Electronic supplementary information

Ferrocenecarboxylic acid: A functional modulator for UiO-66 synthesis and incorporation of Pd nanoparticles

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1. Tables

Table S1 Detailed experimental conditions for preparation of UiO-66-Fc with addition of different equiv. of FcCOOH as modulator.

Runs	$ZrCl_4$		BDC		FcCOOH		FcCOOH/$ZrCl_4$	DMF	t
	mg	mmol	mg	mmol	mg	mmol	mol/mol	mL	h
1	117.6	0.5	83.8	0.5	--	--	0	15	12
2	116.2	0.5	83.2	0.5	115.4	0.5	1.0	15	12
3	118.6	0.5	83.2	0.5	231.5	1.0	2.0	15	12
4	116.6	0.5	83.5	0.5	690.6	3.0	6.0	15	12
5	117.6	0.5	83.4	0.5	1151.2	5.0	10.0	15	12

Table S2 Textural properties of UiO-66-Fc synthesized with different addition equivalent of FcCOOH.

Addition equiv. of FcCOOH	S_{BET} (m^2 g^{-1})	$S_{Langmuir}$ (m^2 g^{-1})	V_{micro} (cm^3 g^{-1})	V_{Total} (cm^3 g^{-1})	Pore size (nm)
0	485	729	0.22	0.30	0.51, 0.60
1	579	913	0.24	0.39	0.53, 0.59
2	658	1060	0.26	0.48	0.51, 0.59
6	1106	1774	0.47	0.85	0.54, 0.61
10	1364	2206	0.56	1.21	0.53, 0.60

Table S3 Content of FcCOOH and Fe/Zr in UiO-66-Fc measured by ICP-AES.

Addition equiv. of FcCOOH	Content of FcCOOH in UiO-66-Fc	Fe/Zr
	wt%	mol/mol
0	0	0
1	3.42	0.06
2	5.56	0.12
6	17.90	0.37
10	27.7	0.44

Table S4 Electrochemical data of UiO-66-Fc synthesized with different FcCOOH/Zr at different scan rate.

Samples	v	E_{pa}[a]	E_{pc}[b]	$E_{1/2}$[c]	ΔE_p[d]	i_{pa}[e]	i_{pc}[f]	i_{pa}/i_{pc}
	V/s	V	V	V	V	μA	μA	
FcCOOH/Zr=2	0.1	0.727	0.692	0.710	0.035	0.968	0.834	1.15
	0.2	0.744	0.686	0.715	0.058	1.595	1.447	1.10
	0.3	0.760	0.677	0.719	0.083	2.134	1.977	1.08
	0.4	0.772	0.673	0.723	0.099	2.640	2.449	1.08
	0.5	0.772	0.668	0.720	0.104	3.099	2.907	1.07
FcCOOH/Zr=6	0.1	0.765	0.659	0.712	0.106	1.982	1.312	1.51
	0.2	0.773	0.666	0.720	0.107	2.625	1.997	1.31
	0.3	0.779	0.664	0.722	0.115	3.210	2.589	1.24
	0.4	0.782	0.663	0.723	0.119	3.762	3.152	1.19
	0.5	0.784	0.664	0.724	0.120	4.250	3.662	1.16
FcCOOH/Zr=10	0.1	0.763	0.663	0.713	0.100	4.013	2.377	1.67
	0.2	0.768	0.663	0.716	0.105	4.886	3.258	1.50
	0.3	0.770	0.666	0.718	0.104	5.397	3.924	1.38
	0.4	0.776	0.666	0.721	0.110	5.951	4.490	1.33
	0.5	0.781	0.671	0.726	0.110	6.578	5.102	1.29

a: E_{pa}: Oxidation peak potential

b: E_{pc}: Reduction peak potential

c: The half wave potential, $E_{1/2}=(E_{pa}+E_{pc})/2$.

d: The difference of the oxidation potential and reduction potential, $\triangle E_p = E_{pa}-E_{pc}$.

