Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

A Cryptand−like Ti−coordination Compound with Visible−Light Activity in CO_2 Storage

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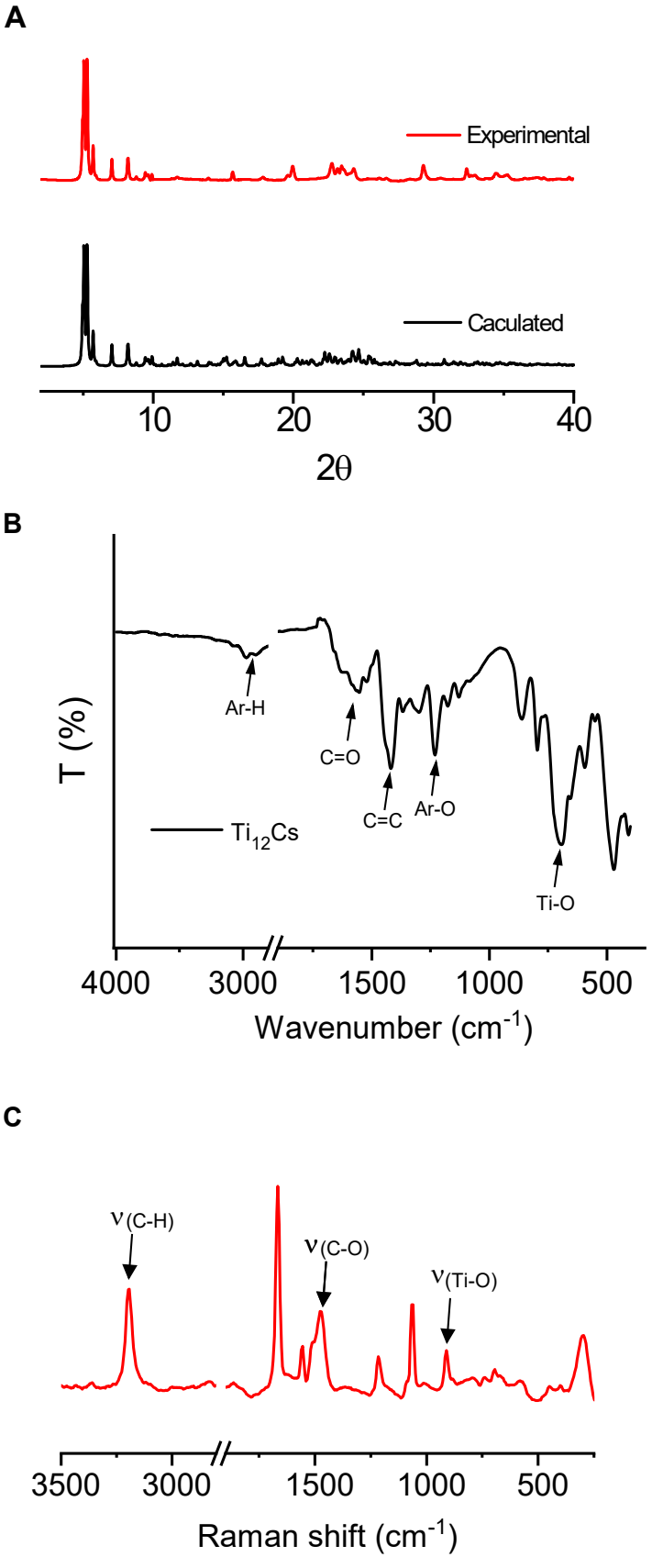


Fig. S1 (A) PXRD, **(B)** FTIR and **(C)** Raman of **Ti_{12}Cs**.

Discussion: In the IR spectra, the peaks ranging from 2800 to 3000 cm^{-1} belong to the stretching vibration of Ar-H bonds on the benzene ring, while the peak at 1632 cm^{-1} belongs to the stretching vibration of C=O bonds. The peaks ranging from 1418 to 1554 cm^{-1} belong to the stretching vibration of C=C bonds on the benzene ring, whereas the peak at 1230 cm^{-1} peak is attributed to Ar-O bonds of flexural vibrations. The broad peaks ranging from 500 to 1000 cm^{-1} belong to Ti-O bonds.

In the Raman spectra, the peaks ranging from 3200 to 3000 cm^{-1} are attributed to the stretching modes of C-H bonds of $Ti_{12}Cs$. The peaks ranging from 2800 to 2600 cm^{-1} are assigned as C-O bonds, while the peaks ranging from 1000 to 894 cm^{-1} are assigned as Ti-O bonds.

