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A new ligand-regulated strategy of highly mesoporous metal–organic framework assembled in ionic liquid/ethanol solvent

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Experimental Section

Materials: ILs, $HmimPF_6$ (purity>99%) were purchased from the Centre of Green Chemistry and Catalysis, LICP, CAS. ILs were dried at 70°C for 48 hours before used, and the water content was less than 0.05wt% as determined by Karl-Fischer method.[S1] Ethanol (A. R. grade), acetone (A. R. grade), H_3BTC (purity 98%), $Cu(NO_3)_2{\cdot}3H_2O$ (purity>99%), Na_2CO_3 (purity>99.8%), $MnCl_2$ (A. R. grade), $ZnCl_2$ (A. R. grade), Benzene dicarboxylic acid (H_2BDC, 98%), and methylbenzene (A. R. grade) were provided by Sinopharm Chemical Reagent Co., Ltd. TEMPO (purity 98%) and N,N-Dimethylformamide (purity>98%) were purchased from Alfa Aesar China Co., Ltd. Benzyl alcohol (99%), Benzaldehyde (98%), benzoic acid (99.5%), 4-methylbenzyl alcohol(98%), p-Methyl benzaldehyde (98%), 4-Methylbenzoic acid (99%), cinnamyl alcohol (98%), 2-Thiophenemethanol (98%), 2-Thiophenecarboxylic (99%), 2-Thiophenecarboxaldehyde(99%), 3-Nitrobenzyl alcohol (98%, 3-Nitrobenzaldehyde (99%), 3-Nitrobenzoic acid (99%), trans-Cinnamaldehyde

(98%), and trans-Cinnamic acid (99%) were purchased from J&K Scientific Co., Ltd.

MOF synthesis: For the synthesis of HKUST-1-1, in a typical experiment, the $HmimPF_6$ (4 g) and ethanol (1 g) were mixed and placed in a conical flask at 25 °C, then H_3BTC (0.01 g) was added into the conical flask under stirring. The following, $Cu(NO_3)_2{\cdot}3H_2O$ (0.02 g) was joined when it was turbidity. After the mixture was stirred at 25 °C for 9 h, the stirrer was stopped. The product was obtained after washing with ethanol and acetone for several times and drying at 60 °C under vacuum for 24 h. To synthesize HKUST-1-2，HKUST-1-3 and HKUST-1-4, the procedures were the similar, the main difference was the H_3BTC mass of 0.02 g, 0.03 g and 0.04 g. Correspond to it, the mass of $Cu(NO_3)_2{\cdot}3H_2O$ was 0.04 g, 0.06 g and 0.08 g, and the other procedures are similar to that described above.

For the synthesis of Zn-BTC MOF, the $[Hmim][PF_6]$ (4 g) and C_2H_5OH (1 g) were mixed and placed in a conical flask at 25 °C, then H_3BTC (0.04 g) was added into the conical flask under stirring. The following, $ZnCl_2$ (0.052 g) was joined when it was turbidity. After the mixture was stirred at 25℃ for 9 h, the stirrer was stopped. The product was obtained after washing with ethanol and acetone for several times and drying at 60 °C under vacuum for 24 h.

For the synthesis of Mn-BDC MOF, the $[Hmim][PF_6]$ (4 g) and C_2H_5OH (1 g) were mixed and placed in a conical flask at 25 °C, then H_2BDC (0.04 g) was added into the conical flask under stirring. The following, $MnCl_2$ (0.042 g) was joined when it was turbidity. After the mixture was stirred at 25 °C for 9 h, the stirrer was stopped. The product was obtained after washing with ethanol and acetone for several times and drying at 60 °C under vacuum for 24 h.

