

Supporting Information

for

Efficient Conversion of CO₂ via Grafting Urea Group into a [Cu₂(COO)₄] Based MOF with Hierarchical Porosity

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1. MOFs Activation

Compound **1** was soaked in DCM solution for 4 h until the crystal color changing from green to deep blue (see Figure S11), suggesting that the guest molecules and the coordinated H₂O was removed.^{S1} The stability of the activated crystal was confirmed by PXRD measurement (see Figure S12). Similar procedures were performed on **1-NH₂**, **1-Urea**, and HKUST-1, respectively, to get the corresponding activated MOFs (see Figures S13 and S14).

2. Ibuprofen Absorption Experiment

Ibuprofen was selected as guest to conduct the absorption experiment to verify the pore stability in solution. The 40 mg activated compound of **1**, **1-NH₂**, or **1-Urea** was soaked in ibuprofen solution of 2.0 mL (0.15 mol/L, in cyclohexane) for 24 h. Then, the product was washed with fresh cyclohexane for three times (3 mL × 3). The crystal phases of the samples contained ibuprofen were characterized by both optical microscope (see Figure S11) and PXRD (see Figure S12-S14). The content of ibuprofen incorporated in MOFs were calculated by the ¹H NMR measurement of the digested sample (Figure S15), the result were summarized in Table S4.

3. Cu(II) Leaking Test after the PO Cycloaddition Experiment

After the reaction PO cycloaddition experiment, **1-Urea** and the organic solution was separated by centrifugation. The obtained organic solution was vaporized under vacuum, the rested oil was treated with conc. HNO₃ (500 uL × 2) and heated at 160 °C for 5 h until near dried, then diluted with ultrapure water. The solution was then transferred into 25 mL flint glass flask volumetric. The ICP-OES analysis giving a Cu(II) content of 0.031 mg/L, which suggested the leak of Cu(II) was 0.02% in compared with the total Cu(II) content of 160 mg/L.

4. Explanation for the Alert B in the checkCIF reports

ALERT_B in checkCIF report of compound **1**:

PLAT420_ALERT_2_B D-H Without Acceptor 01W --H1WB . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 01W --H1WA . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 02W --H2WA . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 02W --H2WB . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 03W --H3WB . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 03W --H3WA . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 04W --H4WB . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 04W --H4WA . Please Check

Discussion: These alerts come from the missing of H-Bond acceptors of H₂O molecules that coordinated to the Cu(II) ions, due to the acceptors (the guest molecules) were found highly disordered with weak X-ray diffraction and were squeezed by *Platon*.^{S15}

PLAT990_ALERT_1_B Deprecated .res/.hkl Input Style SQUEEZE Job ... ! Note

Discussion: This alert come from the use of squeeze program of *Platon* software.

ALERT_B in checkCIF report of compound **1-NH₂**:

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PLAT420_ALERT_2_B D-H Without Acceptor 03W --H3WA . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 04W --H4WB . Please Check
PLAT420_ALERT_2_B D-H Without Acceptor 04W --H4WA . Please Check

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ALERT_B in checkCIF report of compound **1-Urea**:

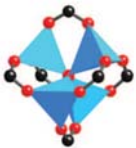
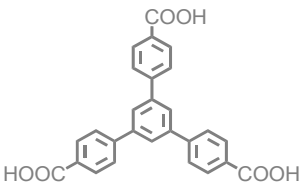
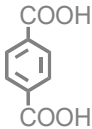
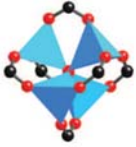
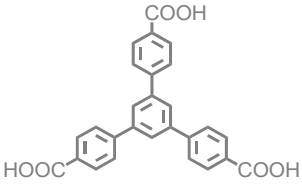
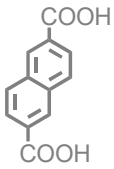
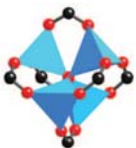
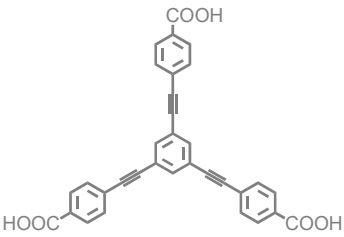
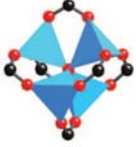
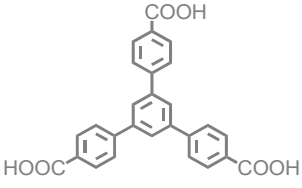
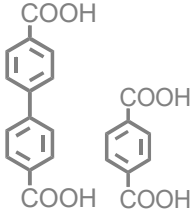
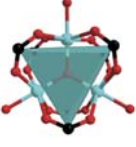
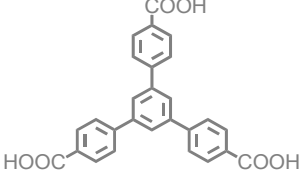
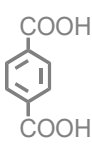
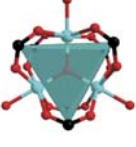
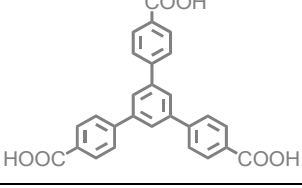
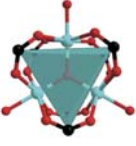
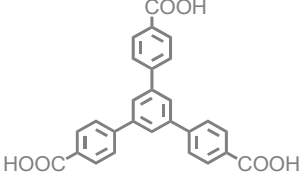
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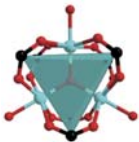
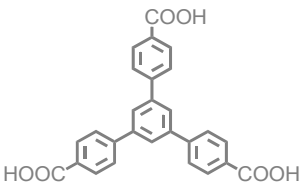
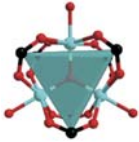
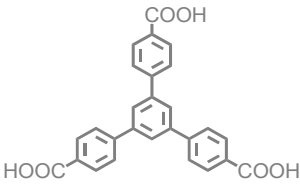
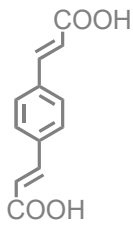
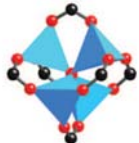
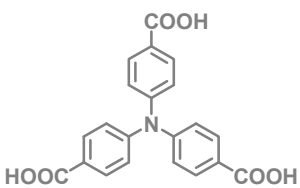
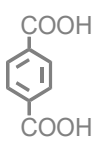
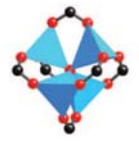
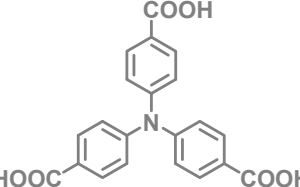
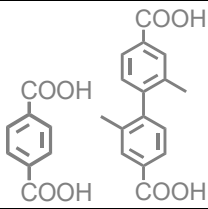
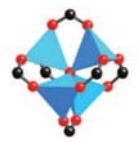
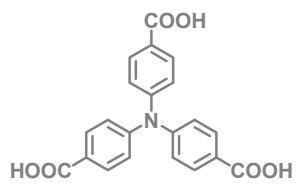
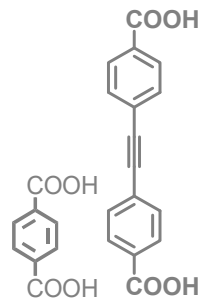
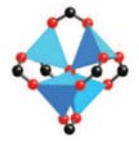
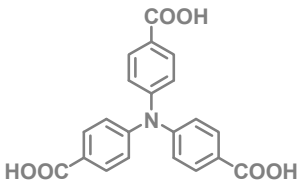
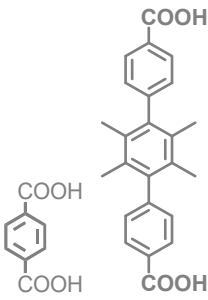
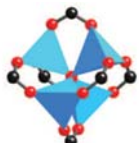
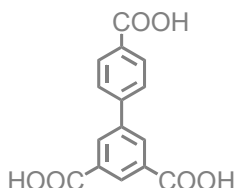
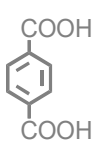
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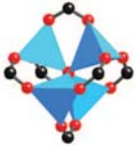
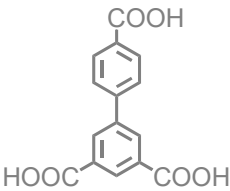
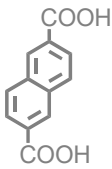
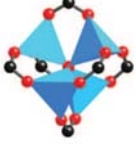
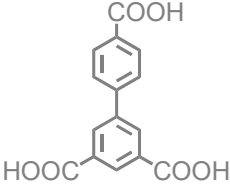
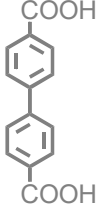
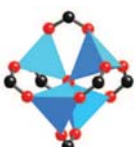
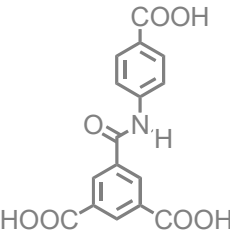
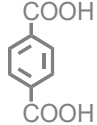
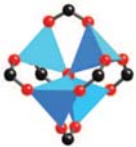
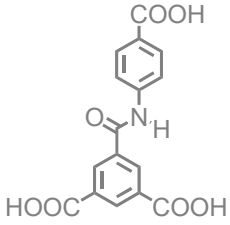
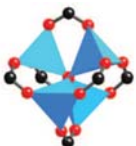
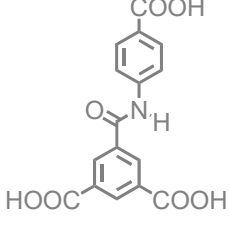
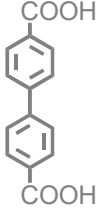
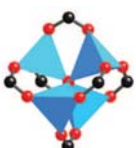
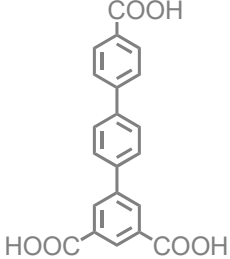
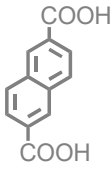
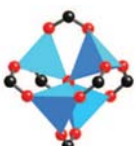
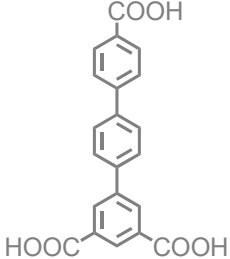
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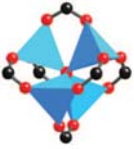
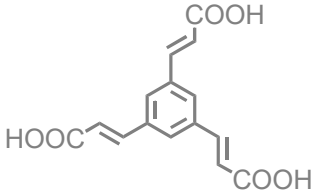
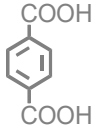
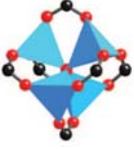
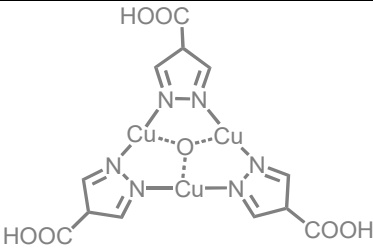
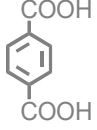
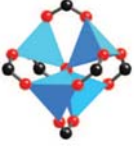
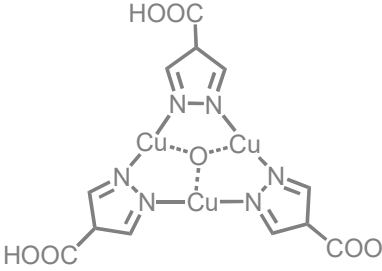
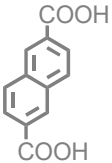
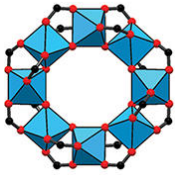
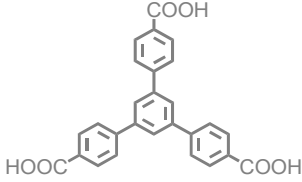
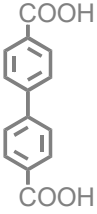
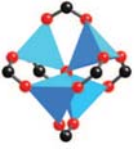
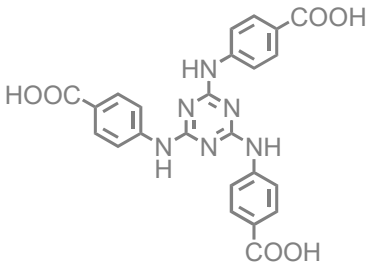
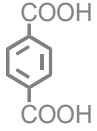
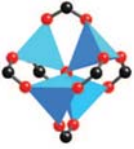
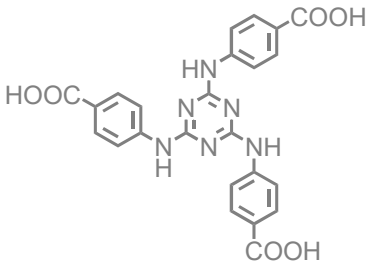
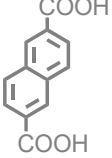
Discussion: This alert come from the use of squeeze program of *Platon* software.

