The Structural and Catalytic Regulation in a Rigid Zr-MOF Through Linker Installation

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Supplementary Information

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1. Materials and Instrumentation

All reagents and solvents utilized in the synthesis studies were commercially available and used without any further purification. ^1H NMR analyses were conducted on a Bruker AVIII-400 instrument. Each MOF sample, weighing 5 mg, was subjected to digestion with 30 μl of deuterated sulfuric acid (D_2SO_4) solution. Following sonication, the solution was further diluted by adding 500 μL of deuterated dimethyl sulfoxide (DMSO). Optical images of the crystals were captured using an OLYMPUS CKX53 microscope. Powder X-ray diffraction (PXRD) patterns were obtained using a PANalytical B.V. X-ray diffractometer (X'Pert Pro) equipped with Cu $K\alpha$ (λ=1.5406 Å). N_2 adsorption isotherms were measured at 77 K using an ASAP-2020 instrument. Prior to the nitrogen adsorption/desorption measurements, the synthesized samples were immersed in dichloromethane and then dried under vacuum at 100 °C. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere using a TA Q50 thermal analyzer with a heating rate of 10 °C min^{-1} in the temperature range of 30-700 °C. X-ray photoelectron spectroscopy (XPS) data were recorded by Nexsa. The morphology and elemental distribution of the crystals were examined using field emission scanning electron microscopy by Quanta FEG 250.
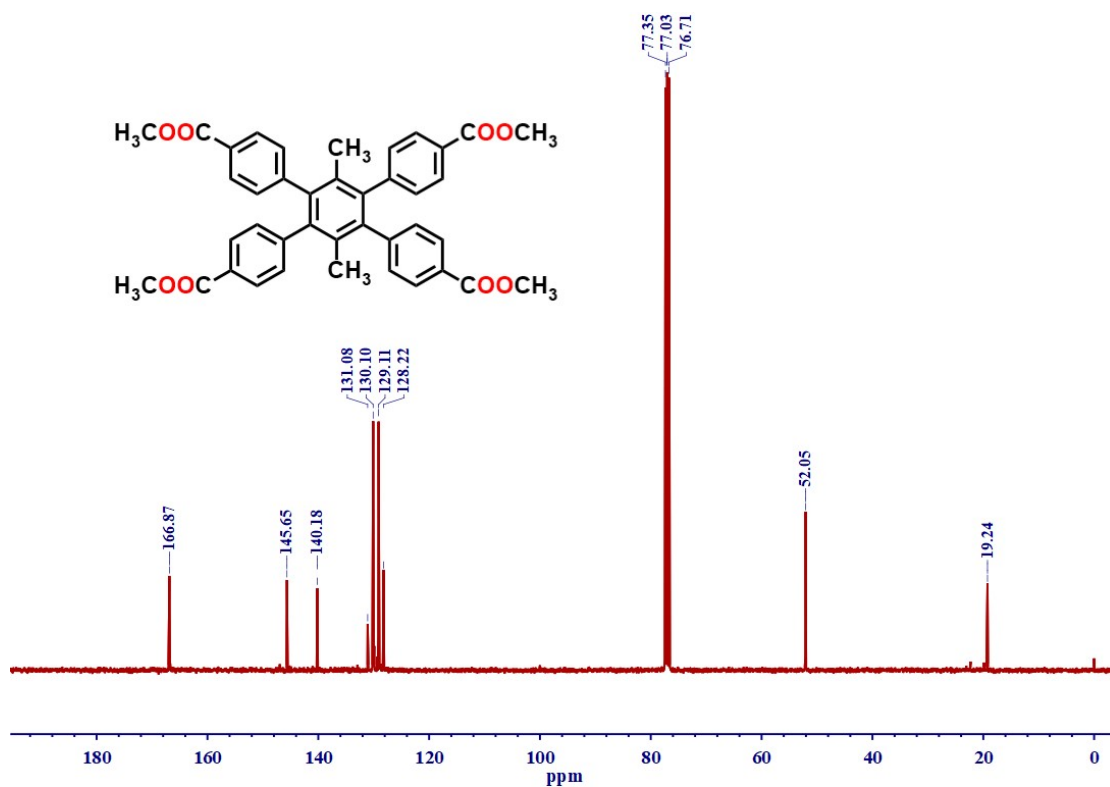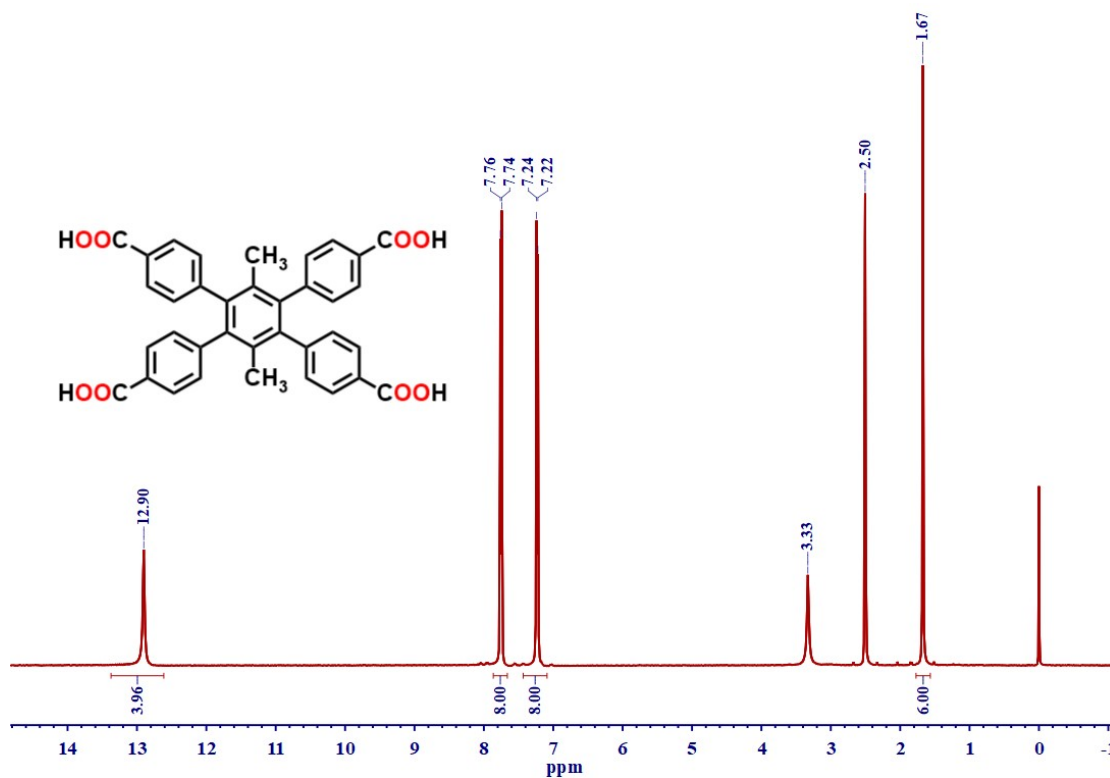
2. ¹H NMR spectrum and Crystallographic data
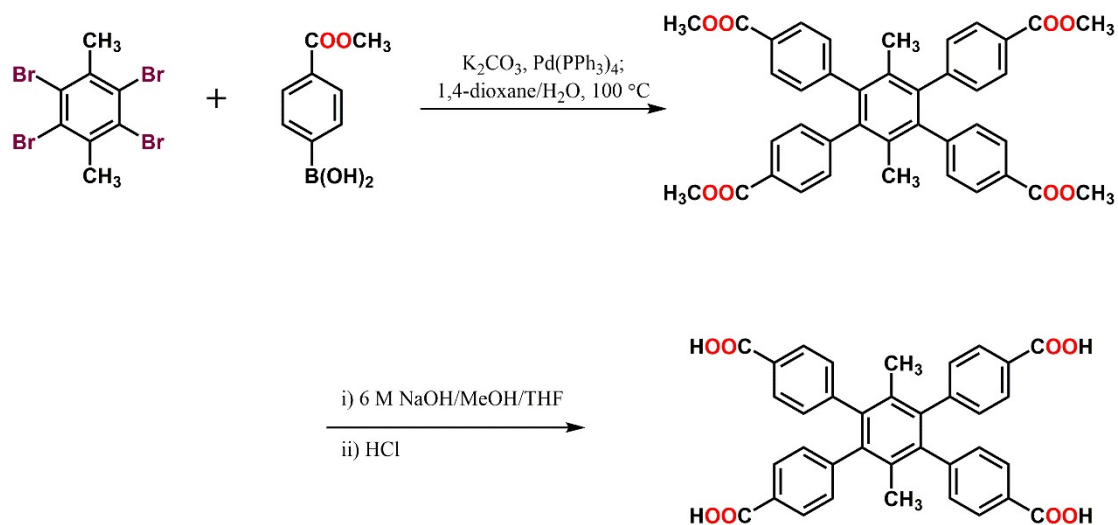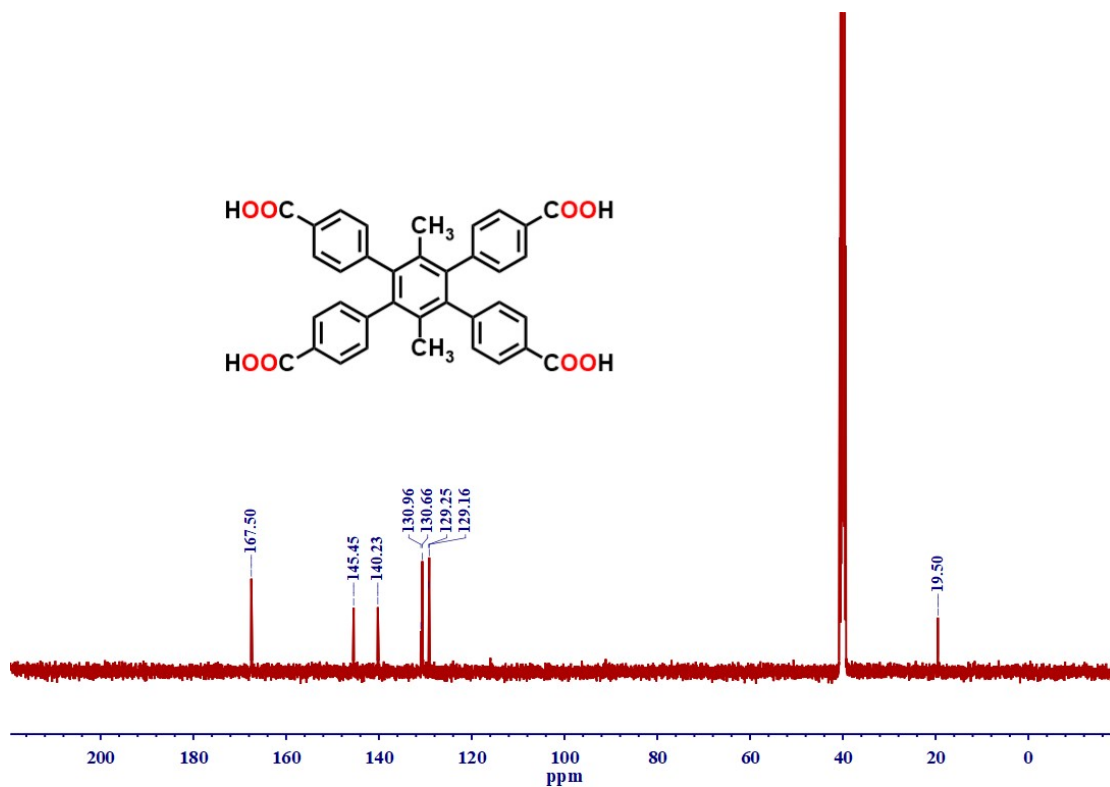

