Supporting Information

Ligands dependent structural diversity and optimizable CO_2 chemical fixation activities of Cu-doped polyoxo-titanium clusters

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1. Single crystal structure of PTC-367 to PTC-370

1.1. Structure determination of PTC-367 to PTC-370.

Table S1 Crystal data and structure refinement summary for **PTC-367** to **PTC-370**.

	PTC-367	**PTC-368**	**PTC-369**	**PTC-370**
CCDC No	2264421	2264422	2264423	2264424
Formula	$C_{52}H_{116}Cu_3O_{29}Ti_6$	$C_{60}H_{116}Br_2Cu_2O_{34}Ti_8$	$C_{70}H_{150}Cu_3O_{57}Ti_{16}$	$C_{91}H_{179}Cu_3O_{101}Ti_{29}$
Mr	1683.46	1026.82	2861.42	4470.06
T[K]	290	293	100	100
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*–1	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	12.9989 (3)	11.6608 (2)	16.0885 (4)	24.5562 (14)
b [Å]	14.2479 (3)	19.3473 (4)	44.2441 (8)	29.6251 (15)
c [Å]	23.6414 (3)	20.8404 (3)	33.1200 (4)	30.6831 (17)
α [Å]	87.179 (2)	90	90	90
β [Å]	82.799 (2)	91.041 (2)	94.1550 (15)	111.029
γ [Å]	72.186 (2)	90	90	90
V [$Å^3$]	4135.47 (15)	4700.92 (14)	23513.5 (7)	20835 (2)
Z	2	4	8	4
ρ_c [gcm^{-3}]	1.352	1.451	1.617	1.425
μ [mm^{-1}]	7.43	6.97	8.91	7.76
Radiation	Ga *K*α	Ga *K*α	Ga *K*α	Ga *K*α
GOOF	1.042	1.063	1.016	0.999
$R_1[I>2\sigma(I)]$ [a]	0.084	0.087	0.091	0.096
$wR_2[I>2\sigma(I)]$ [b]	0.224	0.279	0.277	0.344

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

1.2. Single crystal structures and packing mode of PTC-367 to PTC-370.

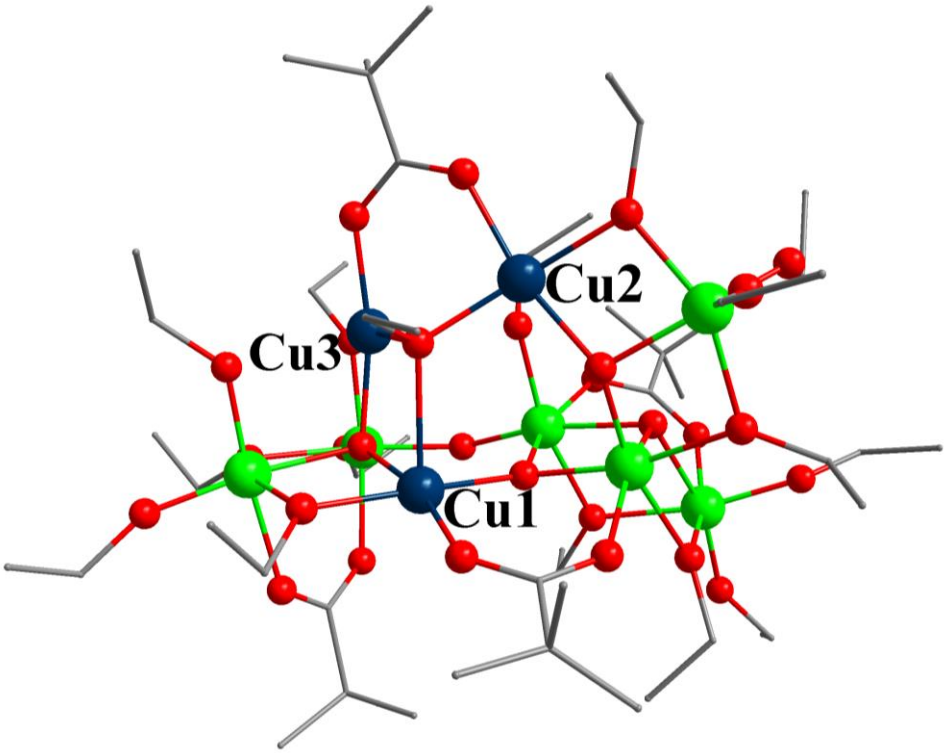

Figure S1. The structure of **PTC-367**. H atoms were omitted for clarity. Atom color code: green Ti; Blue Cu; red O; gray C. Omit H for clarity.

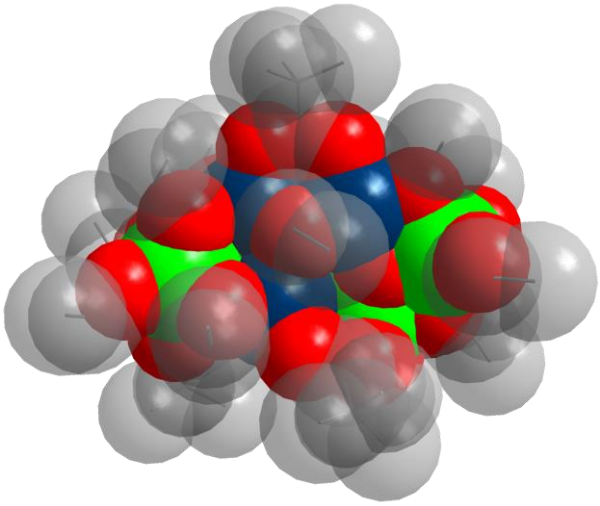

Figure S2 Space-filling model of the structure of **PTC-367**. Atom color code: green Ti; Blue Cu; red O; gray C. Omit H for clarity.

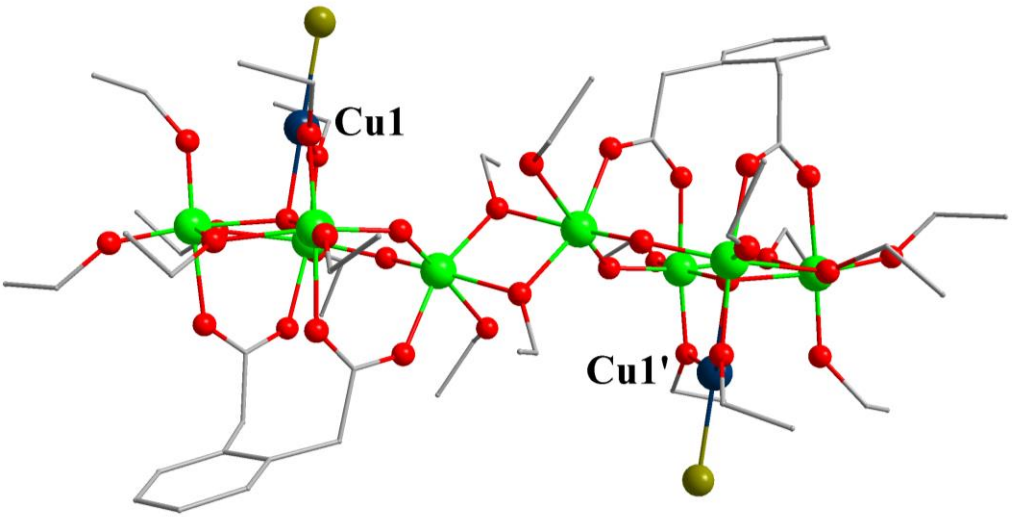

Figure S3 The structure of **PTC-368**. H atoms were omitted for clarity. Atom color code: green Ti; Blue Cu; red O; gray C; brown Br. Omit H for clarity.

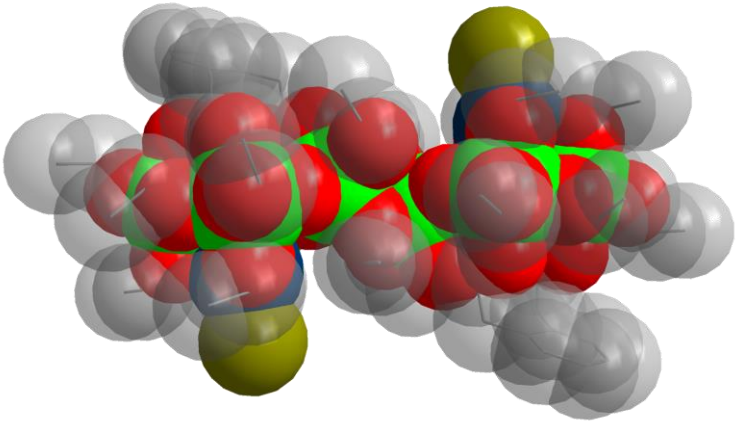

Figure S4 Space-filling model of the structure of **PTC-368**. Atom color code: green Ti; Blue Cu; red O; gray C; brown Br. Omit H for clarity.

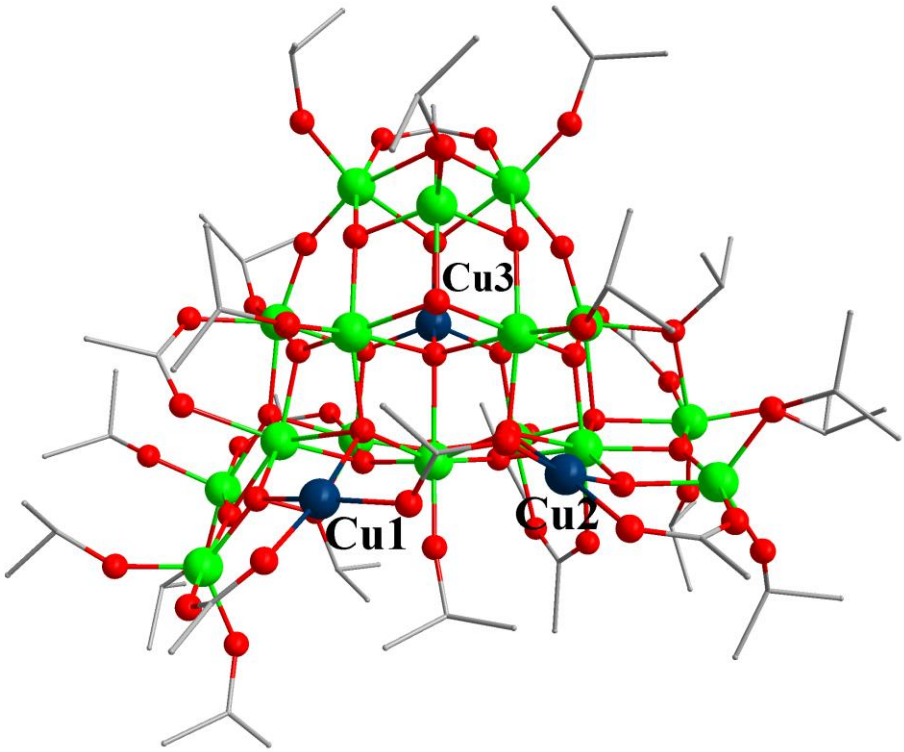

Figure S5 The structure of **PTC-369**. H atoms were omitted for clarity. Atom color code: green Ti; Blue Cu; red O; gray C. Omit H for clarity.

