing a broad variety of functional groups. Photogeneration of $O_2^{\bullet-}$ was verified by EPR analysis, supporting a plausible mechanism in which the reaction cascade goes through a sequence of the capture of radical $O_2^{\bullet-}$ and then H[•], rearrangement, and hydrolysis of borate to afford phenol product. The described work demonstrated an application potential of a previously underexplored COF-based photocatalyst composed exclusively of electron-rich units.

Experimental Section

Unless otherwise noted, all reagents commercially available were used without further purification. ¹H and ¹³C NMR spectra were recorded on 400 MHz Bruker NEO NMR Spectrometer. Mass spectra (ESI analysis) were recorded on an Esquire 6000 spectrometer (LC/ MS). The ¹³C Cross-Polarization Magic Angle Spinning (CP-MAS) NMR spectra were obtained on a Bruker Avance-III HD 400 Hz Solid NMR with 3.2 mm double-resonance MAS probe at 100.6 MHz and a MAS frequency of 10 kHz. The Fourier-transformed infrared (FT-IR) spectra were obtained on a PerkinElmer Spectrum Two spectrometer equipped with an attenuated total reflection (ATR) setup. The scanning electron microscope (SEM) was performed on a JSM-7401F emission scanning electron microscope and the transmission electron microscopy (TEM) on a JEOL JEM-2100 Plus transmission electron microscope. Thermo Graic Analysis (TGA) was performed on a Mettler-Toledo TGA/DSC ³⁺/1100 LF analyzer under N₂, and the samples were heated from 90 $^{\circ}$ C to 800 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/ min. N₂ adsorption/desorption isotherms were measured at 77 K on Micromeritics ASAP 2020 M system. Specific surface areas were determined with the Brunauer - Emmett - Teller (BET) method, and pore size distributions were calculated by was estimated by nonlocal density functional (NLDFT) method. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance instrument with Cu K α radiation ($\lambda = 1.5418$ Å) in the 2 θ range of 1.5–30°. Electron Paramagnetic Resonance (EPR) spectra were collected on a Bruker EPR A300 spectrometer. Elemental analysis was carried out on an Elementar Vario MICRO cube Elemental Analyzer. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded at room temperature on a Shimadzu UV 3600 Spectrophotometer. Photoluminescence (PL) emission spectra and PL decay spectra were obtained from an FLS980 spectrophotometer (Edinburgh Instruments, UK).

Procedure for photocatalytic oxidative hydroxylation of arylboronic acids

To a solution of arylboronic acid (0.20 mmol) and *i*-Pr₂NEt (1.0 mmol) in CH₃CN/D₂O (3.0 mL, 4:1, v/v) was added COF-JLU25 (5.0 mg) resulting in a mixture which was sonicated for 5 min, stirred under air at 25 °C under irradiation with a 20 W white LED. At every designated time point, 400 μ L the reaction mixture was filtered to remove solid, diluted with CH₃CN /D₂O (600 μ L, 4:1, v/v), and subjected to ¹H NMR analysis. As the reactions did not result in identifiable amounts of other products, the conversion was calculated by the following equation.

conversion (%) =
$$\frac{Integral_2}{Integral_1 + Integral_2} \times 100\%$$

Where Integral $_2$ and Integral $_1$ were the peak intensities (integrals) of aromatic CH $_2$ of the phenol product **2** and the unreacted boronic

acid 1 in the ¹H NMR spectrum of the sample collected at a designated time.