Fig. S1. The synthesis scheme of $H_4TCDB-Me_2$.
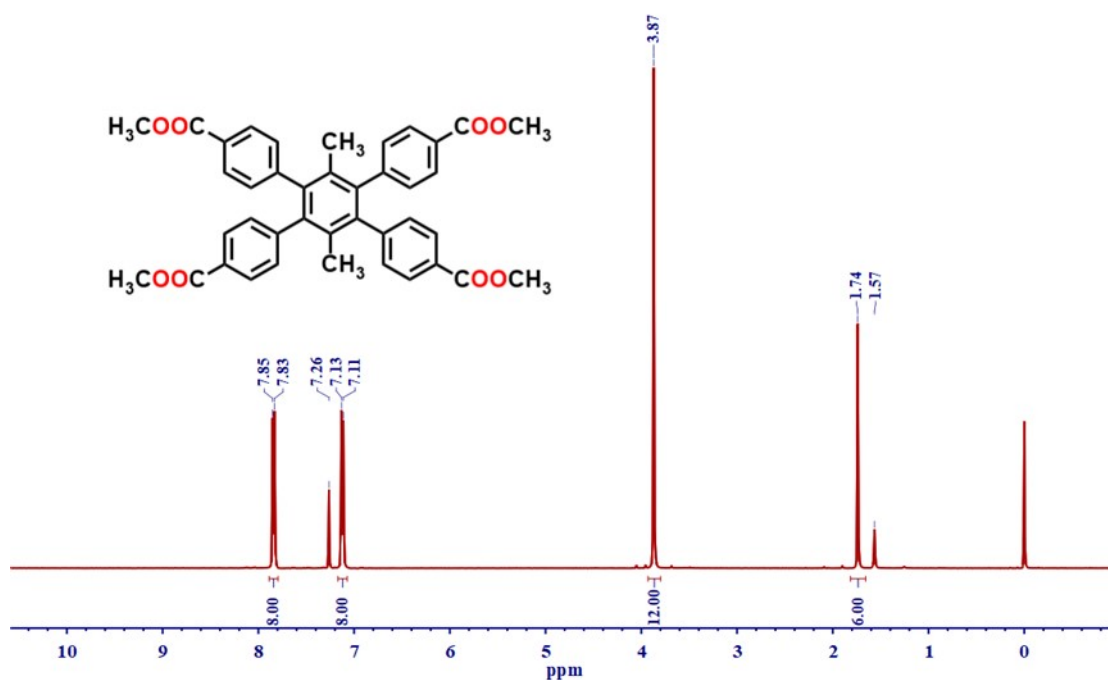
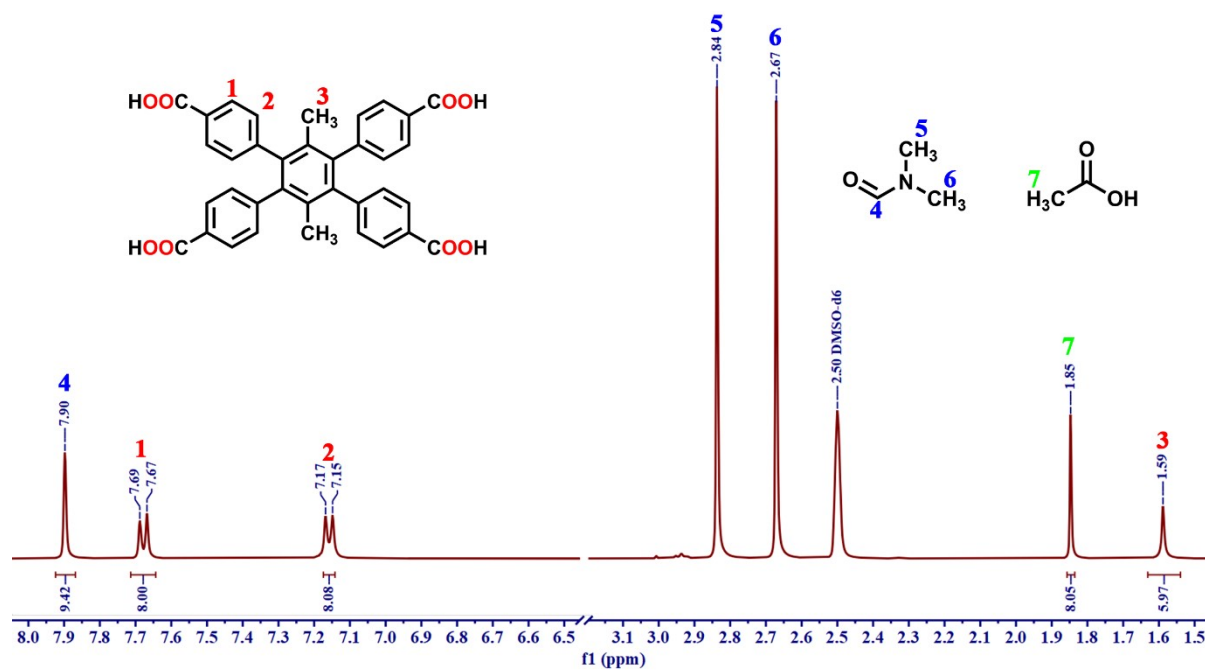**Fig. S2.** The ¹H NMR spectrum of 1,2,4,5-tetrakis(4-methoxycarbonylphenyl) -3,6-dimethyl-benzene in CDCl₃.