e: i_{pa}: Oxidation peak current

f: i_{pc}: Reduction peak current

2. Figures

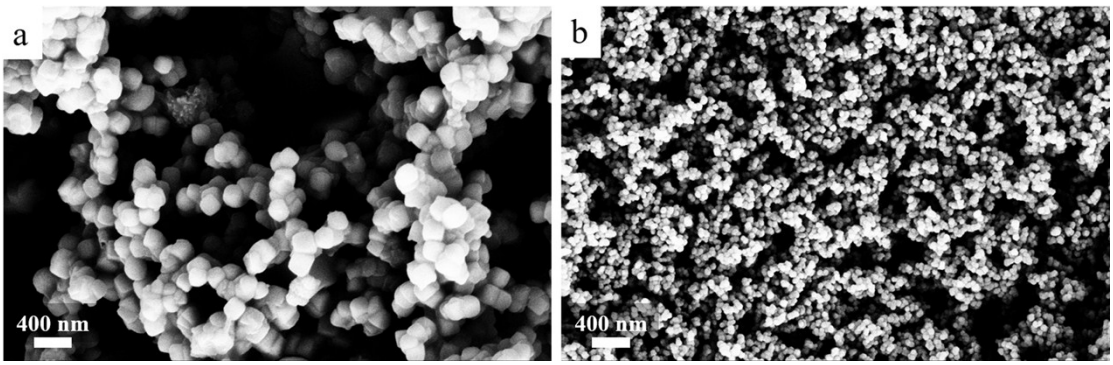

Fig. S1 SEM images of UiO-66 synthesized using 10 equiv. of CH_3COOH (a) and 10 equiv. of FcCOOH (b) as modulators.

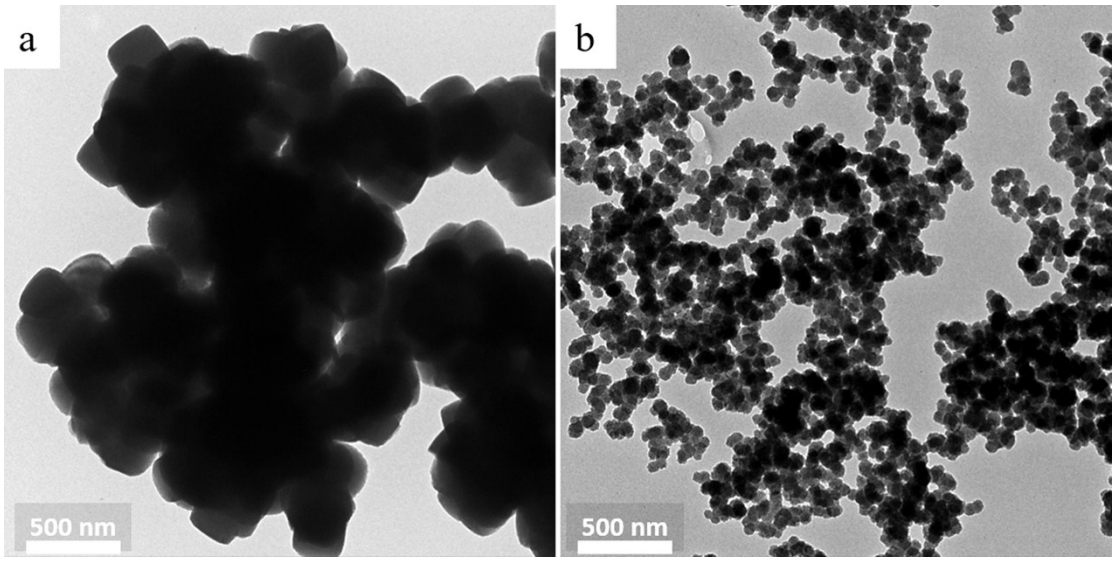

Fig. S2 TEM images of UiO-66 synthesized using 10 equiv. of CH_3COOH (a) and 10 equiv. of FcCOOH (b) as modulators.

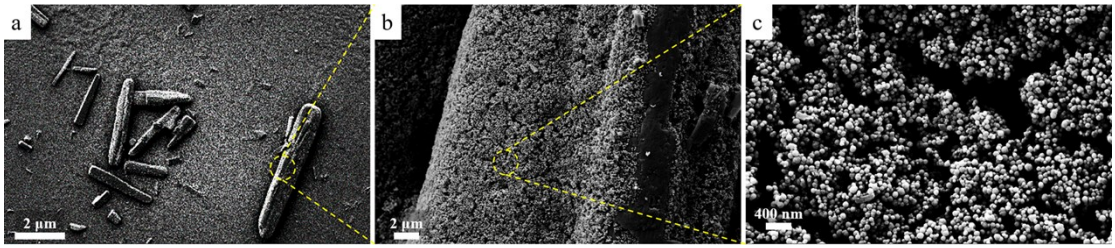

Fig. S3 SEM images (a) and magnified SEM images (b-c) of buck crystals synthesized using 20 equiv. of FcCOOH as a modulator.

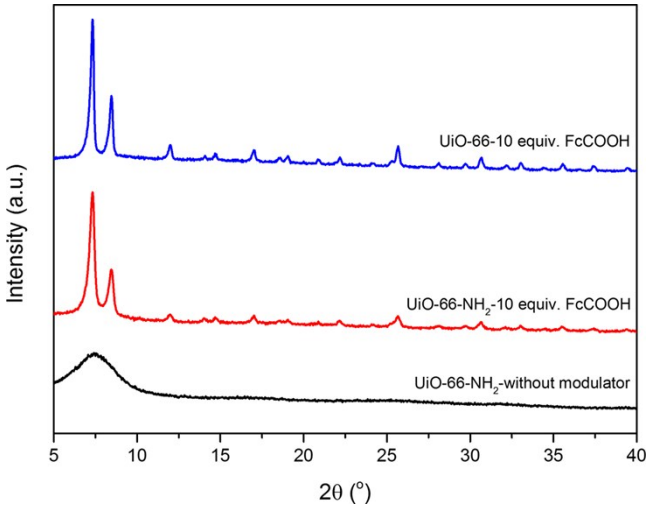

Fig. S4 XRD patterns of UiO-66-NH_2 without modulator and with addition of 10 equiv. of FcCOOH as a modulator. UiO-66 synthesized with 10 equiv. of FcCOOH as a modulator was also listed for comparison.

