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Supporting Information

Repair of missing linker defects in UiO-66 by "molecular patch" boosting 1-hexene hydroformylation reaction

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25 **Experimental section**

26 **Materials**

27 Zirconium (IV) chloride ($ZrCl_4$, 99%), benzene-1,4-dicarboxylic acid (H_2BDC , 99%), 3-
28 Phenylpropionaldehyde (3-PPA, 95%) were brought from Shanghai Aladdin Bio-Chem
29 Technology Co., Ltd. Dimethylformamide (DMF, 99.5%), acetic acid (99.5%), Hydrochloric acid
30 (HCl, 37%) were obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd. (China). All
31 chemicals were directly used without further purification.

32 **Synthesis of UiO-66**

33 UiO-66 was synthesized according to the procedure described by Shearer¹ with minor
34 adjustments. 1.85 mmol H_2BDC and 1.85 mmol $ZrCl_4$ were dissolved in a flask with 45 mL DMF,
35 stirred until the raw materials were completely dissolved and sonicated for 10 min. Then, 185
36 mmol acetic acid and 0.10 mL water were added, mixed well and transferred to a 100 mL Teflon
37 autoclave, sealed and heated to 120 °C and held for 24 h. After cooling to room temperature, the
38 products were separated by centrifugation. Then the white powder was washed well with DMF
39 and water, and finally dried under vacuum at 150 °C for 12 h.

40 **Synthesis of UiO-66-AT**

41 UiO-66-AT was prepared in an intermittent autoclave reactor in the following steps: Firstly,
42 0.1 g of UiO-66 was dispersed in 5 mL of toluene and 200 μ L of 3-PPA was added and sealed.
43 Subsequently, the air in the autoclave was replaced with N_2 three times and all valves were closed.
44 Then the product was heated to 60 °C under atmospheric pressure N_2 , treated for 1h and removed,
45 centrifuged and washed with ethanol 3 times. Finally, the product was dried under vacuum at 80
46 °C for 12 h.

47 **Synthesis of UiO-66-ideal**

48 UiO-66 was synthesized according to the procedure described by Shearer^{1, 2} with some
49 adjustments. 8.1 mmol $ZrCl_4$, 16.2 mmol HCl and 16.2 mmol H_2BDC were sequentially dissolved
50 in a flask containing 48.7 mL DMF. Magnetic stirring at 70 °C to ensure complete dissolution of
51 reagents. The mixture in the flask was then transferred to a 100 mL Teflon autoclave, sealed and
52 heated to 220 °C and held for 20 h. After cooling to room temperature, the products were
53 separated by centrifugation. Then the white powder was washed well with DMF and methanol,
54 and finally dried under vacuum at 150 °C for 12 h.

55 **Preparation of Rh/UiO-66**

56 Rh/UiO-66 was prepared by an ultrasound-assisted incipient wetness impregnation. The
57 loading of Rh in the catalyst was 0.2 wt%. After impregnation, the catalyst was transferred to a
58 vacuum dryer and left to stand for 10 h at room temperature. Then the catalyst was dried at 100 °C
59 for 12h. Finally, the as-obtained catalyst is reduced at 200 °C in hydrogen for 2 h, then cooled to
60 room temperature and passivated with 1%O₂/99%N₂ for 1 h.

