1 2	Electronic Supplementary Information
3	Green and Rapid Synthesis of Two-Dimensional Zn-MOF with Lewis
4	Acid-Base Sites via a Solvent-Free Strategy
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21	Experimental section
22	Materials
23	5-Aminoisophthalic acid (AIP, 99%, C ₈ H ₇ NO ₄ , 5970-45-6), 5-hydroxyisophthalic acid (HIP,

24	99%, C ₈ H ₆ O ₅ , 618-83-7), 5-nitroisophthalic acid (NIP, 99%, C ₈ H ₅ NO ₆ , 618-88-2), zinc acetate
25	dihydrate (Zn(CH ₃ COO) ₂ ·2H ₂ O, 99 %, 5970-45-6), and anhydrous zinc acetate (Zn(CH ₃ COO) ₂ ,
26	99%, 557-34-6) were purchased from Beijing Huawei Ruike Chemical Technology Co., LTD.
27	Deionized water (H ₂ O, 7732-18-5) was purified in the laboratory using a Siemens Ultra Clear TWF
28	water purification system. Dehydrated ethanol (C2H6O, 64-17-5) was purchased from Tianjin Fuyu
29	Fine Chemical. Epichlorohydrin (C ₃ H ₅ ClO, 106-89-8), iron(II) sulphate heptahydrate (FeH ₁₄ O ₁₁ S,
30	7782-63-0) were purchased from Beijing Jiashiteng Trading Co., LTD. Hydrogen peroxide solution
31	(H ₂ O ₂ , 7722-84-1) was purchased from Beijing Tongguang Fine Chemical Co., LTD.
32	Tetrabutylammonium bromide (TBAB, C16H36BrN, 2052-49-5) and deuterium chloroform
33	(CDCl ₃ ,865-49-6) were purchased from Shanghai Dibai Biotechnology Co., LTD. High purity CO ₂
34	was purchased from Beijing Shuangquantianyuan Industrial Gas Co., LTD. Epoxy resin CER1000
35	and curing agent CEH500 were obtained from Guangzhou Weiyee Metallographic Test Instrument
36	Co. Ltd. All chemicals were used without further purification.

37 *Synthesis of Zn(AIP)*

Solvent-free synthesis of Zn(AIP). Zn(CH₃COO)₂·2H₂O (1 mmol, 219.5 mg) and 5-38 aminoisophthalic acid (1 mmol, 181 mg) were added in a mortar and ground for ca. 5 min for initial 39 mixing under ambient conditions. The solid mixture was transferred into a 25 mL Teflon-lined 40 41 stainless-steel autoclave and heated at 120 °C for different time periods to obtain Zn(AIP) crystals. Subsequent washing at room temperature, performed three times with deionized water followed by 42 43 ethanol, was found helpful to refine the crystal structure, but not necessary. The remaining powder after washing was then dried at 80 °C for 12 h. The Zn(AIP) synthesized using this solvent-free 44 45 approach is denoted as F-Zn(AIP) hereafter. To enhance crystallisation efficiency, the reactor was 46 switched from an autoclave to a metal tube for elevated thermal conductivity. The synthesis duration47 was thereby further truncated from hours to just minutes.

48 Hydrothermal synthesis Zn(AIP). As a comparison, Zn(AIP) was also synthesized using a reported.¹ 49 conventional hydrothermal synthesis approach previously Typically, Zn(CH₃COO)₂·2H₂O (0.68 mmol, 150 mg) and 5-aminoisophthalic acid (0.66 mmol, 120 mg) were 50 dissolved in 18 mL H₂O, featuring a pH of 3.90. After vigorous stirring, the aqueous mixture was 51 52 heated at 170 °C for 6 days. Beige crystals were isolated from the solution and washed repeatedly 53 with water and ethanol by centrifugation. Henceforth, the Zn(AIP) acquired from the solvent of 54 water is designated as S-Zn(AIP).

Solvent-free synthesis of Zn(HIP). The synthesis procedure was the same as that of FZn(AIP), with the only difference being the replacement of 5-aminoisophthalic acid with 5hydroxyisophthalic acid.