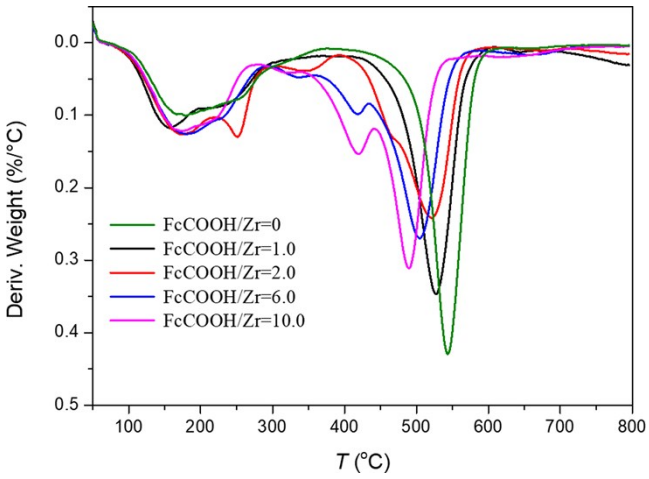

Fig. S5 DTGA curves of UiO-66-Fc synthesized with addition of different equiv. of FcCOOH as a modulator.

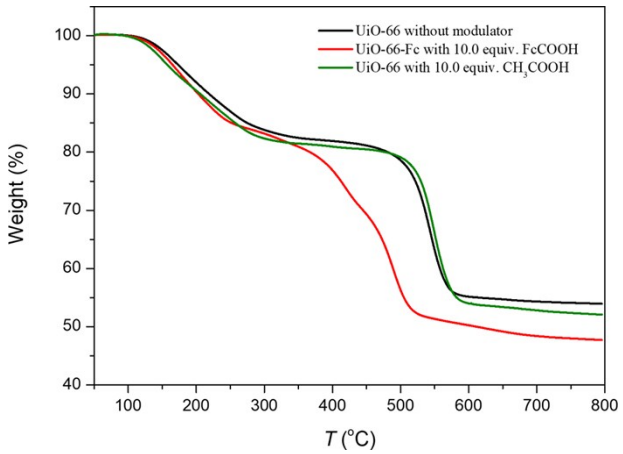

Fig. S6 TGA curves of UiO-66 without addition of modulator and UiO-66 synthesized with addition of 10 equiv. of FcCOOH or CH_3COOH as a modulator.

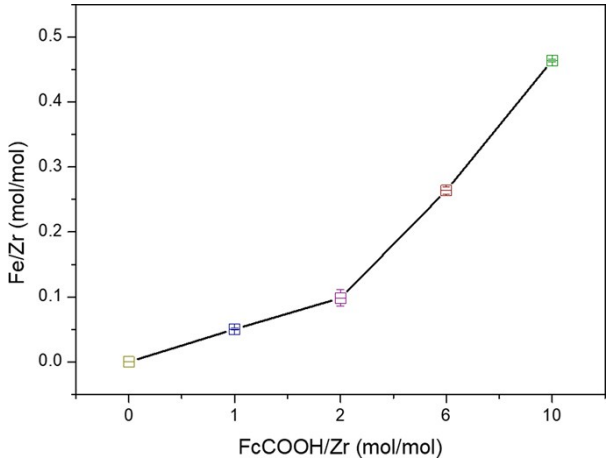

Fig. S7 Calculated Fe/Zr molar ratio of UiO-66-Fc synthesized with addition of different equiv. of FcCOOH as a modulator.