61 **Preparation of Rh/UiO-66-AT**

62 Rh/UiO-66-AT was prepared in agreement with UiO-66-AT.

63 **Catalyst performance evaluation**

64 The hydroformylation reaction was carried out on a batch autoclave reactor (Microreactor,
65 Yanzheng Instrument Ltd. Shanghai) with the following procedure: add a certain amount of
66 catalyst and olefin to the 25 mL autoclave, 5 mL of toluene as solvent, place the autoclave in a
67 heating furnace and seal it. Replace the air in the autoclave with synthesis gas three times, and
68 finally fill the autoclave with a certain pressure of synthesis gas (CO/H₂ volume ratio of 1:1), start
69 heating and magnetic stirring, warm up to the required reaction temperature and start timing the
70 reaction for a specific time. When the reaction was finished, the autoclave was removed from the
71 heating furnace and placed in an ice water bath to cool down. When the temperature of the
72 autoclave dropped below 10 °C, the gas outlet of the autoclave was slowly opened to release the
73 unreacted syngas. The catalyst and the reactants were separated by centrifugation and the liquid
74 was taken for gas chromatography analysis. The products were analyzed offline by flame
75 ionization detector (FID) using a GC4000A (HP-PLOT Al₂O₃ S column). The liquid products
76 were collected in a cold trap, oil phase was analyzed by Shimadzu GC-2014C instrument with a
77 FID detector and all alcohol products in liquid phase were analyzed by GC-7AG (Chromosorb 101)
78 with a FID detector.

79 **Characterization**

80 The X-ray powder diffraction (XRD) patterns were recorded over a 2θ range of 5-50° with
81 step width of 0.02 and speed of 4° min⁻¹ on a D8 Advanced X-ray diffract meter. The Cu Kα
82 radiation generated at 40 kV and 100 mA was used as the X-ray source.

83 N₂ physical adsorption/desorption was performed to investigate the textural properties of
84 samples on a Micrometrics ASAP 2460 instrument. Before the test, all samples were heated to 423

85 K for 2 h to get rid of impurities.

86 TG-DSC-MS measurements were made with a NETZSCH STA 409 PC/PG and QMS 403, in
87 which ca. 10 mg of powder sample was loaded in a platinum crucible. Samples were heated to 800
88 °C at a rate of 10 °C min⁻¹ under a constant and simultaneous flow of air.

89 Dissolution/¹H NMR spectra were recorded with a Bruker AVANCE III NMR Spectrometer
90 (600 MHz). The relaxation delay (d1) was set to 20 s to ensure that reliable integrals were
91 obtained, allowing for the accurate determination of the relative concentrations of the molecular
92 components. The number of scans was 48. First, a quantity of MOF powder was weighed into a
93 1.5 ml vial, and then a D₂O solution of 1 M NaOH was added to the digestion medium. The vial
94 was capped and inverted 2-3 times, and then the sample was allowed to digest for 24 hours. The
95 supernatant from the digestion was tested.

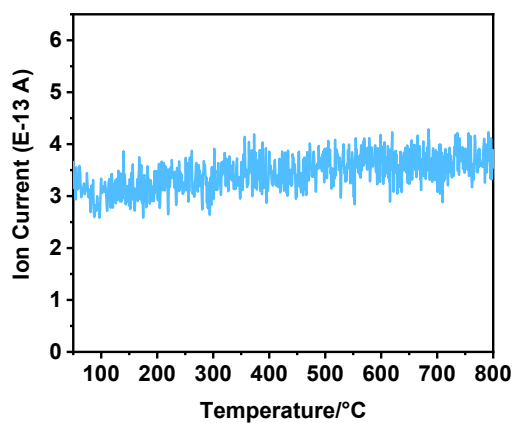
96 X-ray photoelectron spectroscopy (XPS) was performed using Thermo ESCALAB 250XI.
97 All spectra were obtained using Al K α X-ray source.

98 The elemental composition of the oxides was carried out by Inductive Coupled Plasma
99 Emission Spectrometer (ICP) on the ICP-MS 7900 instrument.