Fig. S3. The ^{13}C NMR spectrum of 1,2,4,5-tetrakis(4-methoxycarbonylphenyl) -3,6-dimethyl-benzene in CDCl$_3$.

Fig. S4. The ^{1}H NMR spectrum of H$_4$TCDB-Me$_2$ in DMSO-d_6.

Fig. S5. The ^{13}C NMR spectrum of H$_4$TCDB-Me$_2$ in DMSO-d_6.

Fig. S6. The ^{1}H NMR spectrum of digested SIFE-1.

S6

Table S1. The crystallographic data of SIFE-1.

Empirical formula	$C_{60}H_{78.5}O_{32}Zr_6$
CCDC number	2353447
Formula weight	1859.04
lemperature/K	150.03(10)
Crystal system	cubic
Space group	Pm-3m
a(Å)	32.2925(4)
b(Å)	32.2925(4)
c(Å)	32.2925(4)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
Volume/(Å^3)	33674.9(2)
Z	8
ρ_{calc}g/cm^3	0.733
μ/mm^{-1}	3.254
F(000)	7476.0
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/(°)	7.744 to 134.114
Index ranges	-19 ≤ h ≤ 27, -38 ≤ k ≤ 38, -14 ≤ l ≤ 38
Reflections collected	29016
Independent reflections	5691 [R_{int} = 0.0483, R_{sigma} = 0.0312]
Data/restraints/parameters	5691/104/185
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1229
Final R indexes [all data]]	R_1 = 0.056, wR_2 = 0.1294
Largest diff peak/hole / e Å^{-3}	0.79/-0.71

Table S2. The crystallographic data of SIFE-1-BPYDC.

Empirical formula	$C_{69}H_{51}N_3O_{32}Zr_6$
CCDC number	2353449
Formula weight	1981.45
Temperature/K	150.00(10)
Crystal system	cubic
Space group	Pm-3m
a/Å	32.24423(14)
b/Å	32.24423(14)
c/Å	32.24423(14)
$\alpha/°$	90
$\beta/°$	90
$\gamma/°$	90
Volume/Å3	33524.0(4)
Z	8
ρcalcg/cm3	0.785
μ/mm-1	3.300
F(000)	7856.0
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.756 to 134.154
Index ranges	$-28 \leq h \leq 38, -28 \leq k \leq 15, -37 \leq l \leq 36$
Reflections collected	26337
Independent reflections	5679 [R_{int} = 0.0470, R_{sigma} = 0.0341]
Data/restraints/parameters	5679/414/189
Goodness-of-fit on F2	1.078
Final R indexes [I>=2σ (I)]	R_1= 0.0676, wR_2 = 0.1838
Final R indexes [all data]	R_1= 0.0799, wR_2 = 0.1958
Largest diff. peak/hole / e Å^{-3}	2.12/-1.48

Table S3. The crystallographic data of SIFE-1-INA.

|	
Empirical formula	$C_{73.5}H_{47}N_{3.5}O_{32}Zr_6$
CCDC number	2353450
Formula weight	2038.46
Temperature/K	296.15
Crystal system	cubic
Space group	Pm-3m
a/Å	32.4218(7)
b/Å	32.4218(7)
c/Å	32.4218(7)
$\alpha/°$	90
$\beta/°$	90
$\gamma/°$	90
Volume/Å3	34081(2)
Z	8
ρcalcg/cm3	0.795
μ/mm-1	3.257
F(000)	8068.0
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	4.72 to 133.214
Index ranges	$-35 \le h \le 25, -35 \le k \le 30, -21 \le l \le 36$
Reflections collected	57724
Independent reflections	5516 [R_{int} = 0.0643, R_{sigma} = 0.0329]
Data/restraints/parameters	5516/318/269
Goodness-of-fit on F2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1493
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.1594
Largest diff. peak/hole / e Å^{-3}	0.82/-0.64

Table S4. The crystallographic data of SIFE-1-BPYDC(Cu).

|	
Empirical formula	$C_{72}H_{39}Cu_{0.45}N_6O_{32}Zr_6$
CCDC number	2353448
Formula weight	2075.88
Temperature/K	296.15
Crystal system	cubic
Space group	Pm-3m
a/Å	32.2803(17)
b/Å	32.2803(17)
c/Å	32.2803(17)
$\alpha/°$	90
$\beta/°$	90
$\gamma/°$	90
Volume/Å^3	33637(5)
Z	8
ρ_{calc}g/cm^3	0.820
μ/mm^{-1}	0.455
F(000)	8176.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.55 to 49.986
Index ranges	$-16 \leq h \leq 38, -38 \leq k \leq 33, -33 \leq l \leq 38$
Reflections collected	61324
Independent reflections	5607 [R_{int} = 0.1691, R_{sigma}= 0.0784]
Data/restraints/parameters	5607/378/201
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0817, wR_2 = 0.2281
Final R indexes [all data]	R_1 = 0.1150, wR_2 = 0.2555
Largest diff. peak/hole / e Å^{-3}	1.59/-1.08

Table S5. The crystallographic data of SIFE-1-INA(Cu)-BDC.

Empirical formula	$C_{84}H_{51}Cu_{0.56}I_{0.84}N_3O_{32}Zr_6$
CCDC number	2353451
Formula weight	2303.46
Temperature/K	150.01(10)
Crystal system	cubic
Space group	Pm-3m
a/Å	32.43707(14)
b/Å	32.43707(14)
c/Å	32.43707(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	34129.1(4)
Z	8
ρ_{calc}g/cm^3	0.897
μ/mm^{-1}	4.536
F(000)	9061.0
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.708 to 134.082
Index ranges	-37 $\leq$ h $\leq$ 29, -36 $\leq$ k $\leq$ 20, -13 $\leq$ l $\leq$ 38
Reflections collected	27497
Independent reflections	5777 [R_{int} = 0.0454, R_{sigma} = 0.0345]
Data/restraints/parameters	5777/452/215
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0685, wR_2 = 0.1983
Final R indexes [all data]	R_1 = 0.0805, wR_2 = 0.2103
Largest diff. peak/hole / e Å^{-3}	1.90/-1.48

