Electronic Supplementary Information

Facile synthesis of crystalline viologen-based porous ionic polymers with hydrogen-bonded water for efficient catalytic CO_2 fixation at ambient conditions

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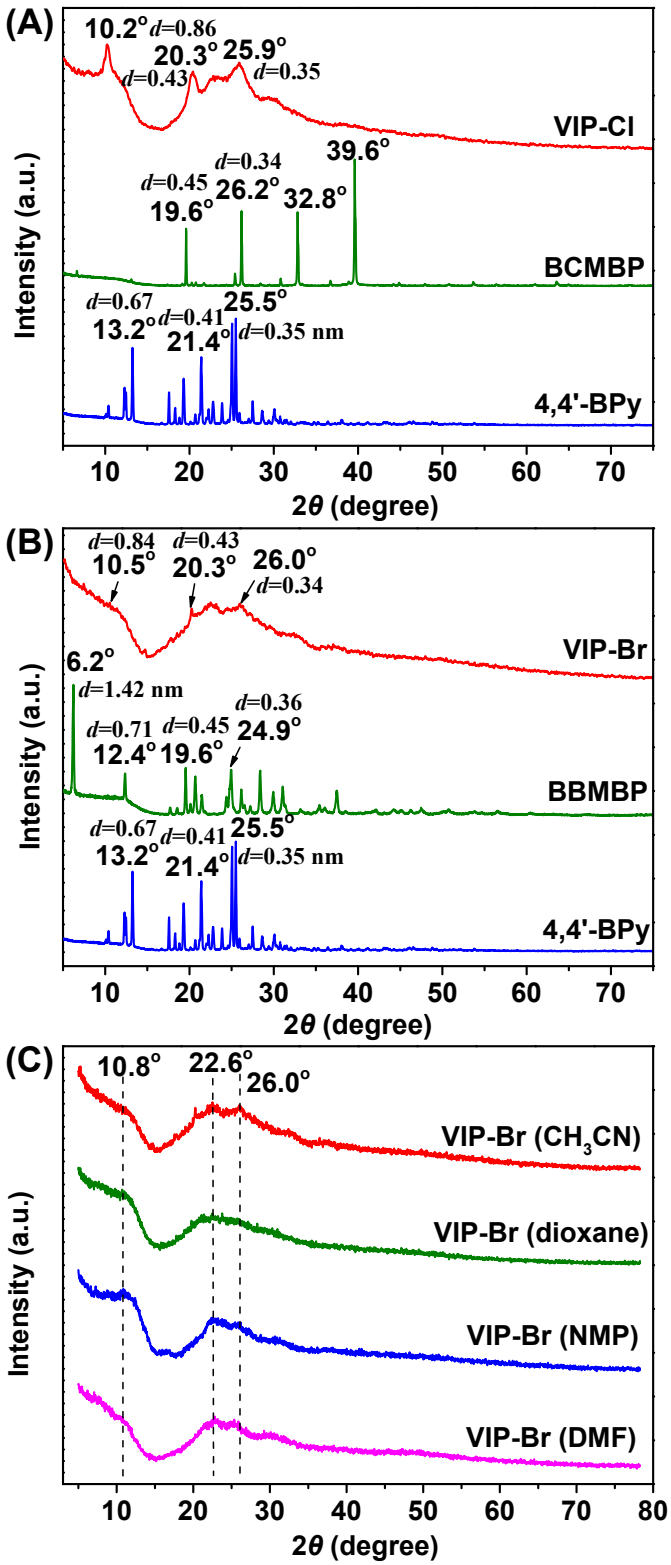

Fig. S1 XRD patterns of (A) 4,4'-BPy, BCMBP and VIP-Cl, (B) 4,4'-BPy, BBMBP and VIP-Br prepared in CH_3CN and (C) VIP-Br series that were synthesized in different solvents.

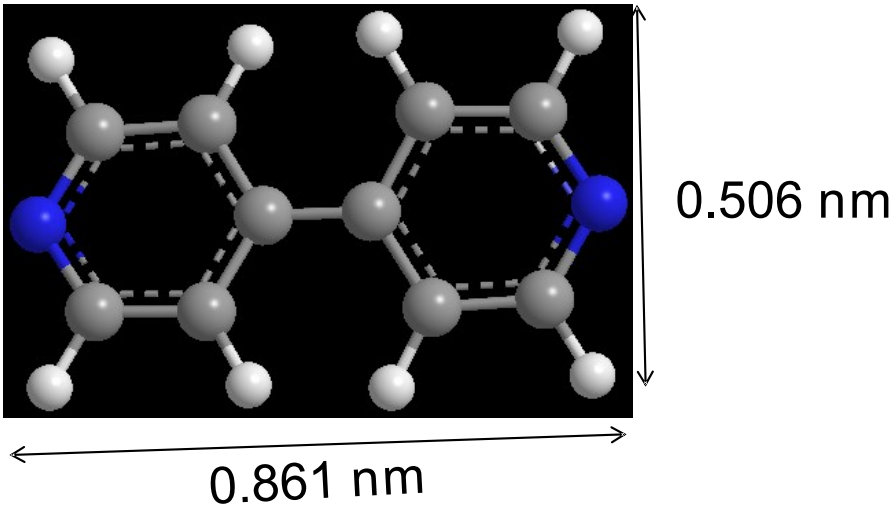

Fig. S2 The optimized molecular structure of 4,4'-BPy (0.861 × 0.506 nm).