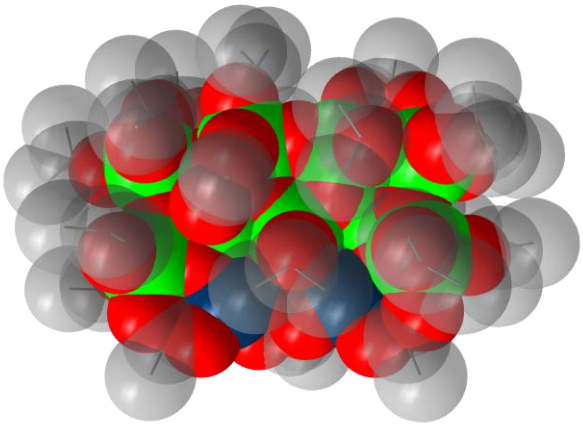

Figure S6 Space-filling model of the structure of **PTC-369**. Atom color code: green Ti; Blue Cu; red O; gray C. Omit H for clarity.

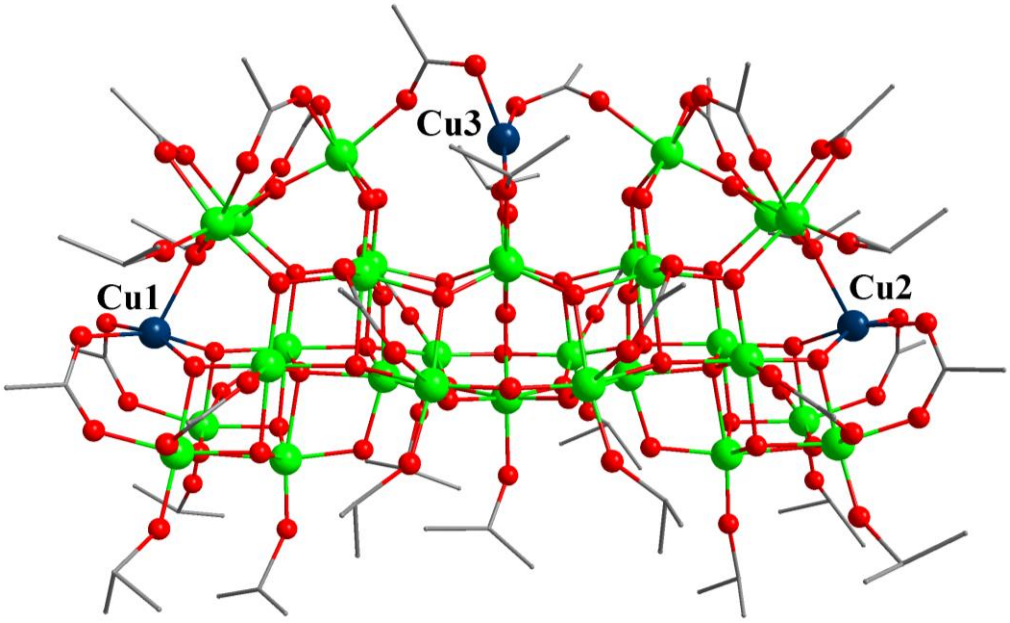

Figure S7 The structure of **PTC-370** H atoms were omitted for clarity. Atom color code: green Ti; Blue Cu; red O; gray C. Omit H for clarity.

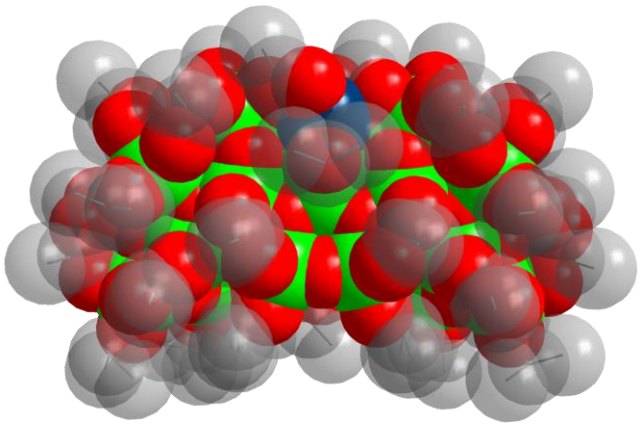

Figure S8 Space-filling model of the structure of **PTC-370**. Atom color code: green Ti; Blue Cu; red O; gray C. Omit H for clarity.

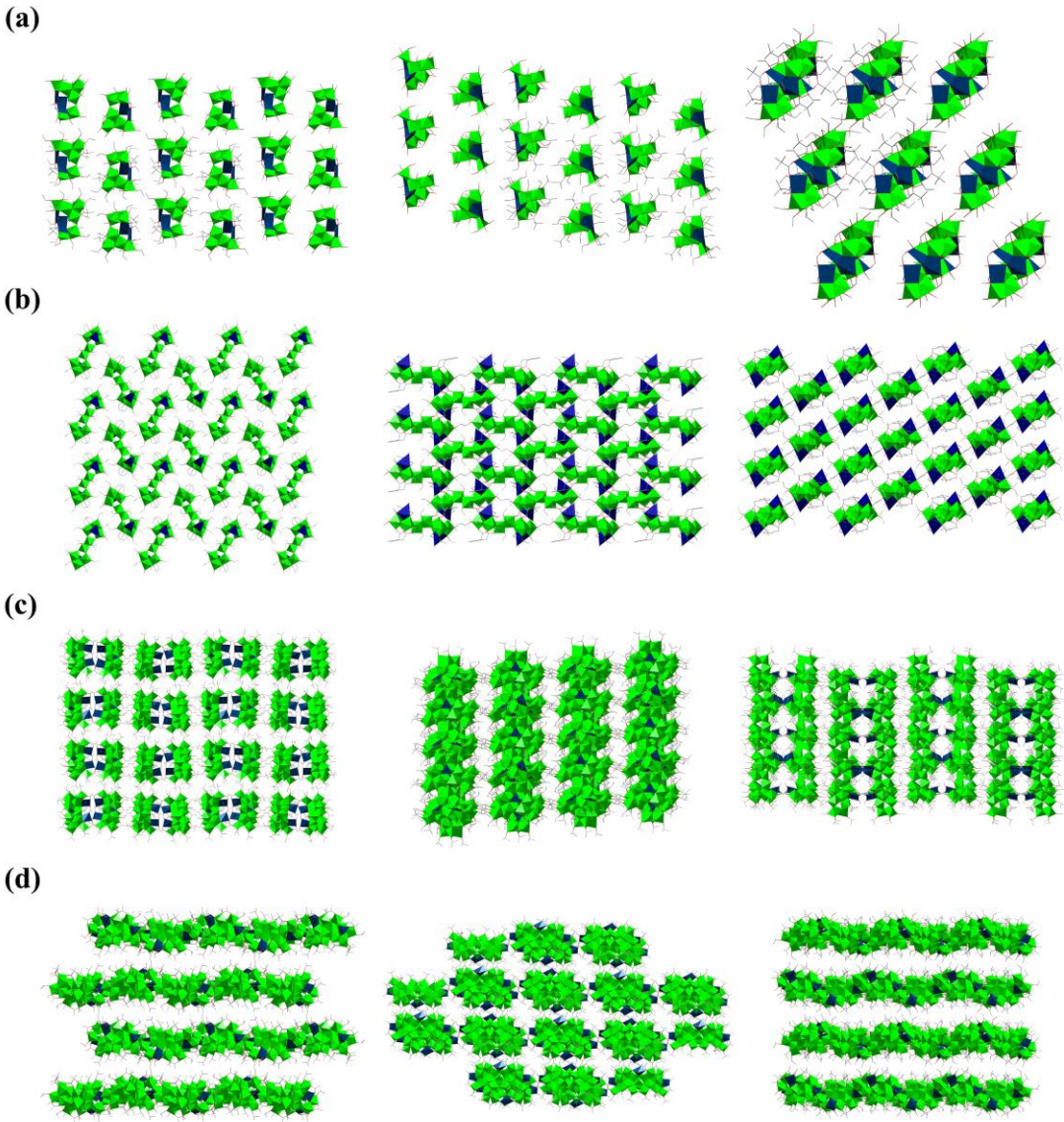

Figure S 9 The packing view of (a) **PTC-367** to (d) **PTC-370** along thea-, c- and b- axis. Color codes: green Ti; green, Cu; gray C; red O; brown Br. Omit H for clarity.