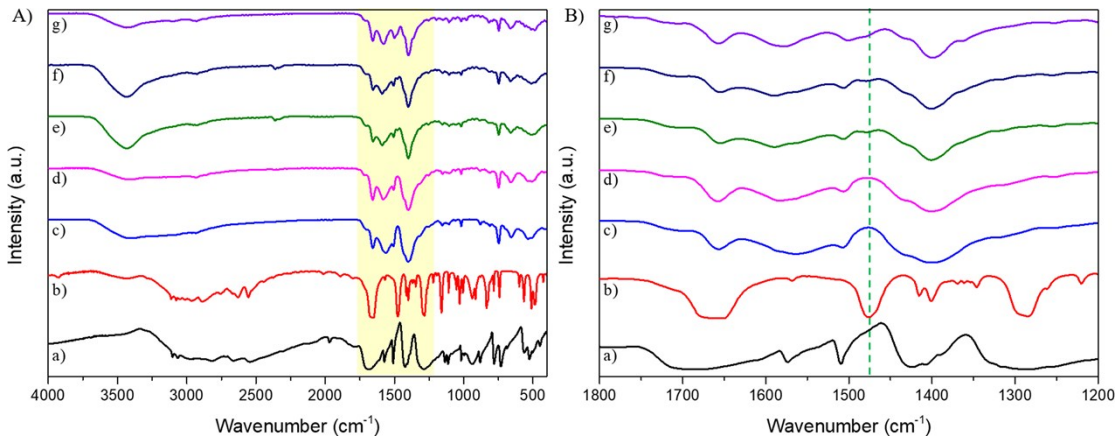

Fig. S8 FT-IR spectra (A) and local magnified FT-IR spectra (B) of a) H_2BDC, b) FcCOOH, UiO-66-Fc synthesized with addition of different equiv. of FcCOOH as a modulator. c) 0 equiv. d) 1 equiv. e) 2 equiv. f) 6 equiv. and g) 10 equiv.

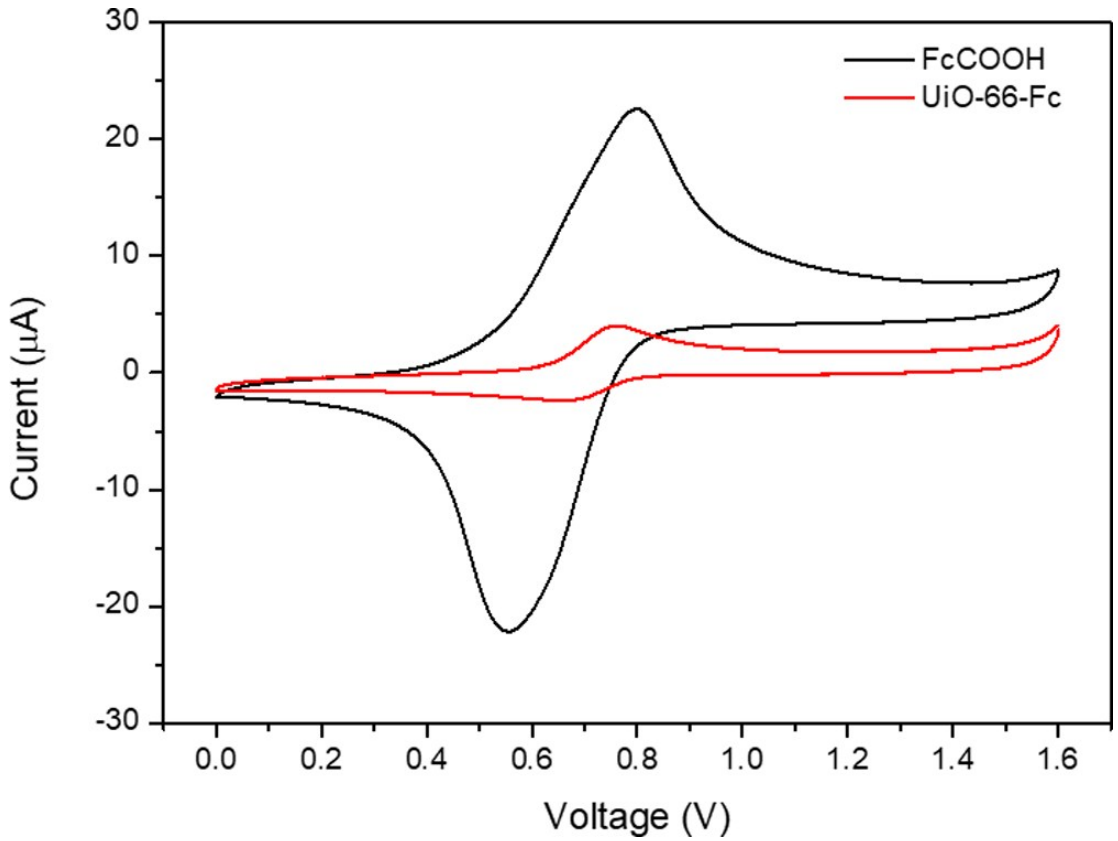

Fig. S9 Cyclic voltammetry curves of FcCOOH and UiO-66-Fc synthesized with addition of 10 equiv. of FcCOOH under a scanning rate 0.1 V/s).