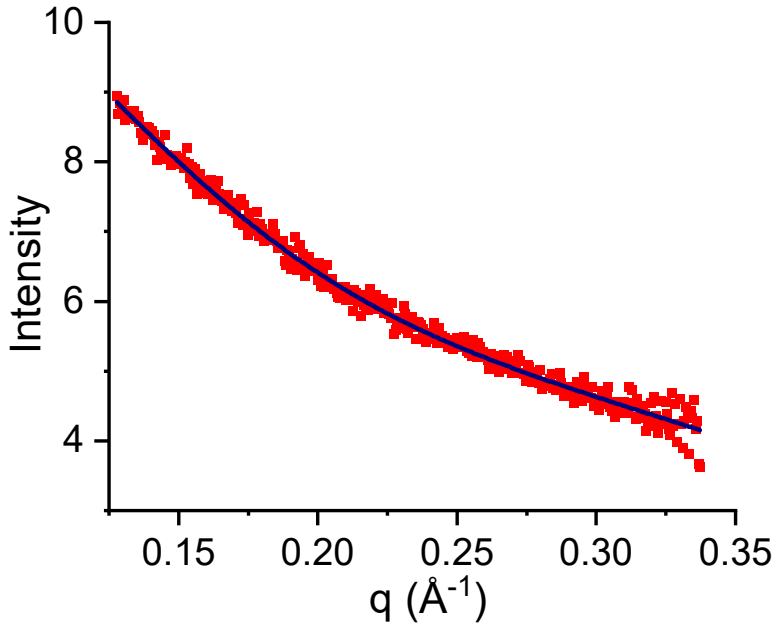


Fig. S2 SAXS analysis of **$Ti_{12}Cs$** in DMF. Color scheme: red scatter, experimental data; navy line, fitted curve.

Table S1. Previous Cs^{+}–enclosing host-guest compounds.

Compounds	**Composition**	**Solvent**	**Internal Standard**	**chemical shift**	**References**
$Ti_{12}Cs$	Ti, Cs, C, O, N, H	DMF	CsCl	11.7 ppm	This work
$Cs@Ti_{12}Ser_6$	Ti, Cs, C, O, Cl, H	H_2O	CsCl	116.4 ppm	1
$Cs@Ti_7Cr_{14}$	Ti, Cs, Cr, C, O, H	CH_2Cl_2	CsCl	-53.4 ppm	2

$CsH_7[Al_8(pdc)_8(OAc)_8O_4]$	Cs, Al, C, O, H	DMSO	$CsClO_4$	-26 ppm	3
$Cs_2(UO_2)(Si_2O_6)$	Cs, Si, C, O, H	H_2O	CsCl	136.5, 61.4, 54.3, and −13.5 ppm	4

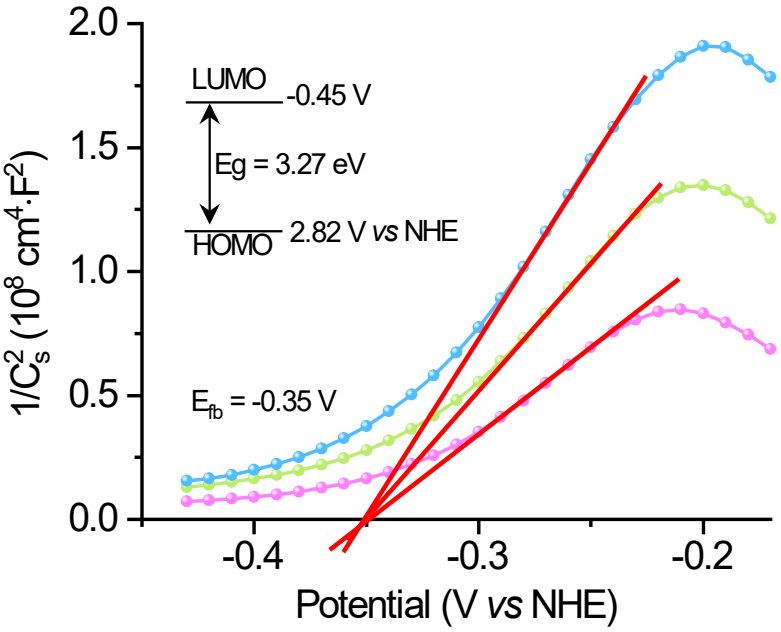


Fig. S3 Mott–Schottky plots of $Ti_8O_8Bz_{16}$ at 70, 100, and 200 Hz.