1.3. Metal coordination mode of PTC-367 to PTC-370.

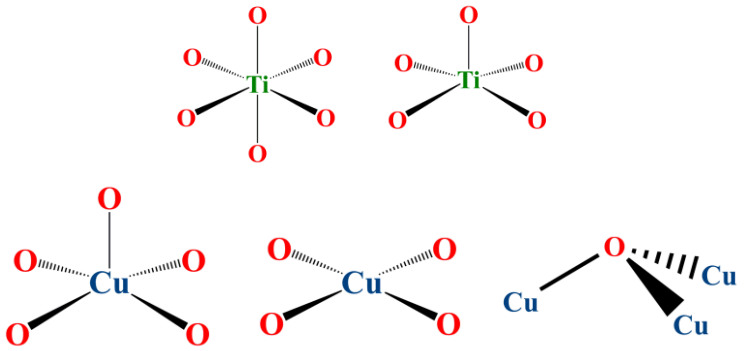

Figure S10 The Ti^{4+} and Cu^{2+} coordination mode and the spatial configuration between Cu^{2+} ions of **PTC-367**.

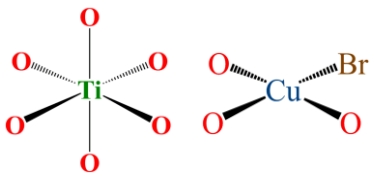

Figure S11 The Ti^{4+} and Cu^{2+} coordination mode of **PTC-368**.

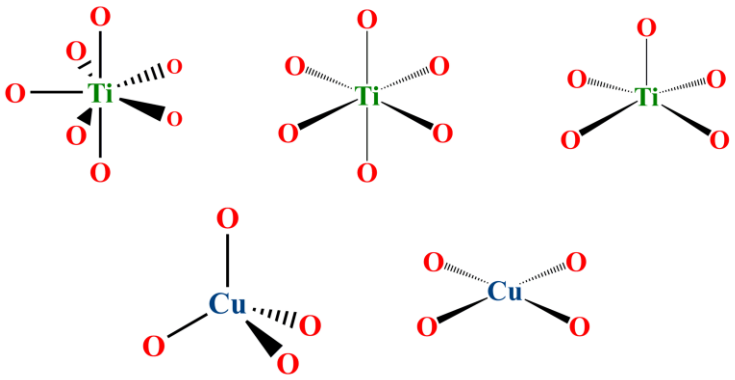

Figure S12 The Ti^{4+} and Cu^{2+} coordination mode of **PTC-369**.

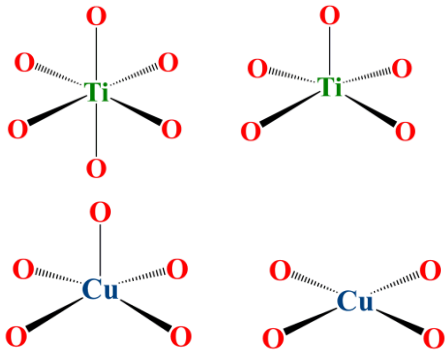

Figure S13 The a) Ti^{4+} and b) Cu^{2+} coordination mode of **PTC-370**.

2. Basic characterization of PTC-367 to PTC-370

2.1. PXRD patterns of PTC-367 to PTC-370.

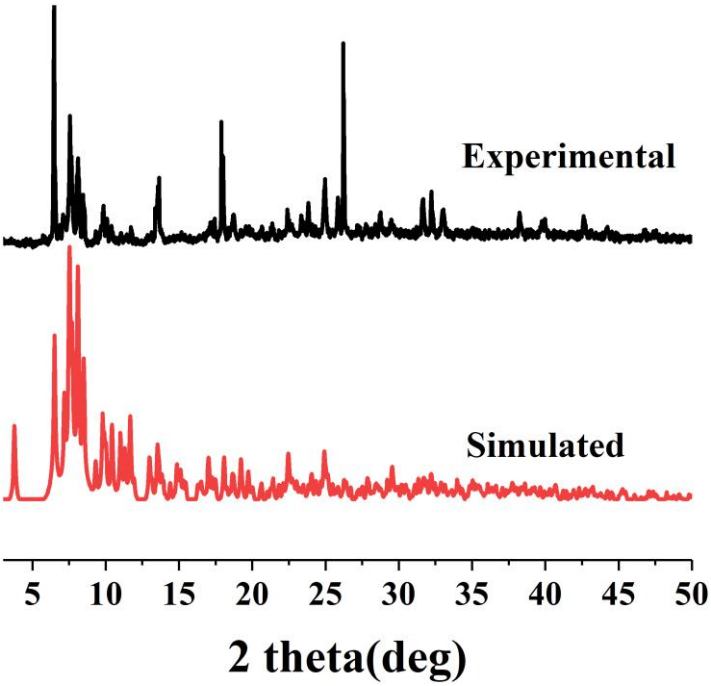

Figure S14 Normalized PXRD pattern of **PTC-367.**

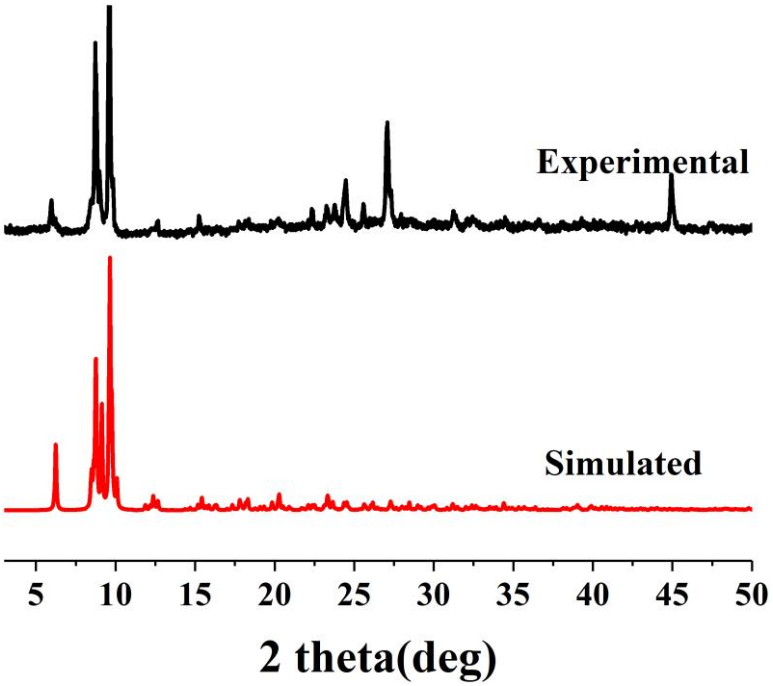

Figure S15 Normalized PXRD pattern of **PTC-368**.

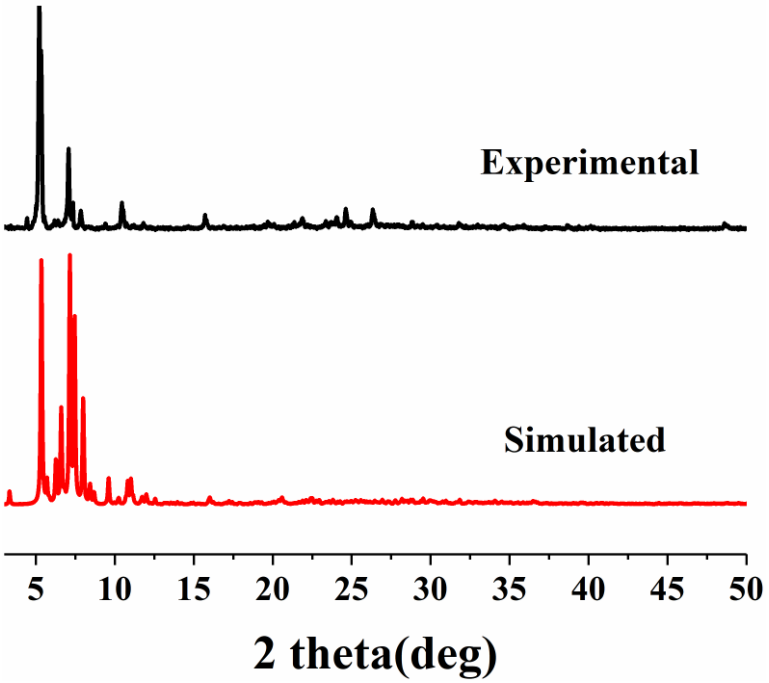

Figure S16 Normalized PXRD pattern of **PTC-369**.

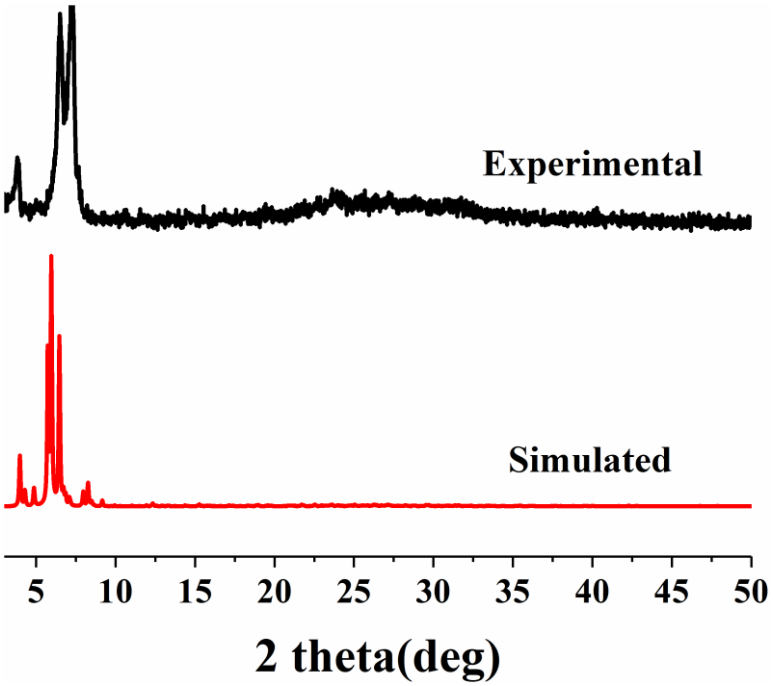

Figure S17 Normalized PXRD pattern of **PTC-370**.