Table S1. Summary of the MOFs Composed of Mixed Tritopic and Ditopic Linkers with SBUs

Year	Code	SBU	Tritopic linker	Ditopic linker
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2009	MOF210 ^{S3}			
2013	MUF-7a ^{S5}			
2013	MIL142a ^{S6}			
2013	MIL142b ^{S6}			
2013 2014	MIL142c ^{S6} PCN280 ^{S7}			

2013 2014	MIL142d ^{S6} PCN285 ^{S7}			
2013	MIL142e ^{S6}			
2014	UMCM-4 ^{S8}			
2014	UMCM-10 ^{S8}			
2014	UMCM-11 ^{S8}			
2014	UMCM-12 ^{S8}			
				

2015 ^{S9}			
			
			
			
			
			
			

2016	MOF905 ^{S10}			
2017	FDM-6 ^{S11}			
2017	FDM-7 ^{S11}			
2017	MOF520-BPDC ^{S12}			
2017	ST-1 ^{S13}			
2017	ST-2 ^{S13}			

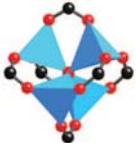
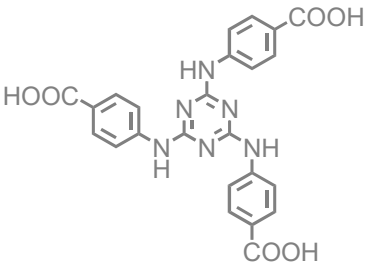
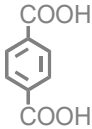
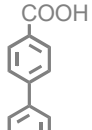
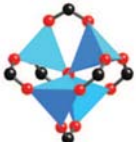
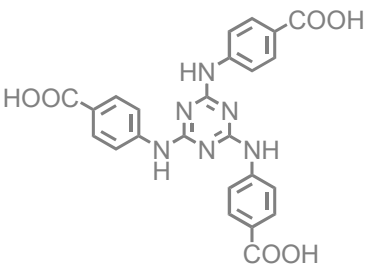
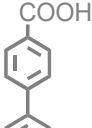
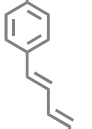
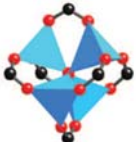
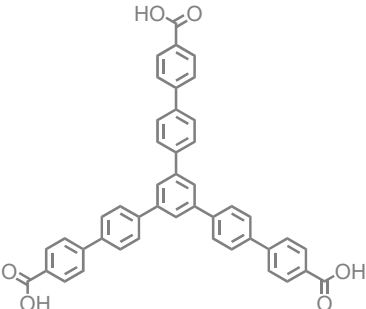
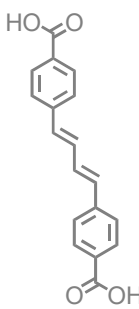
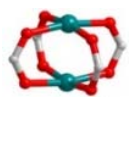
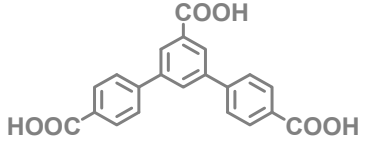
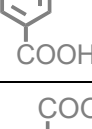
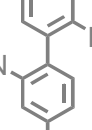
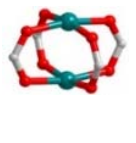
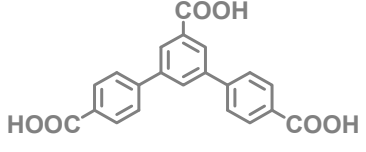
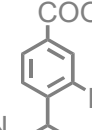
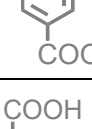
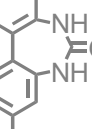
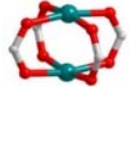
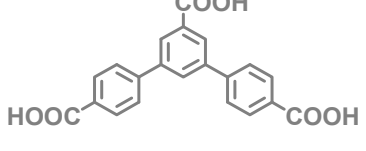
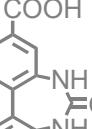
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2017	ST-4 ^{S13}			  
2018	DUT-60 ^{S14}			
2018	This work			  
				  
				  

Table S2. Crystal Data and Structure Refinement for **1**, **1-NH₂**, and **1-Urea**.

Compound	1	1-NH₂	1-Urea
Empirical formula	C ₇₀ H ₄₇ Cu ₅ O ₂₅	C ₇₀ H ₄₅ Cu ₅ NO ₂₅	C ₇₀ H ₄₆ Cu ₅ NO ₂₅
Formula weight	1605.78	1617.77	1618.78
Temperature	298(2) K	298(2) K	150(2)K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system, space group	Orthorhombic, <i>Cmcm</i>	Orthorhombic, <i>Cmcm</i>	Orthorhombic, <i>Cmcm</i>
Unit cell dimensions	<i>a</i> = 57.0005(6) Å,	<i>a</i> = 57.2452(15) Å,	<i>a</i> = 59.0269(14) Å,
	<i>b</i> = 29.6573(3) Å,	<i>b</i> = 29.8895(7) Å	<i>b</i> = 30.4881(15) Å,
	<i>c</i> = 28.7942(4) Å,	<i>c</i> = 28.5403(12) Å,	<i>c</i> = 25.3905(18) Å,
Volume, Z	48676(1) Å ³ , 8	48833(3) Å ³ , 8	45693(4) Å ³ , 8
Absorption coefficient	0.438 mm ⁻¹	0.679 mm ⁻¹	0.726 mm ⁻¹
Reflections collected / unique	48048 / 19653	21038 / 21038	10192 / 23295
	[R(int) = 0.0306]	[R(int) = 0.076]	[R(int) = 0.072]
Data / restraints / parameters	19653 / 0 / 463	21038 / 25 / 448	23295 / 40 / 448
Goodness-of-fit on <i>F</i> ²	1.061	1.000	0.991
Final R indices [I > 2σ(I)]	R ₁ = 0.0557, wR ₂ = 0.1868	R ₁ = 0.0917, wR ₂ = 0.2512	R ₁ = 0.0815, wR ₂ = 0.2532
R indices (all data)	R ₁ = 0.0694, wR ₂ = 0.2004	R ₁ = 0.1463, wR ₂ = 0.2934	R ₁ = 0.1192, wR ₂ = 0.2787
Largest diff. peak and hole	0.352 and -0.289 e·Å ⁻³	0.536 and -1.148 e·Å ⁻³	0.829 and -1.031 e·Å ⁻³

Table S3 Selected bond lengths [Å] and angles [°] for **1**, **1-NH₂**, and **1-Urea**.

