The figures, schemes, and charts in the SI are shown as follows:

Figure S1:

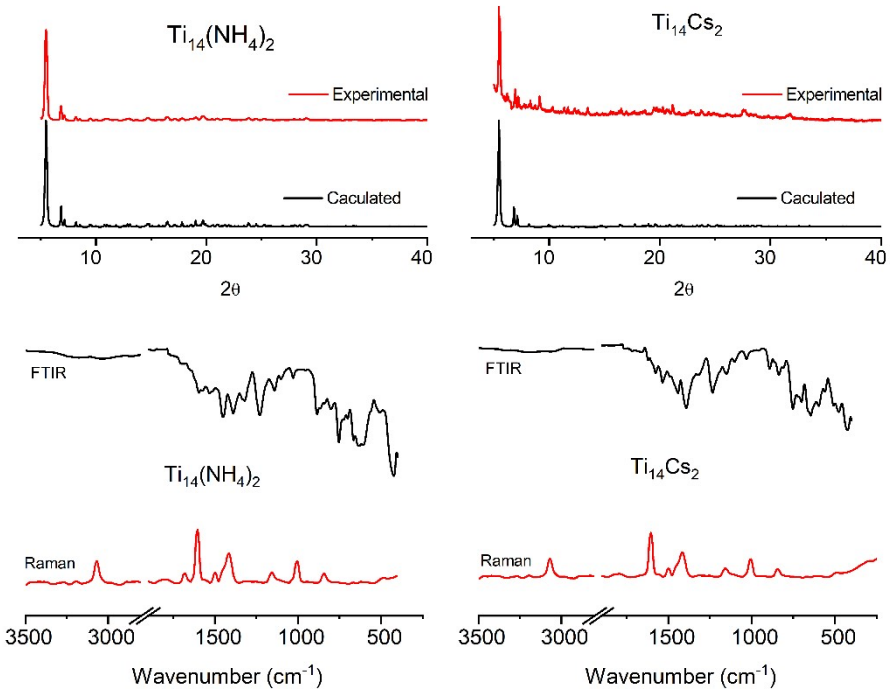


Figure S2:

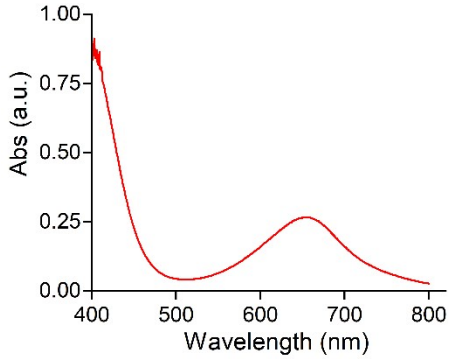


Figure S3:

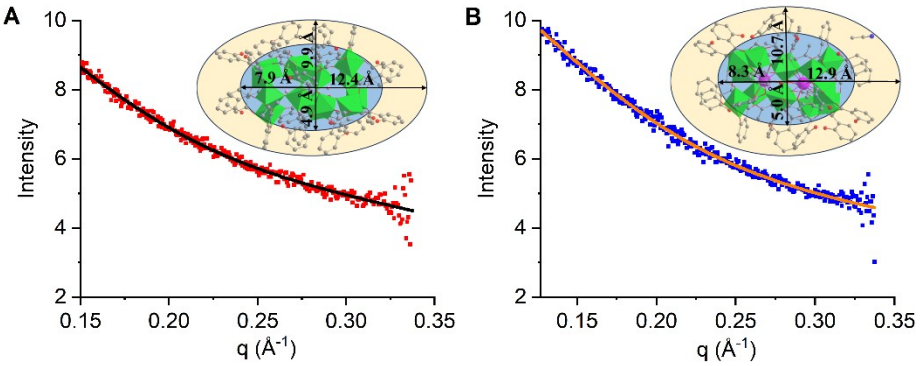


Figure S4:

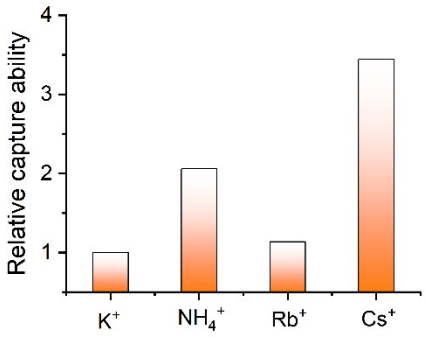


Figure S5:

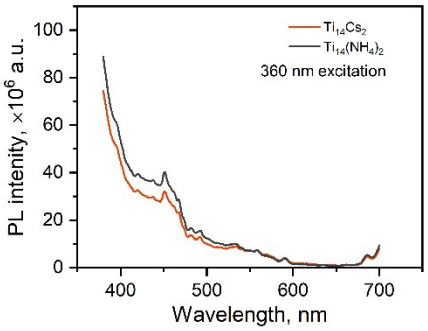
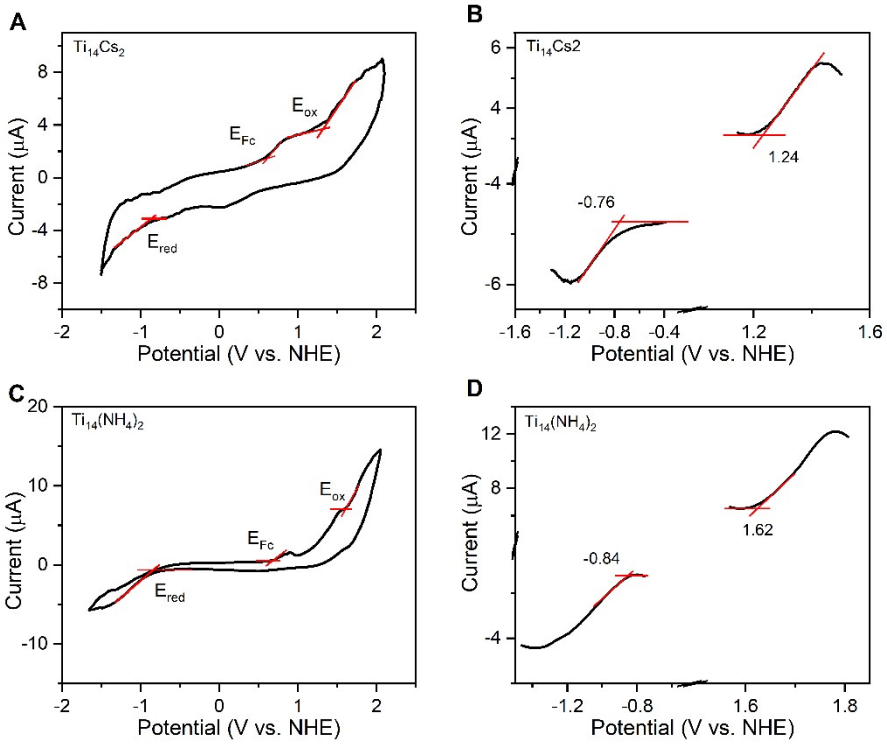


Figure S6:



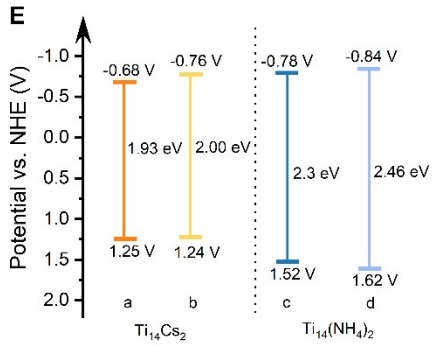


Figure S7:

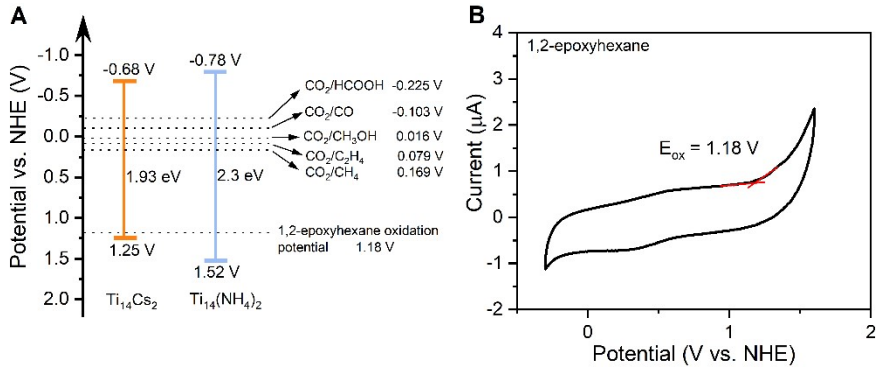


Figure S8:

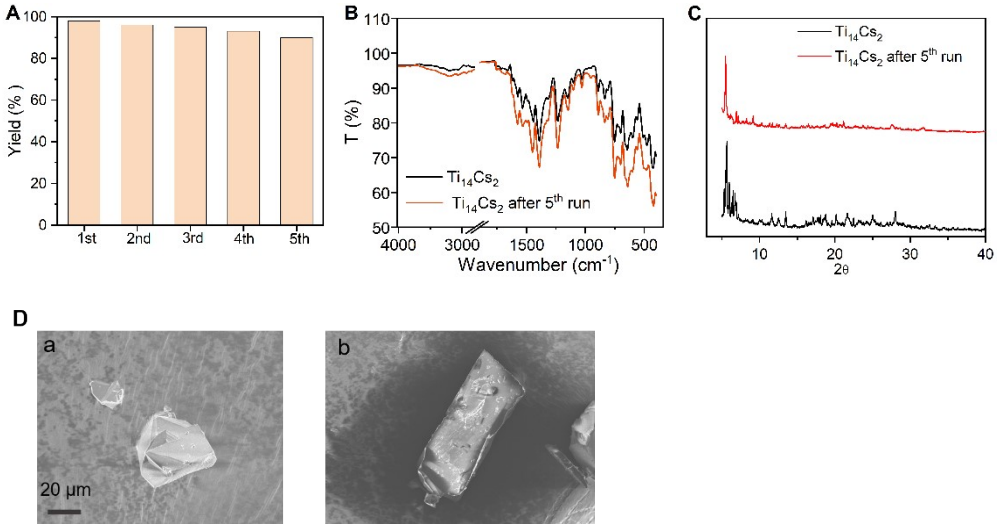
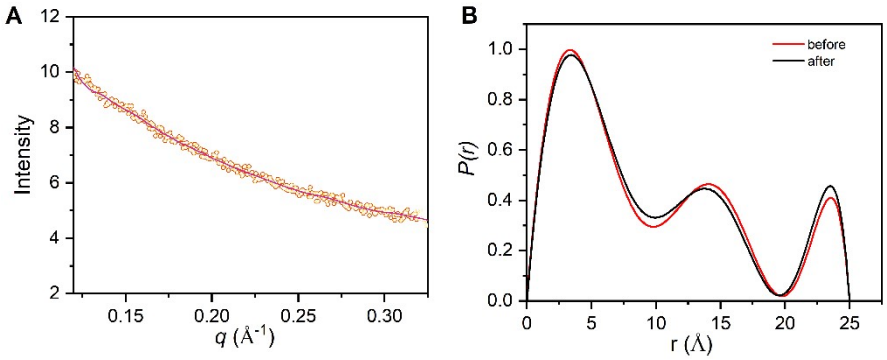


Figure S9:



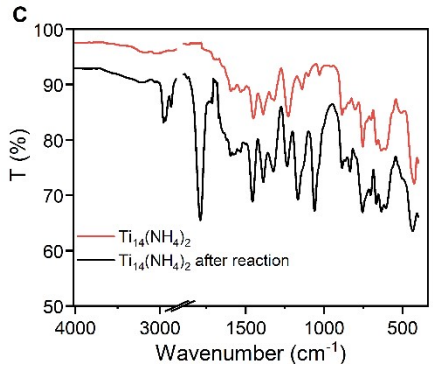


Figure S10:

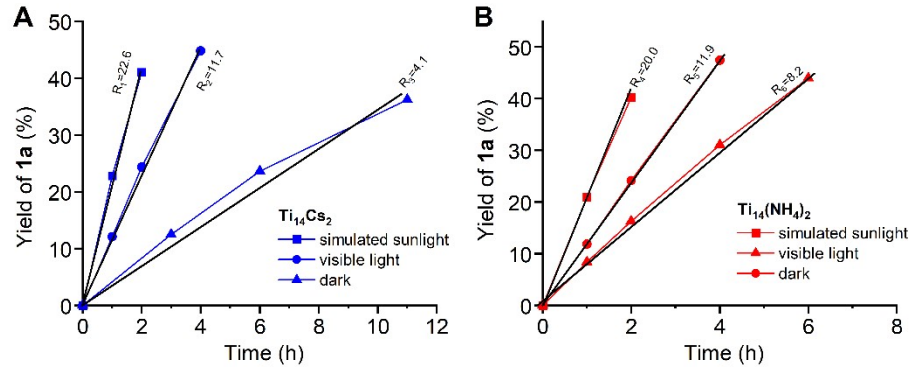


Figure S11:

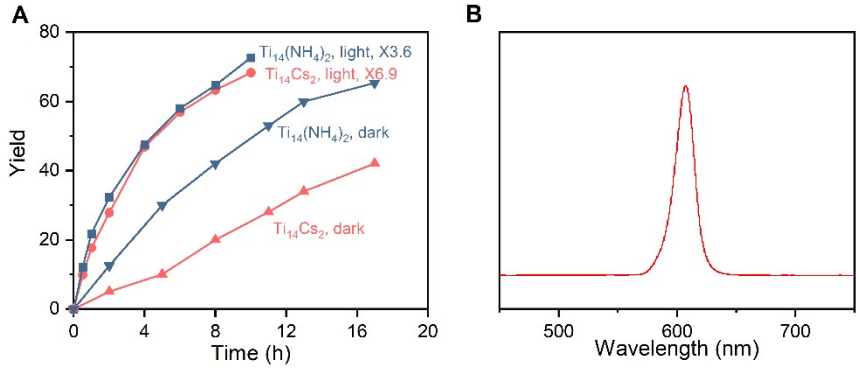


Figure S12:

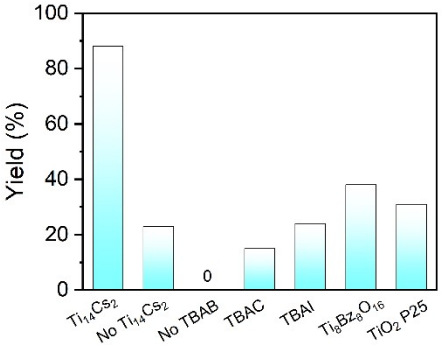


Figure S13:

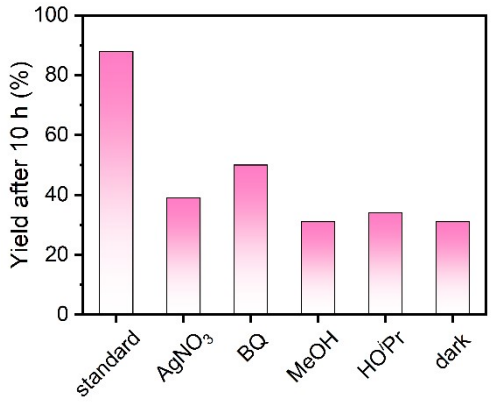


Figure S14:

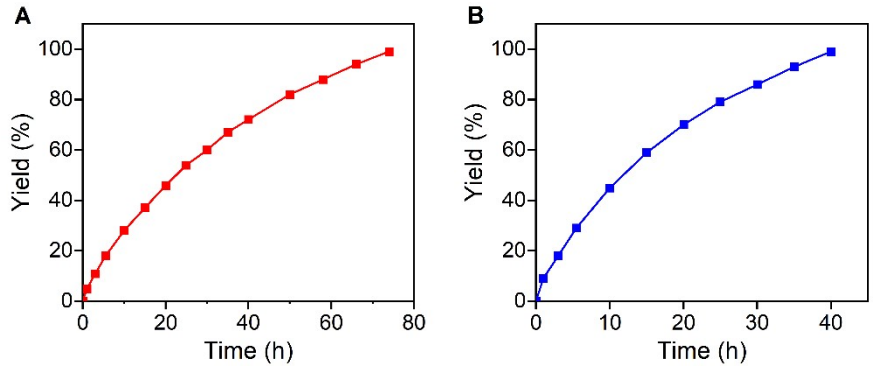
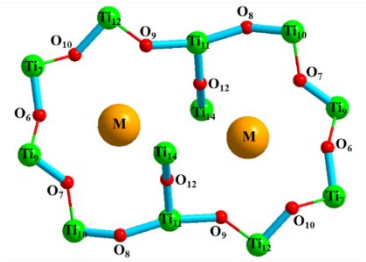


