Supporting Information

Integration of Metalloporphyrin into Cationic Covalent Triazine Frameworks for the Synergistically Enhanced Chemical Fixation of CO_2

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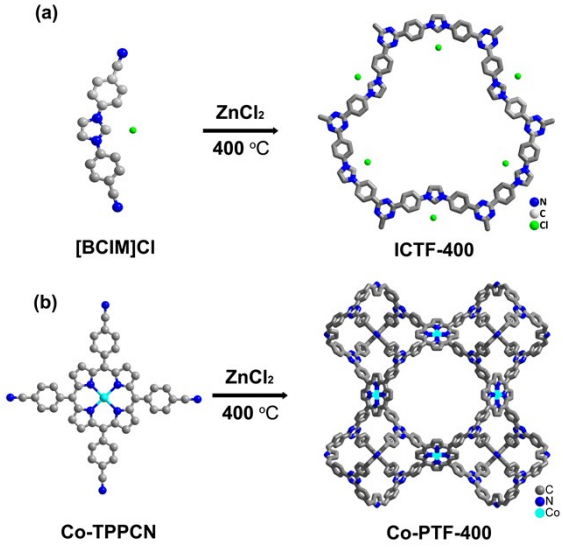

Scheme S1. The synthesis of (a) ICTF-400 and (b) Co-PTF-400.

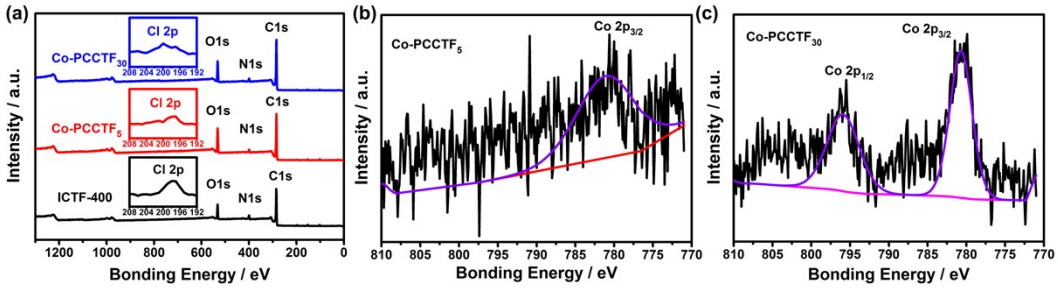

Fig. S1. (a) The XPS spectra of the Co-PCCTF$_s$; (b) The high-resolution XPS spectra (HR-XPS) of Co 2p for the Co-PCCTF$_5$ and (c) Co-PCCTF$_{30}$.

Table S1. Element content of ICTF-400, Co-PCCTF$_5$ and Co-PCCTF$_{30}$.

Sample	N (wt%)	Imidazolium N^+ ratio in N (%)	Cl^- ratio in Cl (%)	Co (wt%)	Zn (wt%)
ICTF-400	8.45	14.69	82.8	0	0.274
Co-PCCTF$_5$	8	11.93	70.4	0.31	0.242
Co-PCCTF$_{30}$	7.76	2.38	48.6	1.41	0.215
Co-PCCTF$_5$-reused				0.278	0.349

Table S2. Catalytic active site content of ICTF-400, Co-PCCTF$_5$ and Co-PCCTF$_{30}$

Catalyst	Co^{2+} content [a] [mmol g^{-1}]	N^+ or Cl^- [b] [mmol g^{-1}]	N^+ or Cl^- : Co^{2+} [c]
ICTF-400	0	0.90	0.90:0
Co-PCCTF$_5$	0.053	0.68	13:1
Co-PCCTF$_{30}$	0.24	0.13	0.50:1

[a] Calculated by ICP analysis. [b] The $N^+ = Cl^-$ content was calculated using the formula:

$$N^+(\text{mmol}g^{-1}) = \frac{(\text{Imidazolium } N^+ \text{ ratio in N}) * (\text{N content in 1g Co - PCCTF}_X) * 1000}{(\text{Atomic mass of N})}$$

[c] The Cl^- : Co^{2+} ratio was calculated from the ICP, EA and XPS results

Table S3. BET and pore volume of Co-PCCTFs.