- 58 Solvent-free synthesis of Zn(NIP). The synthesis procedure mirrored that of F-Zn(AIP), with
 59 the sole modification being the substitution of 5-aminoisophthalic acid with 5-nitroisophthalic acid.
- 60 *CO*₂ cycloaddition of epichlorohydrin (ECH)

All catalytic experiments were performed in a 50 mL Teflon-lined stainless-steel autoclave with a magnetic stirring bar. In a typical reaction, 20 mmol ECH and 0.5 mol% TBAB were mixed with varying molar percentages of MOF catalysts in the autoclave, which was subsequentially pressurized to 1 bar using high-purity carbon dioxide. The reactions were executed at various temperatures and for distinct durations to comprehensively evaluate the impacts of synthesis approaches. After reaction, the resulting product was filtered and analysed with ¹H nuclear magnetic

67 resonance (¹H NMR) spectroscopy.

68 Preparation of Zn(AIP)/EP and bare EP sheets

69	Epoxy resin (EP) sheets were employed in fire resistance tests. The Zn(AIP)/EP composite
70	sheets were prepared by blending EP with 2.0 wt% Zn(AIP) powders (both F-Zn(AIP) and S-Zn(AIP)
71	were used). Typically, 300 mg Zn(AIP) powders were mixed with 10.0 g epoxy resin of CER1000.
72	The resulting suspension was dispersed ultrasonically (1,000 W at 25 °C) for 5 min and then mixed
73	using a vortex mixer (3,000 rpm) for 2 min. This ultrasonic dispersion-vortex mixing cycle was
74	repeated three times to achieve uniform distribution. The suspension was subsequently mixed with
75	5.0 g curing agent of CEH500 (3,000 rpm, 5min) and poured quickly into a 100 mm \times 100 mm \times 2
76	mm curing mould. After curing at 60 °C for 2 h, Zn (AIP)/EP composite sheets were obtained. The
77	bare EP sheets were similarly prepared using 10.0 g CER1000 and 5.0 g CEH500, with Zn(AIP)
78	omitted. The resulting epoxy resin has a Shore hardness of 80 HD as provided by the manufacturer.

79 Materials characterisation

80 Powder X-ray diffraction (XRD) was carried out on a Rigaku XRD-6000 diffractometer with 81 Cu Kα radiation (40 kV, 30 mA, 2θ ranging from 5° to 40°). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed on a Zeiss Supra 55 Sapphire 82 83 field-emission scanning electron microscope at 2.0 kV and a distance of 5.0 mm. Thermogravimetric 84 (TG) analysis was performed on a ZCT-B thermogravimetric analyser (Beijing Jingyi High tech 85 Instrument Co., Ltd; temperature range, 90-800 °C; heating rate, 10 °C min⁻¹). Raman scattering spectra were acquired using a Horiba Jobin-Yvon Lab Ram HR VIS Raman microscope at room 86 87 temperature (633 nm laser as the excitation radiation). The Brunauer-Emmett-Teller (BET) measurements were recorded with a Micromeritics ASAP 2020 surface area and porosimetry 88

analyser. Electron paramagnetic resonance (EPR) spectroscopy was performed on a Bruker EMX 89 PLUS spectrometer to detect the hydroxyl radicals (·OH) generated by a Fenton reaction involving 90 iron(II) sulphate and hydrogen peroxide.² The spin-trapping agent of 5,5-dimethylpyrrolin-1-oxide 91 (DMPO) was employed to form the DMPO-OH adduct in the presence of different MOF crystals. 92 93 ¹H-nuclear magnetic resonance (¹H-NMR) was performed on a 400 MHz NMR spectrometer to 94 characterize the CO₂ conversion in the cycloaddition reaction. Cone calorimetry was performed to 95 examine the flame retardancy performances of the Zn(AIP)/EP and bare EP sheets. The testing protocol was established according to ASTM E1354/ISO 5660 (heat flux, 35 kW m⁻²; separation 96 97 distance, 60 mm; sampling interval, 5 s; sample weight, 15 g).