Material Characterization: XRD analysis of the samples was performed on the X-ray diffractometer (Bruker AXS D8) with Cu-Kα radiation, and the scan speed was 5°/min. The FT-IR spectra of the samples were performed on a Nicolet 5DX spectrometer. The morphologies of the products were characterized by JEOL-1011F transmission electron microscopy (TEM). For the sample preparation, 1 mg sample powder was dispersed in 5 mL acetone, and then 10 μL solution was added on the ultrafine carbon film. The pore properties were obtained from N_2 adsorption-desorption isotherms determined using a Micromeritics ASAP 2020M system.

Catalytic Test: The procedure of catalytic reaction was similar to those reported by Garcia and coworkers[S2]. A 5ml flask was charged with the required amount of catalyst, TEMPO, and sodium carbonate. To this mixture, 1ml DMF was added followed by the appropriate quantity of alcohol. The mixture was stirred at 75 ^{o}C under oxygen atmosphere. After the desired time, the heterogeneous mixture was cooled and centrifuged. The liquid product was analyzed by a gas chromatograph (SP-2100). For the reusability investigation, after some times of reaction the catalyst was recovered by centrifugation, washed with ethanol and dried under vacuum. Then the solid was reused for a consecutive run.

Supplementary Figures

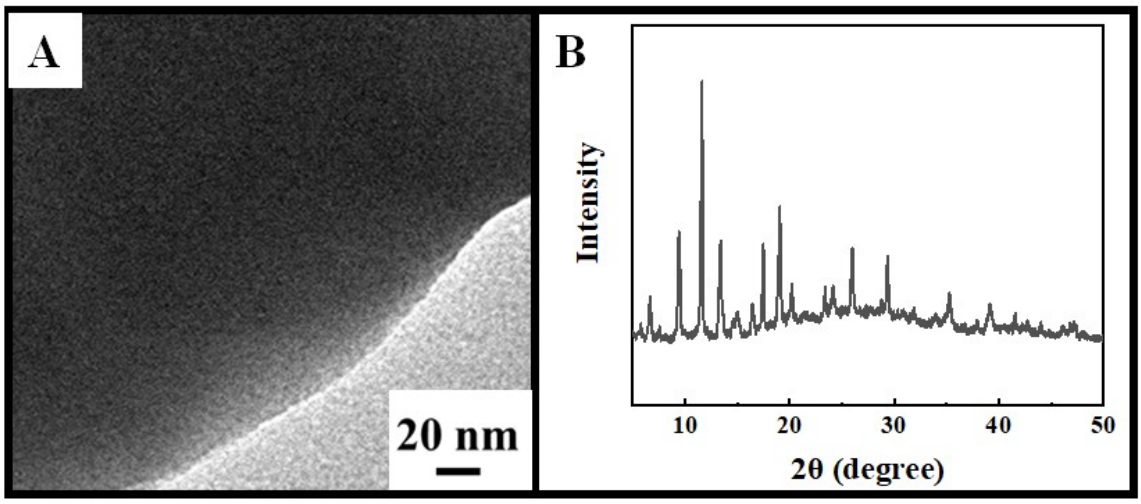

Fig.S1 TEM images (A) and XRD patterns (B) of HKUST-1 synthesized in water.

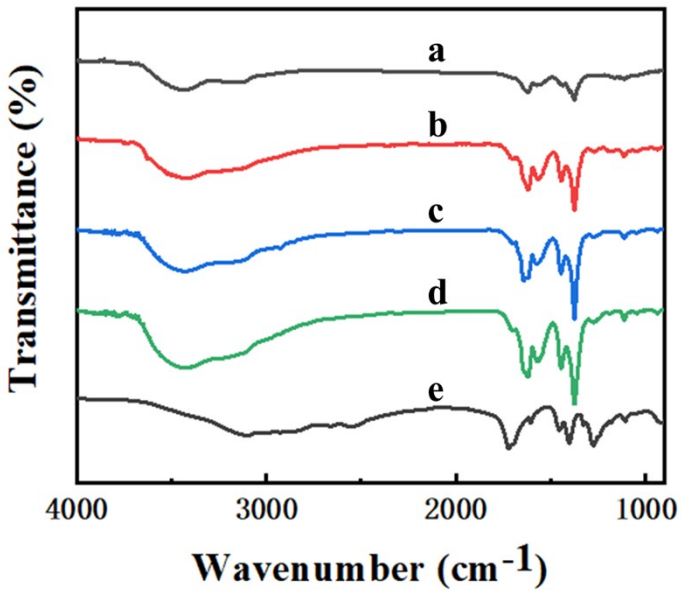

Fig. S2 The FT-IR spectra of the HKUST-1-1 (a), HKUST-1-2 (b), HKUST-1-3 (c), HKUST-1-4 (d) and H_3BTC (e), respectively.