2.2. TGA curves of PTC-367 to PTC-370.

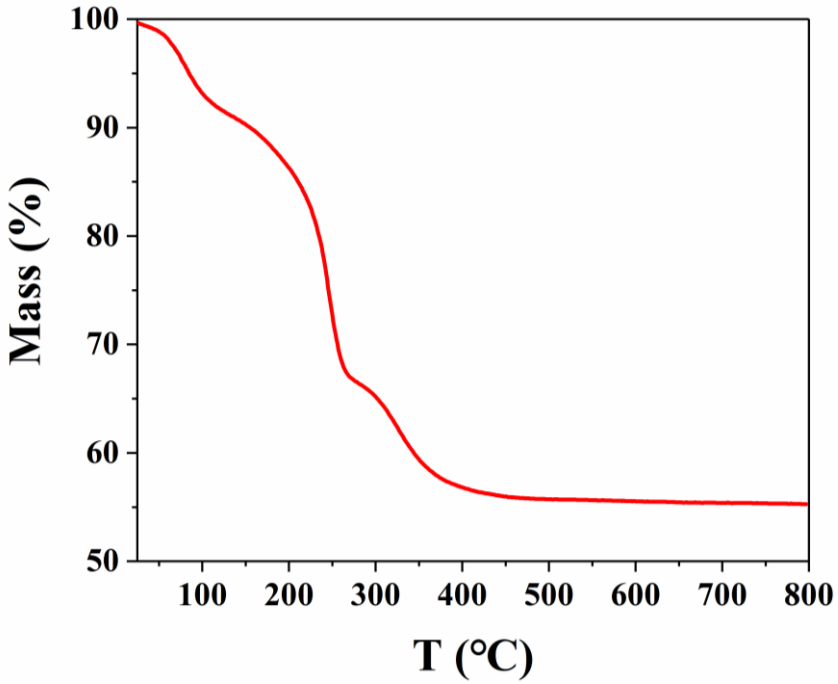

Figure S18 The TGA curve of **PTC-367**.

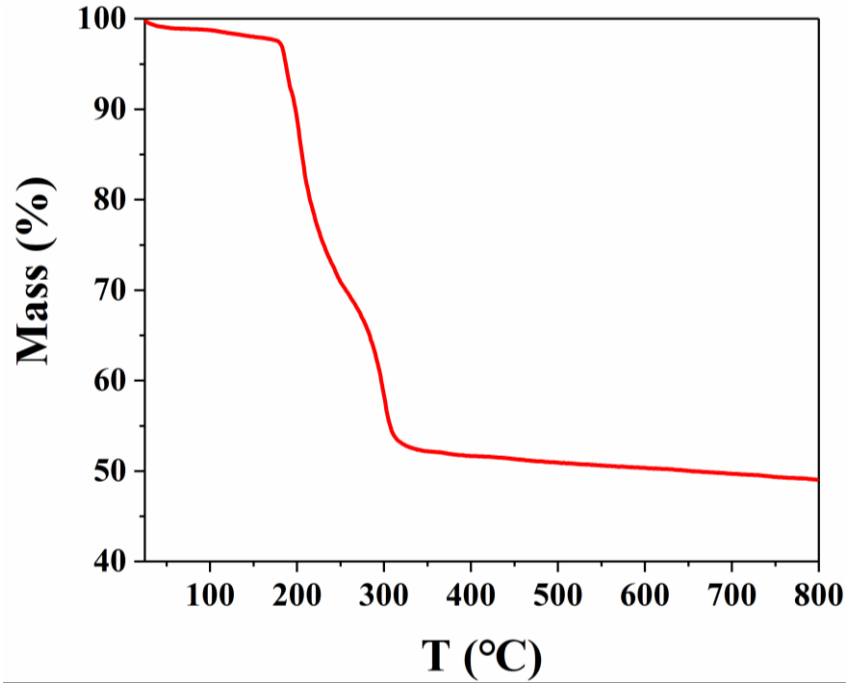

Figure S19 The TGA curve of **PTC-368.**

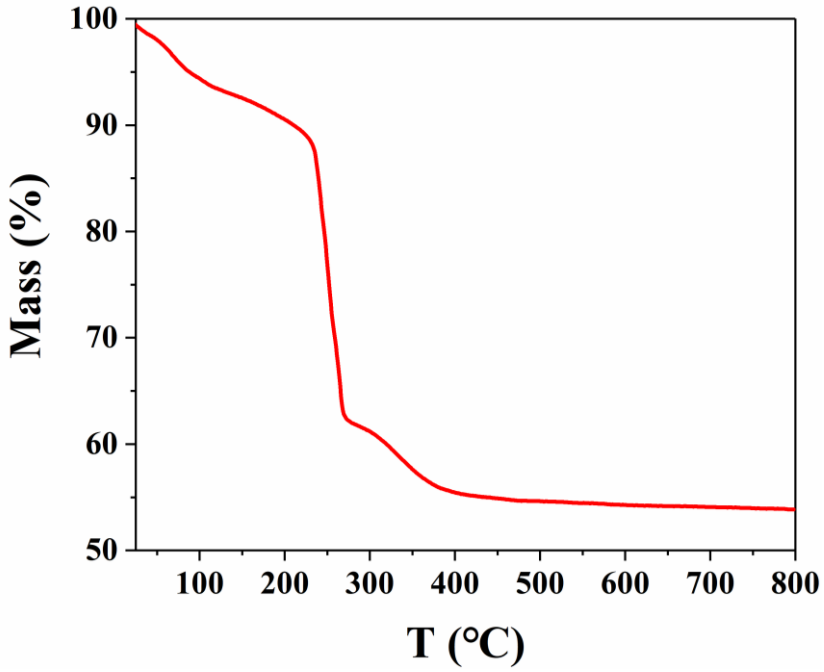

Figure S20 The TGA curve of **PTC-369**.

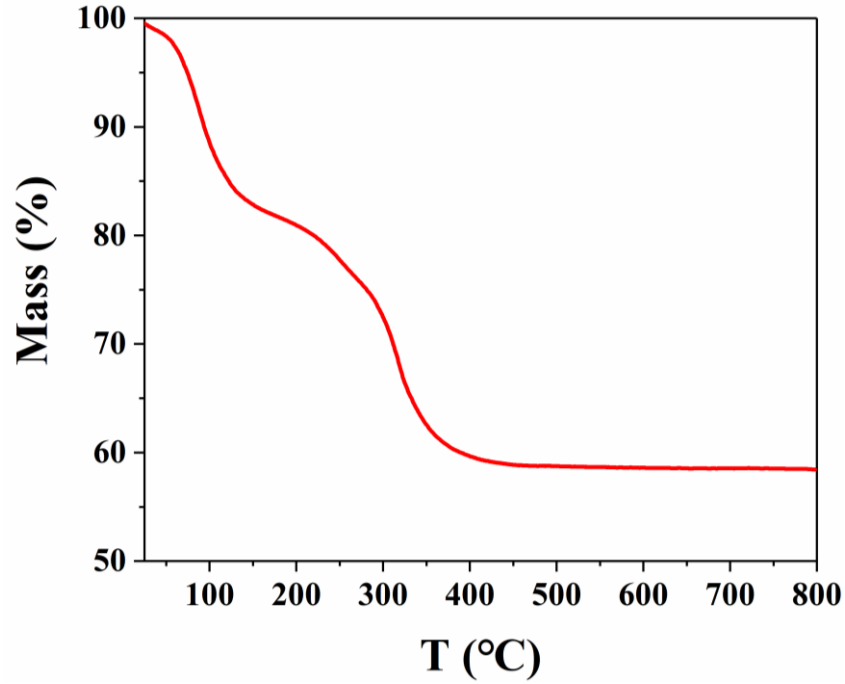

Figure S21 The TGA curve of **PTC-370**.

2.3. Solid UV-vis spectra and Bandgap.

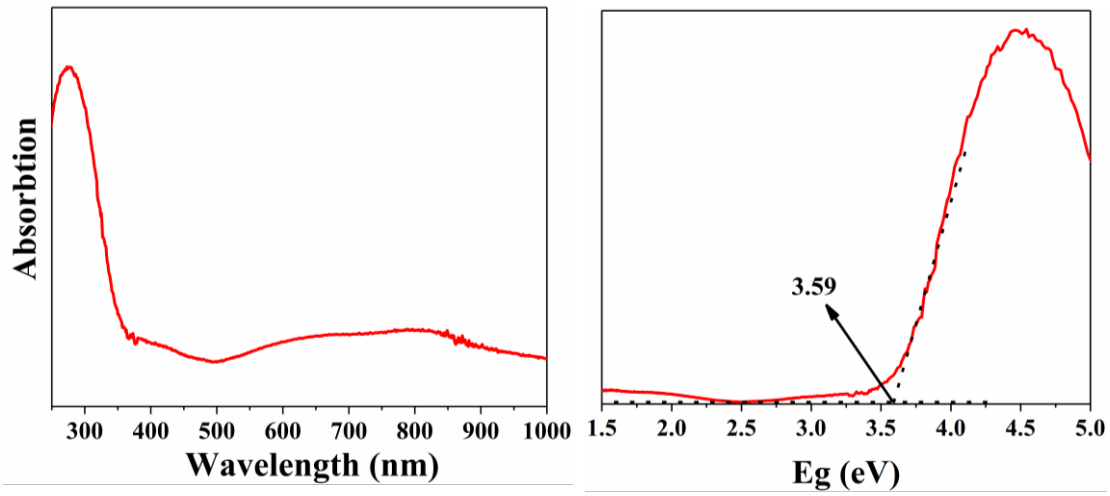

Figure S22 The normalized solid-state UV-vis spectrum and Bandgap of **PTC-367**.