Table S1 Texture parameters of different samples

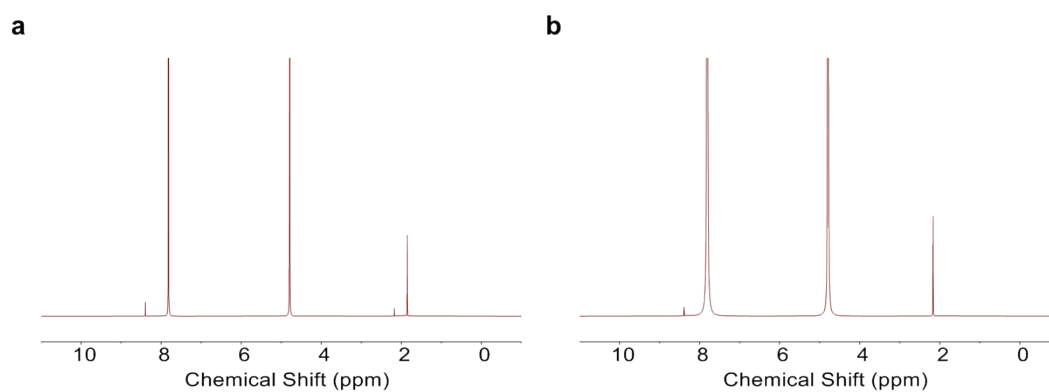
Samples	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)			Average pore size (nm)
		Total	Micro pore	Meso pore	
UiO-66	1107.93	0.61	0.55	0.06	0.51
UiO-66-AT	754.80	0.42	0.38	0.04	0.48
UiO-66-Ideal	726.96	0.40	0.36	0.04	0.45

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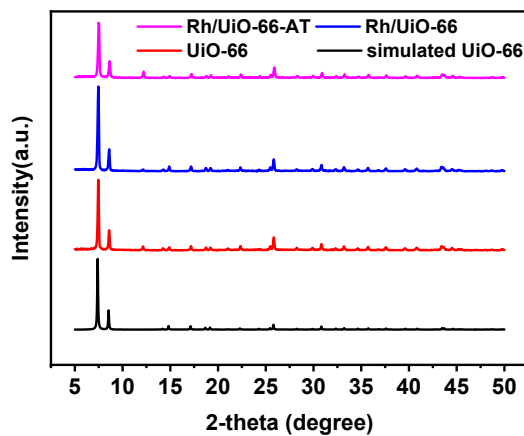
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102 **Fig. S1** 3-PPA signal of TG-MS from UiO-66-AT.



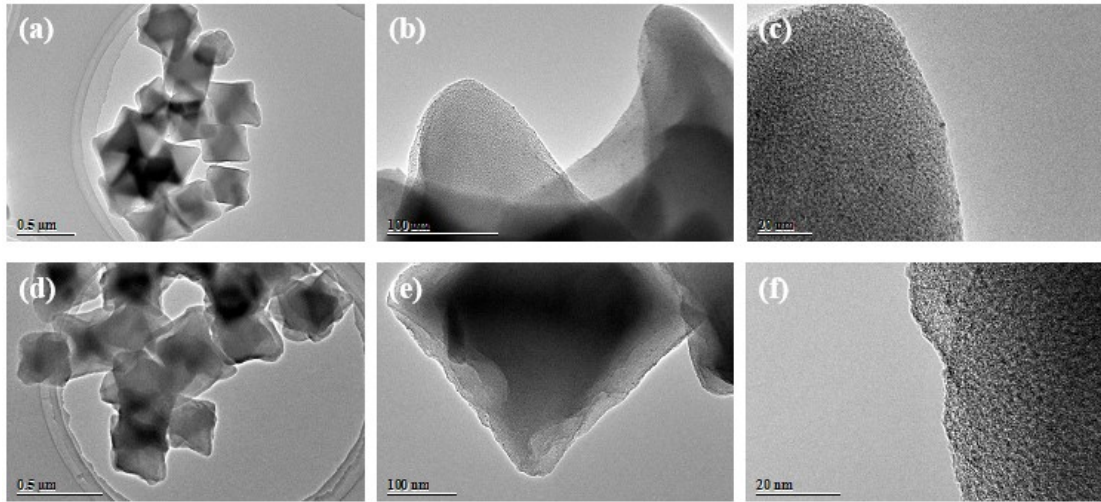
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104 **Fig. S2** The ^1H NMR spectra of UiO-66 (a) and UiO-66-ideal (b).