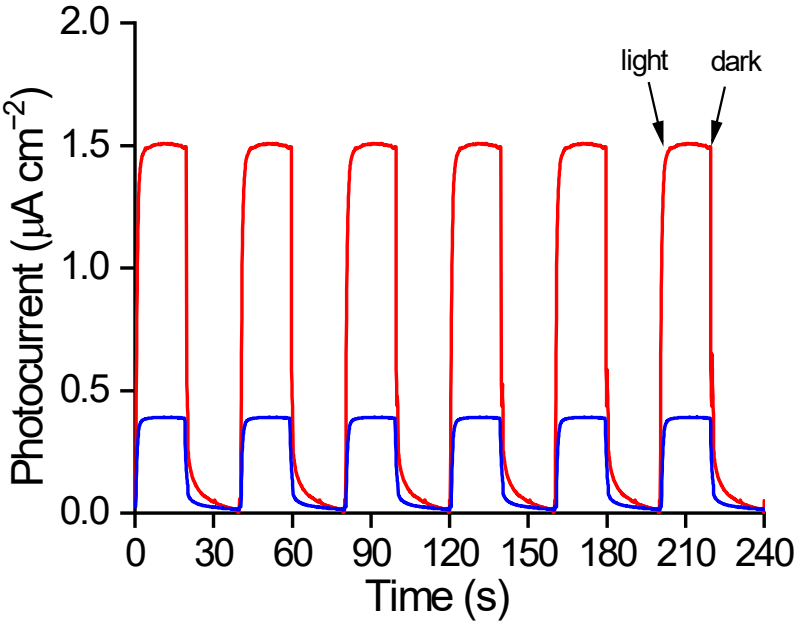
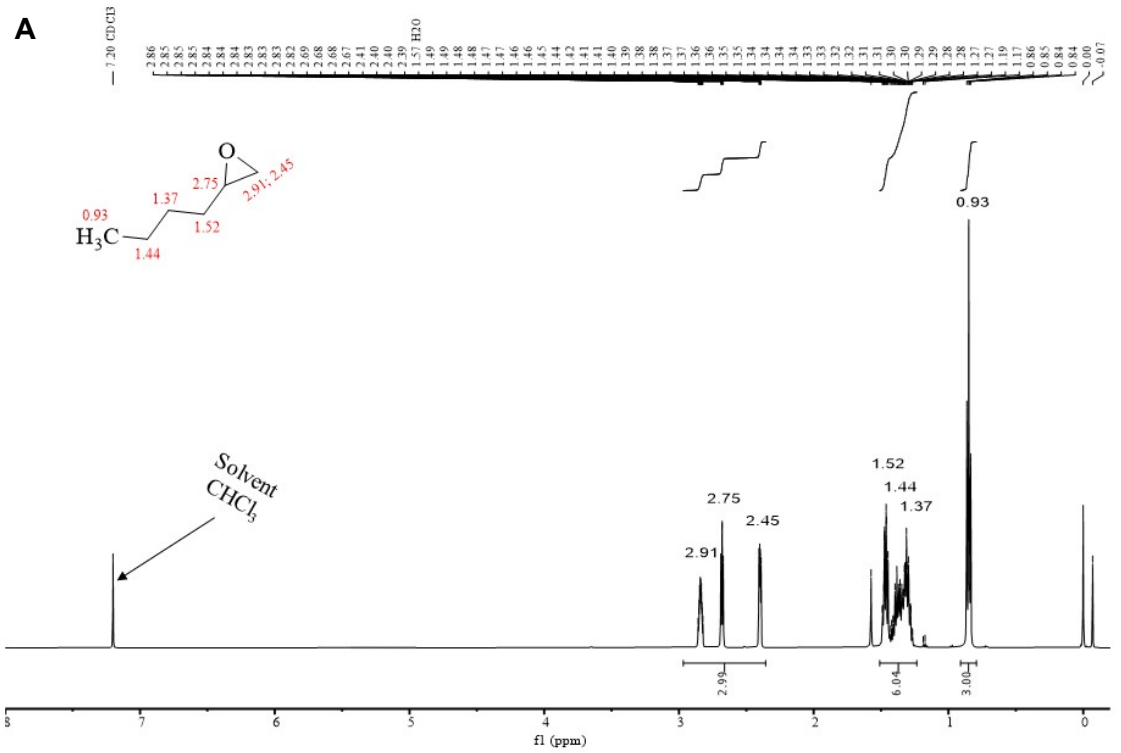
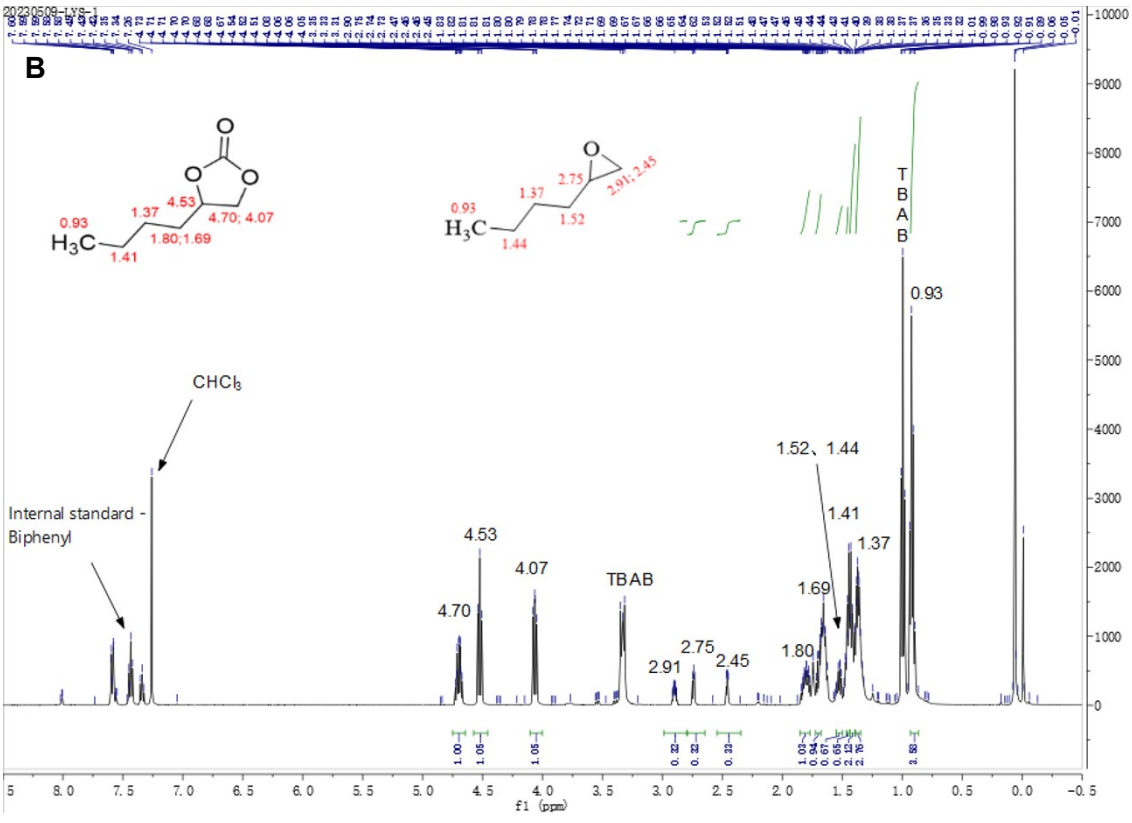