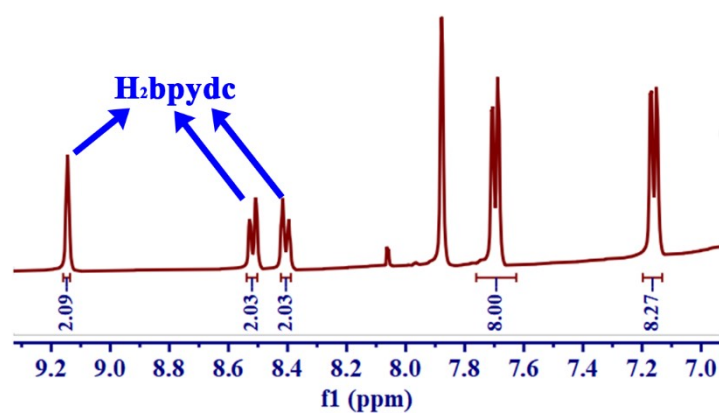**3. MOFs Characterizations.**
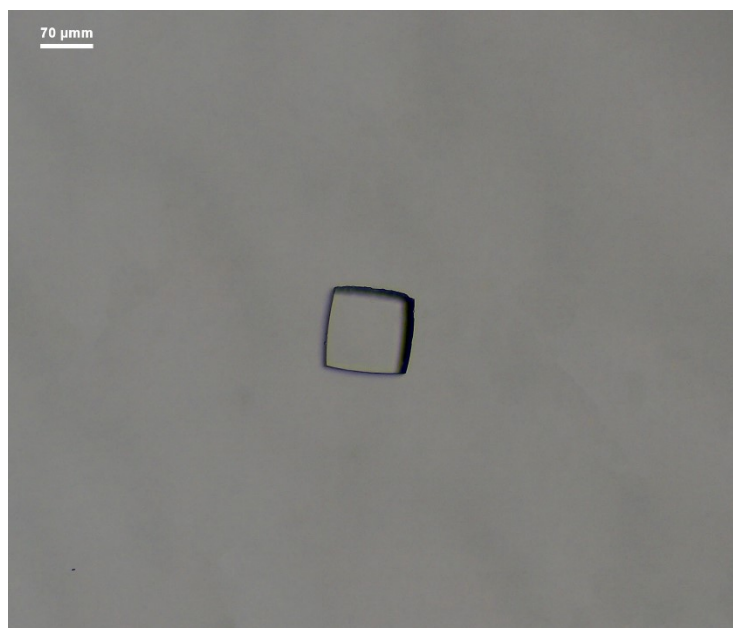
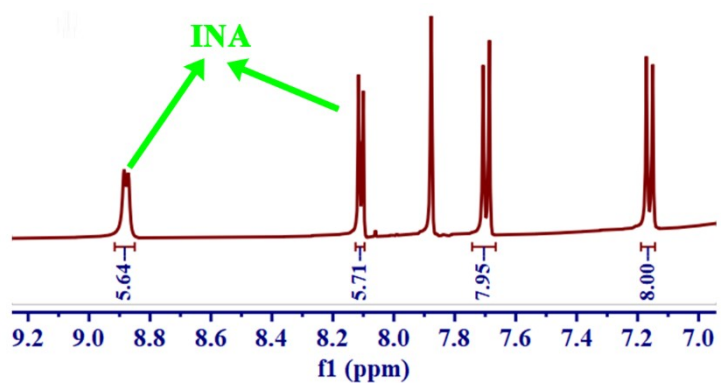**Fig. S7.** Optical image of the block single crystals of SIFE-1.
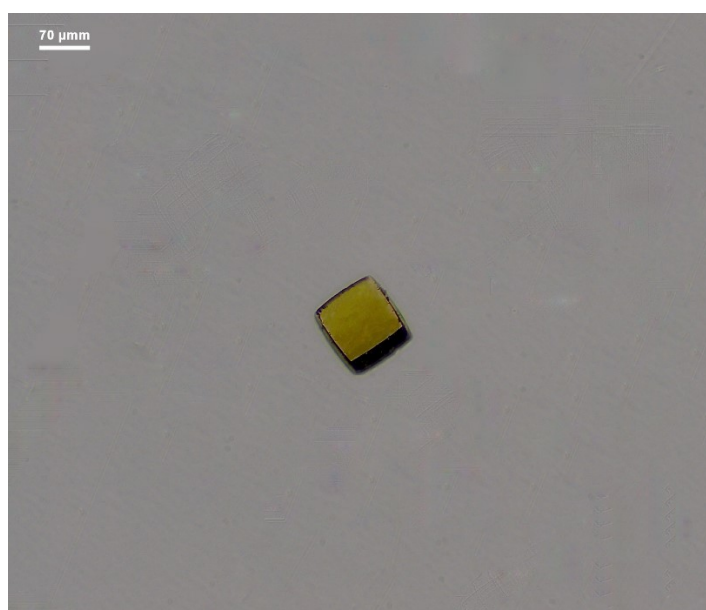
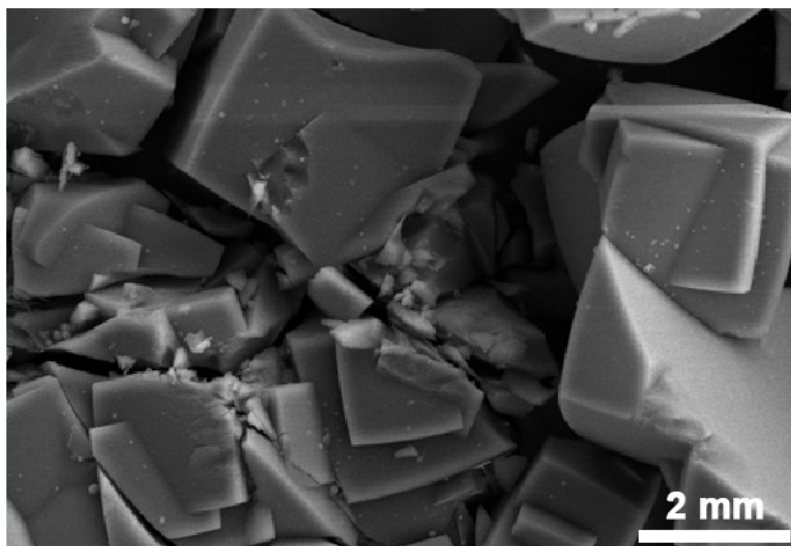**Fig. S8.** Optical image of the block single crystals of SIFE-1-BPYDC(Cu).
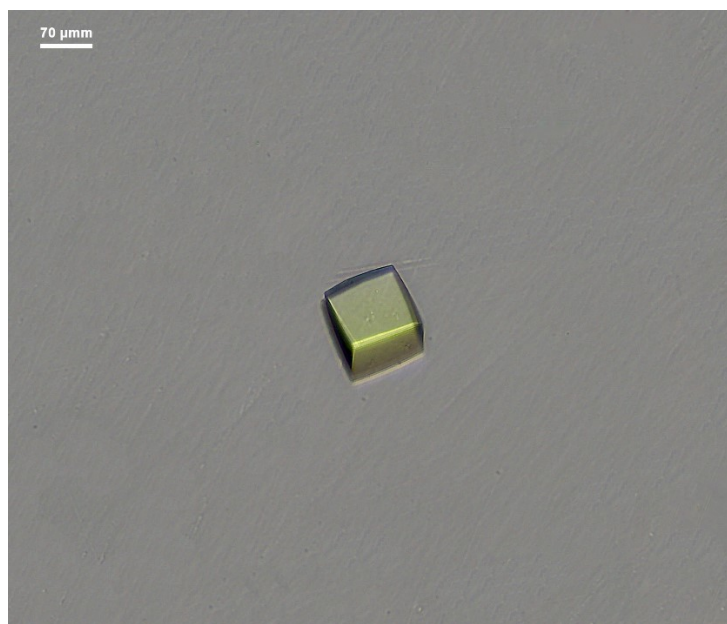
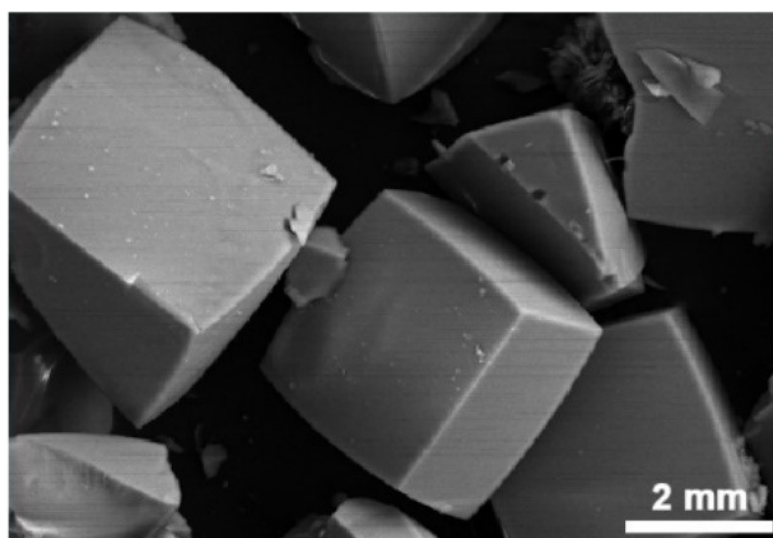**Fig. S9.** Optical image of the block single crystals of SIFE-1-INA(Cu).