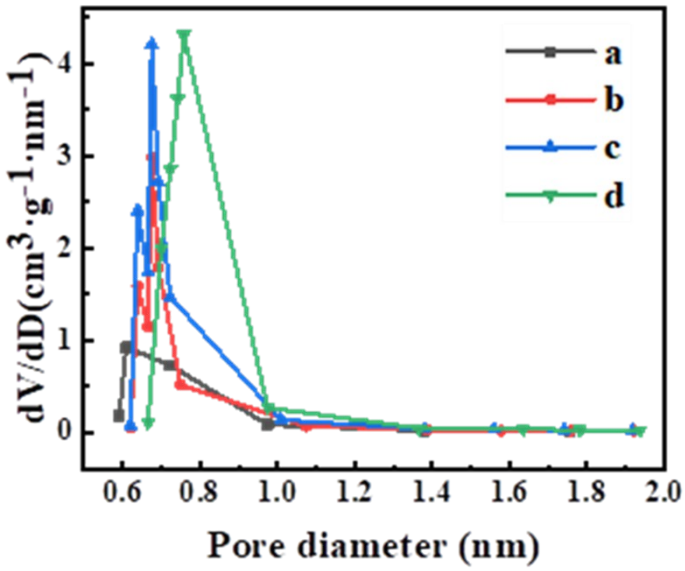

Fig. S3 Micropore size distribution of the HKUST-1-1 (a), HKUST-1-2 (b), HKUST-1-3 (c) and HKUST-1-4 (d), respectively.