Fig. S4 Transient photocurrent response under simulated sunlight at bias = +1.0 V *vs* Ag/AgCl. Color scheme: red, **$Ti_{12}Cs$**; blue, $Ti_8O_8Bz_{16}$.


A
Solvent
CHCl3
2.91
2.75
2.45
1.52
1.44
1.37
0.93
f1 (ppm)


B
CHCl3
Internal standard -
Biphenyl
4.70
4.53
4.07
TBAB
2.91
2.75
2.45
1.80
1.69
1.52、1.44
1.41
1.37
0.93
f1 (ppm)

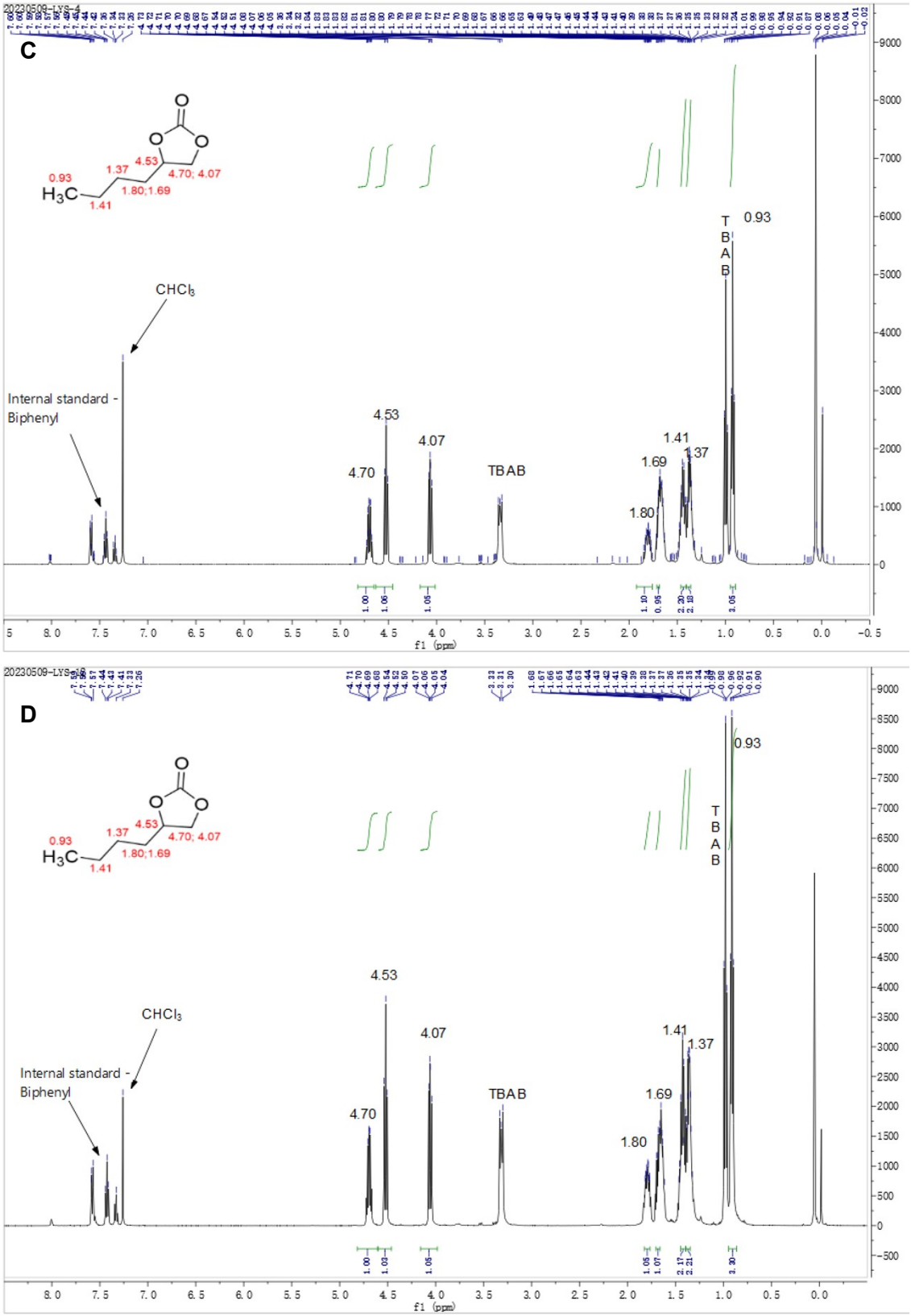
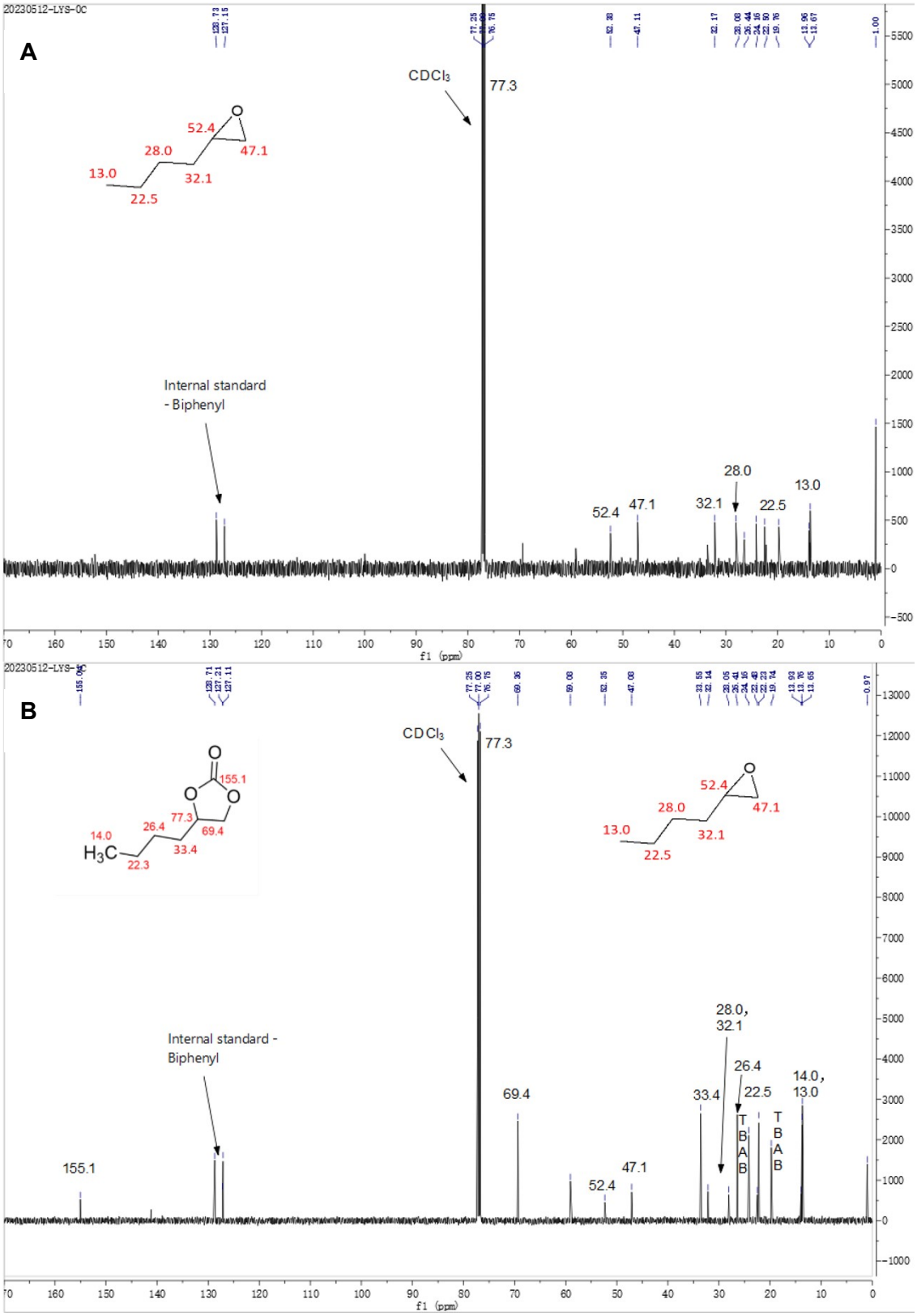


Fig. S5 ^{1}H NMR spectra before and after CO_2/epoxide cycloaddition with **Ti_{12}Cs** in **(A)** 0 h, **(B)** 1 h, **(C)** 4 h, and **(D)** after reaction (12 h).

