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Preparation of MOFs Catalysts Simultaneously Modulated Metal Nodes and Ligands Via One-Pot Method for Optimizing Cycloaddition Reactions

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General information: Commercial reagents were purchased from Sigma-Aldrich (ACS grade) and used as received unless otherwise noted. X-ray diffraction (XRD) patterns of samples were recorded with a Bruker AXS D8 Advance diffractometer using nickel-filtered Cu Kα radiation (λ= 1.5406 Å). Scanning electron microscope (SEM) images were taken by a JEOL JSM-7600 with an accelerating voltage of 5 kV. Transmission electron microscope (TEM) images were taken by JEOL JEM-2100 Plus at an accelerating voltage of 200 kV. Thermo gravimetric analyses (TGA) were performed on a Q500 TGA (TA Instruments) under nitrogen gas flow at 5 $°C \cdot min^{-1}$ from 30 °C to 800 °C. Nitrogen adsorption isotherms of powder samples were measured with a Micromeritics ASAP 2020 adsorption apparatus at 77 K up to 1 bar. Before starting the adsorption measurements, each sample was activated by heating under vacuum at 573 K for 3 h and then at 523 K for 20 h unless otherwise noted. The pore textural properties including specific Langmuir and Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore size were obtained by analyzing nitrogen adsorption and desorption isotherms with Micromeritics ASAP 2020 built-in software. Gas chromatography (GC) spectra were recorded on Agilent Technologies 7890B.

UiO-66 regulated by acetic acid: According to literature with modifications.[1] In a typical synthesis, 23.3 mg zirconium chloride ($ZrCl_4$, 0.01 M), 16.8 mg 1,4-dicarboxybenzene (0.01 M) and 1.37 mL acetic acid were dissolved in 10 mL N,N-Dimethylformamide (DMF) in a 40 mL glass sample vial by ultrasonication for about 1 min, and then the vial was capped and placed into an oven preheated at 120 °C for 24

h. The product was collected by centrifugation and then washed three times with DMF (with 20 mL DMF each time) and then ethanol for three times (with 20 mL ethanol each time). Finally, the resulting white powder was dried at 120 °C for 24 h.

UiO-66 regulated by benzoic acid: According to literature with a few modifications.[2] In a typical synthesis, 80 mg zirconium chloride ($ZrCl_4$, 0.017 M), 56.86 mg 1,4-dicarboxybenzene (0.017 M) and 0.42 g benzoic acid were dissolved in 20 mL DMF in a 40 mL glass sample vial by ultrasonication for about 1 min, and then the vial was capped and placed into an oven preheated at 120 °C for 24 h. The product was collected by centrifugation and then washed three times with DMF (with 20 mL DMF each time) and then ethanol for three times (with 20 mL ethanol each time). Finally, the resulting white powder was dried at 120 °C for 24 h.

UiO-66-OH: 23.3 mg zirconium chloride ($ZrCl_4$, 0.01 M), 18.2 mg 2-hydroxyterephthalic acid (0.01 M) and 1.37 mL acetic acid were dissolved in 10 mL DMF in a 40 mL glass sample vial by ultrasonication for about 1 min, and then the vial was capped and placed into an oven preheated at 120 °C for 24 h. The product was collected by centrifugation and then washed three times with DMF (with 20 mL DMF each time) and then ethanol for three times (with 20 mL ethanol each time). Finally, the resulting white powder was dried at 120 °C for 24 h.

UiO-66-2OH: 23.3 mg zirconium chloride ($ZrCl_4$, 0.01 M), 9.9 mg 2,5-

dihydroxytelephthalic acid (0.005 M) and 1.37 mL acetic acid were dissolved in 10 mL DMF in a 40 mL glass sample vial by ultrasonication for about 1 min, and then the vial was capped and placed into an oven preheated at 120 °C for 24 h. The product was collected by centrifugation and then washed three times with DMF (with 20 mL DMF each time) and then ethanol for three times (with 20 mL ethanol each time). Finally, the resulting white powder was dried at 120 °C for 24 h.