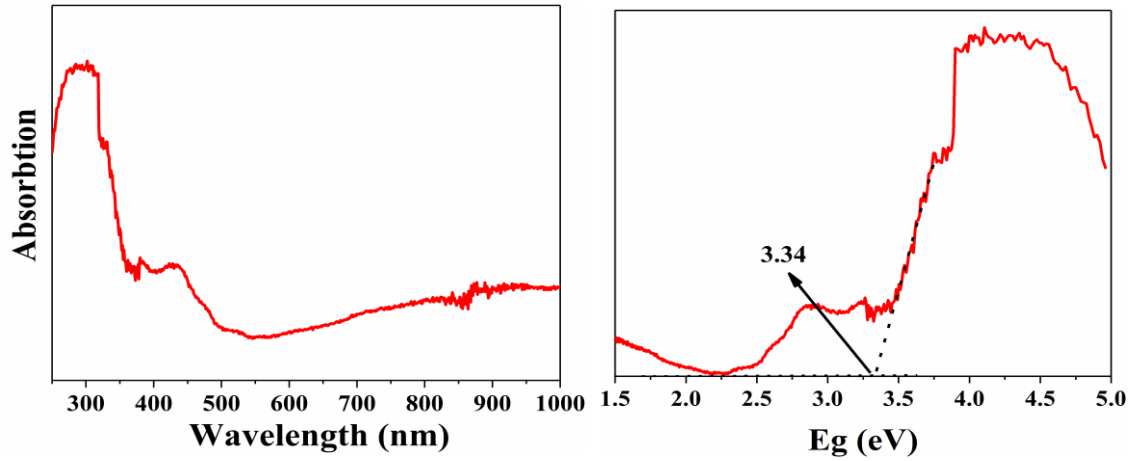

Figure S23 The normalized solid-state UV-vis spectrum and Bandgap of **PTC-368**.

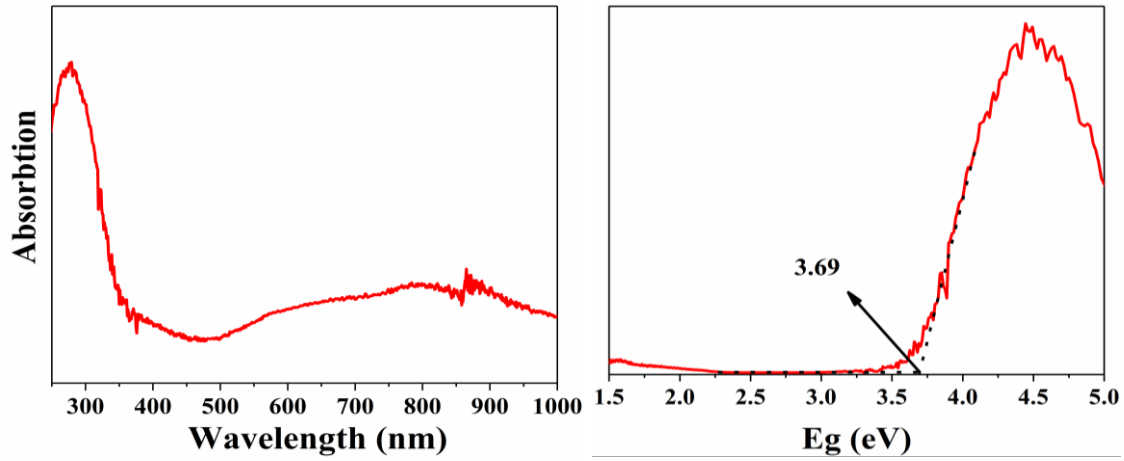

Figure S24 The normalized solid-state UV-vis spectrum and Bandgap of **PTC-369**.

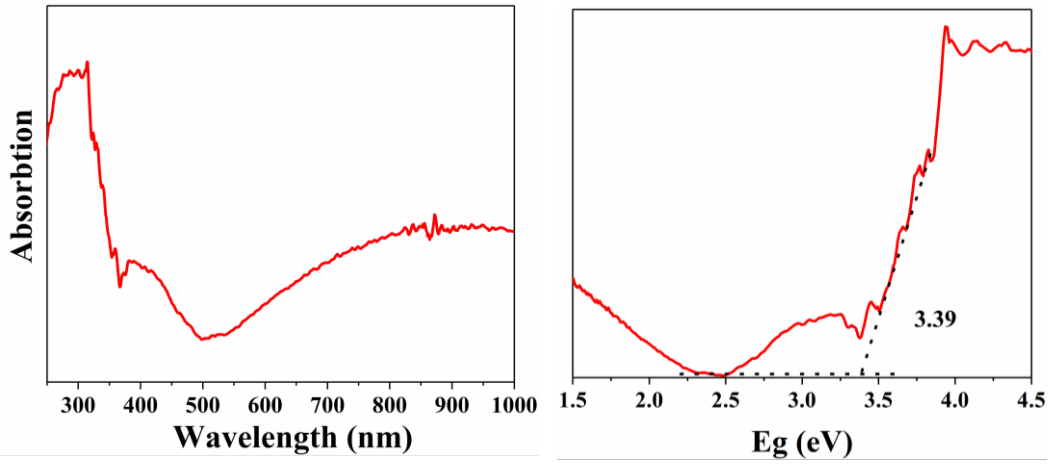

Figure S25 The normalized solid-state UV-vis spectrum and Bandgap of **PTC-370**.

2.4 Energy dispersive spectrometer

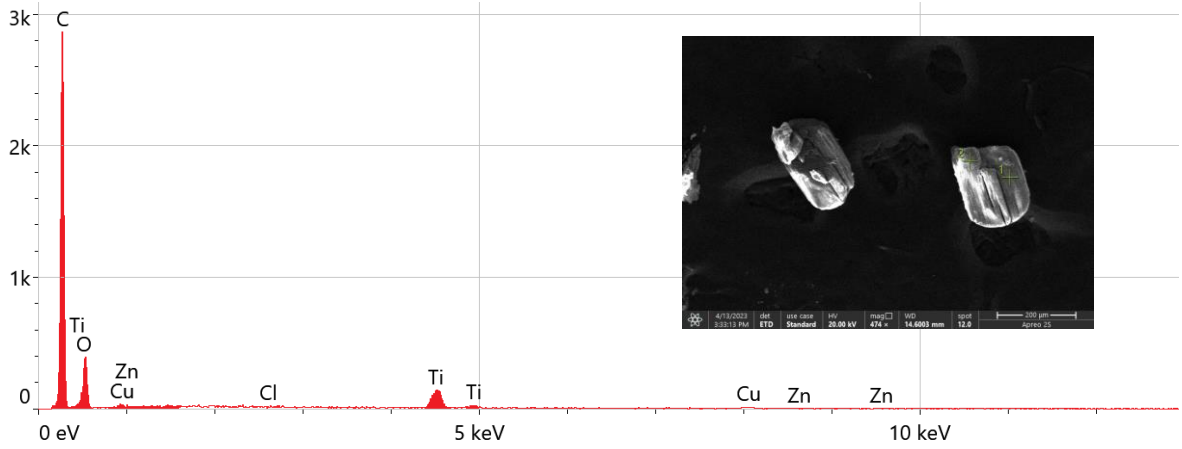

Figure S26 The EDS results of **PTC-367**.

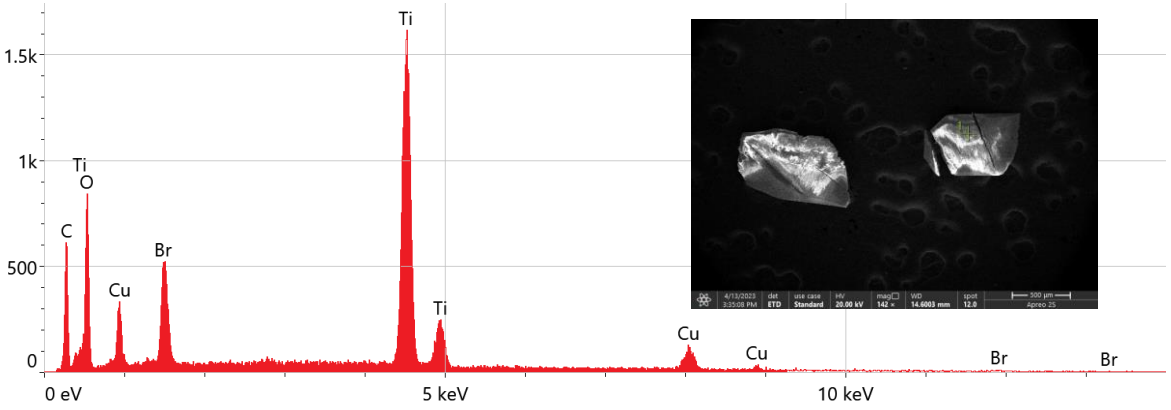

Figure S27 The EDS results of **PTC-368**.

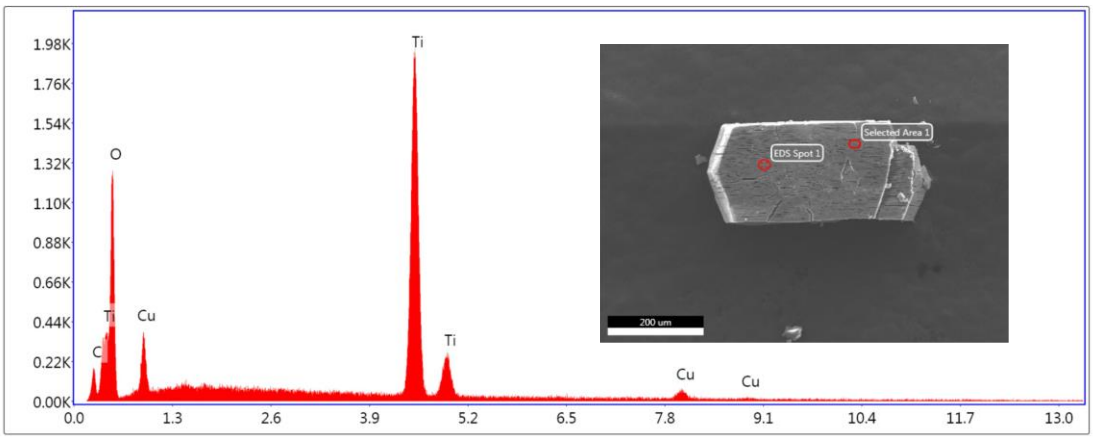

Figure S28 The EDS results of **PTC-369**.