98 Calculation

99 To evaluate the fire retardancy performances of Zn(AIP)/EP sheets, the reduction 100 percentages of the burning parameters including the peak of heat release rate (pHRR), total heat 101 release (THR), the peak of smoke production rate (pSPR), total smoke production (TSP), the 102 peak of the CO production rate (pCOPR), and total CO production (TCOP), were calculated 103 using the following equations:

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$$\varphi_{pHRR} = \frac{pHRR_m - pHRR}{pHRR_m} \times 100\% , \qquad (S1)$$

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$$\varphi_{THR} = \frac{THR_m - THR}{THR_m} \times 100\%, \qquad (S2)$$

106
$$\varphi_{pSPR} = \frac{pSPR_m - pSPR}{pSPR_m} \times 100\% , \qquad (S3)$$

107
$$\varphi_{TSP} = \frac{TSP_m - TSP}{TSP_m} \times 100\%, \qquad (S4)$$

108
$$\varphi_{pCOPR} = \frac{pCOPR_m - pCOPR}{pCOPR_m} \times 100\% , \qquad (S5)$$

$$\varphi_{TCOP} = \frac{TCOP_m - TCOP}{TCOP_m} \times 100\% , \qquad (S6)$$

where pHRRm, THRm, pSPRm, TSPm, pCOPRm, and TCOPm are the burning parameters of the bare EP sheet, and pHRR, THR, pSPR, TSP, pCOPR, and TCOP are the corresponding values experimentally measured for different Zn(AIP)/EP composite sheets.

115 Figures and tables

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Figure S1. Powder XRD patterns of F-Zn(AIP) samples synthesized using anhydrous zinc acetate
as the metal salt. The heating time and washing status of each sample are labelled in the figure. The
F-Zn(AIP) peaks are indicated with red stars.



123 Figure S2. Powder XRD patterns of F-Zn(AIP) samples obtained after 3 h heating with zinc acetate

124 dihydrate as the metal salt. The influence of washing treatment was also illustrated.

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127 Figure S3. Photographs of F-Zn(AIP) and S-Zn(AIP), elucidating their divergent colours.



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129 Figure S4. Powder XRD patterns of F-Zn(AIP) stored under varied conditions, demonstrating



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Figure S5. Powder XRD patterns of Zn(HIP) and Zn(NIP) synthesized using solvent-free "dry

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heating" approach.



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Figure S6. Powder XRD patterns of early-stage F-Zn(AIP) synthesis mixtures before heating
(i.e., 0 min) and heated for 15 min. The small diffraction peaks of the two samples, primarily
constituted of the characteristic peaks of the Zn salt and the ligand, were compared to show
their evolution during the induction period.



Figure S7. Molecular structures of (a) the promoted (0 2 1) surface and (b) the inhibited (2 0 2)
surface. Clear surface N exposure and concealment are presented for the two surfaces,
respectively.



Figure S8. XPS full spectra (a) and high resolution N 1s spectra (b) of S-Zn(AIP) and F-Zn(AIP)
samples, indicating their altered N contents.



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Figure S9. NH₃-TPD spectra of S-Zn(AIP) and F-Zn(AIP), indicating their comparable acid
site amounts. The measured NH₃ desorption temperature is lower for F-Zn(AIP), which might
be attributed the retention of acetate ions on the acid sites, negatively influencing the strength
of Zn-NH₃ interactions.





158 Figure S10. N₂ adsorption isotherm of F-Zn(AIP), compared with that of S-Zn(AIP). Both

159 sample

samples are evidently nonporous.

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Figure S11. Scheme of the CO₂ cycloaddition reaction. 20 mmol epichlorohydrin (ECH) and
0.1 MPa CO₂ were employed as the reactant, producing a pentamonic cyclocarbonate at varied
reaction temperatures. Different amounts of Zn(AIP) samples were used as the catalyst, assisted
by 0.1 mmol co-catalyst of tetrabutylammonium bromide (TBAB).