UiO-66-COOH: UiO-66-COOH was synthesized according to literature with modifications.[3, 4] In a typical synthesis, 1.8 g 1,2,4-benzenotricarboxylic acid, 1.0 g zirconyl nitrate ($ZrO(NO_3)_2 \cdot H_2O$) and 15.8 g benzoic acid was dissolved in 30 mL DMF solution at room temperature via ultrasonication. The mixture was then sealed in a Teflon reactor (100 mL) and allowed to react at 150 °C for 24 h without stirring. After cooling to room temperature, then the white precipitate was recovered by centrifugation and washing with DMF for three times (with 20 mL DMF for each time) and then ethanol for three times (with 20 mL ethanol for each time). Finally, the resulting white powder was dried at 120 °C for 24 h.

UiO-66-2COOH: UiO-66-2COOH was synthesized according to literature with modifications.[3, 4] 1,2,4,5-Benzenetetracarboxylic acid (4.3 g, 0.34 M) and $ZrCl_4$ (2.3 g, 0.2 M) were dissolved in deionized water (50 mL) and then allowed to reflux at 100 °C for 12 h. After cooling to room temperature, the resulting white gel was acquired by filtration, and then washed several times with distilled water for removal of the excess acids. Finally, the UiO-66-2COOH solid was dried at 80 °C overnight.

Zr/UiO-66-COOH: 1.8 g 1,2,4-benzenotricarboxylic acid, 1.0 g zirconyl nitrate ($ZrO(NO_3)_2 \cdot H_2O$), 17 mL trifluoroacetic acid and 1 mL HCl was dissolved in 30 mL DMF solution at room temperature via ultrasonication. The mixture was then sealed in a Teflon reactor (100 mL) and allowed to react at 150 ^{o}C for 24 h without stirring. After cooling to room temperature, then the white precipitate was recovered by centrifugation and washing with DMF for three times (with 20 mL DMF for each time) and then ethanol for three times (with 20 mL ethanol for each time). Finally, the resulting white powder was dried at 120 °C for 24 h.

Catalytic cycloaddition reactions: Typically, a glass bottle (20 mL) was charged with 20 mg catalysts, 1,3-cyclohexanedione (0.06 M) and 3-methyl-2-butenal or cinnamaldehyde (0.03 M) in 4 mL of dichloromethane. The reaction mixture was then stirred at room temperature for 24 h. After the reaction, the catalyst powder was filtered off and the filtrate was analyzed using a gas chromatography equipped with a HP-5 column and flame ionization detector (FID).

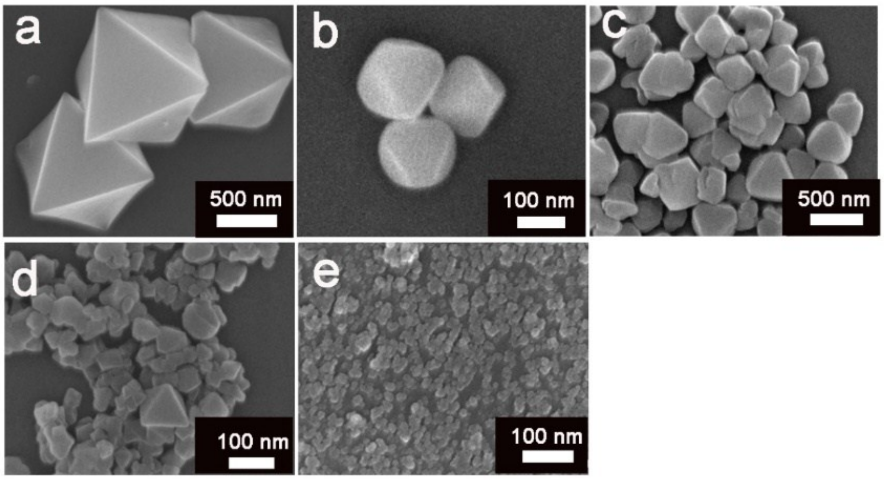


Fig. S1. SEM images of MOFs. (a) UiO-66, (b) UiO-66-OH, (c) UiO-66-2OH, (d) UiO-66-COOH and (e) UiO-66-2COOH.