1					
Cu1-O7	1.9668(18)	O7 ¹ -Cu1-O7	89.66(12)	O3 ⁴ -Cu3-O3	88.90(13)
Cu1-O6	1.9747(17)	O7-Cu1-O6 ¹	168.17(8)	O3-Cu3-O4	168.23(9)
Cu1-O2W	2.153(3)	O7-Cu1-O6	89.39(8)	O3-Cu3-O4 ⁴	89.81(9)
Cu2-O2	1.945(2)	O6 ¹ -Cu1-O6	89.14(11)	O4-Cu3-O4 ⁴	89.06(13)
Cu2-O10	1.958(2)	O7-Cu1-O2W	96.09(9)	O3-Cu3-O4W	96.10(11)
Cu2-O9	1.9637(17)	O6-Cu1-O2W	95.74(9)	O4-Cu3-O4W	95.67(11)
Cu2-O3W	2.142(3)	O2 ² -Cu2-O10	89.70(10)	O8 ¹ -Cu4-O8	89.84(13)
Cu3-O3	1.9504(19)	O2 ² -Cu2-O1 ³	168.38(10)	O8-Cu4-O5	89.27(9)
Cu3-O4	1.9625(19)	O22-Cu2-O9	89.38(8)	O5 ¹ -Cu4-O5	89.21(13)
Cu3-O4W	2.133(4)	O10-Cu2-O9	168.21(10)	O5-Cu4-O1W	95.67(9)
Cu4-O8	1.9461(18)	O2 ² -Cu2-O3	96.30(12)		
Cu4-O1W	2.154(3)	O10-Cu2-O3W	96.77(12)		
Symmetry transformations used to generate equivalent atoms: ¹ +X,+Y,1/2-Z; ² 1/2-X,1/2-Y,-Z; ³ 1/2-X,1/2+Y,+Z; ⁴ 1-X,+Y,+Z.					
1-NH₂					
Cu1-O3	1.933(3)	O7 ¹ -Cu1-O7	89.66(12)	O3-Cu3-O4	168.23(9)
Cu1-O3W	2.174(5)	O7-Cu1-O6 ¹	168.17(8)	O3-Cu3-O4 ⁴	89.81(9)
Cu2-O2	1.933(3)	O7-Cu1-O6	89.39(8)	O4-Cu3-O4 ⁴	89.06(13)
Cu2-O7	1.938(3)	O6 ¹ -Cu1-O6	89.14(11)	O3-Cu3-O4W	96.10(11)
Cu2-O2W	2.131(4)	O7-Cu1-O2W	96.09(9)	O4-Cu3-O4W	95.67(11)
Cu3-O9	1.953(3)	O2 ² -Cu2-O10	89.70(10)	O8 ¹ -Cu4-O8	89.84(13)
Cu3-O10	1.961(3)	O2 ² -Cu2-O1 ³	168.38(10)	O8 ¹ -Cu4-O5 ¹	89.27(9)
Cu3-O4W	2.151(4)	O10-Cu2-O1 ³	89.26(9)	O8-Cu4-O5 ¹	168.22(8)
Cu4-O8	1.961(3)	O2 ² -Cu2-O9	89.38(8)	O8-Cu4-O5	89.27(9)
Cu4-O1	1.962(3)	O10-Cu2-O9	168.21(10)	O8-Cu4-O1W	96.10(10)
Cu4-O1W	2.120(4)	O2 ² -Cu2-O3W	96.30(12)		
Symmetry transformations used to generate equivalent atoms: ¹ 1-X,+Y,+Z; ² +X,1-Y,1-Z; ³ 1-X,1-Y,1-Z; ⁴ 3/2-X,1/2+Y,+Z.					
1-Urea					
Cu1-O1	1.923(3)	O8-Cu1-O1	90.51(17)	O3 ² -Cu3-O9 ³	89.22(12)
Cu1-O8	1.921(3)	O8-Cu1-O1 ¹	167.06(12)	O4-Cu3-O3 ²	167.75(16)
Cu1-O1W	2.122(4)	O8 ¹ -Cu1-O1 ¹	90.51(17)	O4-Cu3-O9 ³	90.07(11)
Cu2-O2	1.958(3)	O8 ¹ -Cu1-O8	88.2(3)	O4-Cu3-O10	89.11(12)
Cu2-O7	1.982(3)	O8-Cu1-O1W	98.10(13)	O4-Cu3-O3W	97.80(14)
Cu2-O2W	2.132(3)	O2-Cu2-O21	88.73(17)	O5 ⁵ -Cu4-O5 ⁴	89.67(16)
Cu3-O4	1.937(3)	O2-Cu2-O7	90.17(12)	O5 ⁵ -Cu4-O6	168.36(14)
Cu3-O3W	2.097(4)	O2-Cu2-O2W	96.48(12)	O5 ⁴ -Cu4-O6 ⁶	168.36(14)
Cu4-O6	1.969(3)	O7 ¹ -Cu2-O7	88.10(18)	O5 ⁴ -Cu4-O6	89.41(12)
Cu4-O4W	2.108(4)	O7-Cu2-O2W	96.25(12)	O5 ⁴ -Cu4-O4W	96.29(12)
Symmetry transformations used to generate equivalent atoms: ¹ +X,+Y,5/2-Z; ² +X,-3-Y,2-Z; ³ 1/2-X,-1/2+Y,+Z; ⁴ +X,-2-Y,2-Z; ⁵ 1-X,-2-Y,2-Z; ⁶ 1-X,+Y,+Z.					

Table S4. Summary of the contents of ibuprofen loaded in the compounds

Compound	Formula	ibuprofen Content
1	$[\text{Cu}_5(\text{TPTC})_3(\text{BPDC})_{0.5}] \cdot 4.8(\text{ibuprofen})$	0.65 g/g
1-NH₂	$[\text{Cu}_5(\text{TPTC})_3(\text{BPDC-NH}_2)_{0.5}] \cdot 5.2(\text{ibuprofen})$	0.70 g/g
1-Urea	$[\text{Cu}_5(\text{TPTC})_3(\text{BPDC-Urea})_{0.5}] \cdot 4.6(\text{ibuprofen})$	0.61 g/g

