

## **Electronic Supplementary Information**

### **One-pot synthesis of conjugated vinylene-extended viologen ionic radical polyacetylenes for visible-light-promoted photocatalytic CO<sub>2</sub> cycloaddition**

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## Experimental

### Materials

1,2-bis(4-pyridyl)ethylene (98%, Bide), 4,4'-bipyridine (98%, Adamas), propargyl bromide (80 wt% in xylene, Aladdin),  $K_2CO_3$ , epoxides, common solvents and reagents were commercially available and used without further purification.

### Methods

Solid-state  $^{13}C$  cross-polarization/magic angle rotation (CP/MAS) NMR spectra were obtained on a Bruker AVANCE III 600 spectrometer. The CHN elemental analysis was conducted on an elemental analyzer Vario EL cube. The chemical compositions and states of polymers were confirmed by the X-ray photoelectron spectroscopy (XPS, thermal scale table 250Xi). Electron paramagnetic resonance (EPR) spectra were recorded on an EMX-10/12 spectrometer on a Bruker at room temperature. Fourier transform infrared spectroscopy (FTIR) was recorded on a Bruker Vertex 80V FTIR instrument (KBr discs) in the region  $4000-400\text{ cm}^{-1}$ . Thermogravimetric analysis (TGA) was carried out with a TA Q50 instrument in a nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  and samples were dried in vacuum at  $100\text{ }^\circ\text{C}$  for 12 h before measurement. The solid ultraviolet-visible-near-infrared absorption diffuse reflectance spectroscopy (UV-vis-NIR) was measured with a SHIMADZU UV-2600 spectrophotometer. X-ray diffraction (XRD) patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu Ka radiation source at 40 kV and 20 mA, from  $5$  to  $80^\circ$  with a scan rate of  $0.2^\circ\text{ s}^{-1}$ . The field emission scanning electron microscopy (FESEM, Hitachi SU8010) was used to observe the morphology.  $N_2$  adsorption-desorption isotherms were measured at 77 K using a Quantachrome autosorb iQ2 analyzer, and the surface areas of samples were calculated using the Brunauer-Emmett-Teller (BET) method and the pore size distributions were determined by the nonlocalized density functional theory (NLDFT) model, while the samples were degassed at  $150\text{ }^\circ\text{C}$  for 12 h in a high vacuum before analysis.

### Photoelectrochemical measurements

The photoelectrochemical measurement was performed by the CHI 660E electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) in a standard three-electrode system with the Ag/AgCl reference electrode, Pt wire counter electrode and  $1 \times 1\text{ cm}^2$  modified indium tin oxide (ITO) as a working electrode. The slurry was prepared by ultrasonically dispersing 5 mg of catalyst into 0.5 mL ethanol, it was drip-coated on the ITO photoelectrode with a fixed area of  $1.0\text{ cm}^2$  and dried under room temperature to get catalyst-modified ITO

photoelectrode. The photoelectrochemical experiment was carried out in 0.1 M phosphate buffer solution (PBS, pH 7.4) containing ascorbic acid (AA, 0.1 mM) as the electron donor in the investigation. The xenon lamp produced the white light as the excitation source, with a spectral range of 200-2500 nm wavelength, and the light source was switched on and off after every 10 s.

### Synthesis of conjugated vinylene-extended viologen ionic radical polyacetylenes

The vinylene-extended viologen ionic radical polyacetylene VIRP-1 was prepared by the quaternization-induced spontaneous polymerization (QISP) reaction between 1,2-bis(4-pyridyl)ethylene (BPE) and propargyl bromide (PGB), as shown in the Scheme 1. In detail, BPE (1 mmol, 0.1822 g) and PGB (2.5 mmol, 0.2974 g) were dissolved in the solvent of CH<sub>3</sub>CN (10 mL). Then, the mixture was transferred into a 25 mL Teflon-lined autoclave. Next, the Teflon-lined autoclave was statically placed in a constant temperature oven at 100 °C for 24 h. After reaction, the solid product was recovered by filtration and thoroughly washed with deionized water (H<sub>2</sub>O), tetrahydrofuran (THF) and ethanol. The black powder VIRP-1 with a high yield of ~100% was obtained by drying in vacuum at 80 °C for 12 h. Elemental analysis found for VIRP-1: C, 43.25; H, 4.43; N, 5.38 wt%. Theoretical calcd. value for VIRP-1 based on the stoichiometric structure ( $n(\text{BPE}):n(\text{PGB})=1:2$ ) with some absorbed H<sub>2</sub>O molecules ( $(\text{C}_{18}\text{H}_{16}\text{N}_2\text{Br}_2 \cdot 4\text{H}_2\text{O})_n$ ): C, 43.92; H, 4.91; N, 5.69 wt%.