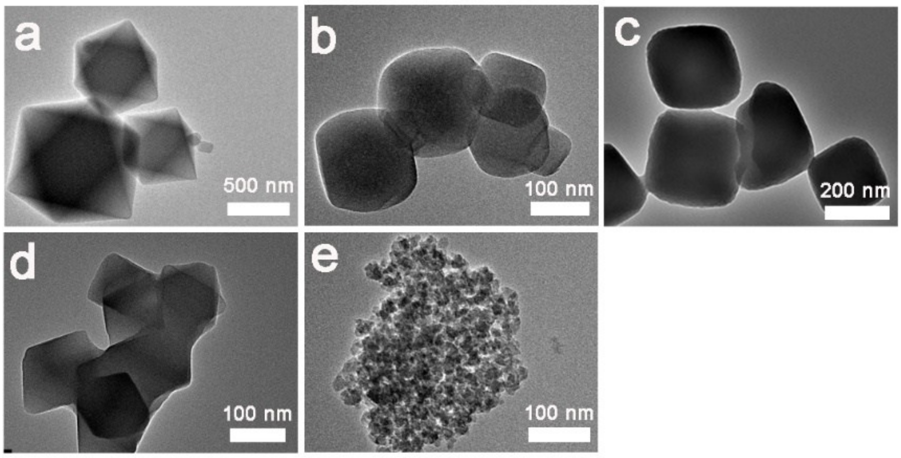


Fig. S2. TEM images of MOFs. (a) UiO-66, (b) UiO-66-OH, (c) UiO-66-2OH, (d) UiO-66-COOH and (e) UiO-66-2COOH.

Table S1. Porosity parameters of UiO-66, UiO-66-OH, UiO-66-2OH, UiO-66-COOH and UiO-66-2COOH.

Samples	BET SA [a] $[m^2 \cdot g^{-1}]$	V_t [b] $[cm^3 \cdot g^{-1}]$	$D_{Micropore}$ [c] [nm]	$D_{Mesopore}$ [d] [nm]
UiO-66	1234.81	0.46	0.68, 0.86	-
UiO-66-OH	1185.52	0.50	0.68, 0.86, 1.48	-
UiO-66-2OH	186.40	0.16	0.64, 1.48	2.73
UiO-66-COOH	324.86	0.31	0.68, 1.23	2.73
UiO-66-2COOH	182.87	0.07	1.59	-

a) BET SA is the Brunauer–Emmett–Teller surface area; b) The pore volume is the total specific pore volume determined by using the adsorption branch of the N_2 isotherm at $P/P_0 = 0.99$; c) Micropore diameter determined by the density functional theory (DFT) method by N_2 adsorption branch at 77 K. Mesopore diameters were determined from the local maximum of the Barrett–Joyner–Halenda (BJH) distribution of pore diameters obtained in the adsorption branch of the N_2 isotherm.

