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Continuous Photocatalytic C–C Coupling Reaction by Palladium Single-Atom Anchored Covalent Organic Framework

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We report, for the first time, the use of a single-atom palladium photocatalyst, Pd-Ace-COF, for a continuous C–C coupling reaction. Under visible light irradiation, Pd-Ace-COF efficiently drives C–C coupling to form biphenyl with a >99% yield. Impressively, Pd-Ace-COF exhibits good stability and high activity in the continuous-flow reactor, highlighting its great potential for practical applications.

Cross-coupling reactions, such as those developed by Sonogashira and Suzuki–Miyaura, have been extensively utilized in organic synthesis due to their effectiveness in the formation of C–C bonds.[1–5] Typically, Pd catalysts are widely employed for catalysing C–C coupling reactions due to their excellent catalytic activity and broad applicability.[6–8] Since the first report of Pd-catalysed Suzuki–Miyaura coupling reactions in 1979, numerous Pd catalysts with various organic ligands have been reported, advancing the field of organic synthesis.[9–13] Despite the progress, coupling reactions usually require elevated temperatures and homogenous Pd salt catalysts,[14] leading to excessive energy consumption, environmental pollution, and precious metal depletion, which severely contradict the principles of green and sustainable organic synthesis.[15] To address these limitations, several attempts have been made to encapsulate Pd nanoparticles within metal-organic frameworks (MOFs) or deposit them on the surface of a two-dimensional material, for improving the recyclability of the catalyst. [16,17] However, only the Pd atoms on the surfaces of the nanoparticles exhibit catalytic activity in these materials, leading to inefficient utilization of precious metals.[18] Therefore, the development of atomic-scale Pd heterogeneous catalysts for C–C coupling reactions under mild conditions is highly desirable but remains a significant scientific challenge.

Covalent organic frameworks (COFs), as a class of crystalline organic porous polymer materials, exhibit unique advantages, including regular structures, low density, large specific surface areas, adjustable pore size, and tailorable structures. Furthermore, COFs are known to possess an exceptional ability to absorb visible light.[19–24] These unique properties endow them with great potential for photocatalytic applications.[25,26] Notably, COFs provide an ideal molecular platform for preparing atomic-level metal catalysts by precisely introducing vacancies into the framework and subsequently trapping metal catalytic centers at these sites.[27–29] However, to the best of our knowledge, single-atom photocatalysts based on COFs have not yet been reported for driving C–C coupling reactions.

Additionally, traditional C–C coupling reactions have been widely studied in laboratory-scale batch reactors, where Pd catalysts are dissolved or dispersed in an Ar-saturated solution. This reaction mode is primarily limited by catalyst separation and the intermittent nature of the process. To overcome the above limitations, we developed a single-atom Pd photocatalyst, Pd-Ace-COF, for continuous photocatalytic cross-coupling reactions. Pd-Ace-COF effectively promotes the coupling reaction between iodobenzene and phenylboronic acid, resulting in the production of biphenyl with a yield >99% at room temperature and under visible light irradiation. Pd-Ace-COF exhibits advantages, including facile synthesis, excellent stability, high activity under mild conditions, and broad substrate tolerance, highlighting its great potential for practical applications.

A triazine-based COF was synthesized by carrying out polymerization of 4,4′4″-(1,3,5-triazine-2,4,6-triyl) trianiline and acenaphthenequinone monomers (Ace-COF). Then, Pd ions were anchored into the Ace-COF platform through a hot solvent post-impregnated approach, resulting in the formation of a single-atom Pd photocatalyst Pd-Ace-COF (Fig. 1a). High-resolution transmission electron microscopy (HRTEM) showed Pd-Ace-COF is composed of multiple layers of stacked nanosheets (Fig. S1). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF–STEM) showed bright dots with average dimensions of 0.1–0.2 nm (Fig. 1d), revealing the existence of atomically dispersed Pd sites in the Pd-Ace-COF framework. The acquired energy-dispersive X-ray (EDX)

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† Electronic supplementary information (ESI) available: Synthesis in detail and additional figures. See DOI: 10.1039/x0xx00000x

Comment [A]: AU: The meaning of the title is not entirely clear. Please provide alternative text. Possible rewrite: "Continuous Photocatalytic C-C Coupling Achieved Using Palladium Anchored to a Covalent Organic Framework."