Further, the viologen ionic radical polyacetylene VIRP-2 was prepared by the K<sub>2</sub>CO<sub>3</sub>-involved QISP reaction. The used of the reducing agent inorganic base K<sub>2</sub>CO<sub>3</sub> can promote the formation of more viologen cationic radicals by one-electron reduction, and affords enriched CO<sub>3</sub><sup>2-</sup> anions within VIRP-2 by the anion exchange with Br<sup>-</sup> anions. In detail, the raw materials BPE (1 mmol, 0.1822 g) and PGB (2.5 mmol, 0.2974 g) were dissolved in the solvent of CH<sub>3</sub>CN (10 mL), and then K<sub>2</sub>CO<sub>3</sub> (4 mmol, 0.5528 g) was added into the mixture solution and stirred thoroughly on a magnetic stirrer for 30 min. Subsequently, the above mixture solution was moved into a 25 mL Teflon-lined autoclave. The autoclave was taken placed in a constant temperature oven at 100 °C for 24 h. After reaction, the solid products were recovered by filtration and thoroughly washed with H<sub>2</sub>O, THF and ethanol. Finally, the black solid VIRP-2 with a yield of 65% was obtained by drying in vacuum at 80 °C for 12 h. Elemental analysis found for VIRP-2: C, 63.73; H, 5.39; N, 8.67 wt%. Theoretical calcd. value for VIRP-2 based on the stoichiometric structure ( $n(\text{BPE}):n(\text{PGB})=1:2$ ) with CO<sub>3</sub><sup>2-</sup> anions and some absorbed H<sub>2</sub>O molecules ( $(\text{C}_{18}\text{H}_{16}\text{N}_2 \cdot 0.5\text{CO}_3^{2-} \cdot 3\text{H}_2\text{O})_n$ ): C, 64.52; H, 6.43; N, 8.13 wt%. Besides, the control conjugated viologen ionic radical polyacetylene VIRP-3 without vinylene linkers was also prepared using a similar reaction process by replacing BPE with 4,4'-bipyridine in term of a black solid with yield of 46%, as shown in Scheme S1.

### **Synthesis of the control BPE-based ionic liquid monomer (BPE-IL)**

The control ethyl-tethered 1,2-bis(4-pyridyl)ethylene (BPE)-based ionic liquid monomer (named as BPE-IL) was prepared by the quaternization reaction of BPE and bromoethane as shown in Scheme S2. First, the raw materials BPE (0.5 mmol, 0.0911 g) and bromoethane (1.5 mmol, 0.2818 g) were dissolved in the solvent of CH<sub>3</sub>CN (10 mL), and then the mixture was added into a 25 mL Teflon-lined autoclave with stirred for 30 minutes at room temperature. Subsequently, the reaction was taken place at 100 °C in a constant temperature oven for 48 h. After reaction, the obtained brown solid was dispersed into ethyl acetate (20 mL) with stirring for 2 h. At last, the above suspension was filtrated, washed with ethyl acetate for several times, and dried at 80 °C for 12 h in vacuum to give a brown powder solid (BPE-IL) with a yield of 75%. BPE-IL: <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) (Fig. S1):  $\delta$ =9.20~9.18 (CH, 4H), 8.42~8.40 (CH, 4H), 8.25 (CH, 2H), 4.66~4.61 (CH<sub>2</sub>, 4H) and 1.58~1.54 ppm (CH<sub>3</sub>, 6H).