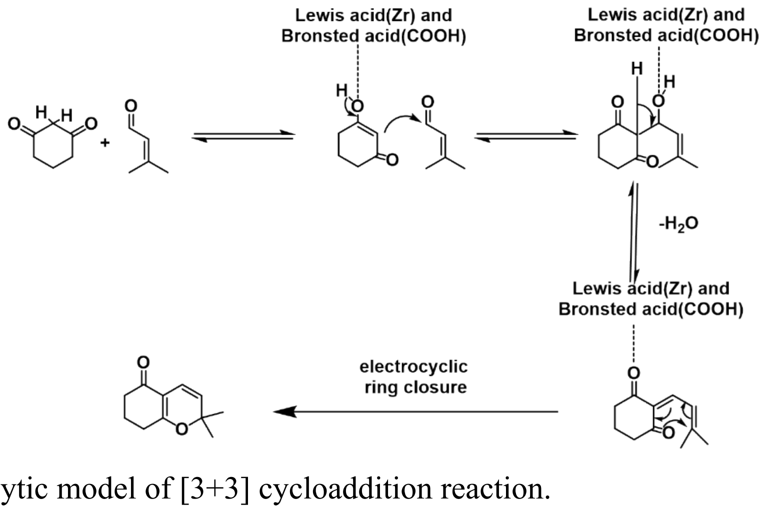


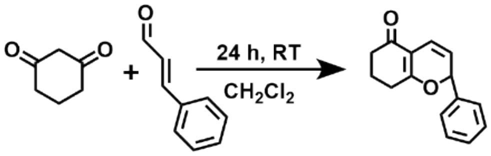
Fig. S3. catalytic model of [3+3] cycloaddition reaction.

Table S2. The amounts of ligands were calculated by the $[Zr_6O_4(OH)_4(BDC\text{-}X)_6]$

(X=OH, 2OH, COOH, 2COOH).

MOF (20 mg)	The amount of ligand (mg)
UiO-66	12.0
UiO-66-OH	12.4
UiO-66-2OH	12.7
UiO-66-COOH	13.0
UiO-66-2COOH	13.8

Table S3. Catalytic properties of UiO-66, UiO-66-OH, UiO-66-2OH, UiO-66-COOH and UiO-66-2COOH in cycloaddition reactions between 1,3-cyclohexanedione and cinnamaldehyde[a]



Entry	Catalysts	Conv. (%)
1	UiO-66	8.51
2	UiO-66-OH	8.03
3	UiO-66-2OH	9.87
4	UiO-66-COOH	**28.07**
5	UiO-66-2COOH	14.24

[a]Reaction conditions: 20 mg of catalyst, 0.06 M 1,3-cyclohexanedione and 0.03 M cinnamaldehyde, 4 mL of dichloromethane, room temperature, t=24 h.

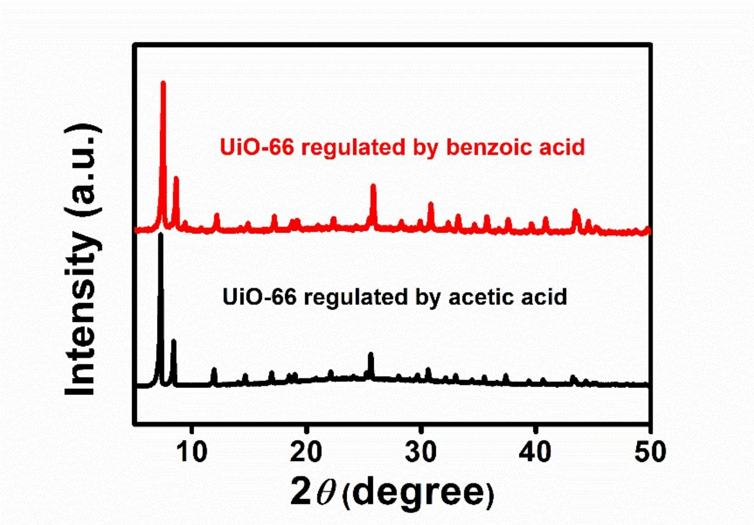


Fig. S4. XRD patterns of UiO-66 regulated by acetic acid and UiO-66 regulated by benzoic acid.

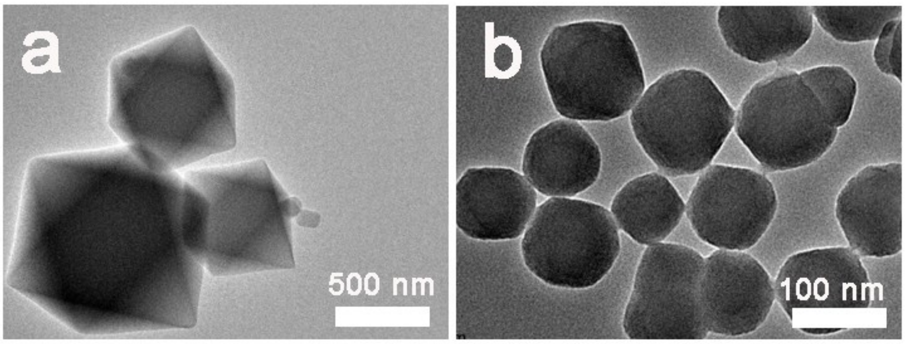


Fig. S5. TEM images of MOFs. (a) UiO-66 regulated by acetic acid and (b) UiO-66 regulated by benzoic acid.