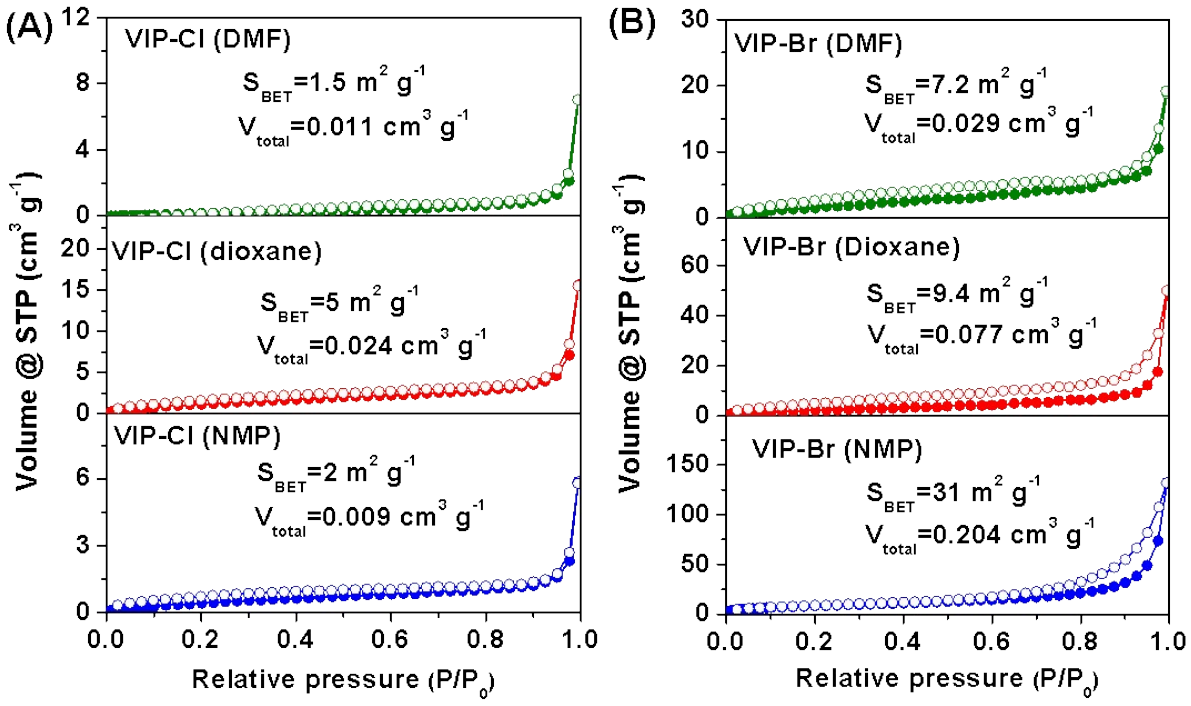

Fig. S3 N_2 adsorption-desorption isotherms of the control samples (A) VIP-Cl (DMF), VIP-Cl (Dioxane) and VIP-Cl (NMP) , (B) VIP-Br (DMF), VIP-Br (Dioxane) and VIP-Br (NMP).

Table S1 The detailed comparisons for surface areas of viologen-based ionic polymers prepared by different synthetic methods.

Entry	Polymers	S_{BET} (m^2 g^{-1})	Synthetic method	Ref.
1	**VIP-Cl**	**56**	**Menshutkin reaction**	**This work**
2	**VIP-Br**	**38**	**Menshutkin reaction**	**This work**
3	iCOP-1	9.01	Menshutkin reaction	S1
4	iCOP-2	12.93	Menshutkin reaction	S1
5	PIN-1	2	Menshutkin reaction	S2
6	COP_1^{++}	None	Menshutkin reaction	S3
7	TBB-Bpy-a	<10	Menshutkin reaction	S4
8	pDAP	41	Menshutkin reaction	S5
9	V-CDP	22	Menshutkin reaction	S6
10	bipy-POP	25	Menshutkin reaction	S7
11	COP_2^{++}	None	Zincke reaction	S3
12	HS	12	Zincke reaction	S8
13	HT	35	Zincke reaction	S8
14	cCTN:Cl^-	30	Zincke reaction	S9
15	COTs	35	Zincke reaction	S10
16	CONs	153	Zincke reaction	S10
17	V-PCIF-Cl	174	Zincke reaction	S11
18	V-PCIF-Br	383	Zincke reaction	S11
19	POP-V1	812	Sonogashira-Hagihara reaction	S12
20	PCP-Cl	755	Sonogashira-Hagihara reaction	S13
21	V-iPHP-11	562	Heck reaction	S14
22	V-iPHP-21	432	Heck reaction	S14
23	cCTF-500	1247	Ionothermal reaction ($ZnCl_2$)	S15
24	HCP-V1	865	Friedel-Crafts reactions ($FeCl_3$)	S16

Table S2 Elemental analysis results of VIP-Cl and VIP-Br.

Sample	Molecular formula	C (wt%)	N (wt%)	H (wt%)	C/N	H_2O (wt%)[a]	V content (mmol g^{-1})[b]
VIP-Cl	$[(C_{24}H_{20}N_2Cl_2)\bullet 4H_2O]_n$	Found: 59.72	Found: 5.77	Found: 5.46	10.35	14.6	2.06
		Calcd: 60.13	Calcd: 5.84	Calcd: 5.89	10.29	15.0	2.08
VIP-Br	$[(C_{24}H_{20}N_2Br_2)\bullet 3H_2O]_n$	Found: 52.08	Found: 5.10	Found: 4.10	10.21	8.5	1.82
		Calcd: 52.38	Calcd: 5.09	Calcd: 4.76	10.29	9.8	1.82

[a] The found content value of H_2O was measured by the TGA result and theoretical value was calculated by the molecular formulas trapped H-bonded water. [b] Viologen (V) ionic content (mmol g^{-1}) = 0.5 × 1000 × N content (wt %) / 14.

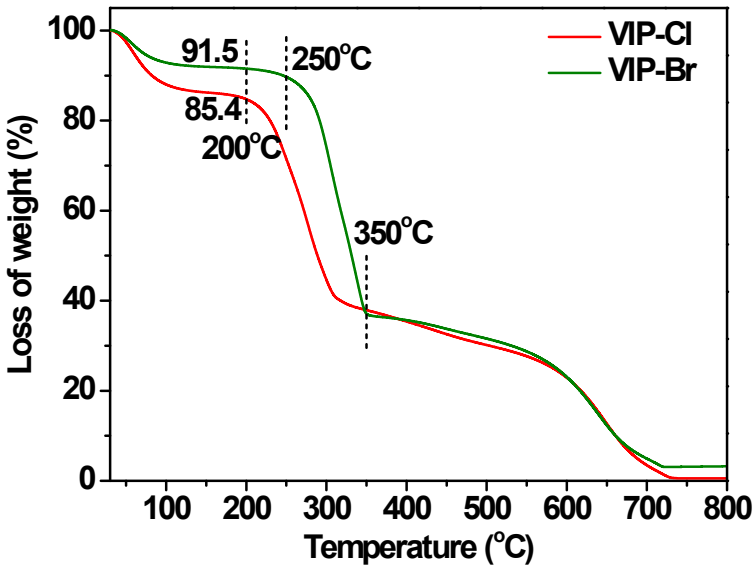

Fig. S4 Thermogravimetric analysis (TGA) curves of VIP-Cl and VIP-Br under N_2 atmosphere.