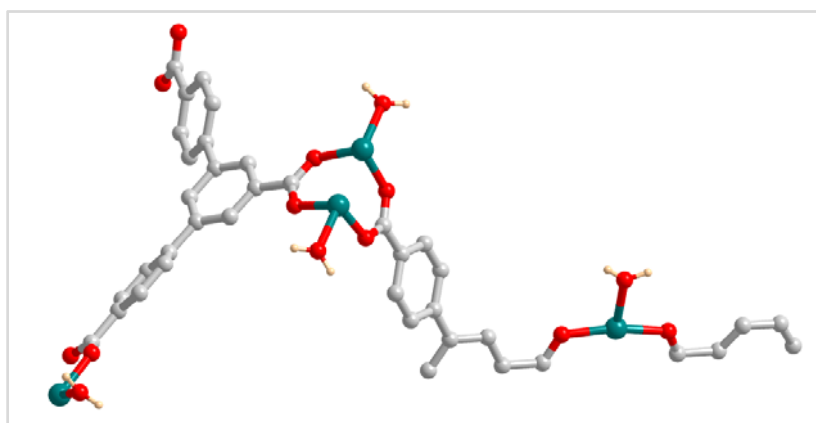


Figure S1. The asymmetry unit of **1**, where $5/2 \text{ Cu}^{2+}$, $3/2 \text{ TPTC}^{3-}$, $1/4$ of BPDC^{2-} and $5/2 \text{ H}_2\text{O}$ were found. (Cu: green, C: light gray, O: red, H: yellow, H atoms in the ligands were omitted for clarity).

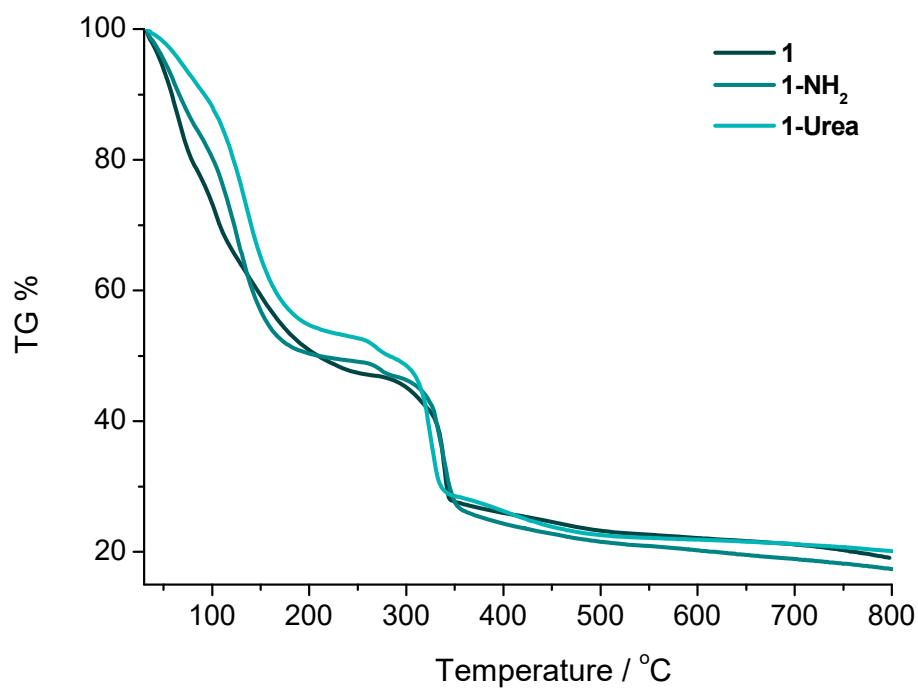


Figure S2. TG curves of compound **1**, **1-NH₂** and **1-Urea**.

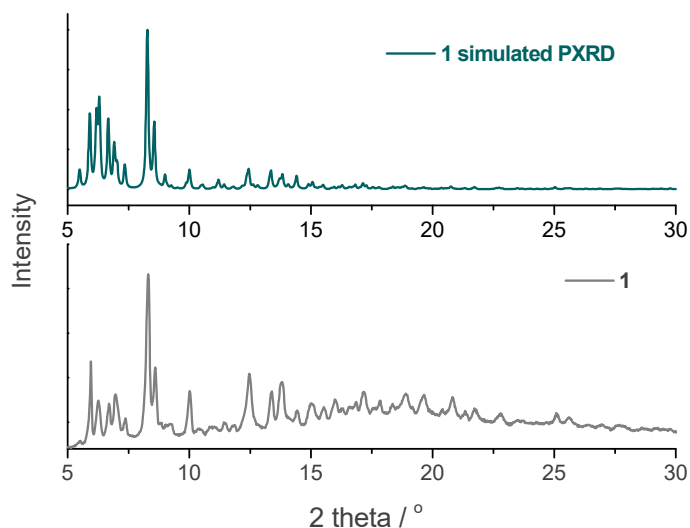


Figure S3. Simulated PXRD pattern (up) and PXRD patterns for pristine **1** (down).

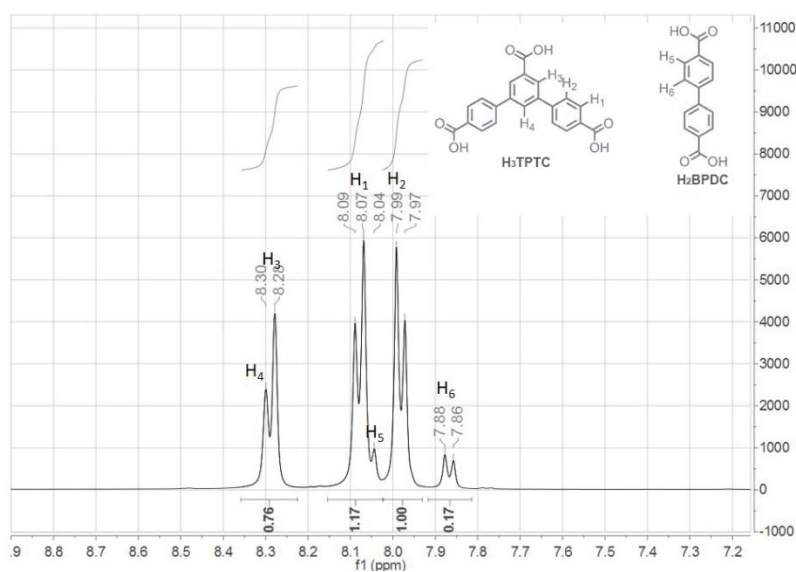


Figure S4. Excerpts of ^1H NMR spectra of compound **1** digest sample dissolved in $\text{DMSO-}d_6$. Ratio of $\text{H}_3\text{TPTC}/\text{H}_2\text{BPDC}=1:0.17$ (5.9:1) comes from the integration of H_2 in H_3TPTC and H_6 in H_2BPDC , which was stoichiometric consistent with the value of 6:1 deduced from the formula of **1**.