Discussion: ^{1}H NMR was measured using a Bruker Avance−500 NMR spectrometer at room temperature using $CDCl_3$ as the solvent. The spectra show some peaks of 1,2-epoxyhexane at

1.52, 2.45, 2.75, and 2.91 ppm before reaction (Fig. S5 A). After the catalytic reaction, these peaks diminished along with the production of new peaks of cyclic carbonate at 4.07, 4.53, and 4.70 ppm (Fig. S5 B, C, D). After 12 h of visible–light irradiation in 1 bar CO_2, the conversion of epoxide to cyclocarbonate approached completion.



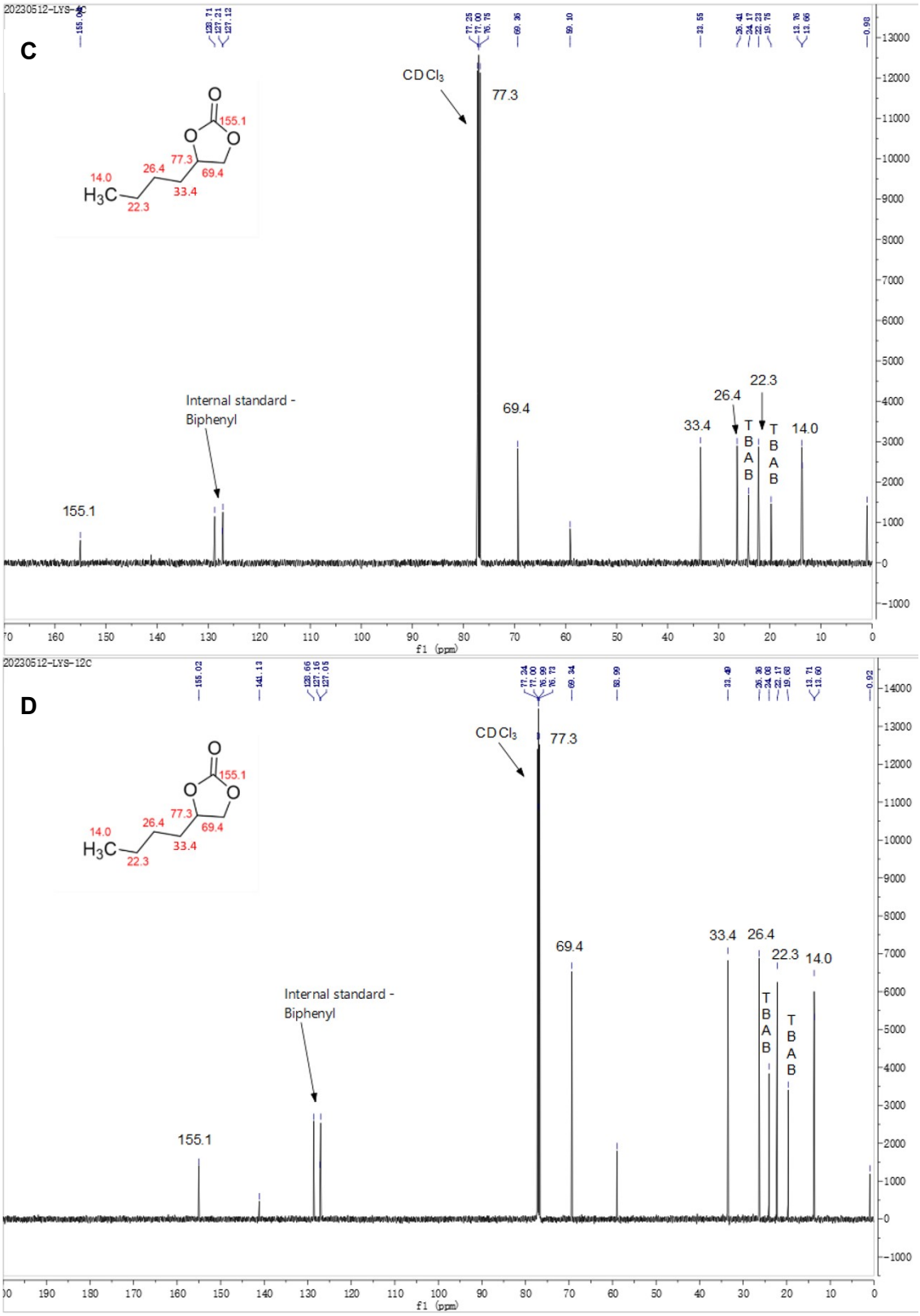


Fig. S6 ^{13}C NMR spectra before and after CO_2/epoxide cycloaddition with **$Ti_{12}Cs$** in **(A)** 0 h, **(B)** 1 h, **(C)** 4 h, and **(D)** after reaction (12 h).