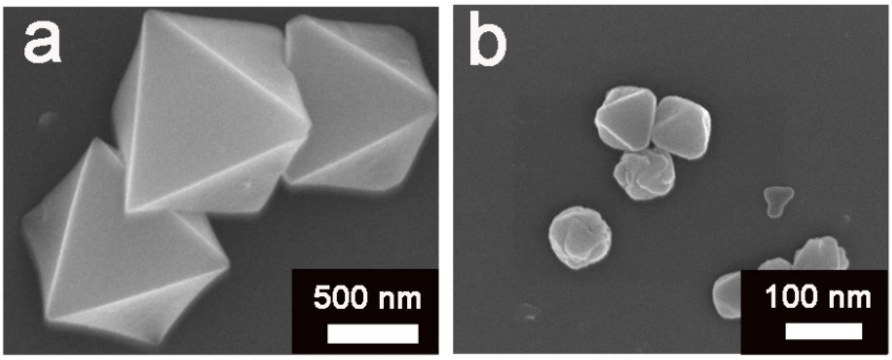


Fig. S6. SEM images of MOFs. (a) UiO-66 regulated by acetic acid and (b) UiO-66 regulated by benzoic acid.

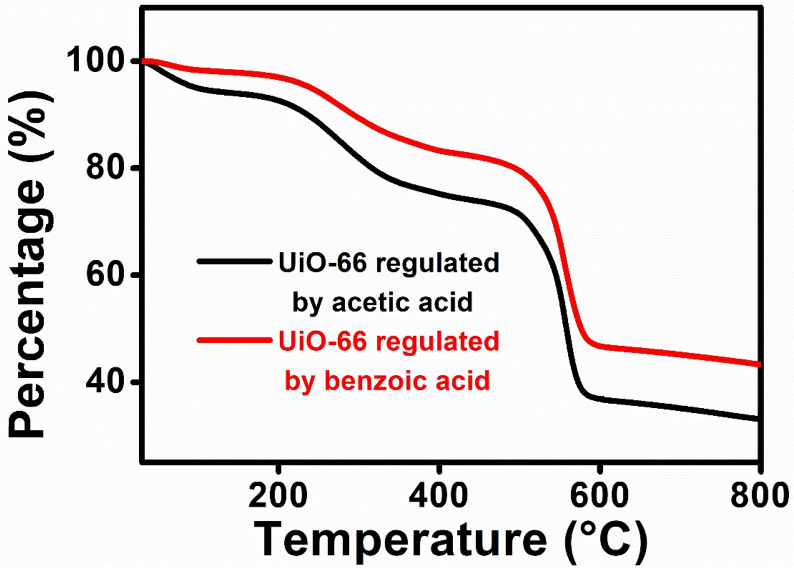


Fig. S7. TGA spectra of UiO-66 regulated by acetic acid and UiO-66 regulated by benzoic acid.

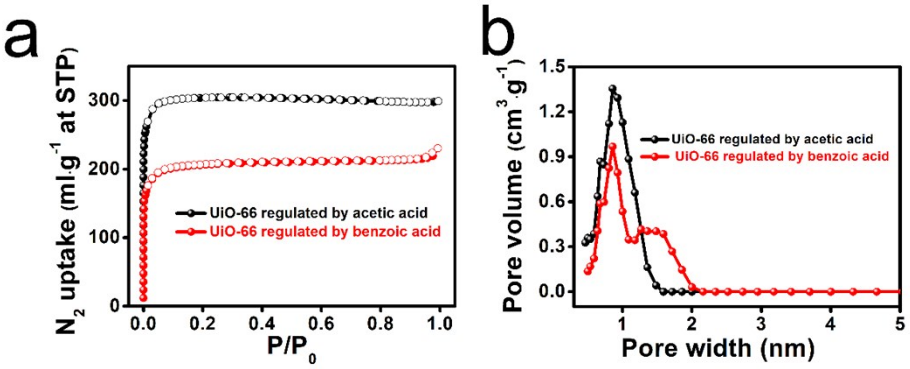


Fig. S8. (a) The nitrogen adsorption–desorption isotherm of UiO-66 regulated by acetic acid and UiO-66 regulated by benzoic acid at 77 K; (b) Pore-size distribution of UiO-66 regulated by acetic acid and UiO-66 regulated by benzoic acid.