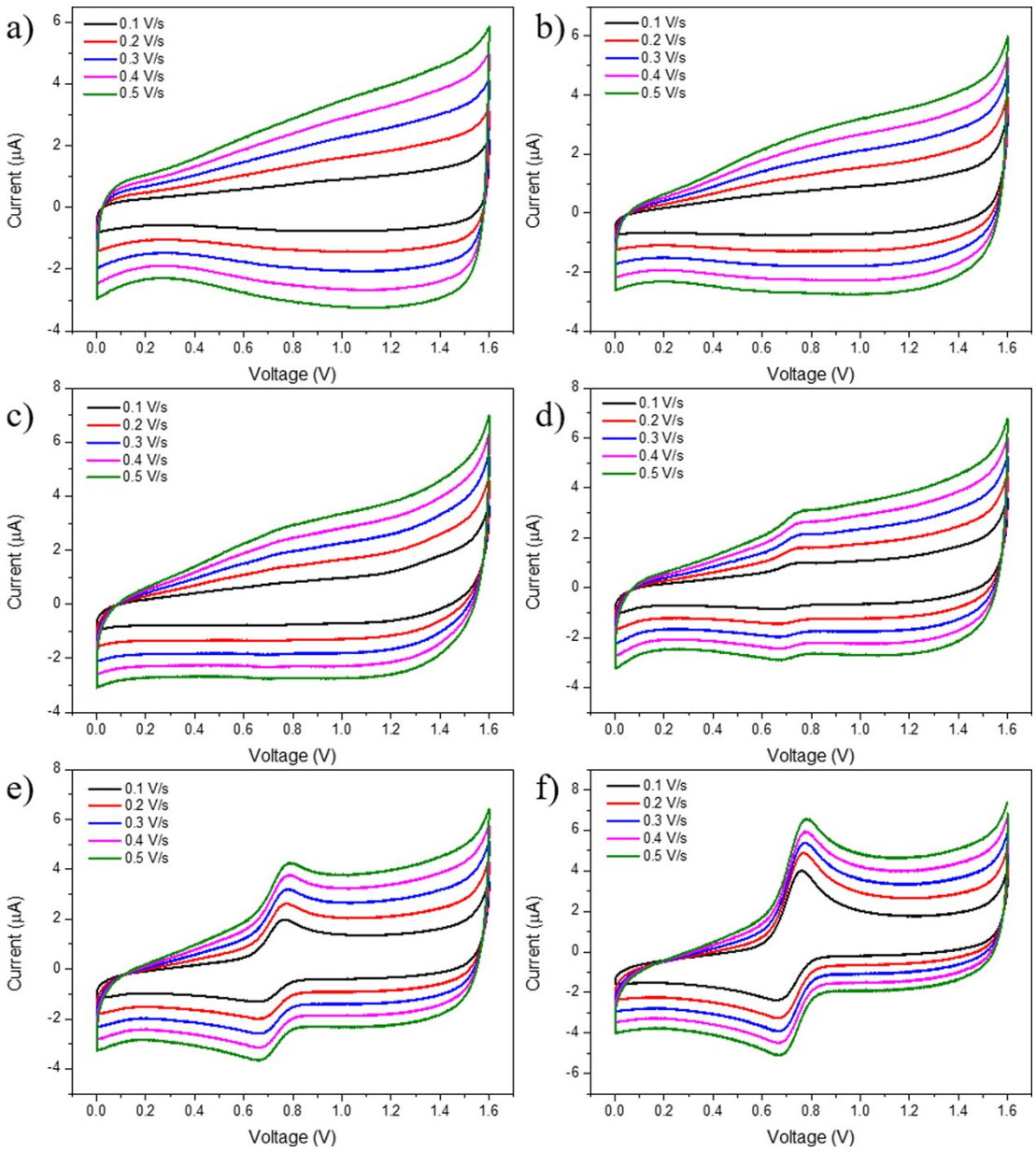

Fig. S10 Cyclic voltammetry curves of blank glass carbon electrode (a) and UiO-66-Fc synthesized with addition of different equiv. of FcCOOH modified glass carbon electrode (b-f) under different scanning rate (0.1-0.5 V/s). b) 0 equiv., c) 1 equiv., d) 2 equiv., e) 6 equiv. and f) 10 equiv.

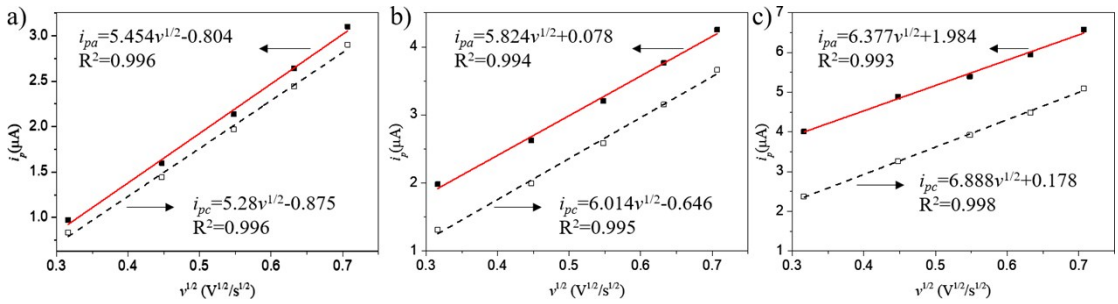

Fig. S11 Relationship between i_p and $v^{1/2}$. a) FcCOOH/Zr=2, b) FcCOOH/Zr=6 and c) FcCOOH/Zr=10.