Discussion: The ^{13}C NMR spectra show that there are some peaks of the 1,2-epoxyhexane at 47.1 and 52.4 ppm before the reaction (Fig. S6 A). After the reaction, these peaks diminished

along with the production of new peaks of cyclocarbonate at 69.4, 77.3, and 155.1 ppm (Fig. S6 B, C, D).

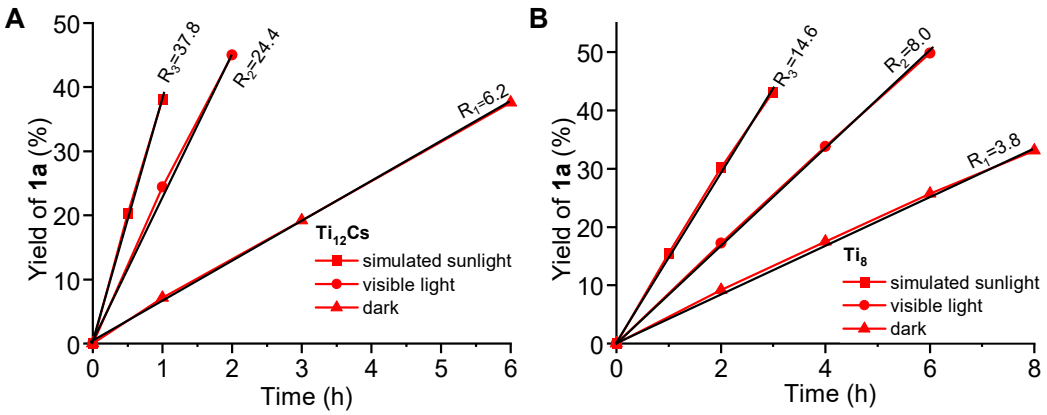
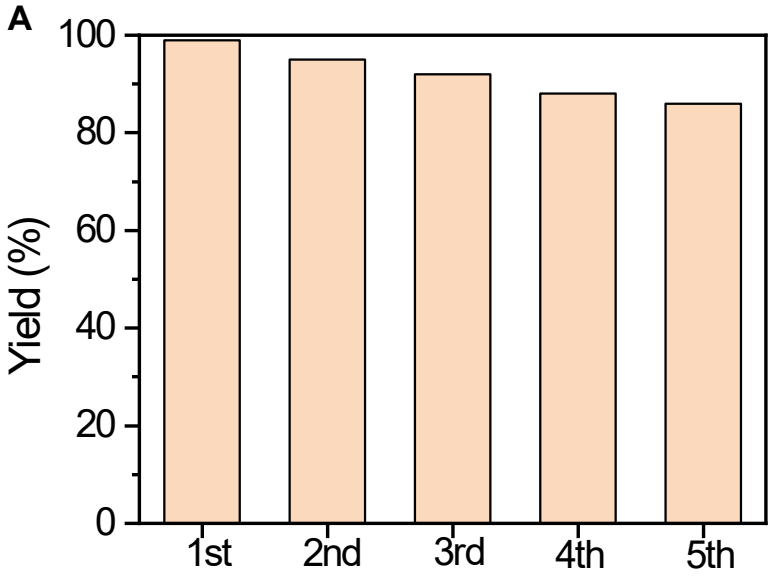


Fig. S7 Calculations of the initial rates. **(A)** The calculated rates data for **$Ti_{12}Cs$** are from Figure 5A. **(B)** The initial rates' data for $Ti_8O_8Bz_{16}$.