Catalyst	S_{BET} [m^2 g^{-1}] [a]	V_p [cm^3 g^{-1}] [b]
ICTF-400	487	0.101
Co-PCCTF$_5$	547	0.110
Co-PCCTF$_{30}$	374	0.106

[a] Surface area calculated on the basis of the BET model from the nitrogen adsorption isotherm (P/P_0 = 0.01-1.0). [b] Total pore volume calculated at P/P_0 = 0.99.

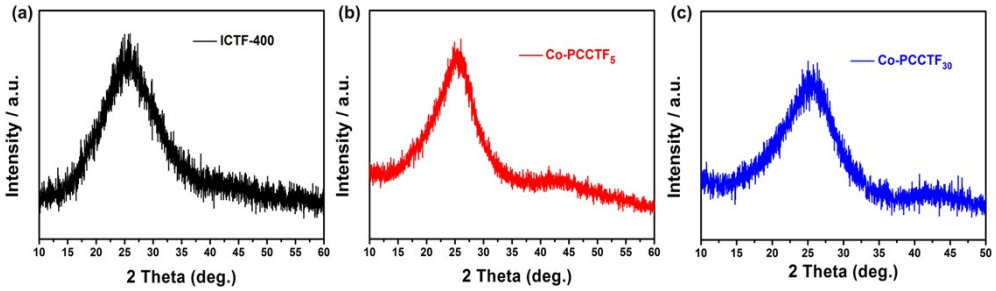

Fig. S2. PXRD patterns of (a) ICTF-400, (b) Co-PCCTF$_5$ and (c) Co-PCCTF$_{30}$.

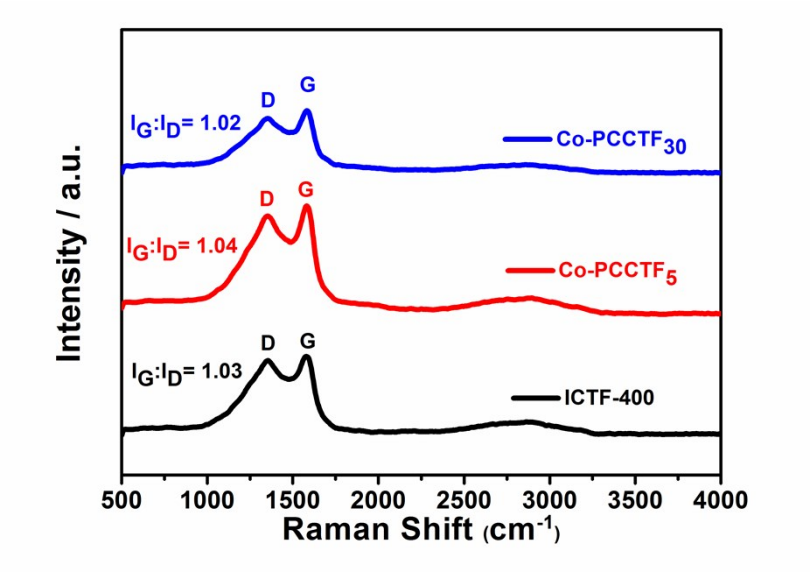

Fig. S3. The Raman spectra of Co-PCCTFs.

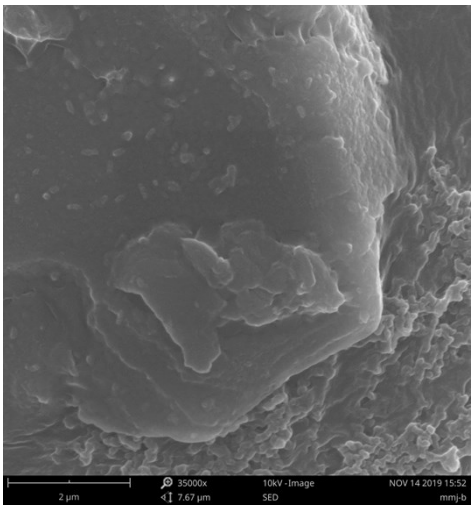

Fig. S4. The SEM image of Co-PCCTF$_5$.