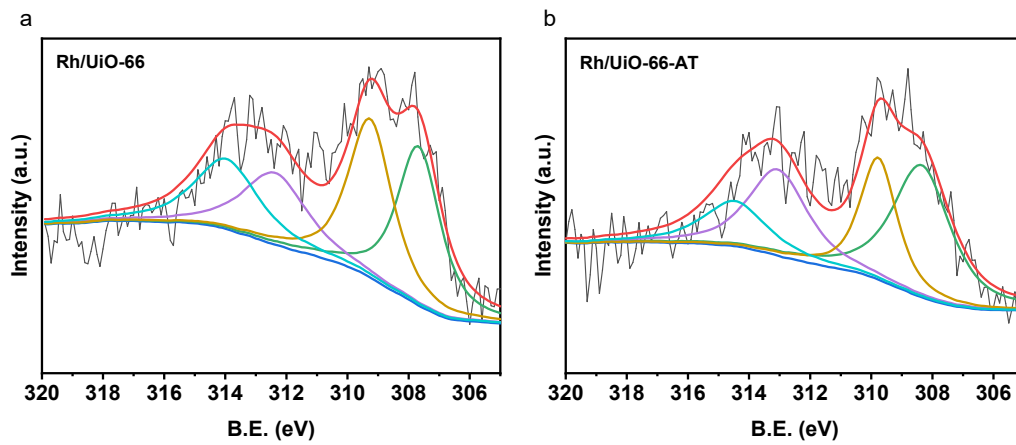
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106 **Fig. S3** The XRD spectra of UiO-66, Rh/UiO-66 and Rh/UiO-66-AT.



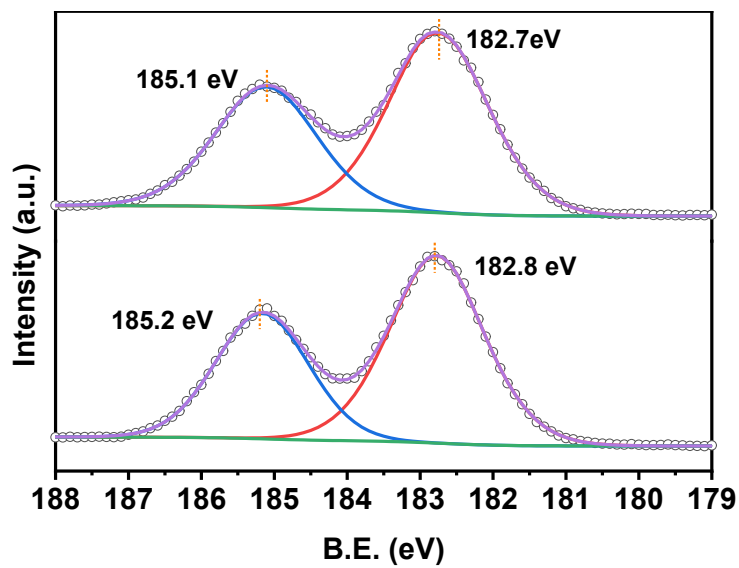
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108 **Fig. S4** TEM images of Rh/UiO-66 catalyst (a)-(c) and Rh/UiO-66-AT (d)-(f) catalyst.