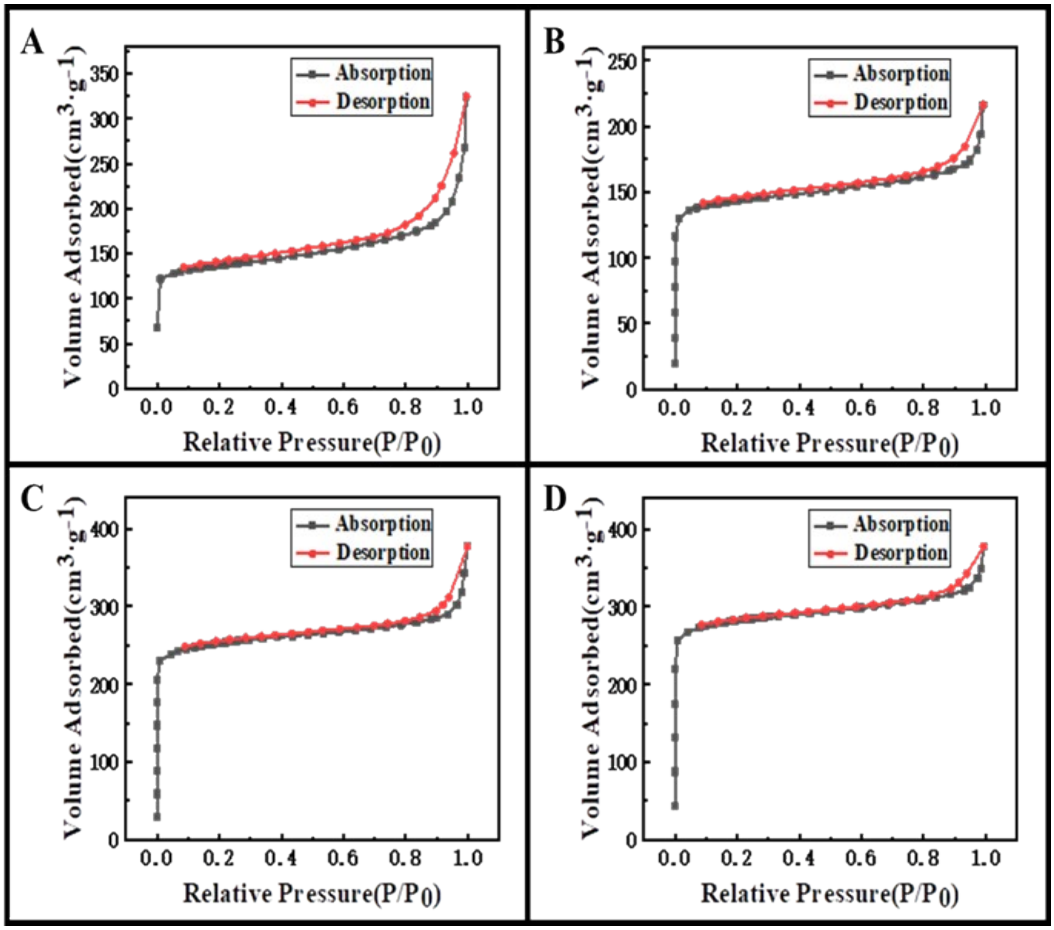

Fig. S4 N_2 adsorption/desorption curve graph of HKUST-1-1 (A), HKUST-1-2 (B), HKUST-1-3 (C) and HKUST-1-4 (D), respectively.

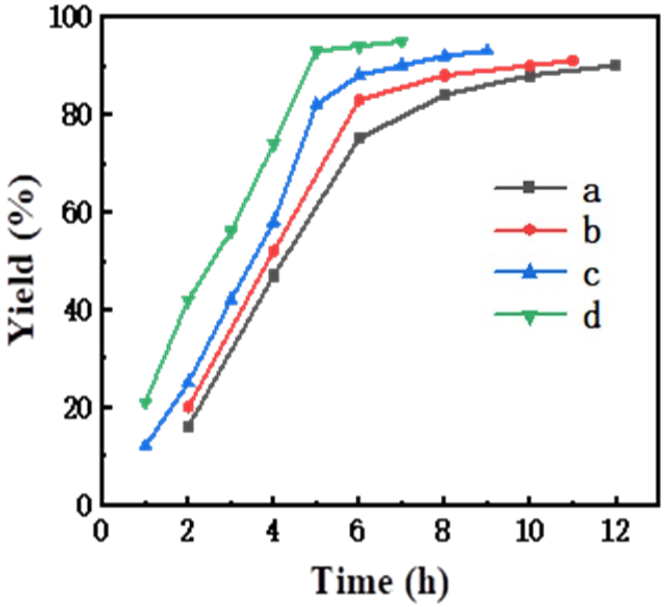

Fig. S5 Time conversion plot for the aerobic oxidation of benzyl alcohol to benzaldehyde catalyzed by HKUST-1-1 (a), HKUST-1-2 (b), HKUST-1-3 (c) and HKUST-1-4 (d), respectively.