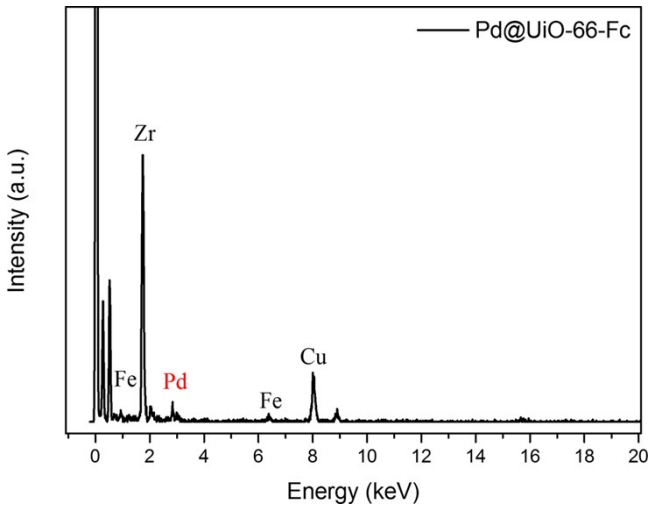

Fig. S12 EDS curve of Pd@UiO-66-Fc. UiO-66-Fc was synthesized with addition of 10 equiv. of FcCOOH as a modulator.

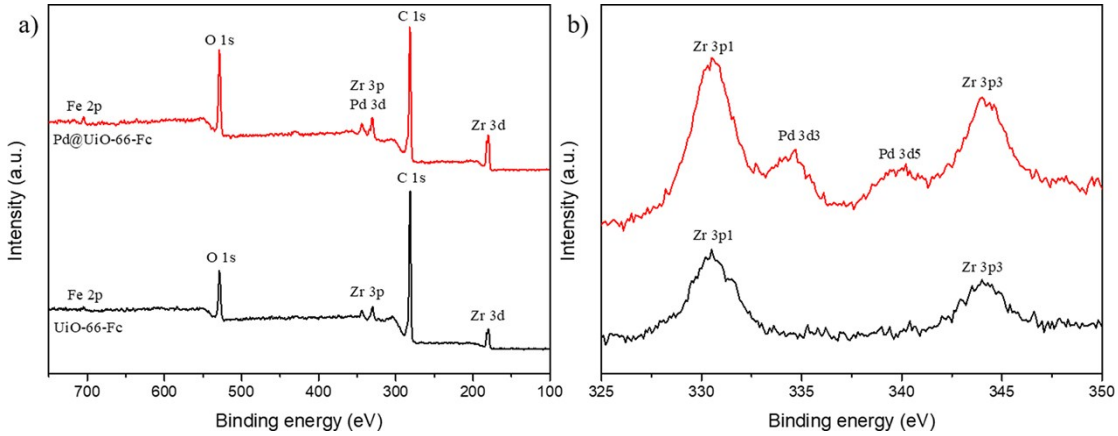

Fig. S13 a) XPS spectra of UiO-66-Fc and Pd@UiO-66-Fc. b) High-resolution XPS Pd 3d and Zr 3p spectra of UiO-66-Fc and Pd@UiO-66-Fc. UiO-66-Fc was synthesized with addition of 10 equiv. of FcCOOH as a modulator.

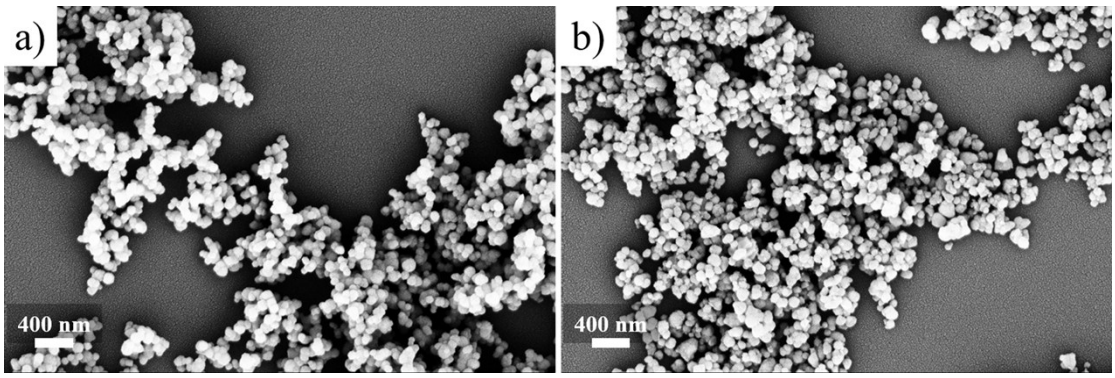

Fig. S14 SEM images of a) UiO-66-Fc and b) Pd@UiO-66-Fc. UiO-66-Fc was synthesized with addition of 10 equiv. of FcCOOH as a modulator.