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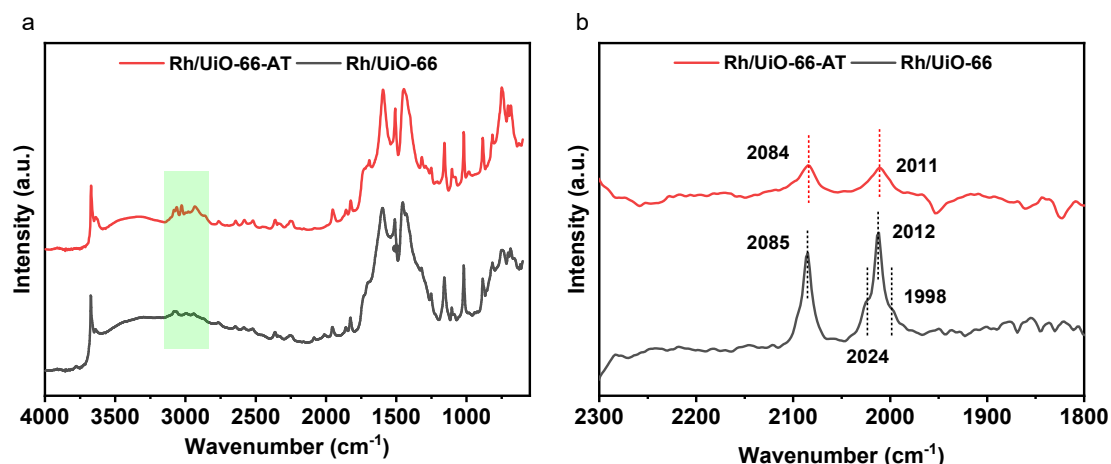
110 **Fig. S5** The Rh 3d spectra of Rh/UiO-66 (a) and Rh/UiO-66-AT (b).



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112 **Fig. S6** The Zr 3d spectra of Rh/UiO-66 (top) and Rh/UiO-66-AT (bottom).

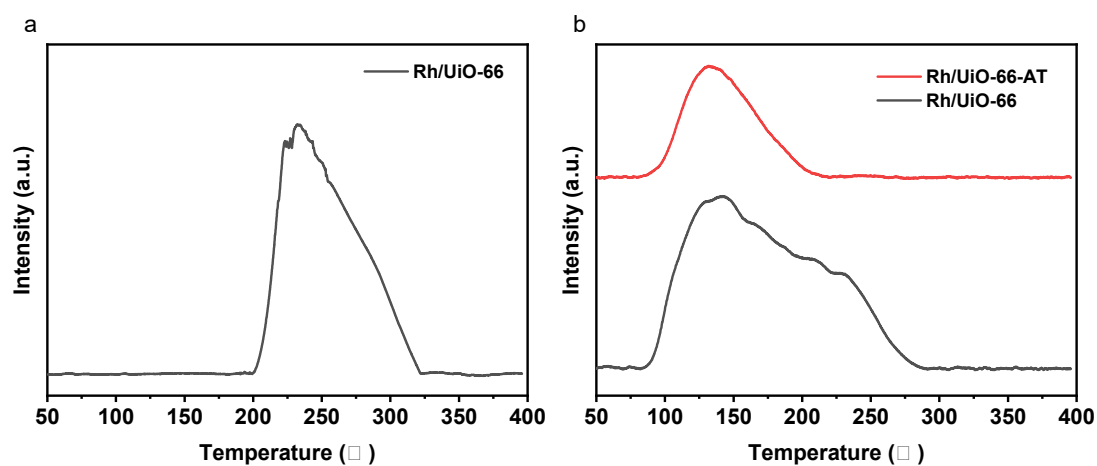
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115 **Fig. S7.** IR spectra of Rh/Uio-66 and Rh/Uio-66-AT(a); In situ DRIFT spectra after the treatment

116 of the samples with CO adsorption at 353 K(b).



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118 **Fig. S8** H₂-TPR profiles of Rh/Uio-66(a); NH₃-TPD profiles of Rh/Uio-66 and Rh/Uio-66-

119 AT(b).

Table S2 The loading amounts of Rh in the as-prepared samples.

Samples	Rh content (wt%)
Rh/Uio-66	0.185
Rh/Uio-66-AT	0.159

120 The loading contents were determined by the ICP-MS.

121 References

122 1. G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye and K. P. Lillerud, *Chemistry of*
 123 *Materials*, 2016, **28**, 3749-3761.

124 2. G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga

125 and K. P. Lillerud, *Chemistry of Materials*, 2014, **26**, 4068-4071.

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