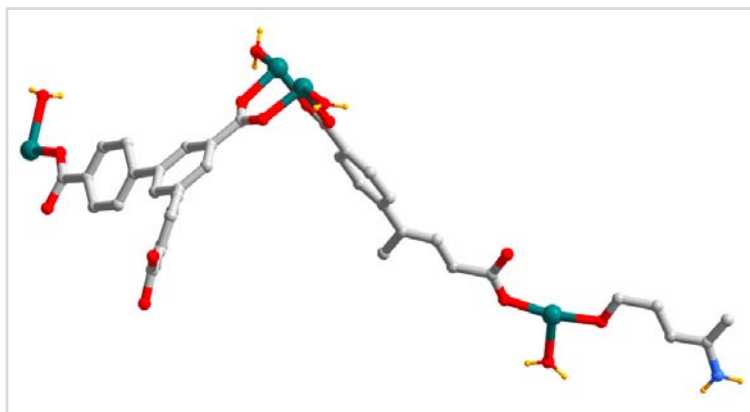


Figure S5. The asymmetry unit of **1-NH₂**, where 5/2 Cu²⁺, 3/2 TPTC³⁻, 1/4 of BPDC-NH₂²⁻ and 5/2 H₂O were found.

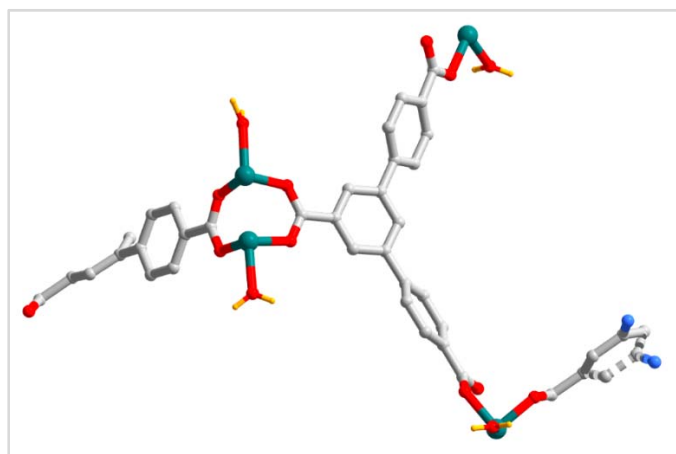


Figure S6. The asymmetry unit of **1-Urea**, where 5/2 Cu²⁺, 3/2 TPTC³⁻, 1/4 of BPDC-Urea²⁻ and 5/2 H₂O were found. BPDC-Urea²⁻ was found two-fold disordered. Due to the weak X-ray diffraction, the C=O group of the urea group cannot be located from the differential map.

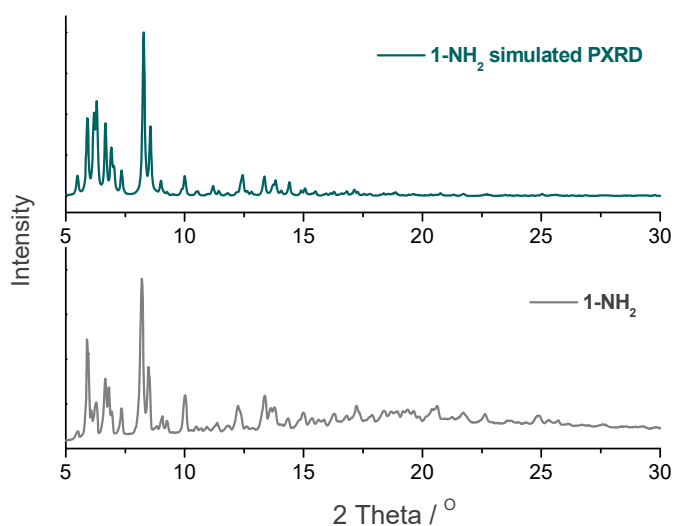


Figure S7. Simulated PXRD pattern (up) and PXRD patterns for pristine **1-NH₂** (down).

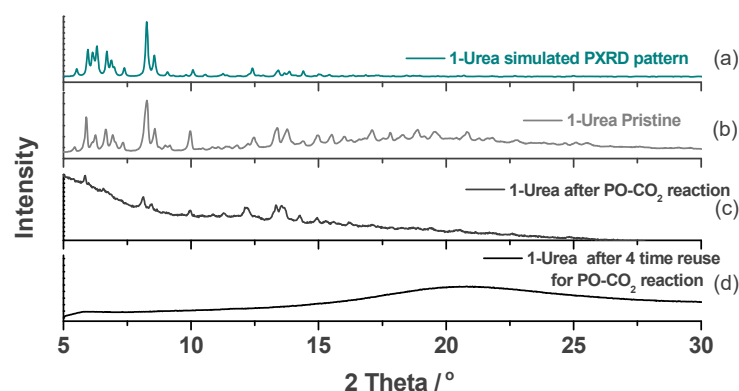


Figure S8. PXRD patterns of **1-Urea**: (a) simulated on the basis of single crystal, (b) as-synthesized sample, (c) recovered sample for 1 running reaction, and (d) recovered sample for 5 running reaction.

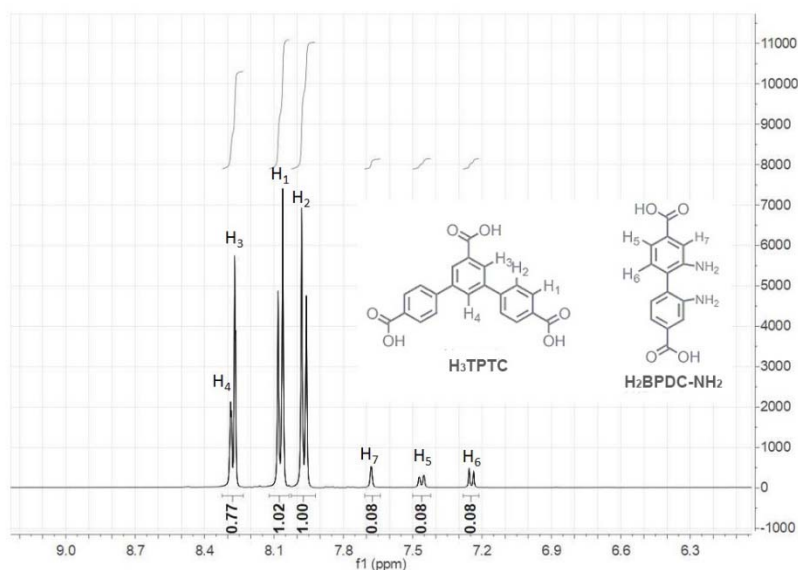


Figure S9. Excerpts of ^1H NMR spectra and the integration of **1-NH₂** digest sample dissolved in $\text{DMSO-}d_6$. Ratio of $\text{H}_3\text{TPTC}/\text{H}_2\text{BPDC-NH}_2 = (1.0/4) : (0.08/2) = 6.2:1$ comes from the integration of H_2 in H_3TPTC and H_6 in $\text{H}_2\text{BPDC-NH}_2$, which was stoichiometric consistent with the value of 6:1 deduced from the formula of **1-NH₂**.