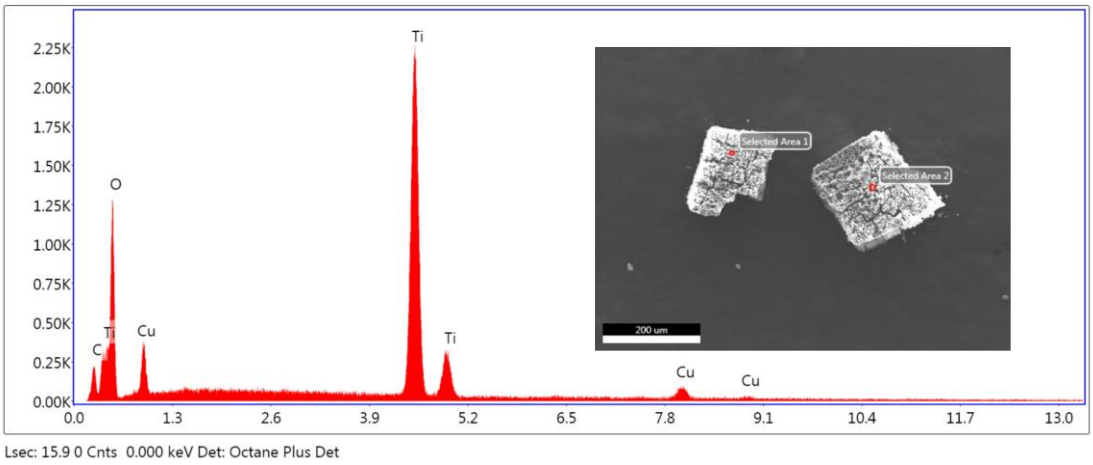

Figure S29 The EDS results of **PTC-370**

3. The summary of ICP-AES results

Table S2 The ICP-AES results of **PTC-367** to **PTC-370**.

	Ti (wt%)	Cu (wt%)	Ti: Cu	Calculated (Ti:Cu)
PTC-367	17.56	13.87	1.68	2.00
PTC-368	18.45	6.03	4.06	4.00
PTC-369	30.67	7.77	5.24	5.33
PTC-370	33.25	4.91	8.99	9.67

4. Bond valence sum calculation

Table S3 Bond valence sum (BVS) analysis of metal ions and μ-O for **PTC-367** to

PTC-370.

PTC-367					
Ti1	+4.178	Ti2	+4.316	Ti3	+4.204
Ti4	4.347	Ti5	+4.369	Ti6	+4.327
Cu1	+2.071	Cu2	+1.928	Cu3	+1.928
O1	-2.154	O4	-2.076	O6	-2.023
O7	-2.040	O8	2.041		
PTC-368					
Ti1	+4.299	Ti2	+4.369	Ti3	+4.334
Ti4	+4.278	Cu1	+2.157		
O2	-2.174	O3	-1.975	O4	-1.992
PTC-369					
Ti1	+4.217	Ti2	+4.211	Ti3	+4.200
Ti4	+4.179	Ti5	+4.157	Ti6	+4.242
Ti7	+4.201	Ti8	+4.289	Ti9	+4.331
Ti10	+4.256	Ti11	+3.992	Ti12	+4.077
Ti13	+4.283	Ti14	+4.313	Ti15	+4.347
Ti16	+4.369				
Cu1	+1.918	Cu2	+1.910	Cu3	+2.849
O1	-2.115	O2	-1.680	O4	-1.962
O5	-1.972	O6	-1.824	O7	-2.086
O8	-1.707	O10	-1.795	O12	-1.855
O15	-2.053	O17	-2.067	O18	-2.100
O19	-2.058	O20	-2.052	O22	-1.974
O24	-1.832	O26	-2.022	O27	-2.092
O29	-2.109	O32	-1.957	O35	-2.128
O37	-2.136	O42	-2.094		
PTC-370					
Ti1	+4.009	Ti2	+4.030	Ti3	+4.160

Ti4	+3.925	Ti5	+4.211	Ti6	+4.189
Ti7	+3.918	Ti8	+4.108	Ti9	+4.367
Ti10	+4.028	Ti11	+4.232	Ti12	+4.139
Ti13	+4.198	Ti14	+4.146	Ti15	+4.257
Ti16	+4.195	Ti17	+4.160	Ti18	+4.100
Ti19	+4.244	Ti20	+4.159	Ti21	+4.206
Ti22	+4.284	Ti23	+4.191	Ti24	+4.200
Ti25	+4.272	Ti26	+4.327	Ti27	+4.184
Ti28	+4.291	Ti29	+4.268		
Cu1	+1.966	Cu2	+2.024	Cu3	+1.994
O1	-2.073	O2	-2.059	O3	-2.197
O4	-2.118	O5	-2.054	O6	-2.183
O7	-2.021	O8	-2.031	O9	-2.038
O10	-1.893	O11	-1.966	O12	-1.892
O13	-1.885	O14	-1.916	O15	-2.233
O16	-2.154	O17	-2.073	O18	-2.081
O19	-2.187	O20	-2.056	O21	-2.113
O22	-1.588	O23	-2.002	O24	-2.065
O25	-1.955	O26	-2.232	O27	-2.127
O28	-1.891	O30	-1.925	O31	-2.048
O33	-1.963	O34	-2.058	O40	-1.945
O41	-1.937	O43	-2.024	O44	-1.967
O45	-2.120	O46	-1.628	O47	-1.858
O56	-2.065	O60	-1.953	O68	-2.002
O77	-1.957	O88	-2.037		

5. CO_2 cycloaddition reaction

Reaction conditions: epichlorohydrin (10 mmol), catalysts (0.005 mmol), $^{n}Bu_4NBr$ (1 mmol), room temperature, 24 h, CO_2 (1 atm gauge pressure). [b] ^1H NMR yields with CH_2Br_2 (1 mmol) as the internal standard.

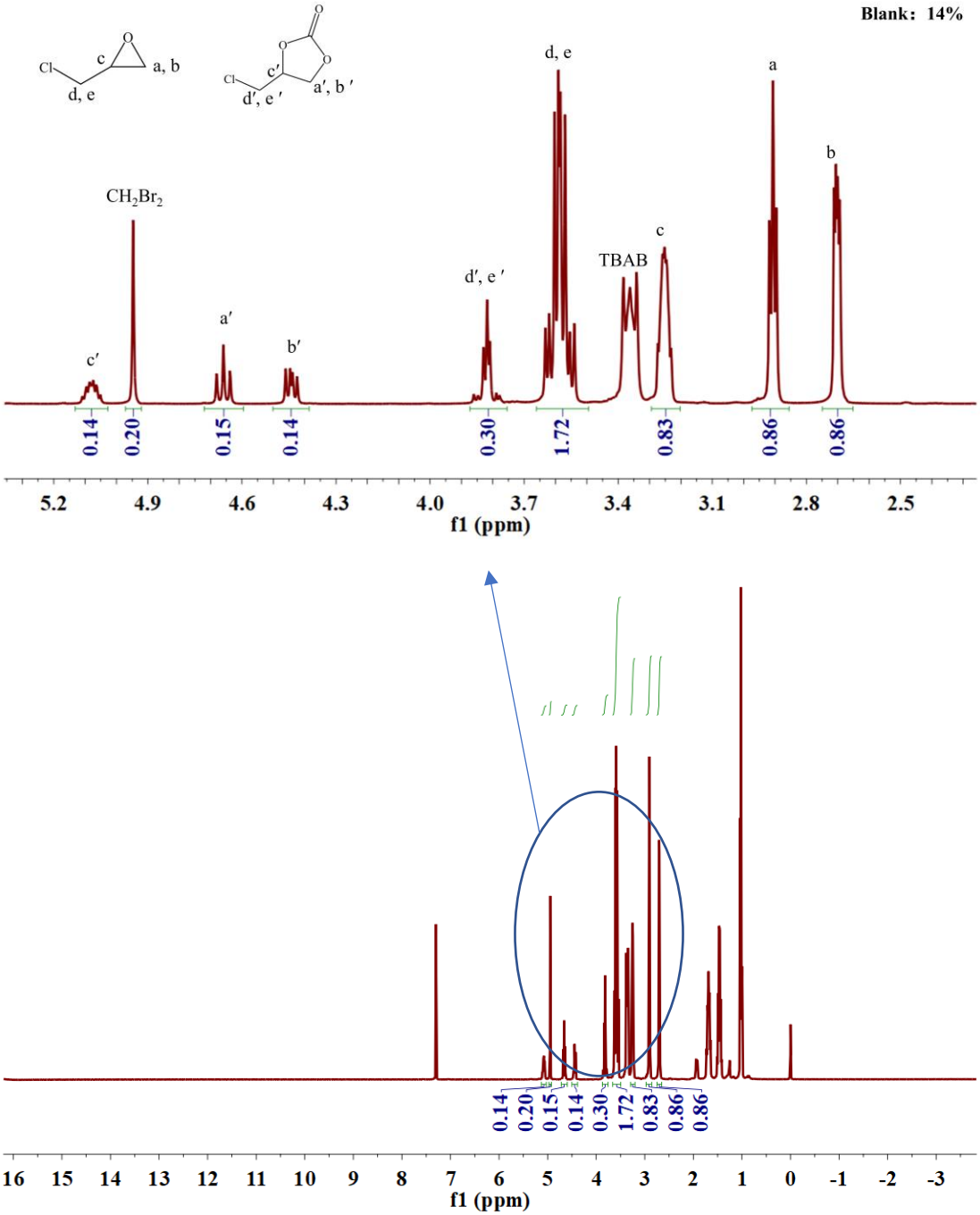

Figure S30 1H NMR spectra after 24 h CO_2 cycloaddition reaction of epichlorohydrin with TBAB as catalyst.