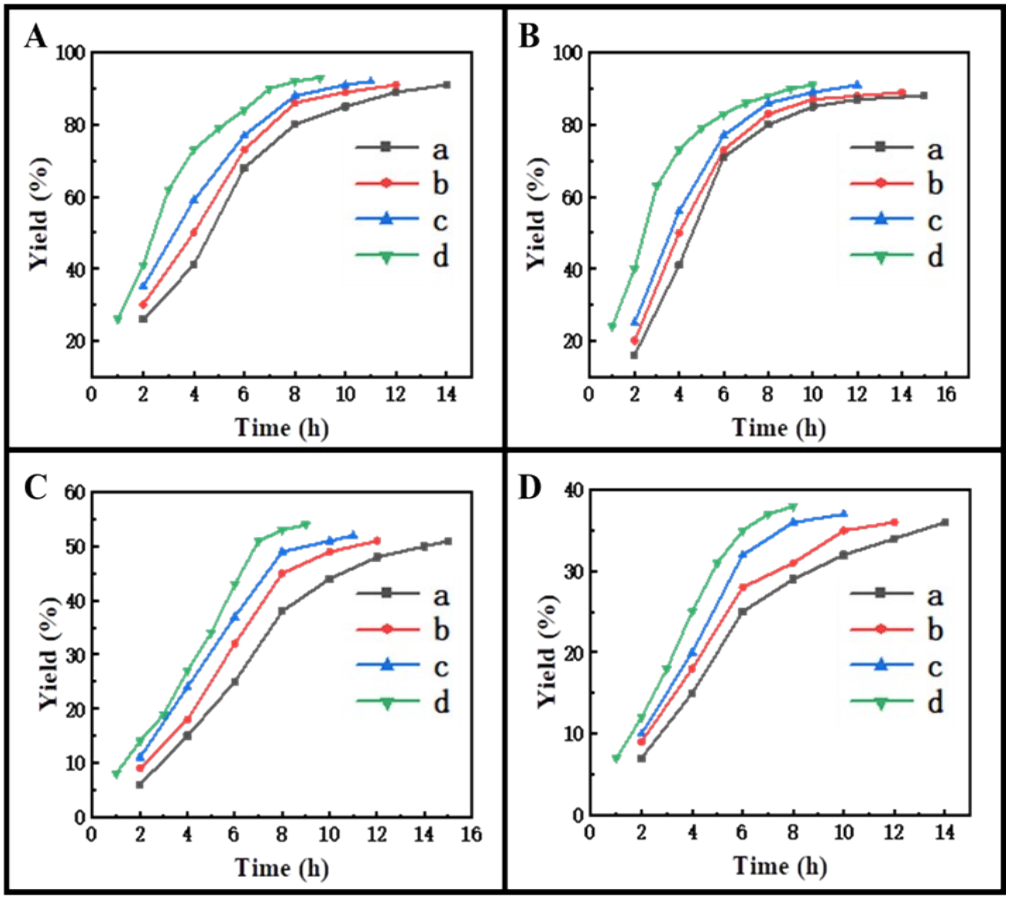

Fig. S6 Time conversion plot for the aerobic oxidation of alcohol to aldehyde catalyzed by HKUST-1-1 (a), HKUST-1-2 (b), HKUST-1-3 (c) and HKUST-1-4 (d), respectivel; the A represents entry 5-8, B blue represents entry 9-12, C represents entry 13-16, and D represents entry 17-20 in Table 2.

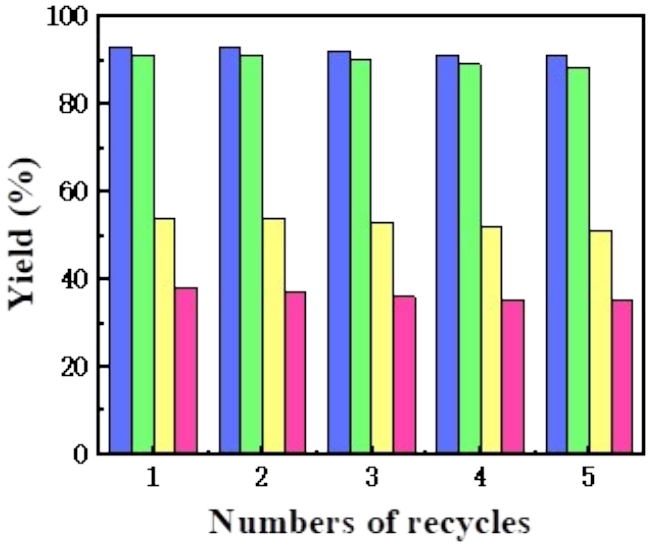

Fig. S7 The dependence of the yield of aldehyde on the reusability of the HKUST-1-4 catalyst under the reaction conditions, the blue represents entry 8, green blue represents entry 12, the yellow represents entry 16, and red represents entry 20 in Table 2.