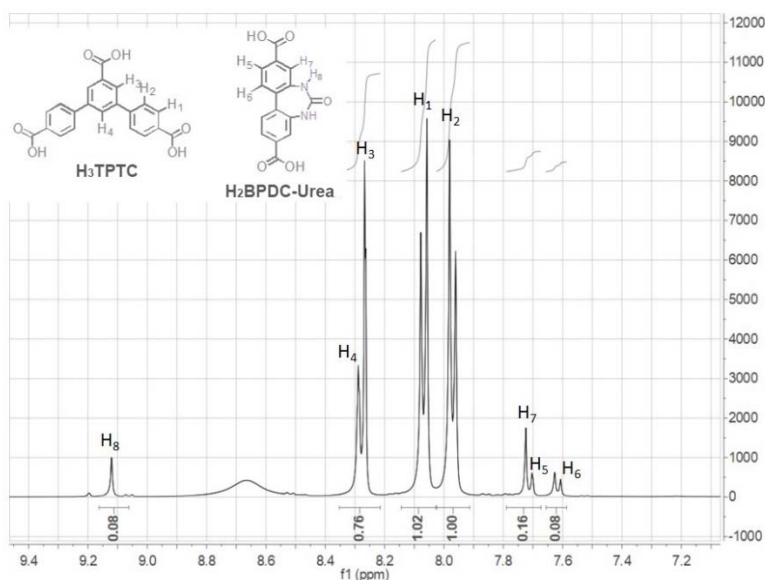


Figure S10. Excerpts of ^1H NMR spectra of **1-Urea** digest sample dissolved in $\text{DMSO-}d_6$. Ratio of

$\text{H}_3\text{TPTC}/\text{H}_2\text{BPDC-Urea} = (1.0/4) : (0.08/2) = 6.2:1$ comes from the integration of H_2 in H_3TPTC and H_6 in $\text{H}_2\text{BPDC-Urea}$, which was stoichiometric consistent with the value of 6:1 deduced from the formula of **1-Urea**.

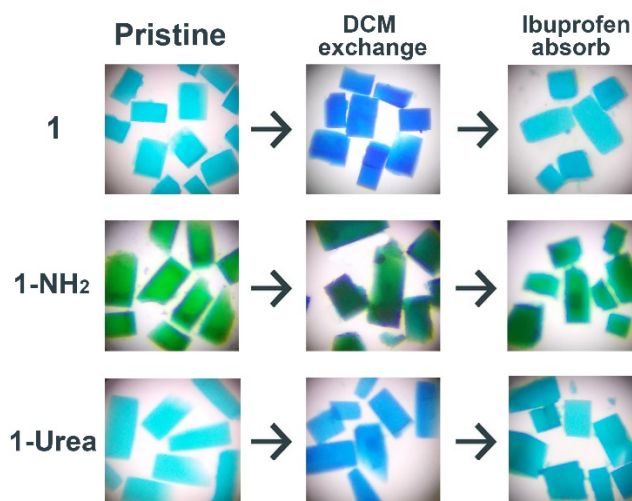


Figure S11. The photographs of single crystal of **1**, **1-NH₂** and **1-Urea** (left), the corresponding DCM exchanged samples (middle), and ibuprofen absorbed samples (right).

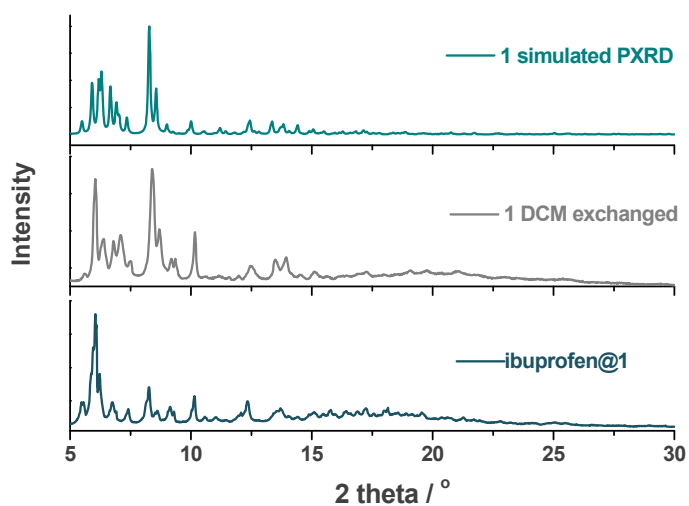


Figure S12. PXRD patterns of **1**, DCM exchanged of **1**, and ibuprofen adsorbed in **1**.

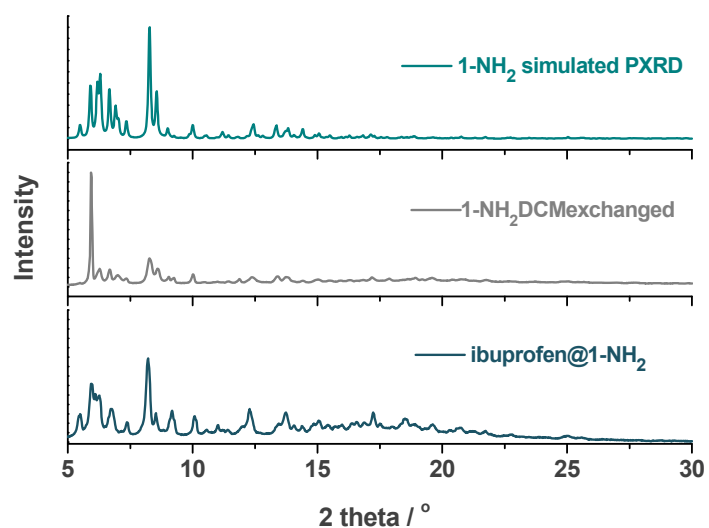


Figure S13. PXRD patterns of **1-NH₂**, DCM exchanged of **1-NH₂**, and ibuprofen adsorbed in **1-NH₂**.