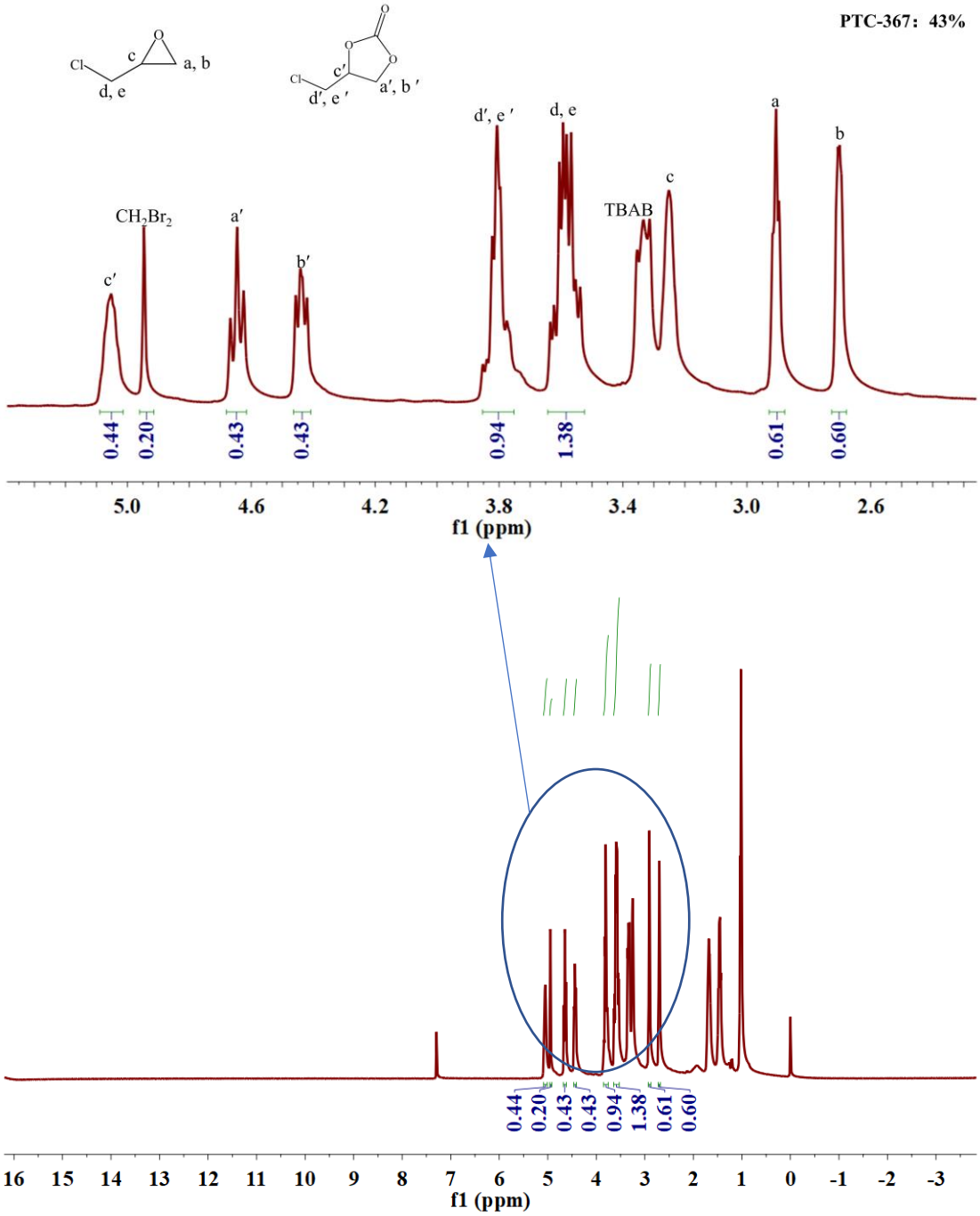

Figure S31 1H NMR spectra after 24 h CO_2 cycloaddition reaction of epichlorohydrin with **PTC-367** and TBAB as co-catalyst.

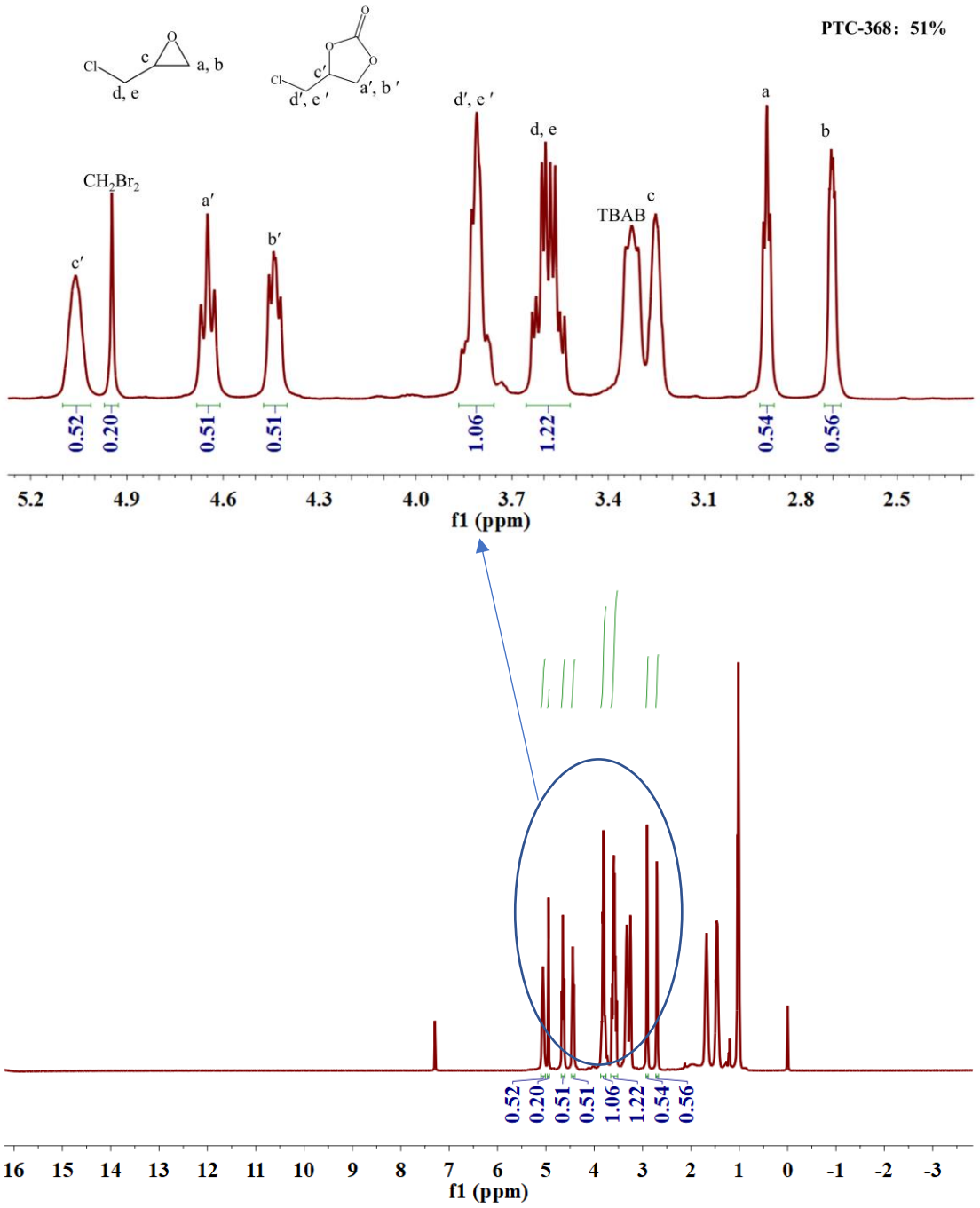

Figure S32 1H NMR spectra after 24 h CO_2 cycloaddition reaction of epichlorohydrin with **PTC-368** and TBAB as co-catalyst.

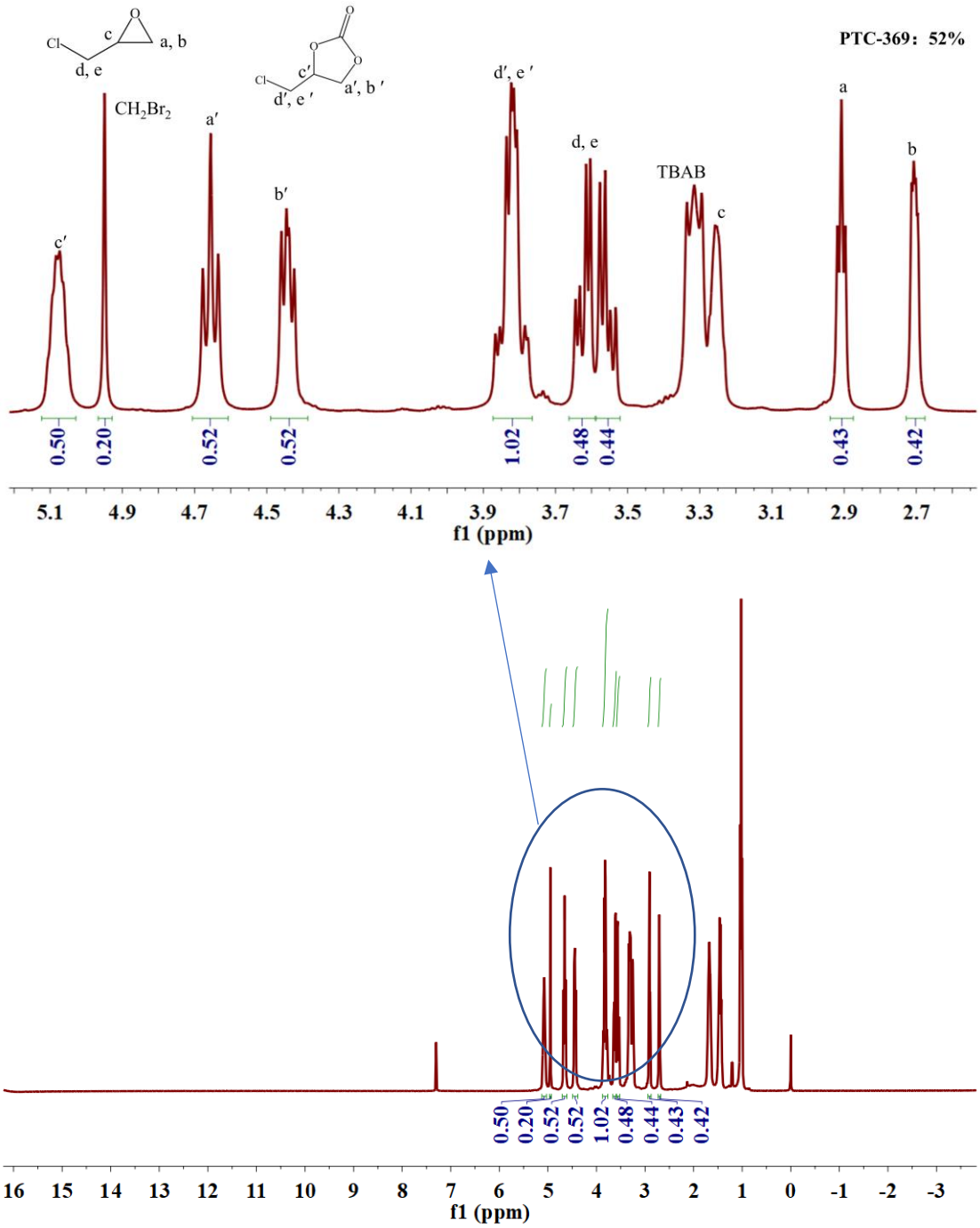

Figure S33 1H NMR spectra after 24 h CO_2 cycloaddition reaction of epichlorohydrin with **PTC-369** and TBAB as co-catalyst.