Comment [A]: AU: In the sentence beginning with “**We report the use**”, and **throughout the abstract and manuscript, please carefully check ALL edits to ensure that they preserve your intended meaning**.

Comment [A]: AU: The meaning of “catalyst separation” in the sentence beginning with “This reaction mode” is not entirely clear. Please provide alternative text. Or should “catalyst separation” be replaced with “catalyst precipitation”?

Comment [A]: AU: The meaning of “hot solvent post-impregnated approach” in the sentence beginning with “Then, Pd ions” is not entirely clear. Please provide alternative text. Or should “hot solvent post-impregnated approach” be replaced with something like “post-impregnation approach using hot solvent”?

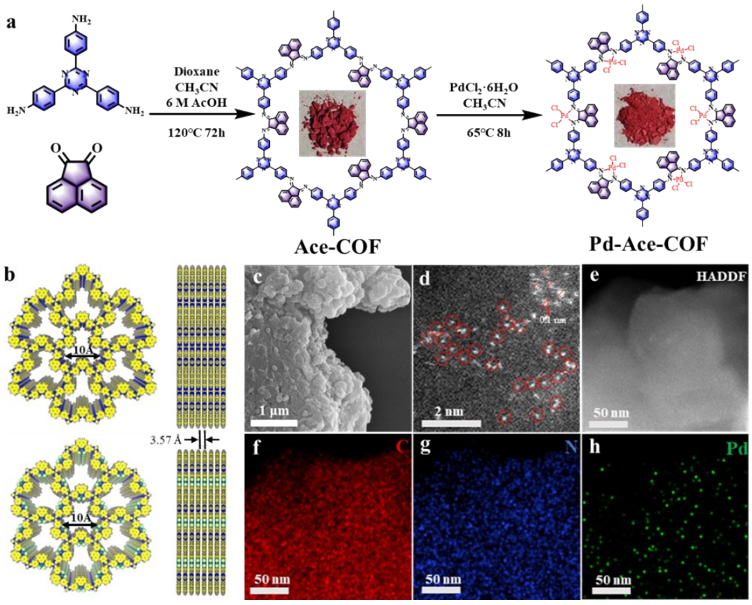

Fig. 1 (a) Schematic of the synthesis of Pd-Ace-COF. (b) Top and side views of Ace-COF and Pd-Ace-COF. (c) SEM image of Pd-Ace-COF. (d) Aberration-corrected HAADF–STEM image and (e–h) element mapping of Pd-Ace-COF.