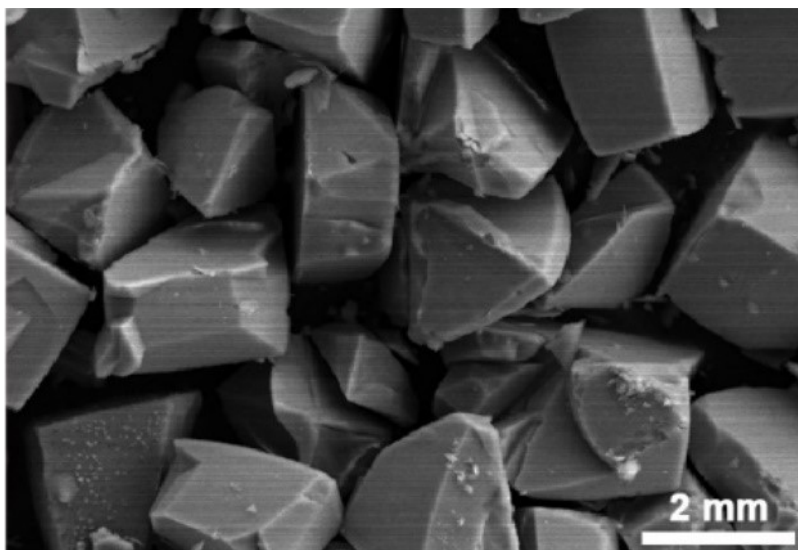**Fig. S10.** The ^{1}H NMR spectrum of digested SIFE-1-BPYDC.

Fig. S11. The ^{1}H NMR spectrum of digested SIFE-1-INA.

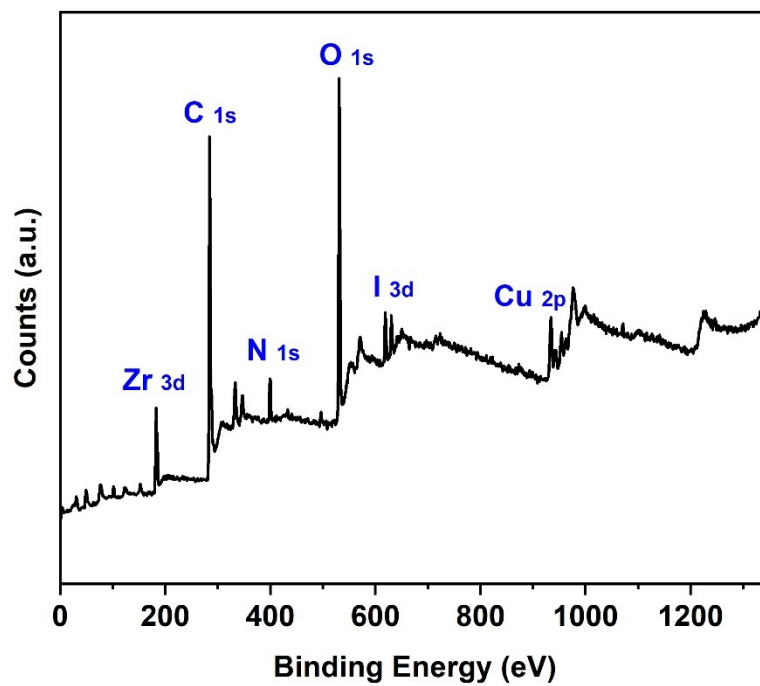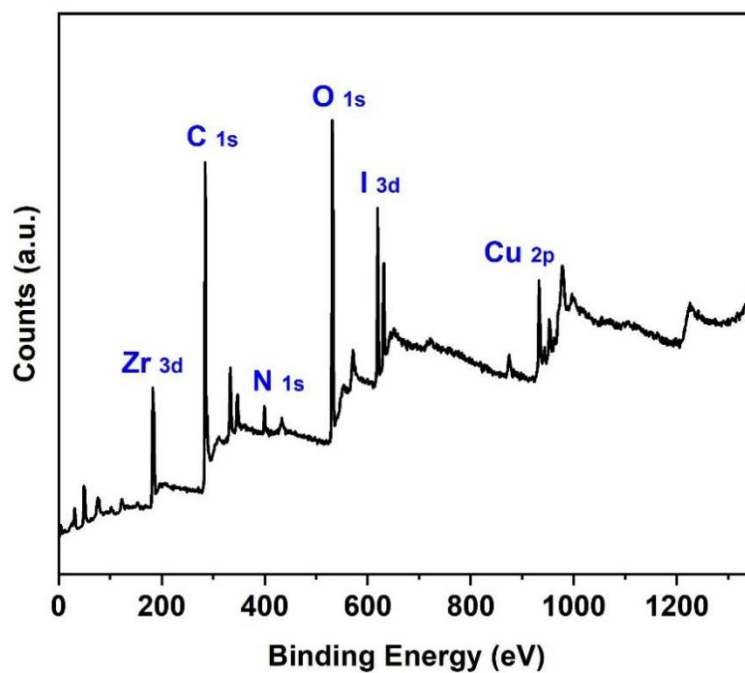**Fig. S12.** SEM image of SIFE-1.

Fig. S13. SEM image of SIFE-1-BPYDC(Cu).
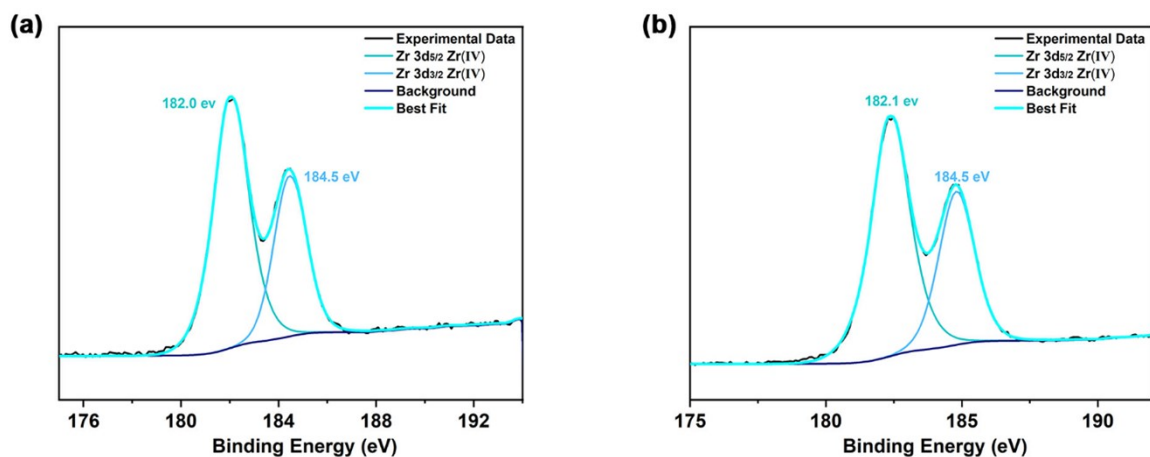
Fig. S14. SEM image of SIFE-1-INA(Cu).