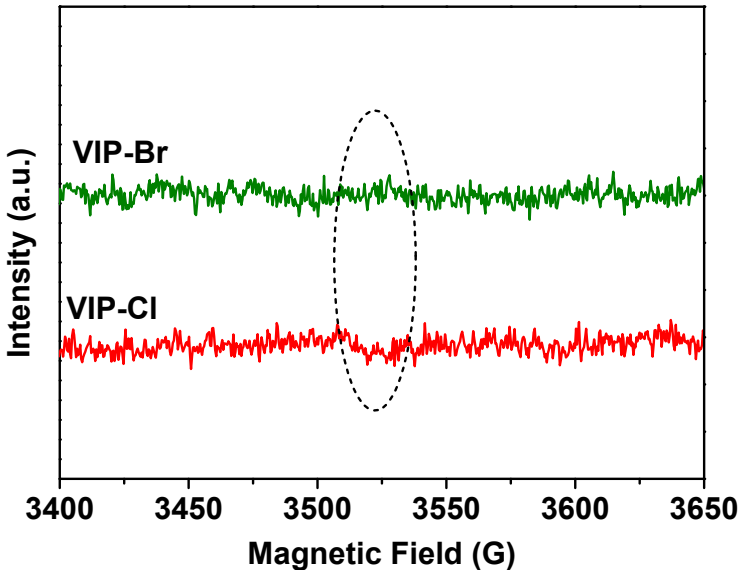

Fig. S5 The solid-state EPR spectra at X-band at room temperature.

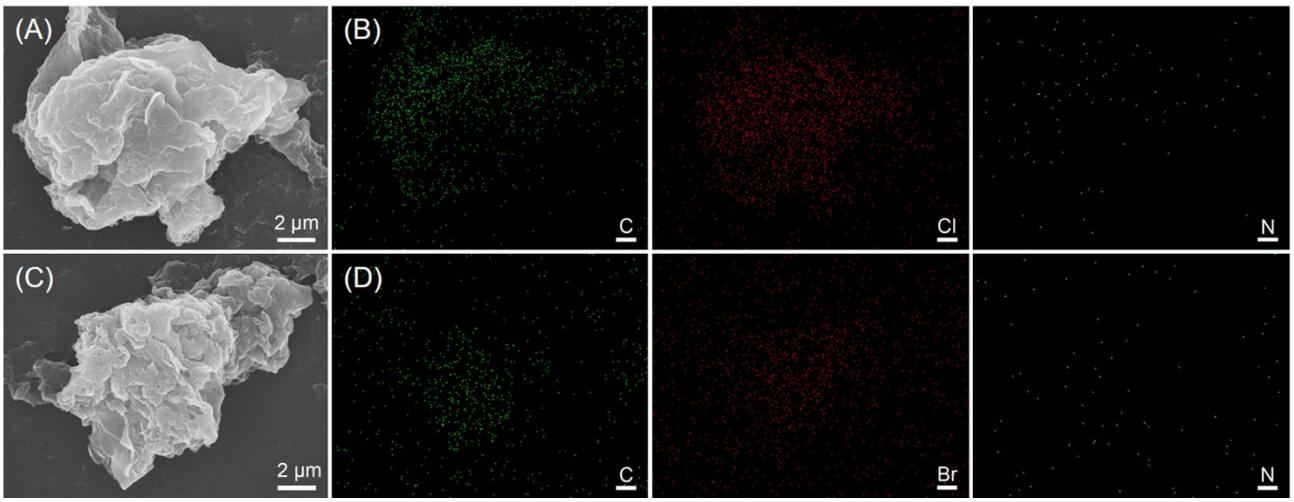

Fig. S6 Energy-dispersive X-ray spectrometry (EDS) elemental mapping images of (A, B) VIP-Cl for C, Cl, N elements, and (C, D) VIP-Br for C, Br, N elements at the SEM mode.

Table S3 The detailed comparisons of catalytic activities over metal-free ionic polymers and IPs with metal sites or HBD groups for CO_2 fixation with ECH without any co-catalysts.*

Catalyst	*P* (MPa)	*T* (°C)	*t* (h)	Yield (%)	Ref.
PCP-Cl	3	100	12	98	S13
PS-DHPIMBr	2	130	1	97	S17
PIM2	1	130	4	92	S18
IT-POP-1	1	120	10	99	S19
poly-imidazoliums	1	110	2	94	S20
POM3-IM	1	120	8	90	S21
TBB-Bpy-a	1	120	4	88	S4
cCTF-500	1	90	12	95	S15
FIP-Im	1	80	10	99	S22
3-IPMP-EtI	1	90	5	90	S23
UIIP	1	90	2	99	S24
CCTF-350	0.1	120	24	93.1	S25
PDMBr	0.1	120	12	91.3	S26
IP3	0.1	100	24	99	S27
PDBA-Cl-SCD	0.1	90	6	99.3	S28
PGDBr-5-2OH	0.1	70	24	91	S29
HIP-Br-2	0.1	70	96	90	S30
PIP-Bn-Cl	0.1	100	3	99	S31
V-PCIF-Br	0.1	80	72	97	S11
V-iPHP-1	0.1	60	72	99	S14
IM-iPHP-2	0.1	60	72	99	S32
PPS-mOH-Bn	0.1	50	72	78	S33
POF-PNA-Br	0.1	40	48	94.1	S34
VIP-Br	**0.1**	**60 (40)**	**48 (72)**	**99 (99)**	**This work**
TBB-Bpy@Salen-Co	1	80	6	95	S35
Al-iPOP-1	1	40	6	99	S36
SYSU-Zn@IL2	1	80	12	99	S37
Al-CPOP	0.1	120	24	95	S38
POF-Zn^{2+}-I^-	1	60	8	92.2	S39
NHC-CAP-1(Zn^{2+})	2	100	3	97	S40
Zn-CIF2-C_2H_4	2.5	120	4	98	S41

* It should be pointed out that different catalysts were evaluated under different conditions. Thus, it is difficult to directly compare the activity between different catalytic systems. The represented catalytic activities using yields of the product in Table S3 should be considered in a reasonable comparison.