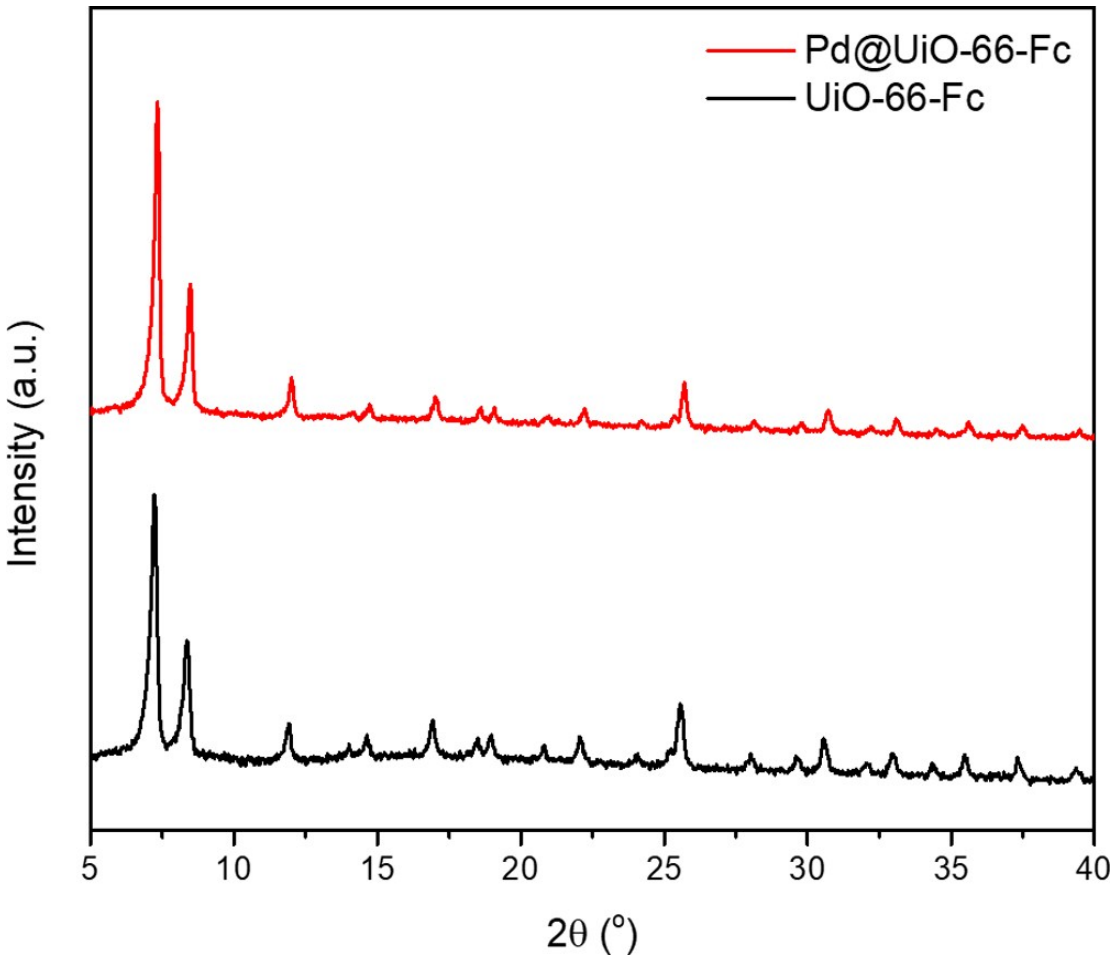

Fig. S15 XRD patterns of Pd@UiO-66-Fc and UiO-66-Fc. UiO-66-Fc was synthesized with addition of 10 equiv. of FcCOOH as a modulator.

