Background: Ambient crystallization conditions are one of the prerequisites in moving metal-organic frameworks (MOFs), especially those based on tetravalent metals, from lab to fab, yet the number of synthesis schemes under mild conditions is rather limited. Current synthetic methods require the addition of a modulator and heating—which is often poisonous and could prevent further applications. Objective: To develop a new strategy for the facile fabrication of Zr-based MOFs.

Methods: Zirconium hydroxide is directly immersed in the concentrated solutions of the ligands, including fumaric acid, H2BDC, H3BTC. The reactions are quenched at certain intervals in order to track the reaction process by ex-situ SEM and PXRD studies.

Results: Phase-pure MOF-801, MOF-808, and UiO-66 crystals could be obtained after 1 hour of reaction, whose morphology could be satisfactorily tuned due to the well-established dissolution-reprecipitation mechanism and Ostwald ripening, which is further confirmed by the Avrami model. All the MOF samples obtained show promising gas absorption capabilities confirmed by the BET absorption isotherm. The 240 kg/(m3*day) yield achieved for the Zr-based MOF-801 is, to the best of our knowledge, the highest space-time yield ever achieved for MOF-801 under room-temperature. Our method could also cope with the low purity and large particle size distribution problems that are common in the current synthesis methods.

Conclusion: We develop a facile method to rapidly synthesize highly-ordered Zr-MOF crystals, which could reach a high space-time yield. We also analyze the reaction kinetics using Avrami Model and show the reason why the sizes and morphology of the synthesized crystals could be well-controlled.