mapping images of Pd-Ace-COF revealed uniform distributions of C, N, and Pd elements in the Pd-Ace-COF framework (Fig. 1e–h). According to the results of inductively coupled plasma mass spectrometry (ICP–MS), the relative amount of the Pd-Ace-COF matrix made up of loaded single Pd atoms was determined to be 2.2 wt%. The surface areas of the Ace-COF and Pd-Ace-COF compounds were determined by acquiring N_2 adsorption–desorption isotherms of the activated samples. As shown in Fig. S2, a sharp increase in the uptake of the gas was observed at low relative pressures ($P/P_0 < 0.1$), indicating the presence of micropores. The Brunauer-Emmett-Teller (BET) surface area values for Ace-COF were 122 $m^2\ g^{-1}$ and 0.26 $cm^3\ g^{-1}$ and only 85 $m^2\ g^{-1}$ and 0.17 $cm^3\ g^{-1}$ for Pd-Ace-COF. The pore dimensions of Ace-COF and Pd-Ace-COF were calculated to be 1.62 nm and 1.15 nm, respectively by using Ar at 87 K with a quenched solid density functional theory (QSDFT) carbon model (Fig. S3). As shown in Fig. S4, thermogravimetric analysis (TGA) showed that neither Ace-COF nor Pd-Ace-COF exhibited any significant mass loss before 300 °C, indicating that both the materials possess permanent porosity and good thermal stability. The planar structure of triazine and Ace building blocks contributed to the formation of the strong π–π interactions between the adjacent layers, thereby facilitating the acquisition of highly crystalline Ace-COF and Pd-Ace-COF (Fig. 1b). The powder X-ray diffraction (PXRD) patterns of Ace-COF and Pd-Ace-COF, illustrated in Fig. 2a, showed several sharp diffraction peaks, indicative of the good crystallinity of Ace-COF. Pd-Ace-COF and Ace-COF exhibited similar PXRD patterns, suggesting that the crystallinity of the COFs was retained even after the incorporation of Pd atoms. The diffraction peaks at 4.0, 7.1, 12.1, and 14.7 can be ascribed to the (100), (110), (130), and (400) facets, respectively, while that at about 25° can be ascribed to π–π stacking interaction between the adjacent layers corresponding to the (001) facet in Pd-Ace-COF. We determined that all the diffraction peaks correspond to the P6 space group, indicating a hexagonal layered structure. The PXRD patterns simulated using the AA stacking mode were found to be in good agreement with the experiment plots—with its unit cell parameters of a = 28.7668 Å, b = 28.7668 Å, c = 3.5734 Å, α = β = 90° and γ = 120° (Table S1) consistent with the experimental results (Rp = 5.52% and Rwp = 7.21%). The Fourier-transform infrared (FT-IR) spectra of Pd-Ace-COF and Ace-COF showed characteristic vibrational bands at 1620 cm^{-1} and 1400 cm^{-1}, corresponding to the ν(−N=C−) vibrational modes in the imine bond and pyridine ring, respectively (Fig. S5). The XPS spectra of Pd-1 and Pd-Ace-COF (Figs. S6 and S7) indicated the same contact positions of Pd-1 and Pd-Ace-COF, suggesting a coordination environment of the synthesized Pd-Ace-COF consistent with that of the ligand. Additionally, compared with the N 1s peak in the XPS spectrum of the original Ace-COF (Fig. S8), the N 1s peak in the Pd-Ace-COF material showed a significant difference in binding energy. This difference can be attributed to the coordination of nitrogen atoms with Pd^{2+}. Scanning electron microscopy (SEM) analyses showed that the morphology of Ace-COF after palladium loading remained consistent with that before loading , indicating no damage to the framework structure of Ace-COF and of good preservation of its original structural integrity (Figs. 1c and S9). Furthermore, X-ray photoelectron spectroscopy (XPS) showed that

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Comment [A]: AU: The sentence beginning with “We determined that all ...” has been altered for clarity. Please check that the meaning is correct.

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the binding energy of Pd in Pd-Ace-COF composites decreased by approximately 0.2 eV when irradiated with visible light (Fig. 2b), indicating the efficient photogenerated electron transfer from the COF framework to Pd^{2+}. To further understand the charge transfer process, steady-state photoluminescence (PL) spectra were recorded for Ace-COF and Pd-Ace-COF. As shown in Fig. 2c, the PL intensity of Ace-COF was significantly reduced upon introducing Pd^{2+}, further suggesting an efficient electron transfer from the COF framework to Pd^{2+} in Pd-Ace-COF. This viewpoint was further supported by photoelectrochemical and electrochemical impedance tests (Figs. S10 and 2d). Pd-Ace-COF exhibited a larger photocurrent intensity and charge transfer resistance than those of Ace-COF in the absence of the Pd atom, suggesting efficient charge transport from the COF framework to Pd^{2+}. Based on the abovementioned analysis, introducing single-atom active sites into Ace-COF can shorten the electron transfer distance, accelerate the rate of transfer, and promote the electron accumulation at the reaction centres, which greatly contributed to facilitating photocatalysis. Based on the above superior properties, Pd-Ace-COF was first employed as a photocatalyst for driving the C–C coupling reaction. Initially, we optimized the reaction conditions using iodobenzene and phenylboronic acid as model substrates (Table S2 and Fig. S11). Pd-Ace-COF exhibited a superior catalytic performance for the formation of biphenyl with a yield >99% within 6 h. When Ace-COF was employed as a photocatalyst, only a trace amount of product was detected, suggesting the crucial role played by the Pd centre in this cross-coupling reaction (Table S2, entry 3). Almost no product formed when the physically mixed system consisting of $PdCl_2$ and Ace-COF was used as the photocatalyst, indicating that anchoring of Pd ions into the Ace-COF is essential for efficient C–C coupling reaction. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) and triethanolamine (TEA) were used as an electron-trapping agent and hole scavenger, respectively. When DMPO and TEA were added to the reaction system, the conversion rate was close to 0 (Fig. S12), indicating that the coupling reaction requires either electron reduction and hole oxidation. Furthermore, we tested additional substrates to evaluate the applicable scope of the Pd-Ace-COF catalyst in Suzuki cross-coupling reactions (Table S3 and Figs. S13–S23). Additionally, Pd-Ace-COF can drive Sonogashira coupling between iodobenzene and phenylacetylene, resulting in the formation of 1,2-diphenylethyne with a yield of 80% (Fig. S24). These findings indicated an excellent substrate tolerance for the Pd-Ace-COF catalyst. Additionally, the catalytic performance of Pd-Ace-COF did not show a significant change over the course of 3 cycles (Fig. S25), demonstrating an excellent photocatalytic stability of Pd-Ace-COF (Figs. S26–S28). The band gap structure revealed the CB position of Pd-Ace-COF to be slightly more negative than that of Ace-COF (Figs. S29–S32), suggesting that introducing Pd has a weak influence on the redox ability of the COF framework. Based on the above photophysical and electrochemical analyses, we proposed a photocatalytic mechanism for the catalytic system containing Pd-Ace-COF (Fig. 3). According to this mechanism, under visible light irradiation, Pd-Ace-COF can efficiently harvest visible light to achieve a population of the excited Ace-COF* state. Then an intra-framework electron transfer occurred from Ace- COF* to the Pd centre, resulting in the formation of a reduced Pd centre. Afterwards, an oxidation addition occurred between iodobenzene (Ph-I) and the Pd active sites, resulting in the formation of the intermediate Ph-Pd-I. When the photogenerated holes diffused to the adsorption site, the adsorbed phenylboronic acid was oxidized and the C–B bond was broken.[30] Finally, the target biphenyl product was obtained as a result of transmetallation and reductive