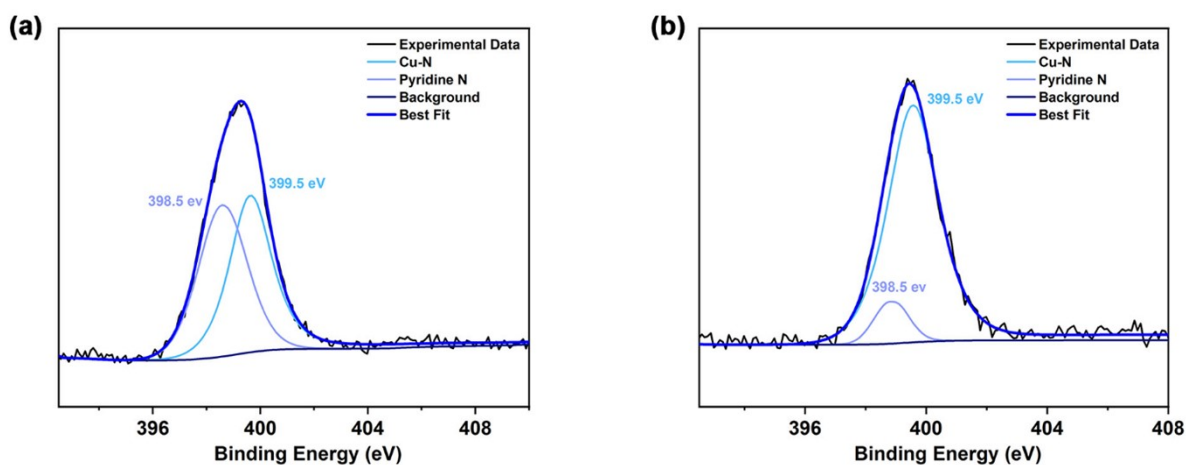**Fig. S15.** X-ray photoelectron spectrum of SIFE-1-BPYDC(Cu).

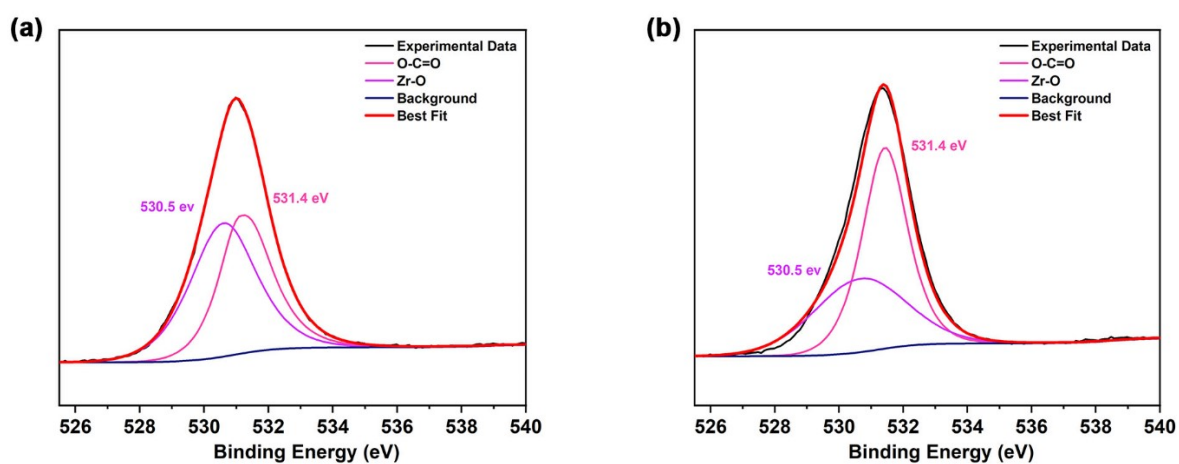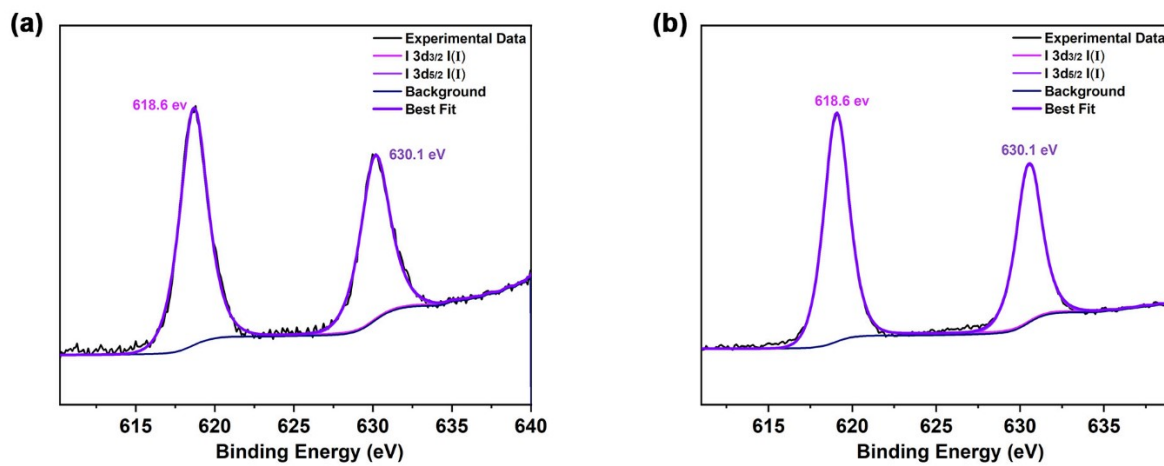**Fig. S16.** X-ray photoelectron spectrum of SIFE-1-INA(Cu).

Fig. S17. XPS spectra of Zr 3d of SIFE-1-BPYDC(Cu)(a) SIFE-1-INA(Cu)(b).
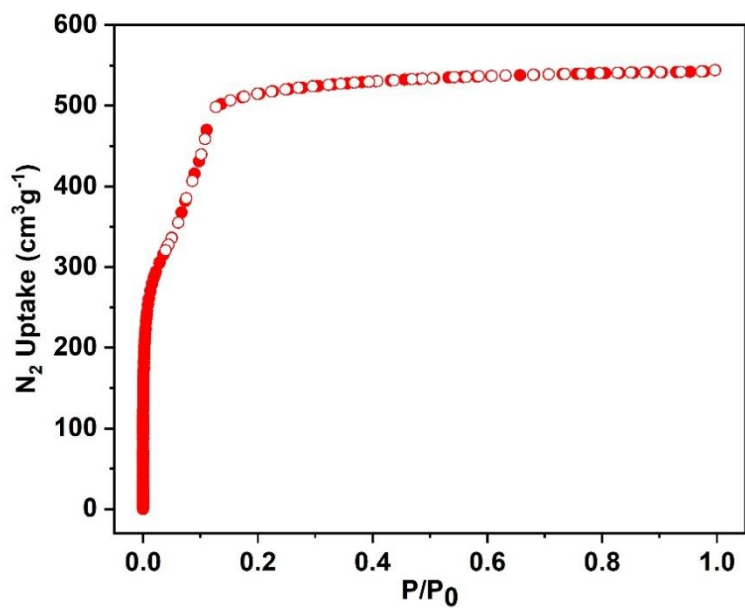

Fig. S18. XPS spectra of N 1s of SIFE-1-BPYDC(Cu)(a) SIFE-1-INA(Cu)(b).
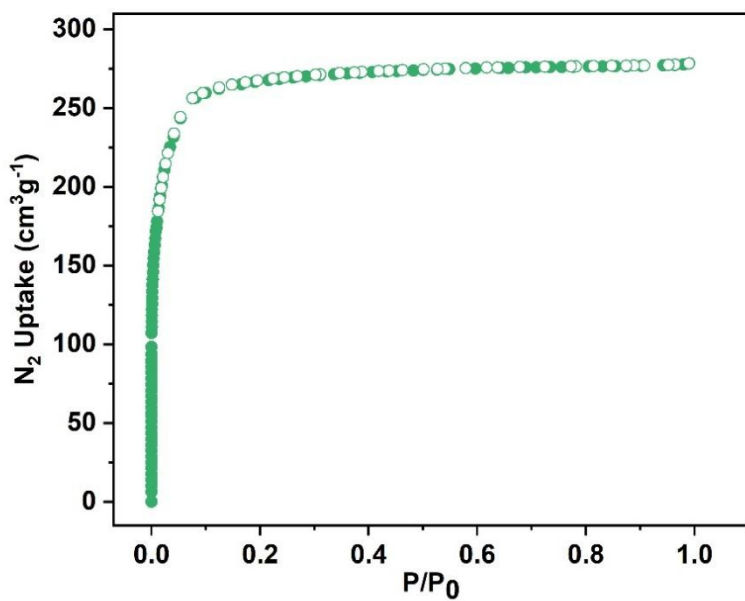