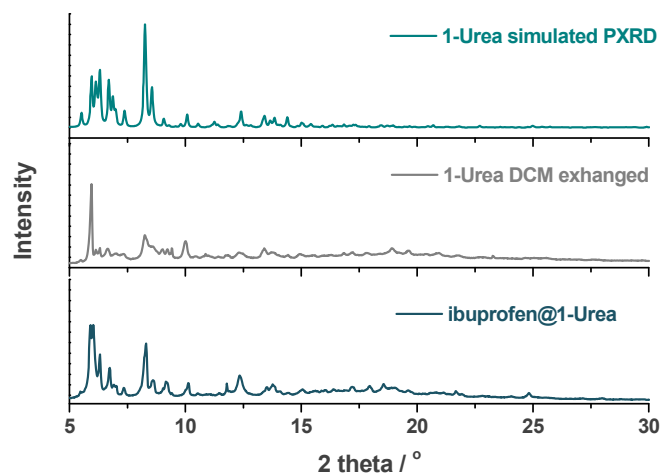


Figure S14. PXRD patterns of **1-Urea**, DCM exchanged of **1-Urea**, and ibuprofen adsorbed in **1-Urea**.

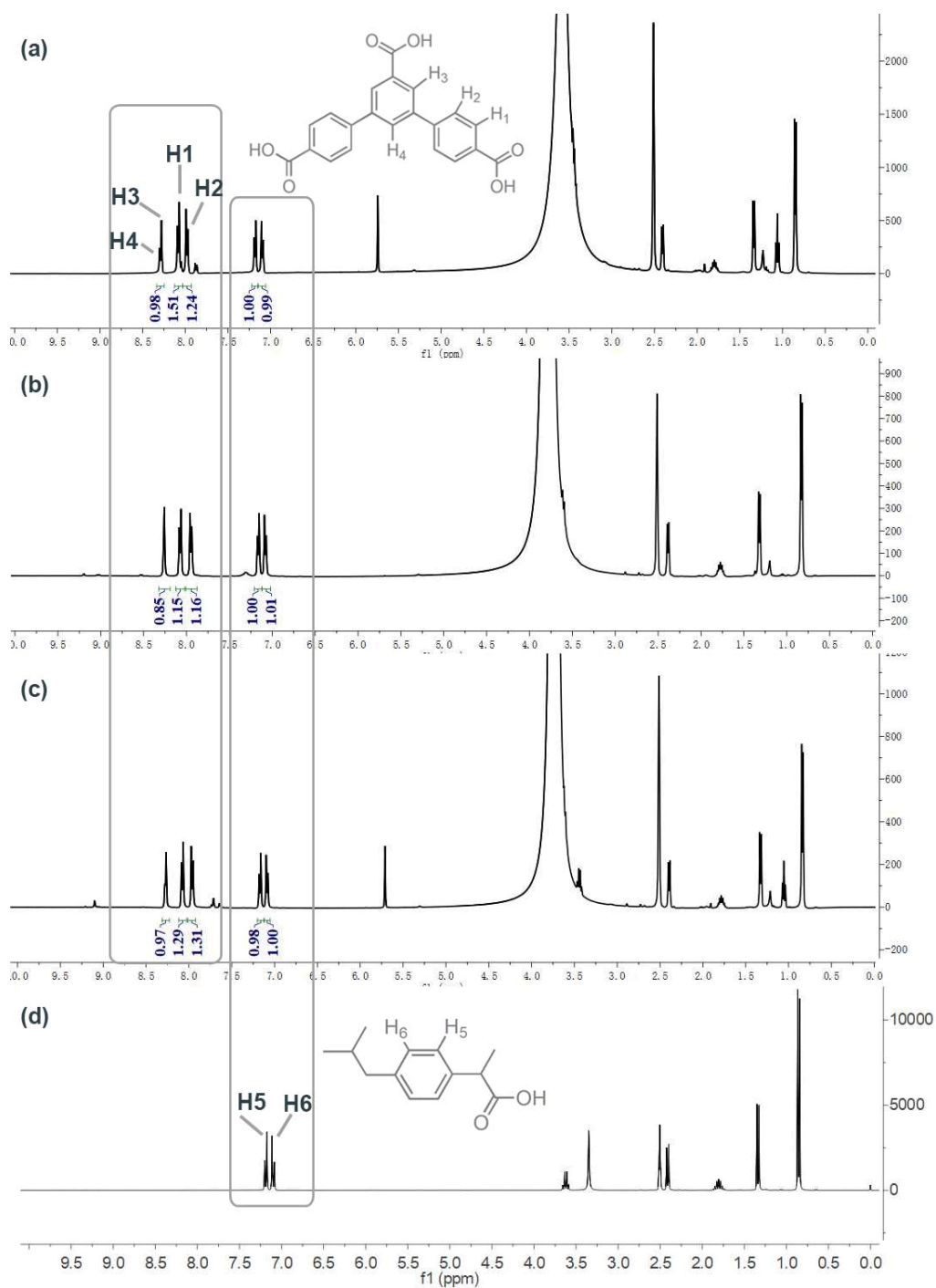


Figure S15. ^1H NMR ($\text{DMSO}-d_6$) spectra for the digested samples of **1** (a), **1-NH₂** (b), and **1-Urea** (c) adsorbed ibuprofen as well as pure ibuprofen (d). The contents of the ibuprofen can be calculated from the integration of H2 in H₃TPTC and H6 in ibuprofen, which give the ratio of ibuprofen /H₃TPTC = 1.61, 1.72 and 1.53 for **1**, **1-NH₂**, and **1-Urea**, respectively.

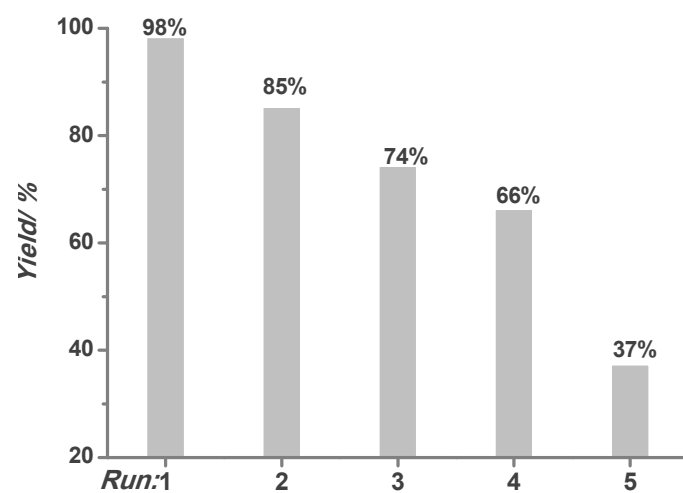


Figure S16. Summary of cycloaddition of PO and CO₂ conversion for the reused catalyst **1-Urea** of the 5 runs.

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