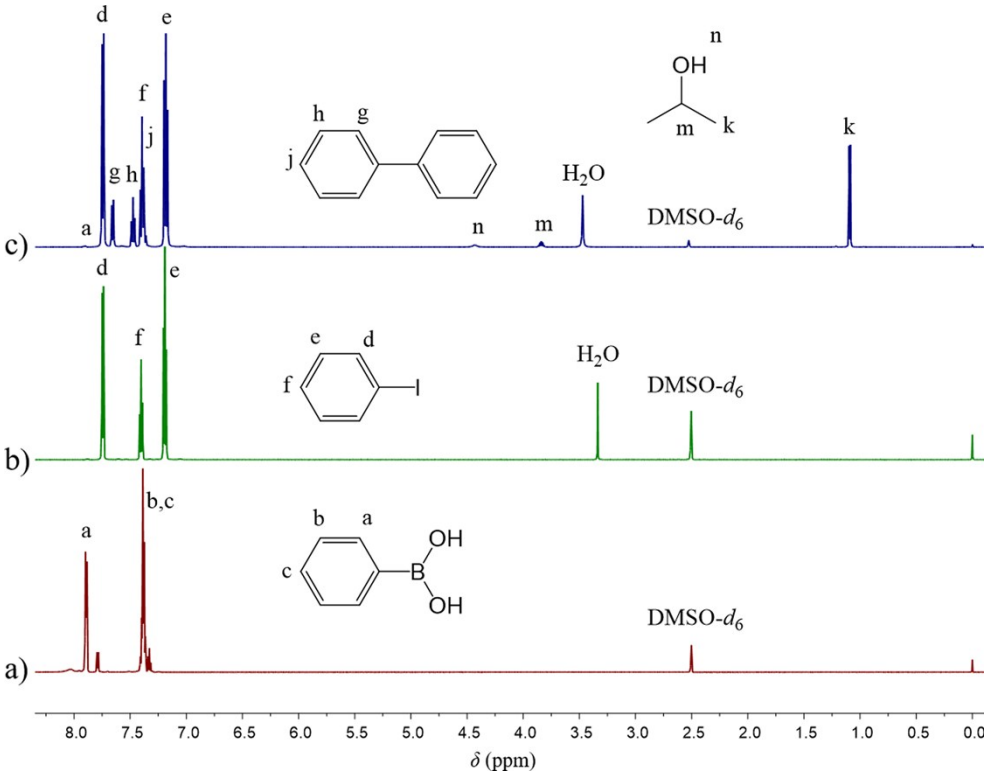

Fig. S16 ^{1}H NMR spectra of pure phenylboronic acid (a), pure iodobenzene (b) and unpurified reaction product (c).

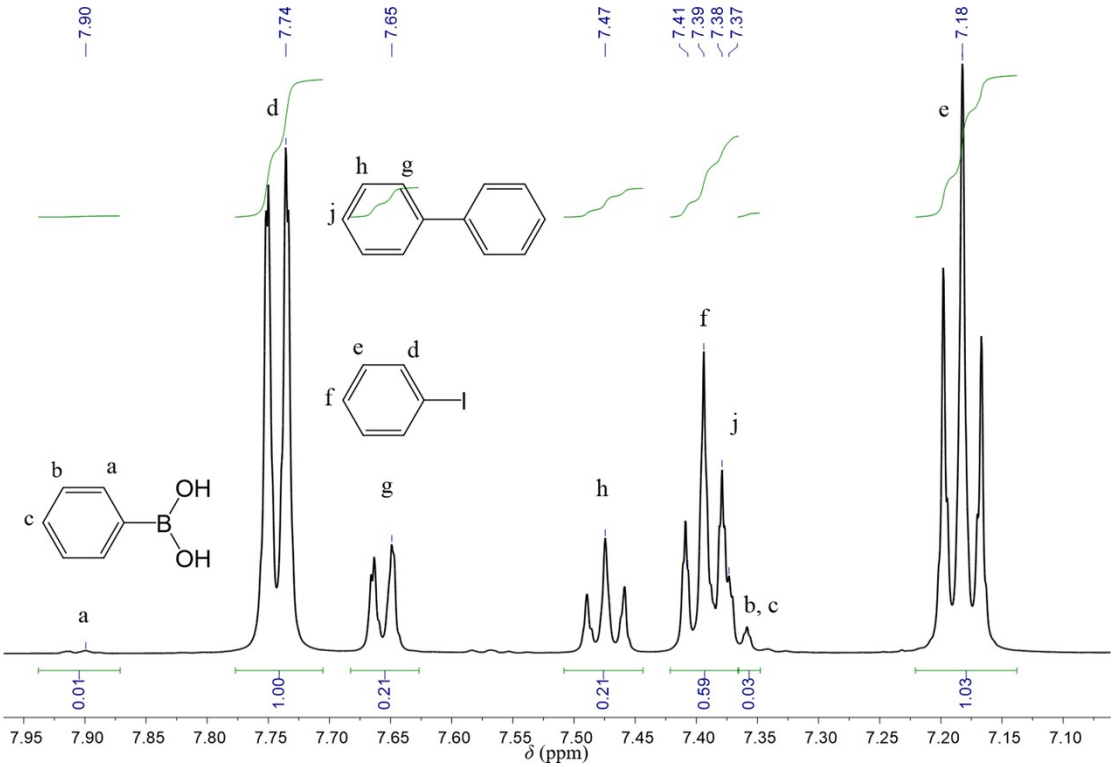

Fig. S17 Local amplification of ^{1}H NMR spectrum of unpurified reaction product.