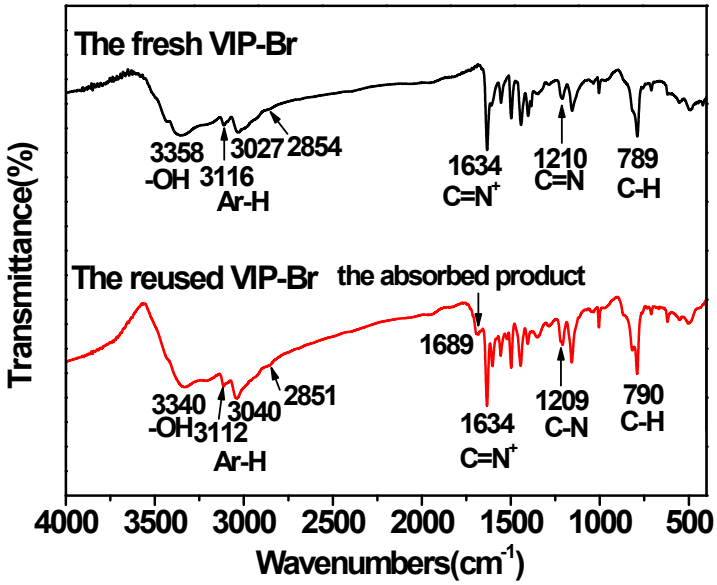

Fig. S7 FTIR of the fresh catalyst VIP-Br and the reused catalyst VIP-Br.

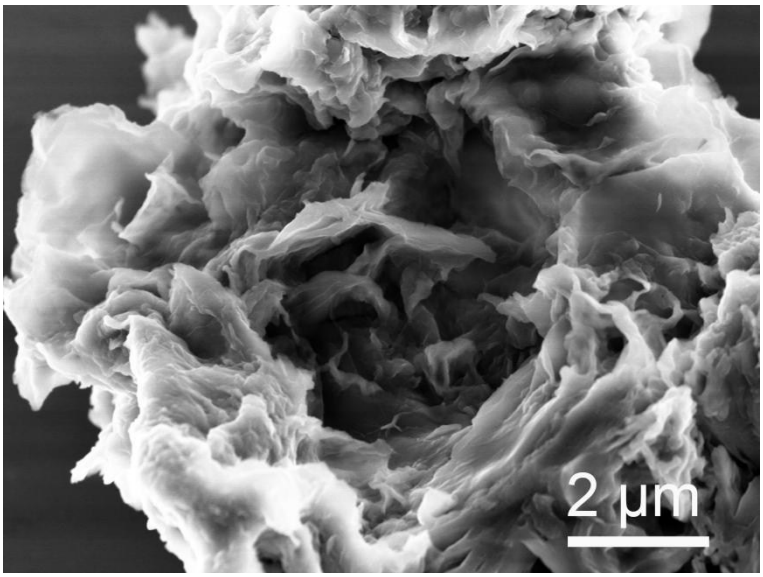

Fig. S8 SEM image of the reused catalyst VIP-Br.

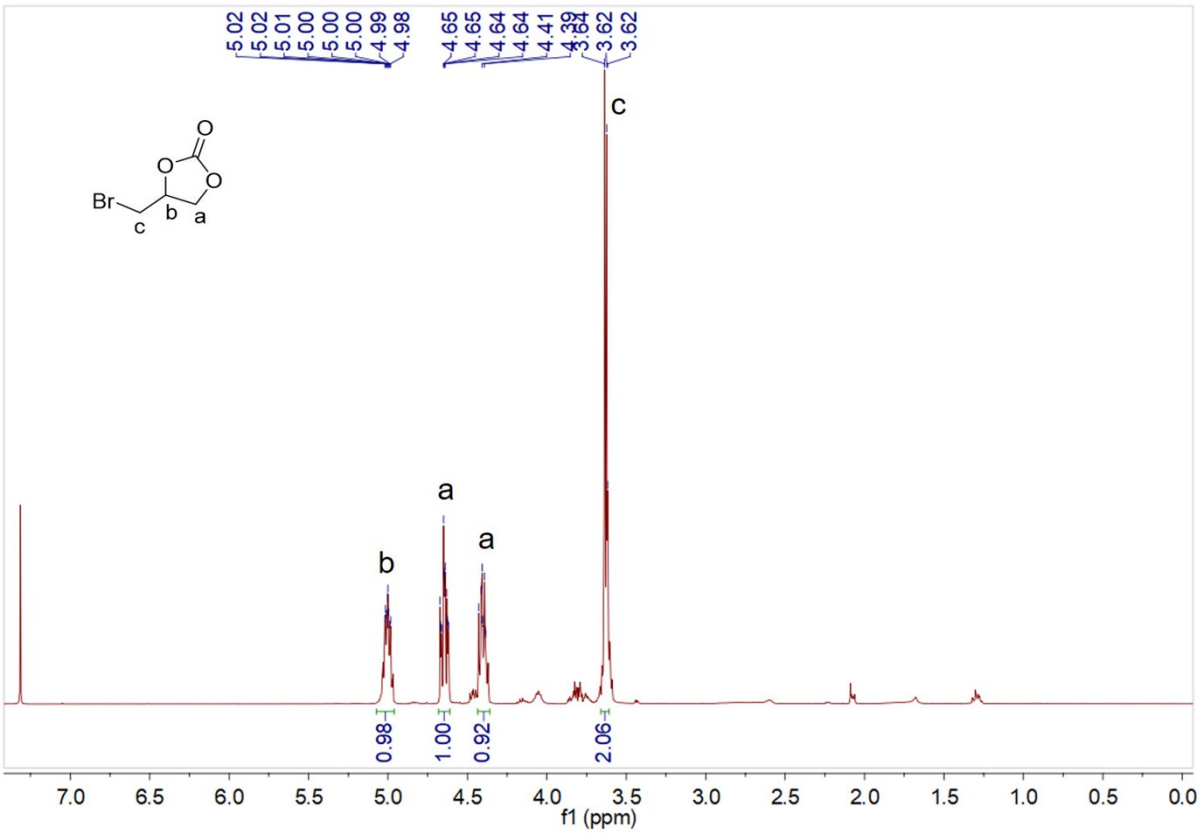

Fig. S9 ^{1}H NMR spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=5.00 (1H, CH), 4.68-4.61 (1H, CH_2), 4.40 (1H, CH_2), 3.66-3.61 (2H, CH_2).