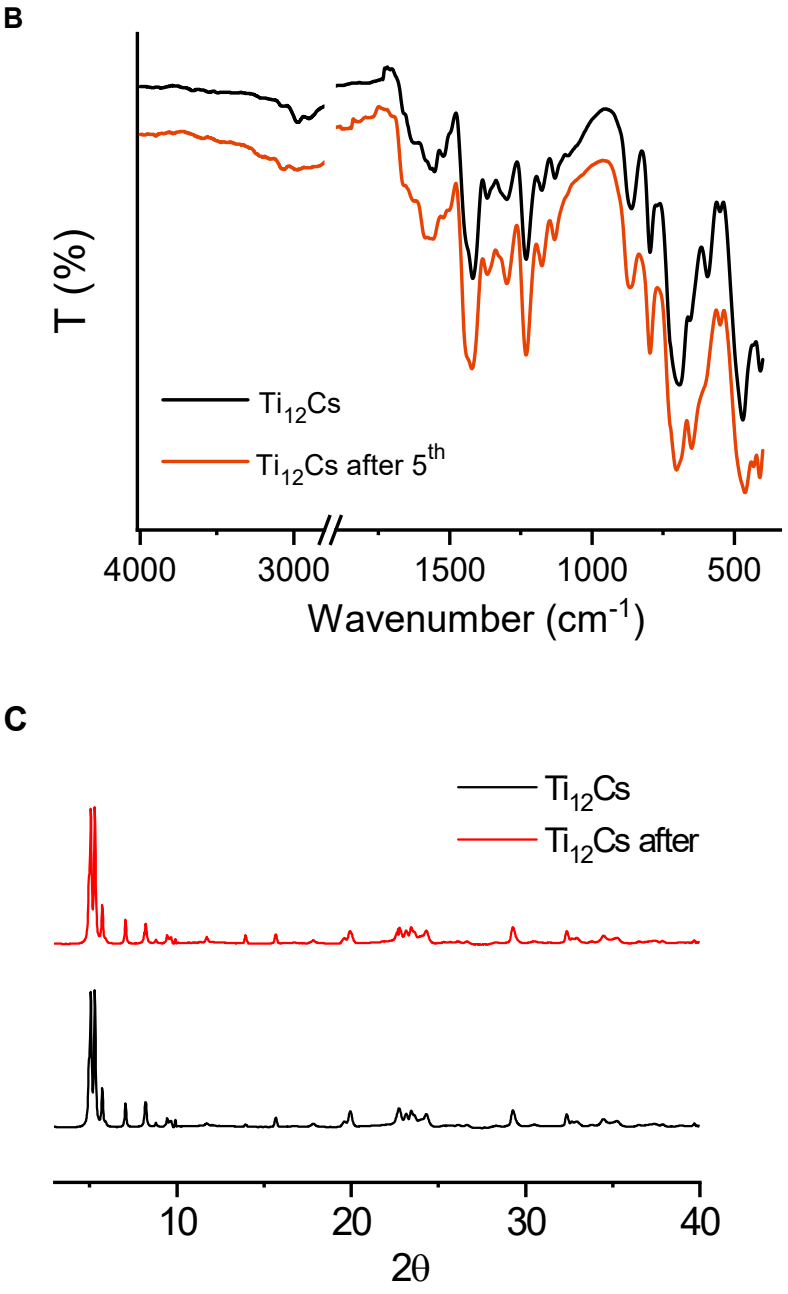


Fig. S8 (A) The cycling experiments under the conditions: 1,2-epoxyhexane (3.0 mmol), **$Ti_{12}Cs$** (100 mg), TBAB (0.5 mmol), CO_2 (1 bar), biphenyl (50 mg), visible−light, and 20 °C. **(B)** FTIR and **(C)** PXRD of **$Ti_{12}Cs$** before and after the cycloaddition reaction.

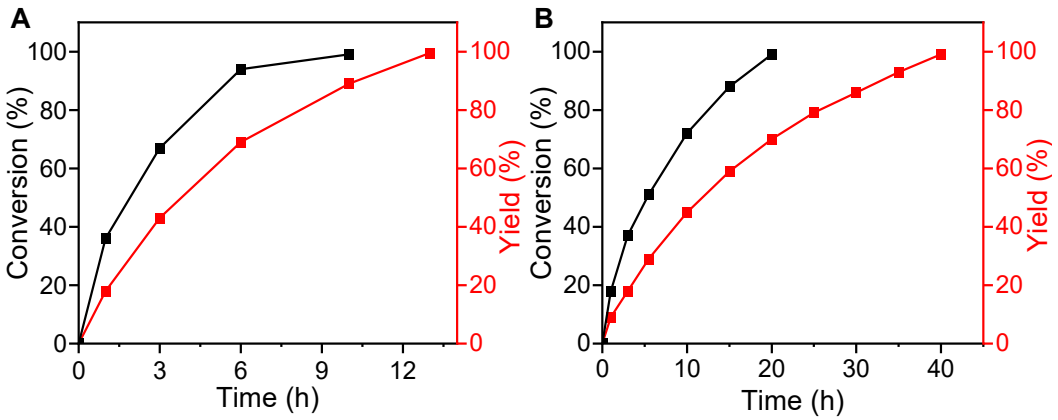


Fig. S9 (A) Reaction kinetics of the standard reaction under natural sunlight. The condition: 1,2-epoxyhexane (3.0 mmol), **$Ti_{12}Cs$** (100 mg), TBAB (0.5 mmol), CO_2 (1 bar), and biphenyl (50 mg). **(B)** Reaction kinetics of the scaleup reaction under natural sunlight. The condition: 1,2-epoxyhexane (30 mmol), and the others were identical to the conditions in panel A.

Reference:

1. G. Zhang, W. Li, C. Liu, J. Jia, C.-H. Tung and Y. Wang, *J. Am. Chem. Soc.*, 2018, **140**, 66-69.
2. D. Wang, A. Said, Y. Liu, H. Niu, C. Liu, G. Wang, Z. Li, C.-H. Tung and Y. Wang, *Inorg. Chem.*, 2022, **61**, 14887-14898.
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