### **Photocatalytic CO<sub>2</sub> cycloaddition reaction**

The photocatalytic CO<sub>2</sub> cycloaddition reactions with epoxides into cyclic carbonates were carried out in a 25 mL Schlenk tube with a magnetic stirrer. In a typical reaction, the epoxide (1 mmol) and VIRP-2 (30 mg) were placed in a 25 mL Schlenk tube connected with a CO<sub>2</sub> balloon (0.1 MPa). Meanwhile, the mixture was irradiated by blue LEDs lamp (8 W) for a desired time. After reaction, 3 mL of ethyl acetate was added into the reaction system and stirred for 30 min. The solid catalyst was separated by centrifugation and the remaining solution was obtained by concentration under a low temperature reduced pressure. Finally, the crude products were directly analyzed by the <sup>1</sup>H NMR spectroscopy to determine the yields of cyclic carbonates by comparison of the integrals of characteristic protons in the substrate and product. For the catalyst recycling experiments, the solid catalyst VIRP-2 was collected by centrifugation, washed with ethanol several time and dried in vacuum and then used for the next run. The reusability of the catalyst VIRP-2 was tested in five-run cycling experiments.

**Table S1** The solubility of a series of VIRPs solid materials.\*

| Samples | Polymer yield (%) | H <sub>2</sub> O (RT) | H <sub>2</sub> O (80 °C) | DMSO (RT) | DMSO (80 °C)     |
|---------|-------------------|-----------------------|--------------------------|-----------|------------------|
| VIRP-1  | 100               | ×                     | ×                        | ×         | ×                |
| VIRP-2  | 65                | ×                     | ×                        | ×         | Slightly soluble |
| VIRP-3  | 46                | ×                     | ×                        | ×         | Slightly soluble |

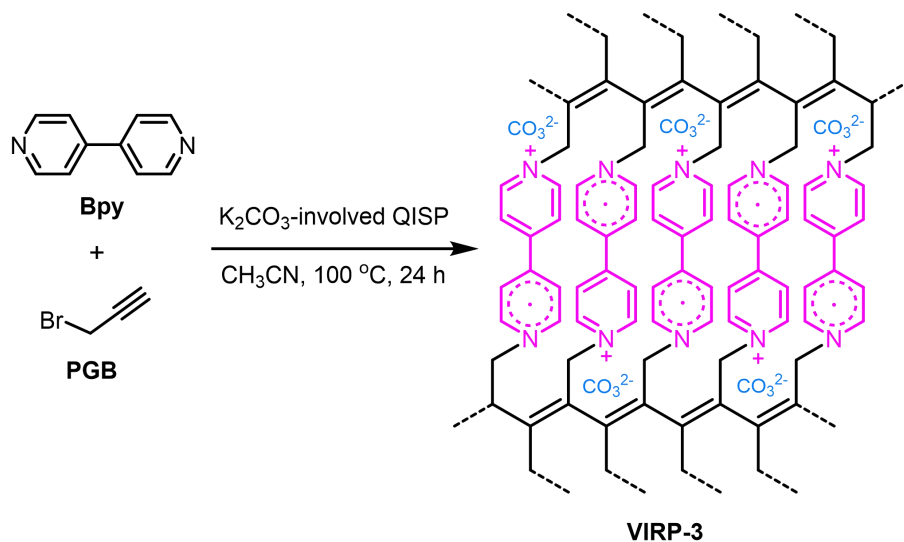
\* The solubility tests were carried out by placing 10 mg the back polymer in 5 mL water or DMSO at room temperature (RT) or 80 °C with stirred for 30 min. The results for the solubility of VIRPs were together determined by the color of solutions and the mass of the remaining solid polymers after centrifugation.

“×” represents insoluble.