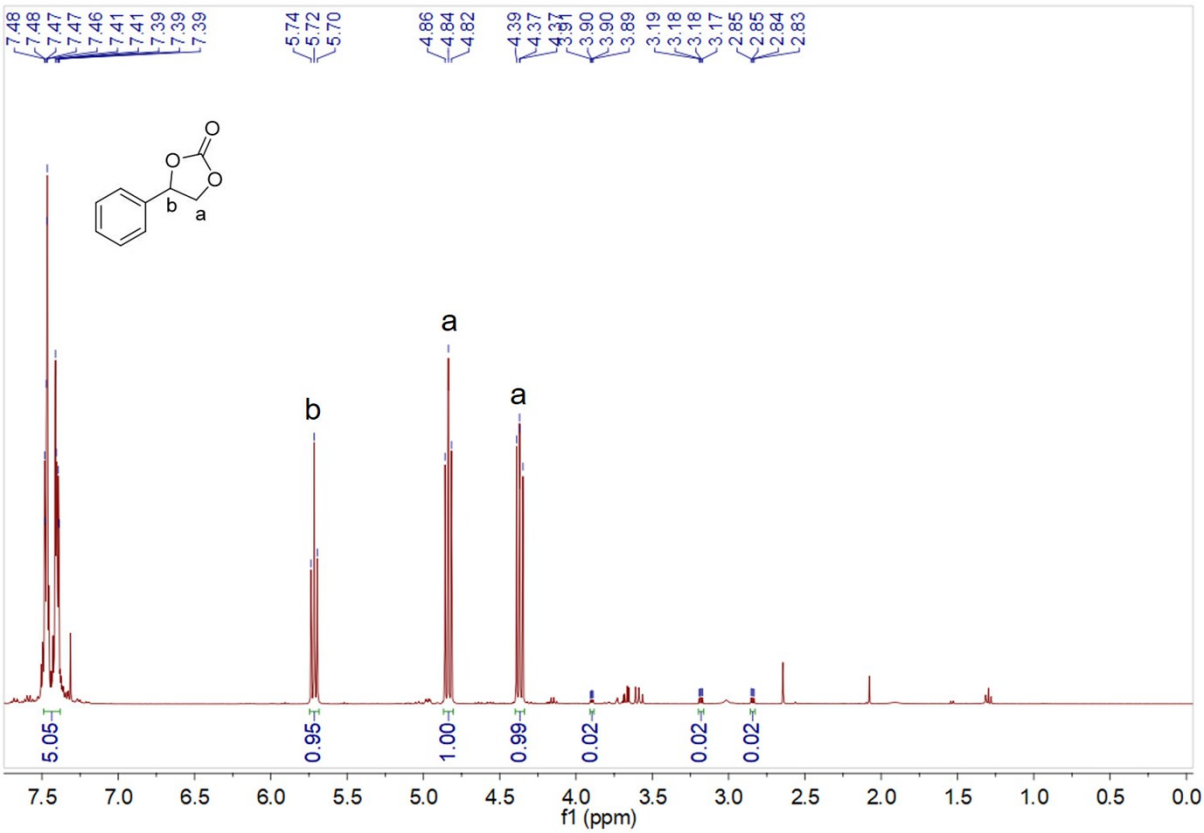

Fig. S10 ^{1}H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=7.49-7.38 (5H, CH), 5.72 (1H, CH_2), 4.87-4.80(1H, CH_2), 4.37 (1H, CH_2).