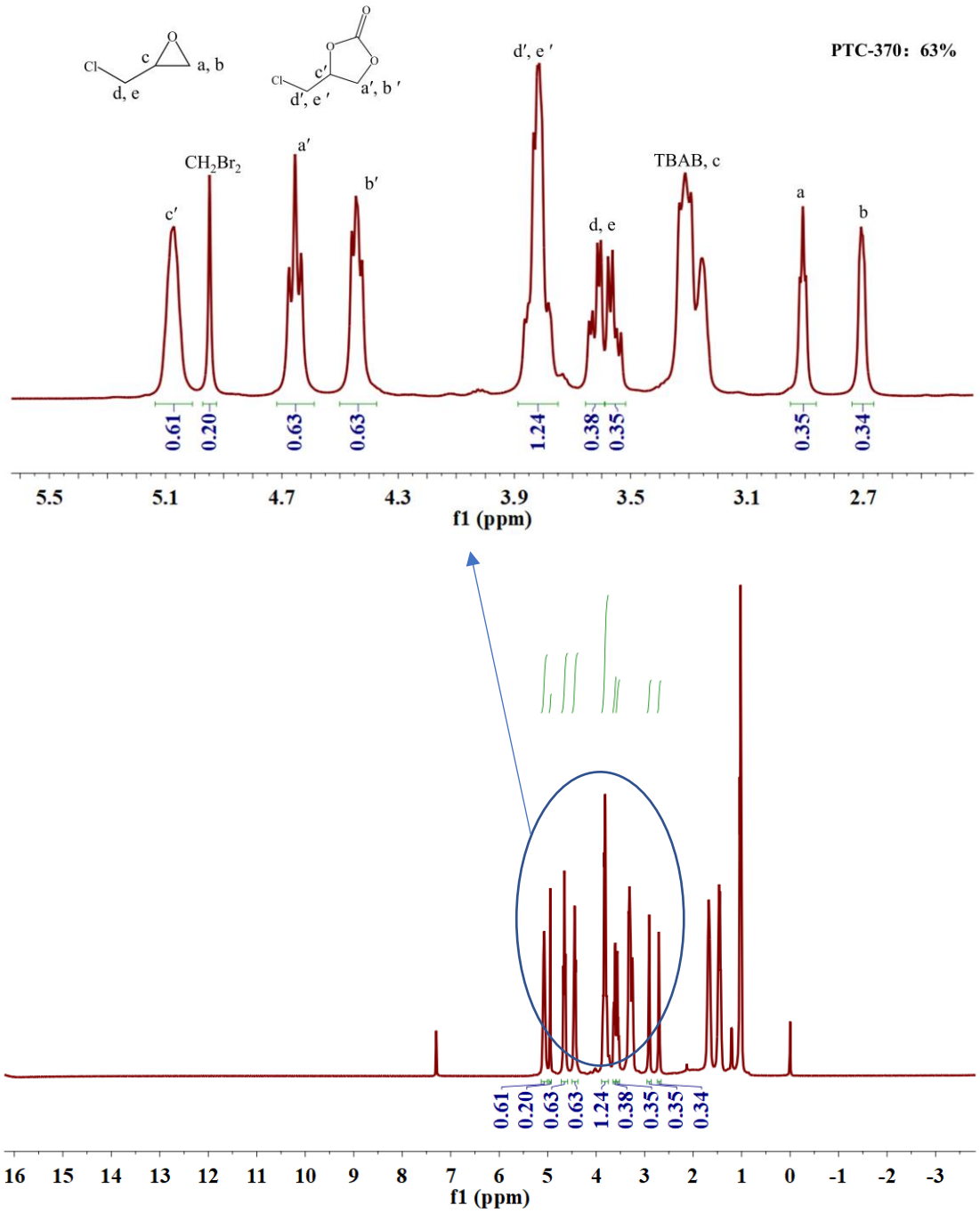

Figure S34 1H NMR spectra after 24 h CO_2 cycloaddition reaction of epichlorohydrin with **PTC-370** and TBAB as co-catalyst.

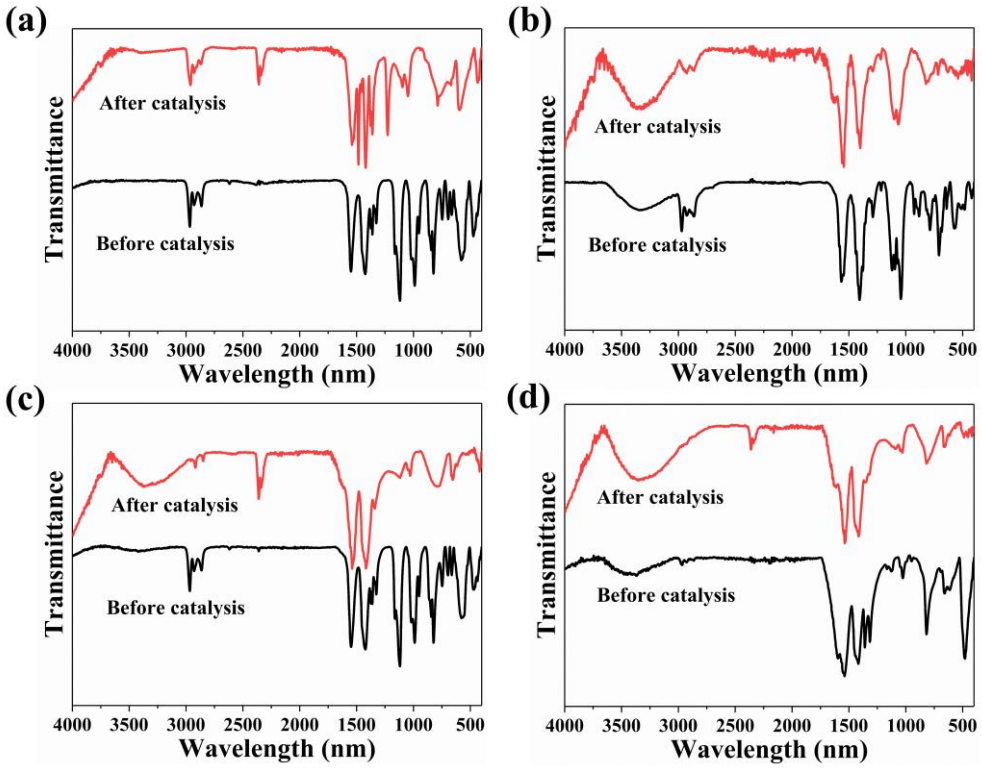

Figure S 35 The solid-state IR spectra of (a) **PTC-367** to (d) **PTC-370** before and after catalytic reaction (powdered crystals were saturated and precipitated after several weeks of standing).

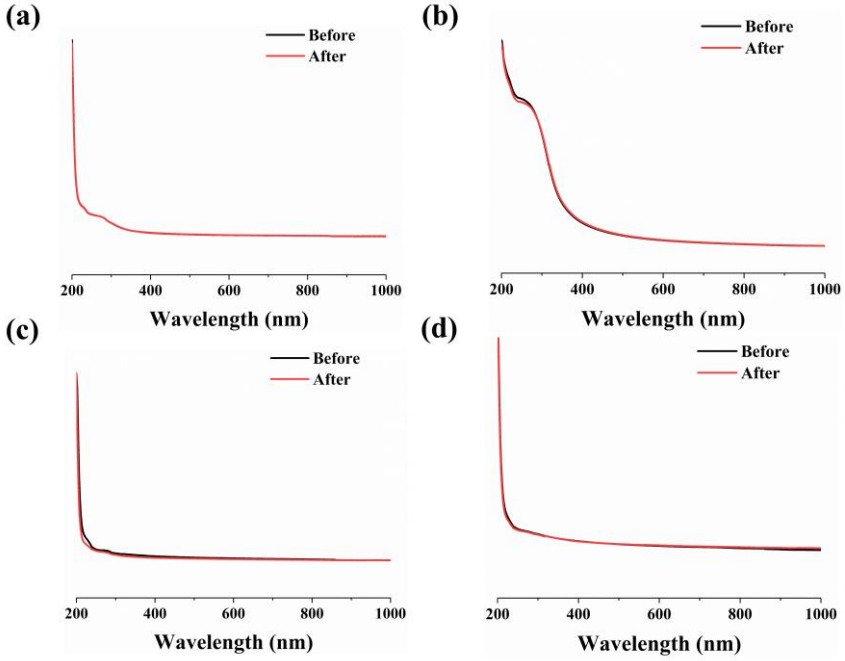

Figure S 36 The solution-state UV-Vis spectra of (a) **PTC-367** to (d) **PTC-370** before and after catalytic reaction.