Acknowledgements

This study was financially supported by National Key Research and Development Program of China (2017YFA0206500), National Natural Science Foundation of China (21871281), Shanghai Sailing Program (19YF1452900), and Science and Technology Commission of Shanghai Municipality (18DZ1100403). We thank the NMR Core Facility, Analytical Instrumentation Center of SPST, ShanghaiTech University for the assistance in NMR analysis.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Arylboronic acids · Covalent organic frameworks · Oxidative hydroxylation · Photocatalysis · Superoxide radical

- a) B. Xia, Y. Zhang, J. Ran, M. Jaroniec, S. Z. Qiao, ACS Cent. Sci. 2021, 7, 39; b) Q. Liu, L.-Z. Wu, Natl. Sci. Rev. 2017, 4, 359; c) G. Han, Y. Sun, Mater. Today Phys. 2021, 16, 100297.
- [2] a) X. Kang, X. Han, C. Yuan, C. Cheng, Y. Liu, Y. Cui, J. Am. Chem. Soc. 2020, 142, 16346; b) S. Bi, P. Thiruvengadam, S. Wei, W. Zhang, F. Zhang, L. Gao, J. Xu, D. Wu, J.-S. Chen, J. Am. Chem. Soc. 2020, 142, 11893; c) P. F. Wei, M. Z. Qi, Z. P. Wang, S. Y. Ding, W. Yu, Q. Liu, L. K. Wang, H. Z. Wang, W. K. An, W. Wang, J. Am. Chem. Soc. 2018, 140, 4623; d) C. Kokotos, I. Sideri, E. Voutyritsa, Synlett 2017, 29, 1324; e) A. A. Atia, M. Kimura, Catalysts 2020, 10, 1262; f) I. G. T. M. Penders, Z. Amara, R. Horvath, K. Rossen, M. Poliakoff, M. W. George, RSC Adv. 2015, 5, 6501; g) T. Toyao, N. Ueno, K. Miyahara, Y. Matsui, T. H. Kim, Y. Horiuchi, H. Ikeda, M. Matsuoka, Chem. Commun. 2015, 51, 16103; h) S. P. Pitre, C. D. McTiernan, H. Ismaili, J. C. Scaiano, J. Am. Chem. Soc. 2013, 135, 13286; i) J. A. Johnson, J. Luo, X. Zhang, Y.-S. Chen, M. D. Morton, E. Echeverría, F. E. Torres, J. Zhang, ACS Catal. 2015, 5, 5283; j) Y. Q. Zou, J. R. Chen, X. P. Liu, L.Q. Lu, R. L. Davis, K. A. Jorgensen, W. J. Xiao, Angew. Chem.

Int. Ed. **2012**, *51*, 784; k) X. Yan, H. Liu, Y. Li, W. Chen, T. Zhang, Z. Zhao, G. Xing, L. Chen, *Macromolecules* **2019**, *52*, 7977.