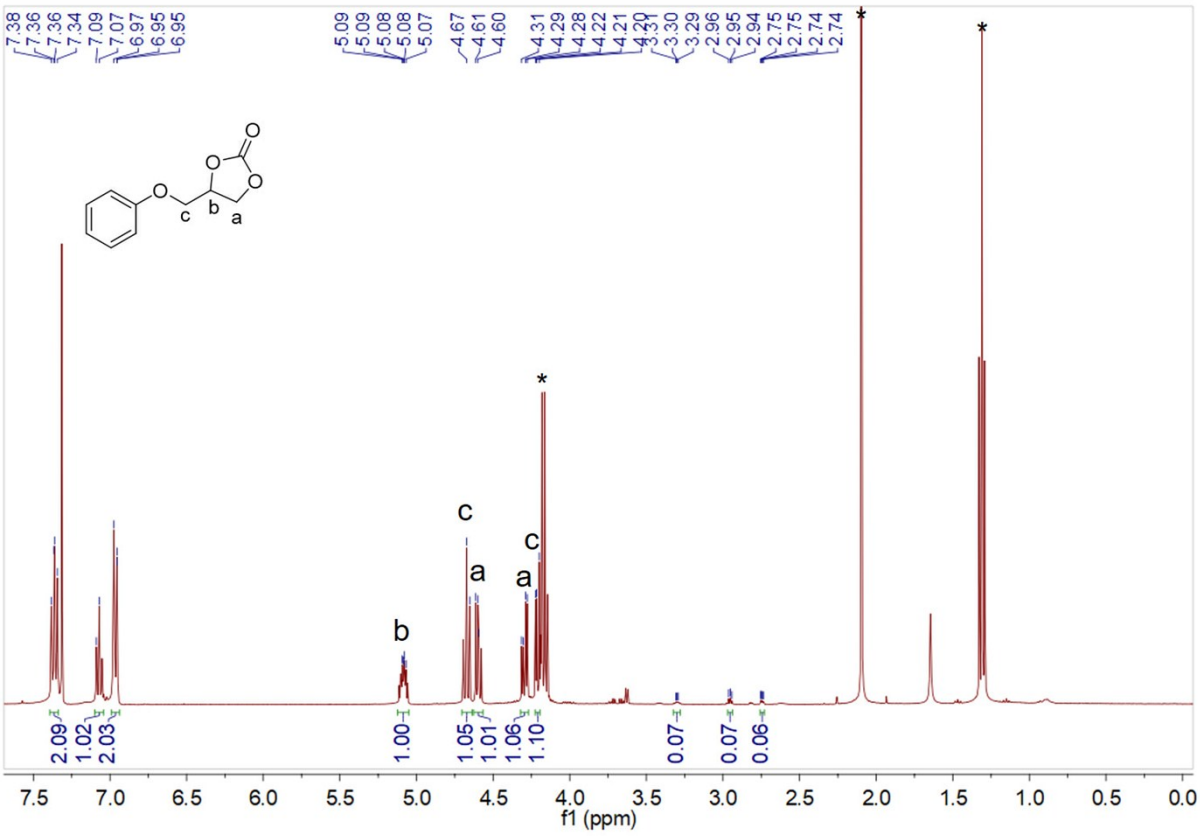

Fig. S11 ^{1}H NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=7.36 (2H, CH), 7.08 (1H, CH), 6.99–6.94 (2H, CH), 5.12-5.05 (1H, CH), 4.66 (1H, CH_2), 4.63-4.57 (1H, CH_2), 4.30 (1H, CH_2), 4.23-4.19 (1H , CH_2).

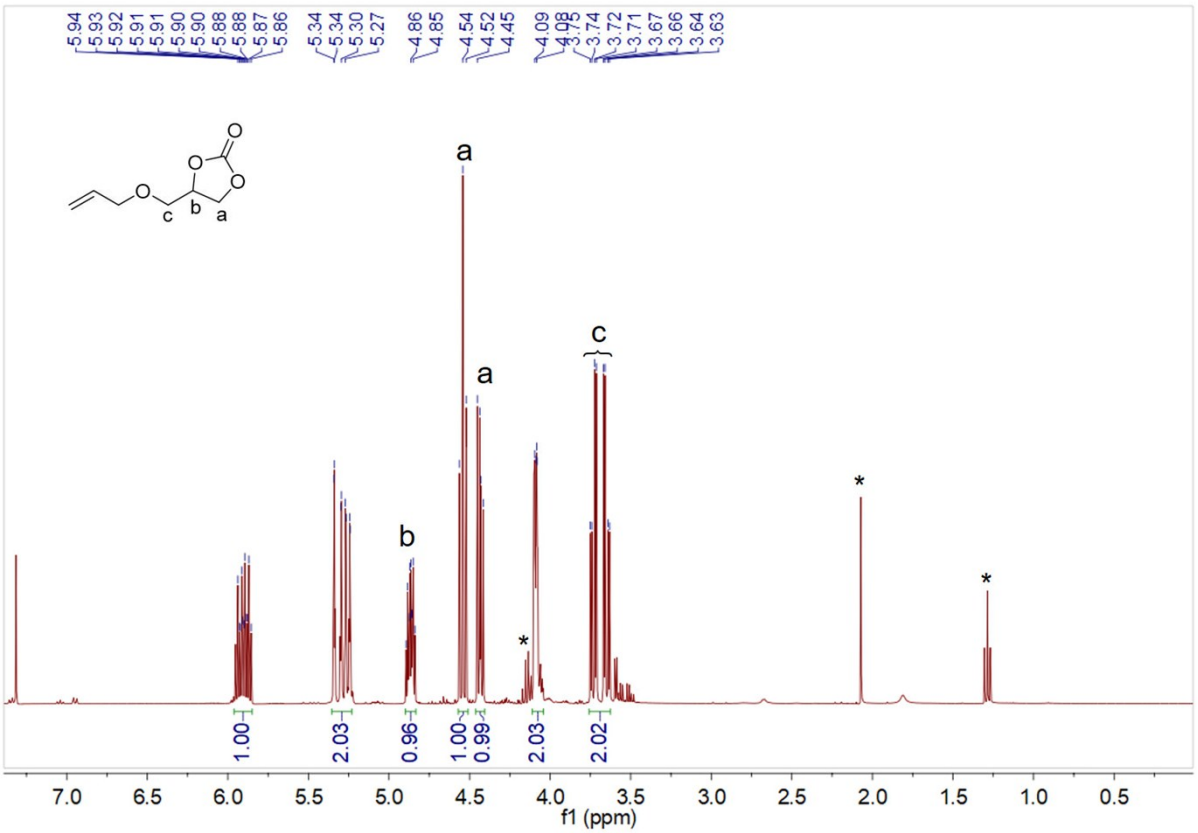

Fig. S12 ^{1}H NMR spectrum of allyloxymethyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=5.96-5.85 (1H, CH), 5.36–5.23 (2H, CH_2), 4.90– 4.83 (1H, CH), 4.54 (1H, CH_2), 4.43 (1H, CH_2), 4.09 (2H, CH_2), 3.69 (2H, CH_2)