Table S4. Porosity parameters of UiO-66 regulated by acetic acid and UiO-66 regulated by benzoic acid.

Samples	BET SA $^{a)}$ $[\mathrm{m}^2\cdot\mathrm{g}^{-1}]$	V_t $^{b)}$ $[\mathrm{cm}^3\cdot\mathrm{g}^{-1}]$	$D_{\mathrm{Micropore}}$ $^{c)}$ [nm]
UiO-66 regulated by acetic acid	1,234.81	0.46	0.68, 0.86
UiO-66 regulated by benzoic acid	811.90	0.36	0.86

a) BET SA is the Brunauer–Emmett–Teller surface area; b) The pore volume is the total specific pore volume determined by using the adsorption branch of the N_2 isotherm at $P/P_0 = 0.99$; c) Micropore diameter determined by the density functional theory (DFT) method by N_2 adsorption branch at 77 K. Mesopore diameters were determined from the local maximum of the Barrett–Joyner–Halenda (BJH) distribution of pore diameters obtained in the adsorption branch of the N_2 isotherm.

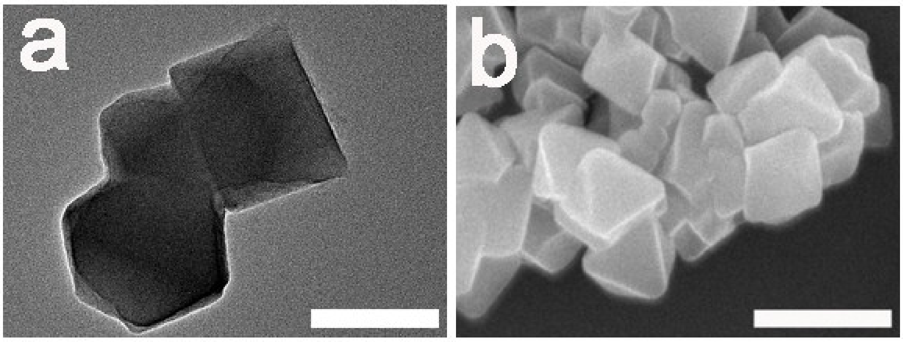


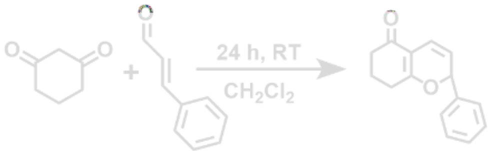
Fig. S9. (a) TEM image of Zr/UiO-66-COOH; (b) SEM image of Zr/UiO-66-COOH. Scarle bar is 100 nm.

Table S5. Porosity parameters of UiO-66-COOH and Zr/UiO-66-COOH.

Samples	BET SA a) [$m^2 \cdot g^{-1}$]	V_t b) [$cm^3 \cdot g^{-1}$]	$D_{Mesopore}$ c) [nm]	$V_{Mesopore}$ d) [$cm^3 \cdot g^{-1}$]	$V_{Meeopore}/V_{Micropore}$ e)
UiO-66-COOH	324.86	0.31	2.73	0.19	1.58
Zr/UiO-66-COOH	592.82	0.49	2.52,9.31	0.35	2.50

a) BET SA is the Brunauer–Emmett–Teller surface area; b) The pore volume is the total specific pore volume determined by using the adsorption branch of the N_2 isotherm at $P/P_0 = 0.99$; c) Mesopore diameters were determined from the local maximum of the Barrett–Joyner–Halenda (BJH) distribution of pore diameters obtained in the adsorption branch of the N_2 isotherm; d) Mesopore volumes were obtained from the BJH cumulative specific adsorption volume of pores of 1.70–300.00 nm in diameter; e) Micropore volume calculated by subtracting Vmeso from Vt (total specific pore volume determined by using the adsorption branch of the N_2 isotherm at $P/P_0= 0.99$)