171 Figure S12. ¹H-NMR of the liquid product of CO₂ cycloaddition reaction when the catalyst







Figure S13. ¹H-NMR of the liquid product of CO₂ cycloaddition reaction catalysed by 2 mol %
F-Zn(AIP) at 80 °C (i.e., entry 6 of Table 1).





178 Figure S14. TG curves of S-Zn(AIP) and F-Zn(AIP) in N₂ atmosphere. F-Zn(AIP) decomposed

- 179 slightly earlier, a phenomenon commonly observed in smaller particles.
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- **183** Figure S15. Bare EP, S-Zn(AIP)/EP and F-Zn(AIP)/EP sheets before (a) and after (b) curing.



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185 Figure S16. Electron micrographs and EDX elemental mapping of (a) bare EP, (b) S-

186 Zn(AIP)/EP and (c) F-Zn(AIP)/EP sheets.



188 Figure S17. Time-elapsed (a) THR, (b) HRR, (c) TCOP, (d) COPR, (e) TSP, and (f) SPR curves
189 of bare EP, S-Zn(AIP)/EP, and F-Zn(AIP)/EP sheets, measured by cone calorimetry.



191 Figure S18. (a) TG curves of bare EP, S-Zn(AIP)/EP, and F-Zn(AIP)/EP sheets in N₂
192 atmosphere. (b) Mass percentage of carbon residue of each sheet after TG measurements.

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199 Figure S19. (a) TG curves of bare EP, S-Zn(AIP)/EP, and F-Zn(AIP)/EP sheets in air (i.e., 20%

 $\label{eq:O2} \textbf{O2}). (b) \ \text{Mass percentage of carbon residue of each sheet after cone calorimetry measurements}.$



Figure S20. (a) Powder XRD pattern of bare EP, S-Zn(AIP)/EP, and F-Zn(AIP)/EP sheets after 203 204 combustion. The (002) plane of graphite results in a characteristic diffraction peak at 26°, which 205 can be used as an indicator for the formation of graphitised carbon. A higher degree of graphitisation 206 would shift the peak closer to 26° . Obviously, the carbon residues of the two Zn(AIP)/EP sheets 207 manifested diffraction peaks closer to this value, indicating their elevated contents of graphitized 208 carbon in relative to the bare EP sheet. No characteristic diffraction peaks of Zn(AIP) were observed, 209 suggesting complete decomposition of the MOF. (c-d) Raman spectra of bare EP (b), S-210 Zn(AIP)/EP (c) and F-Zn(AIP)/EP sheets (d) after combustion. The D and G peaks were located at 1366 and 1595 cm⁻¹, respectively. The ratios of the two peak areas are listed in each panel. 211 212 213

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Table S1. Basic site amounts of S-Zn(AIP) and F-Zn(AIP) samples, measured by CO₂-TPD.

Catalyst	Lewis basic sites (mmol g ⁻¹)
S-Zn(AIP)	0.04
F-Zn(AIP)	0.22

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Table S2. CO₂ cycloaddition activities of Zn(AIP) samples under different reaction conditions.

221 Several previously reported MOF catalysts using the same reactant of ECH were also listed in

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222	the	table	tor	comparison.
			101	•omparison.

Entry	Catalyst	Time (h)	Temperature (°C)	Conversion (%)
1	No catalyst	10	50	36.6
2	F-Zn(AIP) ^c	10	50	39.7
3	F-Zn(AIP) ^d	10	50	46.5
4	F-Zn(AIP) ^e	10	50	51
5	F-Zn(AIP) ^f	10	50	55.2
6	$S-Zn(AIP)^{f}$	10	50	41.5
7	F-Zn(AIP) ^b	5	80	87.7
8	S-Zn(AIP) ^b	5	80	82
9	F-Zn(AIP) ^a	10	80	94.3
10	F-Zn(AIP) ^b	10	80	97.1
11	S-Zn(AIP) ^b	10	80	90.9
12	F-Zn(AIP) ^c	10	80	98
13	S-Zn(AIP) ^c	10	80	96.2
14	Co-btc ^a	2	120	78 ³
15	MOF-801(D) ^j	15	80	78.8^{4}
16	Ni(HBTC)(4,4-bipy) ^h	6	80	60 ⁵
17	MOF-5-MIX ^k	8	110	94 ⁶

223 Catalyst amounts: ^a 0.5 mol %, ^b 1 mol %, ^c 2 mol%, ^d 4 mol %, ^e 8 mol %, ^f 15 mol %, ^j 0.4 mol %,

224 ^h 0.6 mol %, ^k 0.7 mol %. Percentages were calculated based on the molar amount of ECH.