Table S1.:



$Ti_{14}Cs_2$			$Ti_{14}(NH_4)_2$		
Atom 1	Atom 2	Bond length	Atom 1	Atom 2	Bond length
Ti_{11}	O_{12}	1.7428	Ti_{11}	O_{12}	1.7366
	O_8	1.9277		O_8	1.9249
	O_9	1.9331		O_9	1.9302
Ti_{10}	O_8	1.7426	Ti_{10}	O_8	1.7393
	O_7	1.8324		O_7	1.8439
Ti_{14}	O_{12}	1.939	Ti_{14}	O_{12}	1.9273
Ti_9	O_6	1.7887	Ti_9	O_6	1.795
	O_7	1.7991		O_7	1.7946
Ti_7	O_{10}	1.7682	Ti_7	O_{10}	1.7705
	O_6	1.8285		O_6	1.8187
Ti_{12}	O_9	1.7297	Ti_{12}	O_9	1.7349
	O_{10}	1.8764		O_{10}	1.8694

Table S2.:

Compound	Composition	Solvent	Standard	Chemical shift, ppm	Ref.
$Ti_{14}Cs_2$	Ti, Cs, C, O, N, H	DMF	CsCl	9.64	This work
$Ti_{12}Cs$	Ti, Cs, C, O, N, H	DMF	CsCl	11.7	[10]
$Cs@Ti_{12}Ser_6$	Ti, Cs, C, O, Cl, H	H_2O	CsCl	116.4	[11]
$Cs@Ti_7Cr_{14}$	Ti, Cs, Cr, C, O, H	CH_2Cl_2	CsCl	-53.4	[6]
$CsH_7[Al_8(pdc)_8(OAc)_8O_4]$	Cs, Al, C, O, H	DMSO	$CsClO_4$	-26	[12]
$Cs_2(UO_2)(Si_2O_6)$	Cs, Si, C, O, H	H_2O	CsCl	136.5, 61.4, 54.3, −13.5	[13]

Table S3.:

Catalyst	Reaction conditions	Time, h	Conv., %	Yield, %	References
$Ti_{14}Cs_2$	Catalyst (50 mg); TBAB (0.5 mmol); epoxide (3 mmol); 1 atm CO_2; 20 ºC; simulated solar light.	23 h	100	>99	***This work***
$Ti_{14}Cs_2$	Catalyst (50 mg); TBAB (0.5 mmol); epoxide (3 mmol); 1 atm CO_2; 80 ºC; simulated solar light.	14 h	100	>99	***This work***
$Ti_{12}Cs$	Catalyst (50 mg); TBAB (0.5 mmol); epoxide (3 mmol); 1 atm CO_2; 50 ºC; visible light.	7.5 h	100	>99	*Dalton Trans.,* **2024**, *53*, 1989-1998
$Ti_{12}Pb_2$	Catalyst (50 mg); TBAB (0.5 mmol); epoxide (3 mmol); 1 atm CO_2; 20 ºC; visible light.	24 h	100	>99	*Dalton Trans.,* **2024**, *53,* 3666-3674
Ti_{14}	Catalyst (50 mg); TBAB (0.5 mmol); epoxide (3 mmol); 1 atm CO_2; 20 ºC; visible light.	30 h	100	>99	*Dalton Trans.,* **2024**, *53,* 3666-3674
Zn-NTTA	Catalyst (5 µmol); TBAB (0.3 mmol); epoxide (20 mmol); 10 bar CO_2; 100 ºC.	8 h	-	98.2	*ACS Appl. Mater. Interfaces,* **2016**, *8*, 31746-56.
Al–N_4–C	Catalyst (20 mmol); TBAB (0.8 mmol); epoxide (0.67 mmol); DMF; 1 bar CO_2; visible light.	60 h	-	80	*Adv. Mater.,* **2021**, *33*, 2103186.
MOF-801 (D)	Catalyst (0.6 mol%); TBAB (0.5 mol%); epoxide (19.2 mmol); 0.1 MPa CO_2; 80 °C.	15 h	92.4	92.4	*J. Mate. Chem. A*, **2022**, *10*, 10051–10061.
V_8-1	Catalyst (2 mol %); TBAB (0.5 mmol,	16 h	-	>99	*J. Am. Chem.*