Fig. S19. XPS spectra of O 1s of SIFE-1-BPYDC(Cu)(a) SIFE-1-INA(Cu)(b).
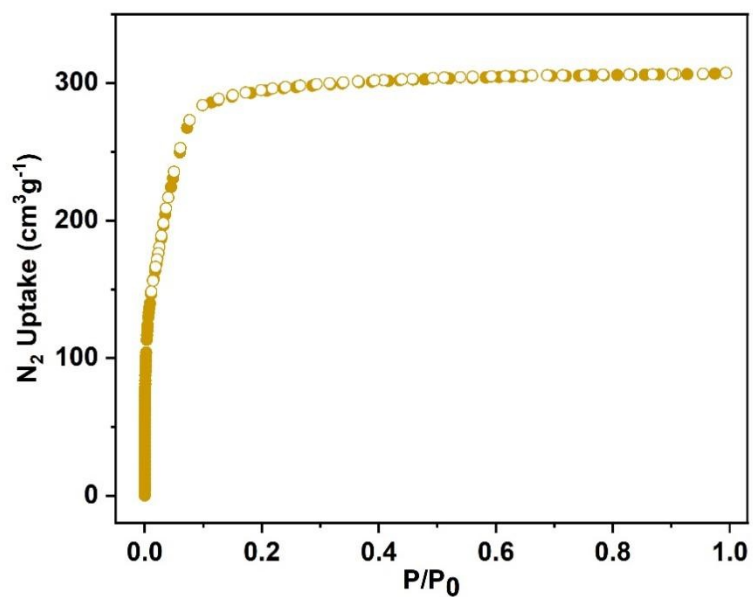
Fig. S20. XPS spectra of I 3d of SIFE-1-BPYDC(Cu)(a) SIFE-1-INA(Cu)(b).
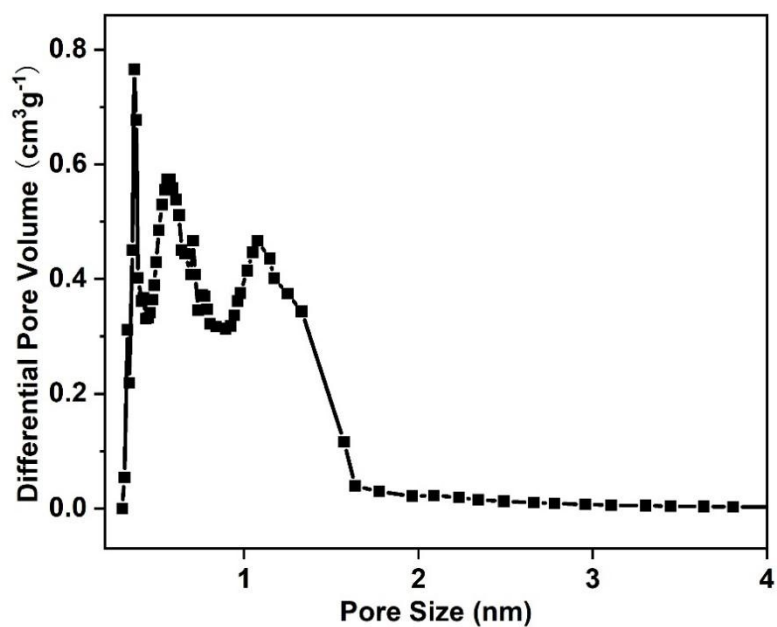
Fig. S21. The N_2 adsorption–desorption isotherms of SIFE-1 at 77 K.

Fig. S22. The N_2 adsorption–desorption isotherms of SIFE-1-BPYDC(Cu) at 77 K.

Fig. S23. The N_2 adsorption–desorption isotherms of SIFE-1-INA(Cu) at 77 K.

Fig. S24. Pore size distribution of SIFE-1 from N_2 adsorption isotherms using a density functional theory (DFT) model.
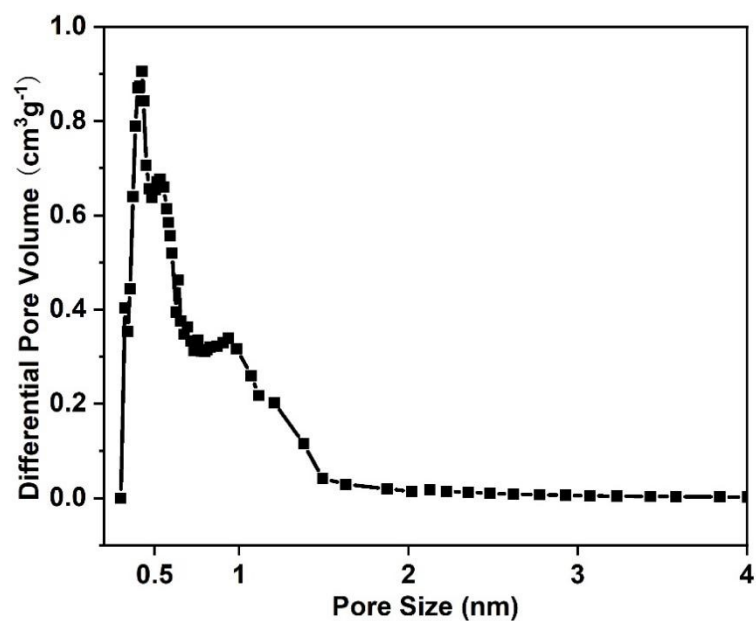
Fig. S25. Pore size distribution of SIFE-1-BPYDC(Cu) from N_2 adsorption isotherms using a density functional theory (DFT) model.
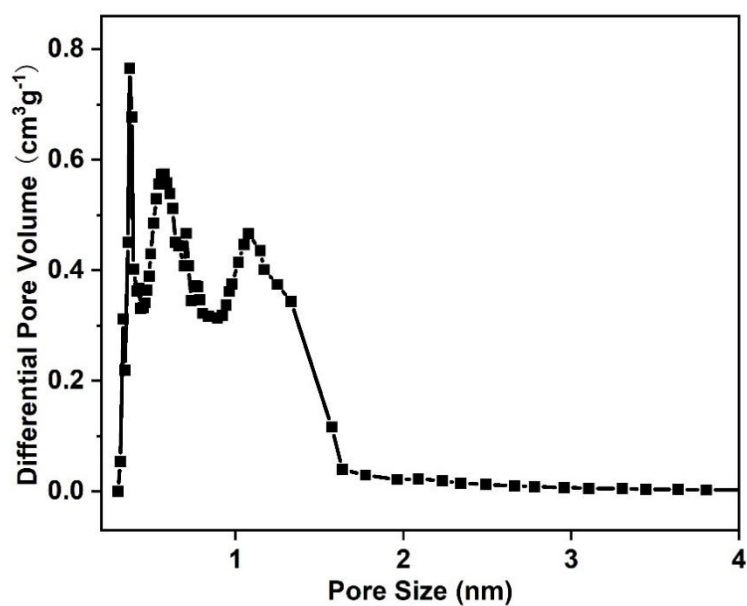
Fig. S26. Pore size distribution of SIFE-1-INA(Cu) from N_2 adsorption isotherms using a density functional theory (DFT) model.

Fig. S27. Experimental PXRD patterns of SIFE-1-BPYDC(Cu) after catalytic reaction.

Fig. S28. Experimental PXRD patterns of SIFE-1-INA(Cu) after catalytic reaction.