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Table S3. Cone calorimetry results for bare EP, S-Zn(AIP)/EP, and F-Zn(AIP)/EP sheets.

Parameters	Bare EP	S-Zn(AIP)/EP	Decrement (%)	F-Zn(AIP)/EP	Decrement (%)
pHRR (kW m ⁻²)	628.2	410.9	34.6	356.2	43.3
THR (MJ m^{-2})	37.6	26.3	30.0	20.8	44.7
$pSPR (m^2 s^{-1})$	0.4	0.2	35.7	0.3	29.4
$TSP(m^2)$	19.7	14.7	25.1	11.7	40.5
pCOPR (mg s^{-1})	33.0	21.0	35.9	19.0	42.0
TCOP (g)	2.1	1.4	34.2	1.1	49.2
Remaining mass (%)	6.0	12.0	-	14.7	-

233 Table S4. Reduction percentages of the burning parameters (φ) after the addition of varied

234 MOFs. The performances of F-Zn(AIP) are compared with those of S-Zn(AIP) and other MOFs

235	reported	in	previous	flame	retardancy	studies.
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Sample	Loading (wt%)	$arphi_{ ext{pHRR}}$	$arphi_{ ext{THR}}$	$arphi_{ ext{pSPR}}$	$arphi_{ ext{TSP}}$	$arphi_{ extsf{p} extsf{COPR}}$	$arphi_{ ext{TCOP}}$	Ref.
Y-BTC	4	28.2	12.7	20.7	15.2	30	11.9	7
MOF-3	2	45.0	7.0	24.4	-	-	-	8
UIO-66	3	39.1	-	-	18.5	-	-	9
UIO-66-NH ₂	2	30.2	-	8.9	-	21.4	2.3	10
Mo-MOF	2	41.9	5.4	13.3	10.5	38.1	-	11
Co-MOF	2	28.4	2.6	-	9.9	-	-	12
P-MOF	2	28.1	18.6	23.4	14.9	-	-	13
ZIF-(Zn/Co)	2	10.9	-	-	-	37	-	14
Fe-BDC	2	18.6	7.9	32	-	-	-	15
ZIF-67(Co)	2	15.4	7.9	-	17.3	-	-	16
ZIF-8(Zn)	2	24.8	-	-	23.8	-	-	17
PN-MOF	2	29.9	24.1	14.1	-	-	-	18
S-Zn(AIP)	2	34.6	30.0	35.7	25.1	35.9	34.2	This work
F-Zn(AIP)	2	43.3	44.7	29.4	40.1	42	49.3	This work

Table S5. Experimental and theoretical residual mass percentages of S-Zn(AIP), F-Zn(AIP),

_	Sample	Experimental residual mass (%)	Theoretical residual mass ^a (%)
	S-Zn(AIP)	44.3	-
	F-Zn(AIP)	43.8	-
	Bare EP	10.0	-
	S-Zn(AIP)/EP	14.1	10.7 ^b
	F-Zn(AIP)/EP	16.1	10.7 ^b

240 bare EP, S-Zn(AIP)/EP and F-Zn(AIP)/EP sheets, measured by TG.

a. The theoretical residual mass of the composite was estimated using the experimental residual

242 mass of each component and their respective weight percentages in the composite (e.g. for S-

243 Zn(AIP)/EP, 10.0*98% + 44.3*2% = 10.7%).

244 b. These theoretical values were calculated based on the TG results in N_2 atmosphere. When in

245 air, the theoretical values should be < 8.0 % (i.e., 6.0 % residue for the bare EP sheet in air and

the added Zn-MOF amounting to 2.0 % in total).

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