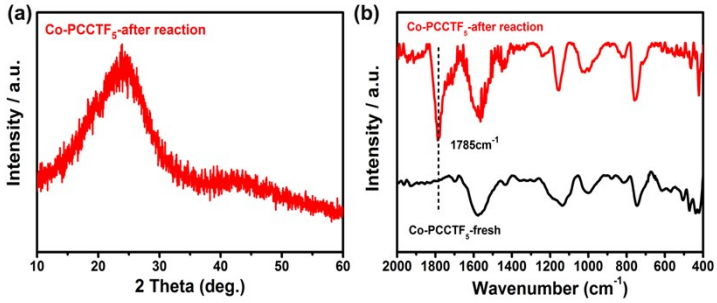

Fig. S5. PXRD and IR patterns of Co-PCCTF$_5$ after reaction.

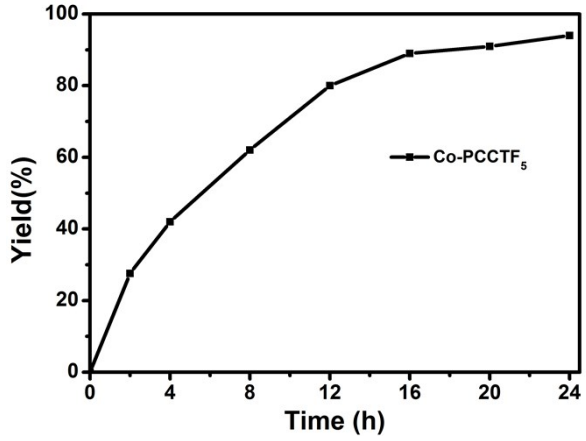

Fig. S6. Time course of the production of Chloropropene Carbonate. Reaction conditions: Co-PCCTF$_5$ (15 mg), epichlorohydrin (10 mmol), CO_2 (0.1 MPa), 120 °C.

Table S4. Comparison of TON of various catalysts for CO_2 cycliaddition reaction without addition of co-catalyst.

Catalyst	T (°C)	Expoxide	Time (h)	CO_2 (bar)	Yield (%)	TON	Reference	Year
Co-PCCTF$_5$	120	ECH	24	1	94	940	This work	
MIL-101 -N(n-Bu)$_3$Br	80	PO	8	20	99	110	[S1]	2015
FJI-C10	80	ECH	12	1	87	247	[S2]	2017
UiO-67-IL	90	ECH	8	1	85.5	57	[S3]	2017
ZnTCPP⊂ (Br$^-$)Etim-UiO-66	140	AGE	14	1	90	94.7	[S4]	2017
(I$^-$)Meim-UiO-66	120	ECH	24	1	93	125	[S5]	2018
ZIF-68	120	SO	12	10	93	-	[S6]	2014
CZ-ZIF	100	ECH	4	7	92	138.6	[S7]	2016
Ti-ZIF	100	SO	8	25	99	99	[S8]	2016
IL-ZIF-90	120	PO	3	1	95	194	[S9]	2016
ZIF-67	120	ECH	6	10	71	190	[S10]	2016
Fe/ZIF-8	120	SO	8	7	97	-	[S11]	2020
ZIF-8	100	ECH	4	7	98	40.9	[S12]	2012
PPS⊂COF -TpBpy-Cu	40	ECH	24	1	95	690	[S13]	2019
COF-IL	80	SO	48	1	98	32.7	[S14]	2019

Al-CPOP	120	ECH	24	1	95	95	[S15]	2016
SYSU-Zn@IL_2	80	PO	16	10	99	618	[S16]	2017
MTS-1(3)-AT-2	120	ECH	6	16	96	240	[S17]	2018
POF-PNA-Br^-	60	PO	8	10	99.4	340.8	[S18]	2018
66Pym-iPrI	100	BO	24	5	92.7	655	[S19]	2020

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