4. Catalytic Reaction

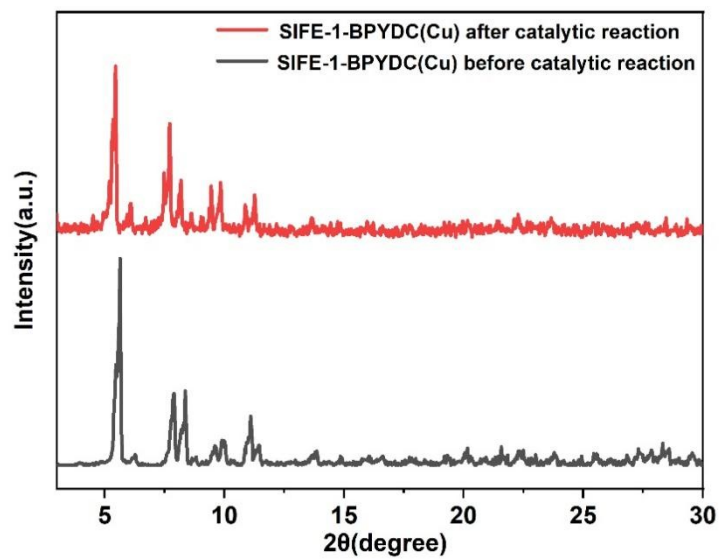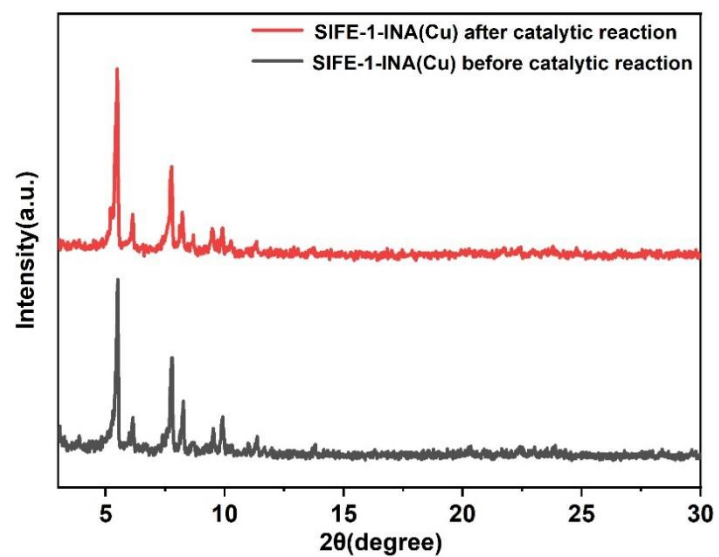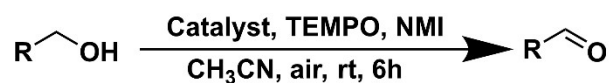$$R\diagdown OH \xrightarrow[\text{CH}_3\text{CN, air, rt, 6h}]{\text{Catalyst, TEMPO, NMI}} R\diagup O$$

In a classical alcohol-formaldehyde conversion reaction, alcohol (0.5 mmol), TEMPO (0.05 mmol, TEMPO = 2,2,6,6-etramethylpiperidine-N-oxyl), N-methylimidazole (NMI, 0.05 mmol), CH_3CN (5.0 mL), and catalyst (10 mg, SIFE-1-BPYDC(Cu) or SIFE-1-INA(Cu)) were combined in a 20 mL vial. The mixture was stirred in an open-air environment at room temperature for 6 hours to ensure complete exposure to atmospheric oxygen. Following the reaction, the crude reaction mixture was concentrated and subjected to purification using silica column chromatography. The resulting product was analyzed using ^{1}H NMR spectroscopy to determine the conversion rate of the reaction.

To confirm the essential catalytic function of the (bpy)Cu catalysis centers in the aforementioned reaction, SIFE-1, SIFE-1-BPYDC, and SIFE-1-INA were employed as substitutes for the catalytic component in the initial reactants. The reaction was subsequently repeated under identical conditions. The resulting products were analyzed using ^{1}H NMR spectroscopy, revealing minimal formation of the corresponding aldehydes, as outlined in Table S6. These findings unequivocally establish the indispensability of (bpy)Cu in facilitating this reaction.

The recoverability of the SIFE-1-BPYDC(Cu) and SIFE-1-INA(Cu) catalysts was evaluated in this study. At the completion of the reaction, the catalysts were easily recovered from the mixture through centrifugation. The resulting solids were washed thoroughly with CH_3CN and subsequently reused in the subsequent reaction cycles. Benzyl alcohol was employed as the alcohol substrate in the aforementioned reaction, and the reaction underwent cyclic experimental tests while maintaining identical conditions. The yields obtained from three repetitive runs were provided in Table S7. To ensure the integrity of the crystal structure, the powder PXRD patterns of the fresh catalyst and after the third cycle were examined (as

depicted in Fig. S27 and S28). The comparison of these patterns confirmed that the catalytic process did not result in any significant damage to the crystal structure.

5. Additional Tables

**Table S6.** Verification of the catalytic function of (bpy)Cu catalytic centers[a].

Entry	Substrate	Catalyst	Time(h)	Conversion(%)
1	Benzyl alcohol	SIFE-1	6	<1
2	1-Naphthalenemethanol	SIFE-1	6	<1
3	9-Anthracenemethanol	SIFE-1	6	<1
4	Benzyl alcohol	SIFE-1-BPYDC	6	<1
5	1-Naphthalenemethanol	SIFE-1-BPYDC	6	<1
6	9-Anthracenemethanol	SIFE-1-BPYDC	6	<1
7	Benzyl alcohol	SIFE-1-INA	6	<1
8	1-Naphthalenemethanol	SIFE-1-INA	6	<1
9	9-Anthracenemethanol	SIFE-1-INA	6	<1

(a) Reaction condition: alcohol (0.5 mmol), TEMPO (0.05 mmol), N-methylimidazole (NMI, 0.05 mmol), CH_3CN (5.0 mL), and catalyst (10 mg), room temperature, 6h.

Table S7. Recyclability test of SIFE-1-BPYDC(Cu) and SIFE-1-INA(Cu)[a].

Cycle	Substrate	Catalyst	Time(h)	Conversion(%)
1	Benzyl alcohol	SIFE-1-BPYDC(Cu)	6	99
	Benzyl alcohol	SIFE-1-INA(Cu)	6	99
2	Benzyl alcohol	SIFE-1-BPYDC(Cu)	6	99
	Benzyl alcohol	SIFE-1-INA(Cu)	6	80
3	Benzyl alcohol	SIFE-1-BPYDC(Cu)	6	88
	Benzyl alcohol	SIFE-1-INA(Cu)	6	65

(a) Reaction condition: Benzyl alcohol (0.5 mmol), TEMPO (0.05 mmol), N-methylimidazole (NMI, 0.05 mmol), CH_3CN (5.0 mL), and catalyst (10 mg), room temperature, 6h.
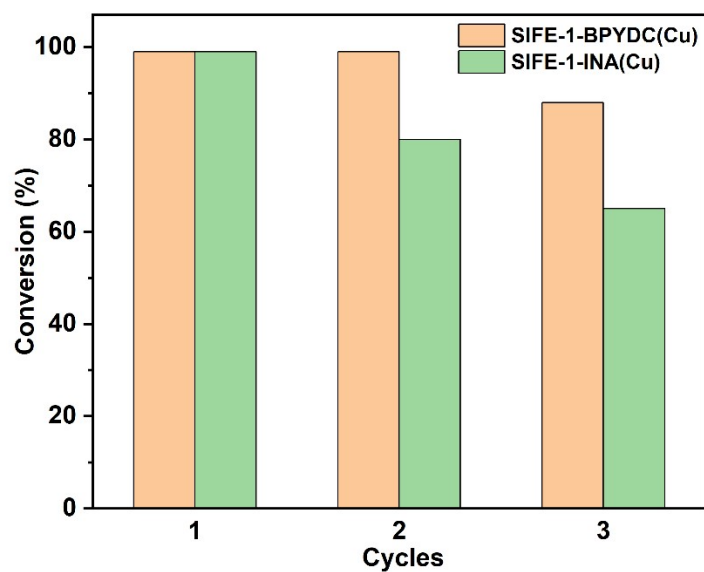
Figure S29. Cycle test of SIFE-1-BPYDC(Cu) and SIFE-1-INA(Cu).