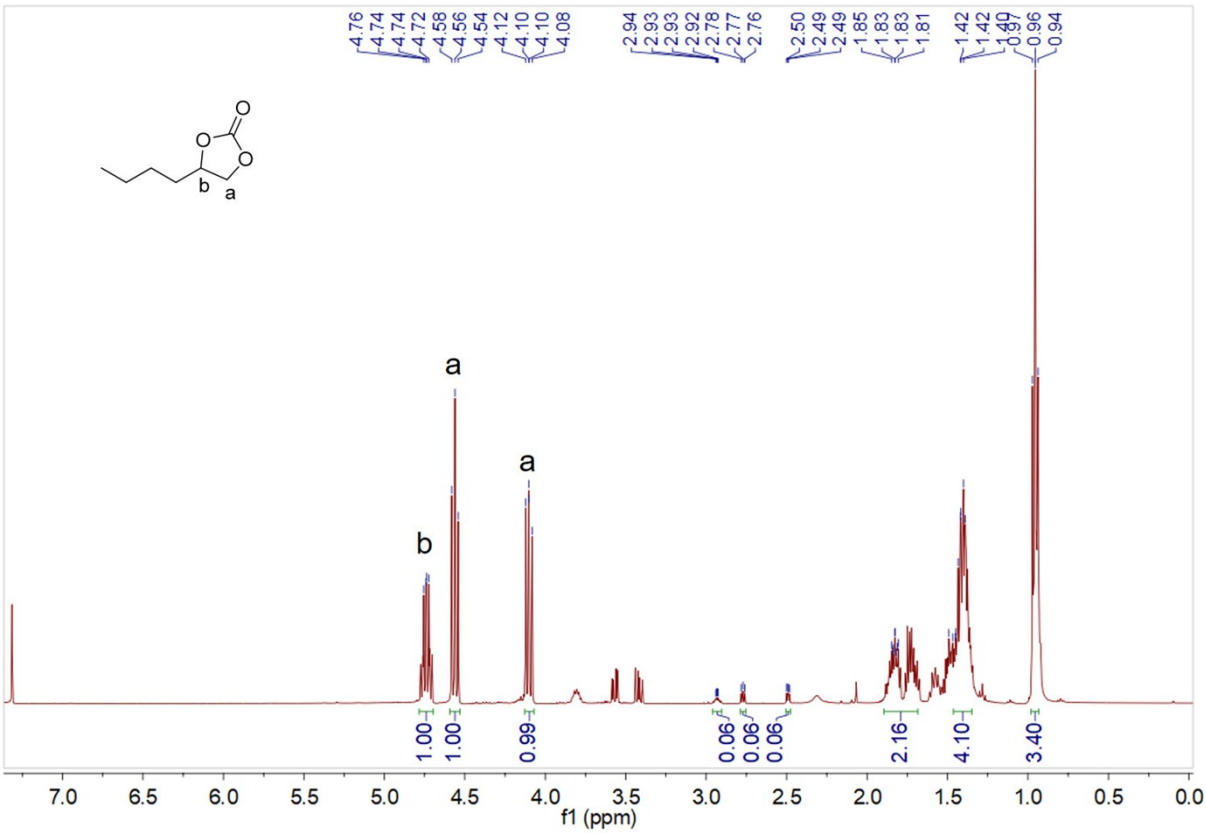

Fig. S13 ^{1}H NMR spectrum of 4-butyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.74 (1H, CH_2), 4.56 (1H, CH_2), 4.10 (1H, CH_2), 1.83 (2H, CH_2), 1.42 (4H, CH_2), 0.95 (3H, CH_3).

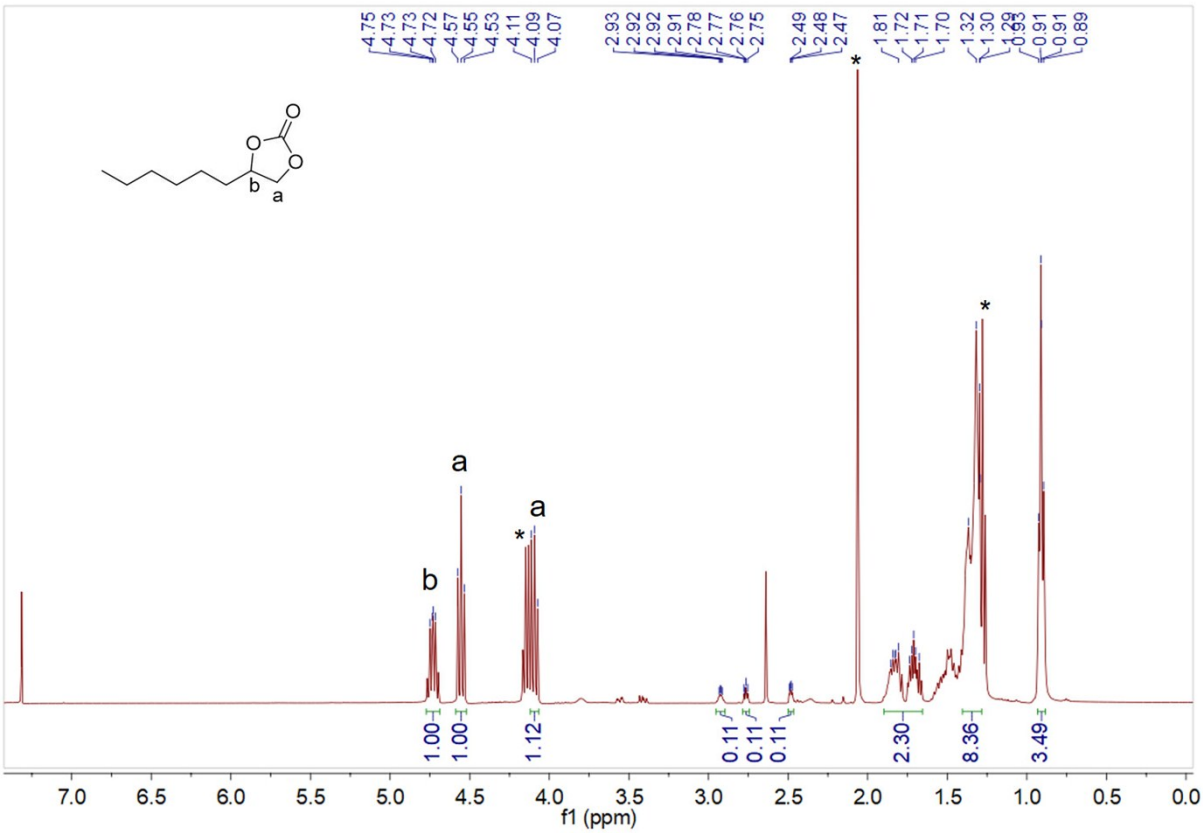

Fig. S14 ^{1}H NMR spectrum of 4-hexyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.73 (1H, CH_2), 4.55 (1H, CH_2), 4.12-4.07(1H, CH_2), 1.90-1.66 (2H, CH_2), 1.33 (8H, CH_2), 0.91 (3H, CH_3).