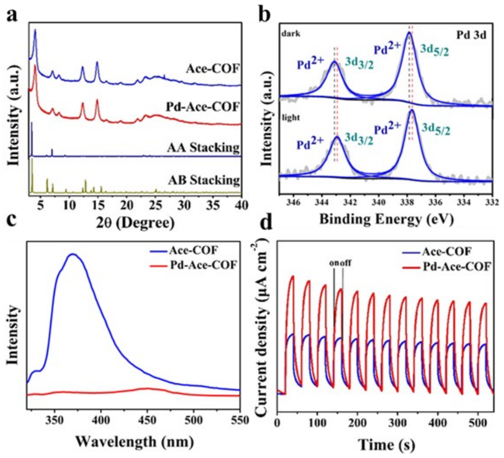

Fig. 2 (a) Experimentally obtained PXRD patterns of Ace-COF (blue) and Pd-Ace-COF (red), and PXRD patterns simulated using eclipsed AA stacking (deep blue) and staggered AB stacking (faint yellow). (b) XPS spectra of Pd-Ace-COF (top: under dark; bottom: under the light). (c) Steady-state PL spectra of Pd-Ace-COF and Ace-COF and (d) Photocurrent response (I-t) plots for Pd-Ace-COF and Ace-COF.

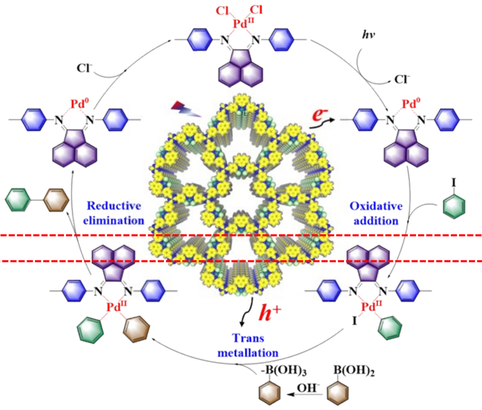

Fig. 3 Mechanism for Pd-Ace-COF–catalyzed Suzuki–Miyaura cross-coupling reactions.

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Comment [A]: AU: The sentence beginning with "When DMPO and TEA were added" is not entirely clear. Should "When DMPO and TEA were added" be replaced with "When either DMPO or TEA was added"? Also, please replace "either electron reduction and hole oxidation" with "either electron reduction or hole oxidation" or "both electron reduction and hole oxidation". And please check the edit to "was close to".