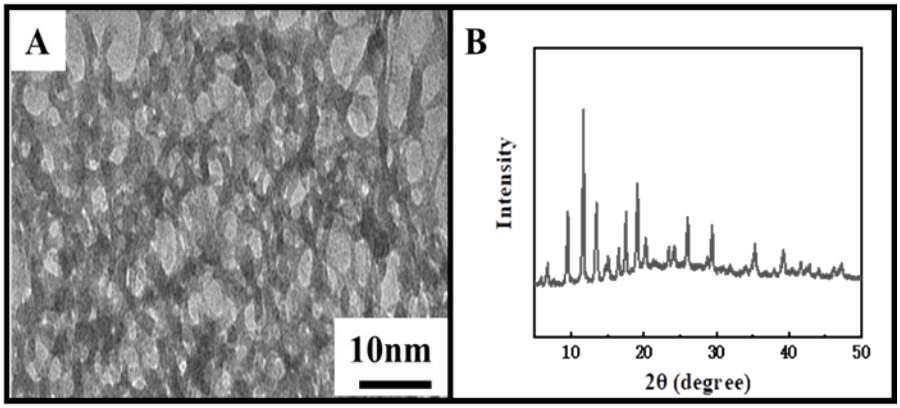

Fig. S8 TEM images of the after being used five times (A), XRD pattern of HKUST-1-4 after being used five times (B).

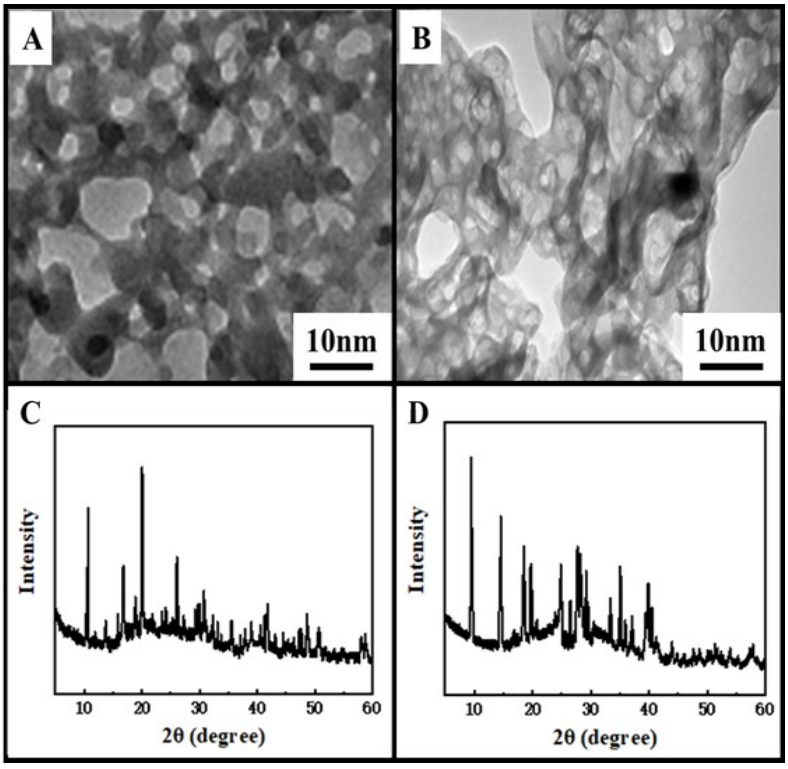

Fig.S9 TEM images and XRD patterns of Zn-BTC MOF (A,C) and Mn-BDC MOF (B,D), respectively.

References

1. X. F. Sun, Q. Q. Tian, Z. M. Xue, Y. W. Zhang, T. C. Mu, *RSC Adv.*, 2014, **4**, 30282.
2. A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *ACS Catal*., 2011, **1**, 48-53.