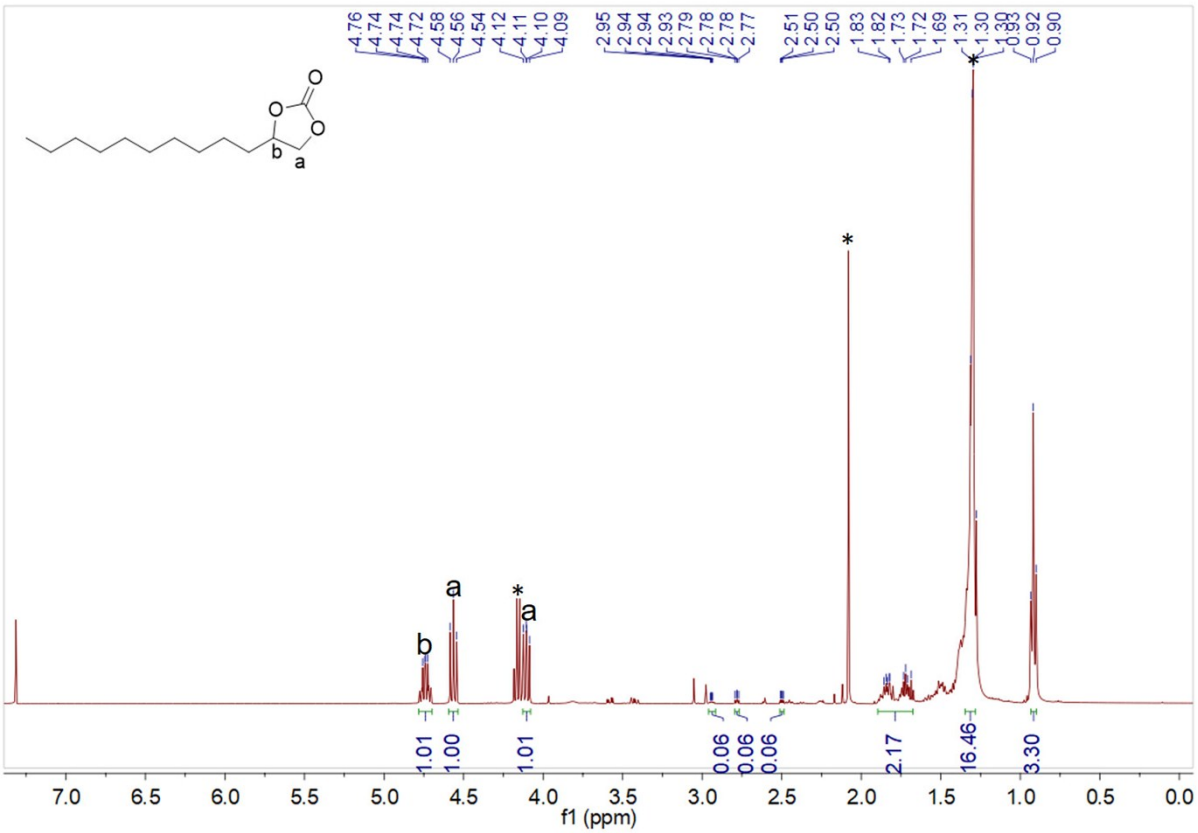

Fig. S15 ^{1}H NMR spectrum of 4-decyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.74 (1H, CH_2), 4.56 (1H, CH_2), 4.10 (1H, CH_2), 1.90-1.68 (2H, CH_2), 1.35-1.28 (16H, CH_2), 0.91 (3H, CH_3).

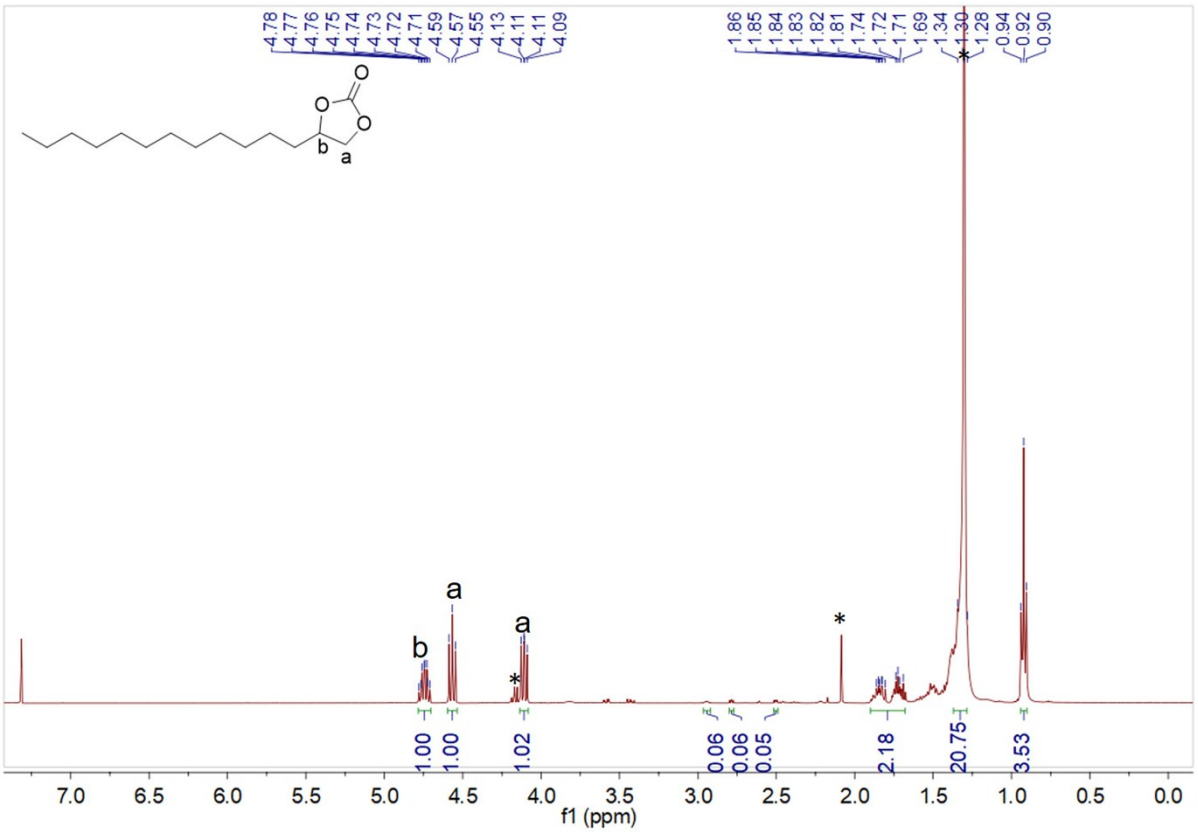

Fig. S16 ^{1}H NMR spectrum of 4-dodecyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.74 (1H, CH_2), 4.57 (1H, CH_2), 4.11 (1H, CH_2), 1.90-1.68 (2H, CH_2), 1.32 (16H, CH_2), 0.92 (3H, CH_3).

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