	2.5 mol %); epoxide (28 mmol); CO_2 (0.5 Mpa); 70 °C.				*Soc.,* **2019**, *141*, 19487−19497.
Ni−TCPE1	Catalyst (10 μmol; based on Ni); epoxide (20 mmol); TBAB (0.3 mmol); CO_2 (1 MPa), 100 °C.	12 h	-	>99	*J. Am. Chem. Soc.,* **2015**, *137*, 15066−15069.
Mn-MOF	Catalyst (10 mg); TBAB (0.028 mmol); epoxide (1.429 mmol); 1 bar CO_2; visible light; 80 °C.	24 h	-	90	*ACS Omega,* **2022**, *7*, 9958-9963.
PMo_{12}@Zr-Fc MOFs	catalyst (5 mg, 10.26 wt%); TBAB (0.25 mmol); epoxide (12.5 mmol); 1 atm CO_2; 80 °C; 900 rpm.	8 h	80	86.77	*Appl. Catal. B,* **2021**, *296*, 120329.
$CoPc/TiO_2$	Catalyst (100 mg); TBAB (0.1 mmol); epoxide (1.0 mmol); 1 bar CO_2; solvent (CH_3CN+MeOH); 20 W white cold LED, 25 °C.	24 h	96.7	94	*ACS Sustain. Chem. Eng.,* **2018**, *6*, 7799–7809.
Bi-PCN-224	Catalyst (30 mg); TBAB (0.5 mmol); epoxide (4.5 mmol); 1 bar CO_2; 300 W Xenon lamp.	6 h	>99	-	*ACS Catal.,* **2021,** *11*, 1988-1994.
$\{Cu_4[(C_{57}H_{32}N_{12})(COO)_8]\}_n$	Catalyst (0.2 mol%); TBAB (0.65 g, 10 mol %); CO_2 (1 atm); r.t.	48 h	-	96	*J. Am. Chem. Soc.,* **2016**, *138*, 2142−2145.
$Au_{19}Ag_4$(S-Adm)$_{15}$	Catalyst (5 mg); TBAB (10 mol%); epoxide (0.3 mmol); 3 ml solvent; 60 °C.	24 h	-	78	*Angew. Chem. Int. Ed.,* **2021**, *60*, 10573–10576.
IHEP-9	Catalyst (0.05 mmol); TBAB (0.5 mmol); epoxide (1 mmol); 1 bar CO_2; visible light; r.t.	12 h	-	>99	*Inorg. Chem.,* **2021**, *60*, 651-659.
Zr-MOF	Catalyst (30 mg); TBAB (0.5 mmol); epoxide (4.5 mmol); 1 bar CO_2; Xe lamp; r.t.	6 h	>99	-	*ACS Catal*. **2021**, *11*, 1988.
$Ti_{18}Bi_4$	Catalyst (100 mg); TBAB (0.5 mmol); epoxide (3.0 mmol); 1 bar CO_2; Xe lamp, r.t.	14 h	100	>99	*ACS Catal., **2022**, 12*, 8202−8213.
$BiNbO_4$/r-GO	Catalyst (50 mg); TBAB (9 mg); epoxide (100 μl); CO_2 (1.48 MPa); 353 K.	24 h	-	65	*ACS Sustain. Chem. Engin.,* **2020**, *8*, 12072-12079.
NUC-38Yb	Catalyst (0.5 mol %); TBAB (4 mol%); epoxide (20 mmol); CO_2 (1 atm); 60 °C.	10 h	-	96	*ACS Catal.,* **2021**, *11*, 14916−14925.