Table S6. Catalytic properties of UiO-66-COOH and Zr/UiO-66-COOH in cycloaddition reactions between 1,3-cyclohexanedione and cinnamaldehyde[a]



Entry	Catalysts	Conv. (%)
1	UiO-66-COOH	28.07
2	UiO-66-2COOH	**43.24**

[a] Reaction conditions: 20 mg of catalysts, 0.06 M 1,3-cyclohexanedione and 0.03 M cinnamaldehyde, 4 mL of dichloromethane, room temperature, t=24 h.

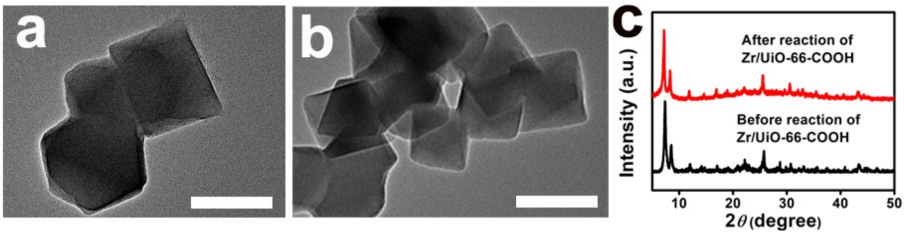


Fig. S10. (a) TEM image of Zr/UiO-66-COOH composites before [3+3] cycloaddition reaction; (b) TEM image of Zr/UiO-66-COOH composites after [3+3] cycloaddition reaction. Scale bar is 100 nm; (c) XRD patterns of Zr/UiO-66-COOH composites before and after [3+3] cycloaddition reaction for three consecutive runs.

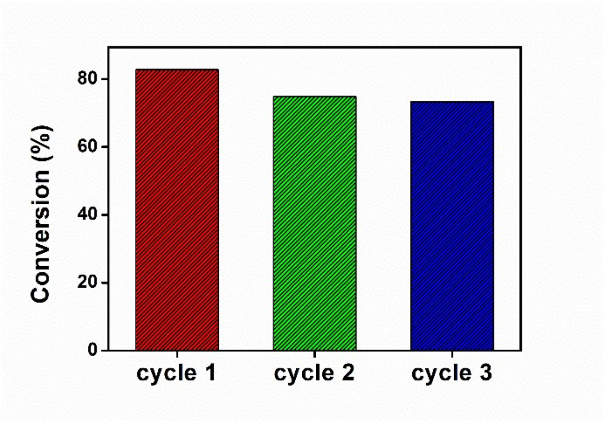


Fig. S11. The reusability of Zr/UiO-66-COOH composites in the [3+3] cycloaddition reaction for three consecutive runs.

1. W. Zhang, G. Lu, C. Cui, Y. Liu, S. Li, W. Yan, C. Xing, Y. R. Chi, Y. Yang, F. Huo, *Adv. Mater.* 2014, **26**, 4056-4060.
2. A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke,P. Behrens, *Chem. Eur. J.* 2011, **17**, 6643-6651.
3. S. Biswas, J. Zhang, Z. Li, Y.Y. Liu, M. Grzywa, L. Sun, D. Volkmer, P.V.D. Voort, *Dalton Trans*. 2013, **42**, 4730-4737.
4. Q. Yang, S. Vaesen, F. Ragon, A.D. Wiersum, D. Wu, A. Lago, T. Devic,C. Martineau, F. Taulelle, P.L. Llewellyn, H. Jobic, C. Zhong, C. Serre,G.D. Weireld, G. Maurin, *Angew. Chem. Int.* 2013, **52**, 10316-10320.