Comment [A]: AU: The sentence beginning with "Furthermore, we tested additional substrates" has been altered for clarity. Please check that the meaning is correct.

Comment [A]: AU: In Figure 2a, please replace the x-axis label with "Two-theta (°)", and could you supply a corrected version (preferably as a TIF file at 600 dots per inch) with your proof corrections.

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elimination steps. With a clear catalytic mechanism, high catalytic activity and excellent catalytic stability, the Pd-Ace-COF photocatalyst was further immobilized within a continuous-flow reactor for carrying out a continuous photocatalytic C–C coupling reaction (Figs. 4 and S33). To enhance the absorption of incident light and strengthen the interfacial contact between the catalyst and substrates during the flow process, the photocatalyst was coated onto the surface of a non-woven fabric in a reaction tube. Under visible light irradiation, this continuous-flow system with Pd-Ace-COF was found able to efficiently drive the C–C coupling reaction between iodobenzene and phenylboronic acid, achieving the synthesis of 312 mg of biphenyl with a yield of over 90%.

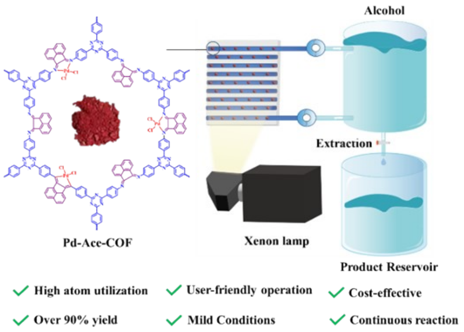

Fig. 4 Schematic of the visible-light–driven continuous-flow system with Pd-Ace-COF.

In conclusion, we developed a single-atom palladium photocatalyst, Pd-Ace-COF, for carrying out a continuous C–C coupling reaction. Under visible light irradiation, Pd-Ace-COF efficiently drove C–C coupling to form biphenyl with a 99% yield. In addition, Pd-Ace-COF exhibited a good catalytic stability and substrate tolerance. Impressively, a mass of 312 mg of biphenyl was obtained with high yield (90%) by immobilizing Pd-Ace-COF within a continuous-flow reactor. This work provides new insight for developing an efficient and sustainable catalytic system by immobilizing a single-atom Pd photocatalyst within a continuous-flow reactor.

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Data availability

The data supporting this article have been included as part of the ESI.

Conflicts of interest

The authors declare no competing interests.