- [3] a) T. Zhang, G. Xing, W. Chen, L. Chen, *Mater. Chem. Front.* 2020, 4, 332;
 b) T.-X. Wang, H.-P. Liang, D. A. Anito, X. Ding, B.-H. Han, *J. Mater. Chem.* A 2020, 8, 7003.
- [4] a) H. Liu, J. Tang, H. Liu, C. Li, H. Li, Y. Ren, Q. Yang, C. Li, Y. Ren, J. Chen, J. Tang, ACS Appl. Mater. Interfaces. 2020, 12, 20354; b) S. Li, L. Li, Y. Li, L. Dai, C. Liu, Y. Liu, J. Li, J. Lv, P. Li, B. Wang, ACS Catal. 2020, 10, 8717; c) W. Hao, D. Chen, Y. Li, Z. Yang, G. Xing, J. Li, L. Chen, Chem. Mater. 2019, 31, 810; d) W. Chen, L. Wang, D. Mo, F. He, Z. Wen, X. Wu, H. Xu, L. Chen, Angew. Chem. Int. Ed. 2020, 59, 16902; e) W. Li, X. Huang, T. Zeng, Y. A. Liu, W.-B. Hu, H. Yang, Y.-B. Zhang, K. Wen, Angew. Chem. Int. Ed. 2020, 60, 1869.
- [5] a) Z. Li, Z. Ye, L. Chen, J. Cui, J. Chen, ACS Appl. Nano Mater. 2020, 3, 10720; b) J.-Z. Cheng, Z.-R. Tan, Y.-Q. Xing, Z.-Q. Shen, Y.-J. Zhang, L.-L. Liu, K. Yang, L. Chen, S.-Y. Liu, J. Mater. Chem. A 2021, 9, 5787.
- [6] Y. Zhi, Z. Yao, W. Jiang, H. Xia, Z. Shi, Y. Mu, X. Liu, ACS Appl. Mater. Interfaces. 2019, 11, 37578.
- [7] Y. Zhang, L. Zhang, X. Zhang, D. Yang, C. Du, L. Wan, C. Au, J. Chen, M. Xie, New J. Chem. 2020, 44, 15202.
- [8] a) X. Chen, K. Geng, R. Liu, K. T. Tan, Y. Gong, Z. Li, S. Tao, Q. Jiang, D. Jiang, Angew. Chem. Int. Ed. 2020, 59, 5050; b) C. S. Diercks, O. M. Yaghi, Science 2017, 355; c) X. Feng, X. Ding, D. Jiang, Chem. Soc. Rev. 2012, 41, 6010; d) H. Wang, H. Wang, Z. Wang, L. Tang, G. Zeng, P. Xu, M. Chen, T. Xiong, C. Zhou, X. Li, D. Huang, Y. Zhu, Z. Wang, J. Tang, Chem. Soc. Rev. 2020, 49, 4135; e) S. Y. Ding, W. Wang, Chem. Soc. Rev. 2013, 42, 548; f) Y. Li, W. Chen, G. Xing, D. Jiang, L. Chen, Chem. Soc. Rev. 2020, 49, 2852; g) X. Chen, K. Geng, R. Liu, K. T. Tan, Y. Gong, Z. Li, S. Tao, Q. Jiang, D. Jiang, Angew. Chem. Int. Ed. 2020, 59, 5050; h) H. Wang, H. Wang, Z. Wang, L. Tang, G. Zeng, P. Xu, M. Chen, T. Xiong, C. Zhou, X. Li, D. Huang, Y. Zhu, Z. Wang, J. Tang, Chem. Soc. Rev. 2020, 49, 4135.
- [9] a) G.-B. Wang, S. Li, C.-X. Yan, F.-C. Zhu, Q.-Q. Lin, K.-H. Xie, Y. Geng, Y.-B. Dong, J. Mater. Chem. A 2020, 8, 6957–6983; b) Z. Li, Y. Zhi, P. Shao, H. Xia, G. Li, X. Feng, X. Chen, Z. Shi, X. Liu, Appl. Catal. B 2019, 245, 334; c) S. Wang, Q. Sun, W. Chen, Y. Tang, B. Aguila, Y. Pan, A. Zheng, Z. Yang, L. Wojtas, S. Ma, F.-S. Xiao, Matter 2020, 2, 416; d) Y. Zhi, Z. Wang, Q. Zhang, H.-L. Zhang, Q. Zhang, Small 2020, 16, e2001070; e) Y. Zhi, Z. Li, X. Feng, H. Xia, Y. Zhang, Z. Shi, Y. Mu, X. Liu, J. Mater. Chem. A 2017, 5, 22933.
- [10] Z. Li, S. Han, C. Li, P. Shao, H. Xia, H. Li, X. Chen, X. Feng, X. Liu, J. Mater. Chem. A 2020, 8, 8706.

Manuscript received: February 11, 2021 Revised manuscript received: March 8, 2021 Accepted manuscript online: March 11, 2021

FULL PAPERS

G. Xiao, W. Li, T. Chen, W.-B. Hu, Prof. Dr. H. Yang, Dr. Y. A. Liu, Prof. Dr. K. Wen*

1 – 7

Application of Electron-Rich Covalent Organic Frameworks COF-JLU25 for Photocatalytic Aerobic Oxidative Hydroxylation of Arylboronic Acids to Phenols

COF-JLU25, a COF-based photocatalyst comprised solely of electrondonating units, 1,3,6,8-tetrakis(4-aminophenyl)pyrene (PyTA) and 4-[4-(4formylmethyl)-2,5-dimethoxyphenyl] benzaldehyde (TpDA), demonstrated excellent photocatalytic activity with high efficiency, robust reusability, and low catalyst loading when used in catalyzing the oxidative hydroxylation of arylboronic acids.