Notes and references

1 J. P. Corbet, G. Mignani, *Chem. Rev.*, 2006, **106**, 2651- 2710.
2 C. C. C. J. Seechurn, M. O. Kitching and T. J. Colacot, *Angew. Chem. Int. Ed.*, 2012, **51**, 5062- 5085.
3 N. A. Weires, E. L. Baker and N. K. Garg, *Nat. Chem.*, 2016, **8**, 75-79.
4 S. Handa, Y. Wang, F. Gallou and B. H. Lipshutz, *Science*, 2015, **349**, 1087-1091.
5 A. A. Thomas, S. E. Denmark, *Science*, 2016, **352**, 329- 332.
6 S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su and W. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 19816-19822.
7 J. G. Liu, H. Zhan, N. Wang, Y. P. Song, C. G. Wang, X. M. Wang, L. L. Ma and L. G. Chen, *ACS Appl. Nano Mater.*, 2021, **4**, 6239-6249.
8 X. X. Jia, J. W. Zhao, Y. J. Lv, X. L. Fu, Y. J. Jian, W. Q. Zhang, Y. Y. Wang, H. M. Sun, X. X. Wang, J. L. Long, Q. Gu and Z. W. Gao, *Appl. Catal., B*, 2021, **300**, 120756.
9 M. Kou, W. Liu, Y. Y. Wang, J. D. Hung, Y. L. C hen, Y. Zhou, Y.Chen, M. Z. Ma, K. Lei, H. Q. Xie, P. K. Wong and L. Q. Ye, *Appl. Catal., B*, 2021, **291**, 120146.
10 V. Hasija, S. Patial P. Raizada, A. A. P. Khan, A. M. Asiri., Q. V. Le, V. H. Nguyen and P. Singh, *Coor. Chem. Rev.*, 2022, **452**, 214298.
11 P. Y. Dong, Y. Wang, A. C. J. Zhang, T. Cheng, X. G. Xi and J. L. Zhang, *ASC Catal.*, 2021, **11**, 13266-13279.
12 Z. W. Li, S. Qiu, Y. R. Song, S. Y. Huang, J. F. Gao, L. C. Sun and J. G. Hou, *Sci. Bull.*, 2022, **67**, 197-1981.
13 Y. X. Hou, X. M. Zhang, J. S. Sun, S. Lin, D. D. Qi, R. R. Hong, D. Q. Li, X. Xiao and J. Z. Jiang, *Mic. Mes. Mat*, 2015, **214**, 108-114.
14 Y. F. Jiang, Q. Liu, B. Q. Xie and J. S. Zhang, *Ind. Eng. Chem. Res.*, 2024, **63**, 10532-10543.
15 C. H. Han, D. E. Gómez, Q. Xiao and J. S. Xu, *J. Catal.*, 2021, **397**, 205-211.
16 M. Y. Chen, Q. Y. Li, X. Y. Xu, D. W. Liu, Z. J. Ma, Y. X. Li, Y. J. Zhang, D. J. Li, Q. Chen and R. J. Sa, *Chem. Eng. J.*, 2024, **494**, 153133.
17 Y. Y. Qian, H. L. Jiang, *Acc. Chem. Res.*, 2024, **57**, 1214-1226.
18 C. S. More, A. K. Kar and R. Srivastava, *Inorg. Chem.*, 2022, **61**, 19010–19021.
19 L. Y. Qin, C. D. Ma, J. Zhang and T. H. Zhou, *Adv. Funct. Mater.*, 2024, **34**, 2401562.
20 Z. Z. Lang, R. C. Hance, Y. H. Ng, Y. Fu, T. Y. Ma, P. Zhang, Y. J. Li and X. Li, *Chem. Catalysis.*, 2022, **2**, 2157-2228.
21 X. L. Xu, N. N. Wang, Y. H. Zou, X. Qin, P. Wang, X. Y. Lu, X. Y. Zhang, W. Y. Sun and Y. Lu, *Nat. Commun.*, 2024, **15**.
22 J. Yang, Z. Chen, L. Zhang and Q. Zhang, ACS Nano., 2024, **18**, 21804-21835.
23 C. I. Yeo, Y. S. Tan, H. T. A. Awan, A. Hanan, W. P. Wong, R. Walvekar, B. H. Goh and M. Khalid, *Coor. Chem. Rev.*, 2024, **521**, 216167.
24 H. Ran, Q. Xu, Y. Yang, H. Li, J. Fan, G. Jiu, L. Zhang, J. Zou, H. Jin and S. Wang, *ACS Catal.*, 2024, **14**, 11675-11704.
25 M. Y. Chen, Q. Y. Li, X. Y. Xu, D. W. Liu, Z. J. Ma, Y. X. Li, Y. J. Zhang, D. J. Li, Q. Chen, R. J. Sa, *Chem. Eng. J.*, 2024, **494**, 153133.
26 A. Shetty, D. Sunil, T. Rujiralai, S. P. Maradur, A. N. Alodhayb and G. Hegde, *Nanoscale Adv.*, 2024, **6**, 2516-2526.
27 F. P. Ma, Q. P. Tang, S. B. Xi, G. Q. Li, T. Chen, X. C. Ling, Y. Lyu, Y. P. Liu, X. L. Zhao, Y. Zhou and J. Wang, *Chin. J. Catal.*, 2023, **48**, 137-149.
28 T. He, Z. F. Zhao, R. Y. Liu, X. Y. Liu, B. Ni, Y. P.Wei, Y. L. Wu, W. Yuan, H. J. Peng, Z. Y. Jiang and Y. L. Zhao, *J. Am. Chem. Soc.*, 2023, **145**, 6057-6066

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29 L. Ran, Z. W. Li, B. Ran, J. Q. Cao, Y. Zhao, T. Shao, Y. R. Song, M. K. H. Leung, L. C. Sun and J. G. Hou, *J. Am. Chem. Soc.*, 2022, **144**, 17097-17109.

30 Y. Q. Ren, Y. Chen, Q. F. Zhao, Z. M. Xu, M. J. Wu and Z. F. Bian, *Appl. Catal., B*, 2023, **324**, 122264.