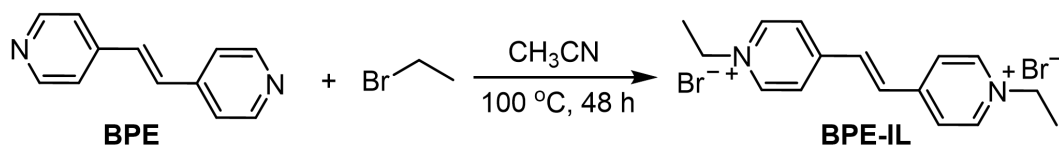
**Table S2** The elemental compositions of VIRP-1 and VIRP-2 detected from the XPS spectra.<sup>a</sup>

| Samples | C (at%) | N (at%) | O (at%) | Br (at%) |
|---------|---------|---------|---------|----------|
| VIRP-1  | 79.01   | 7.58    | 6.28    | 7.14     |
| VIRP-2  | 79.50   | 7.92    | 11.53   | 1.05     |

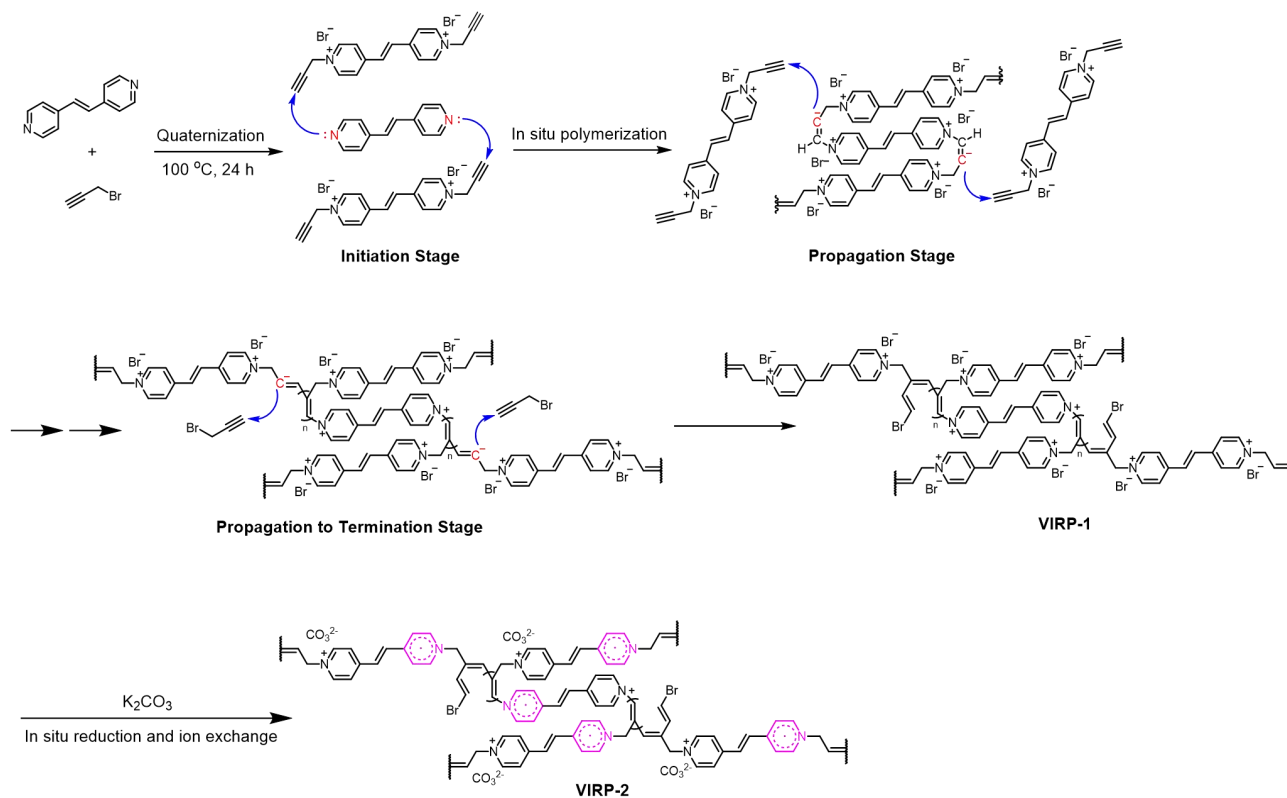
<sup>[a]</sup> All the elemental compositions were presented by the atomic concentration (at%) from the XPS survey spectra.



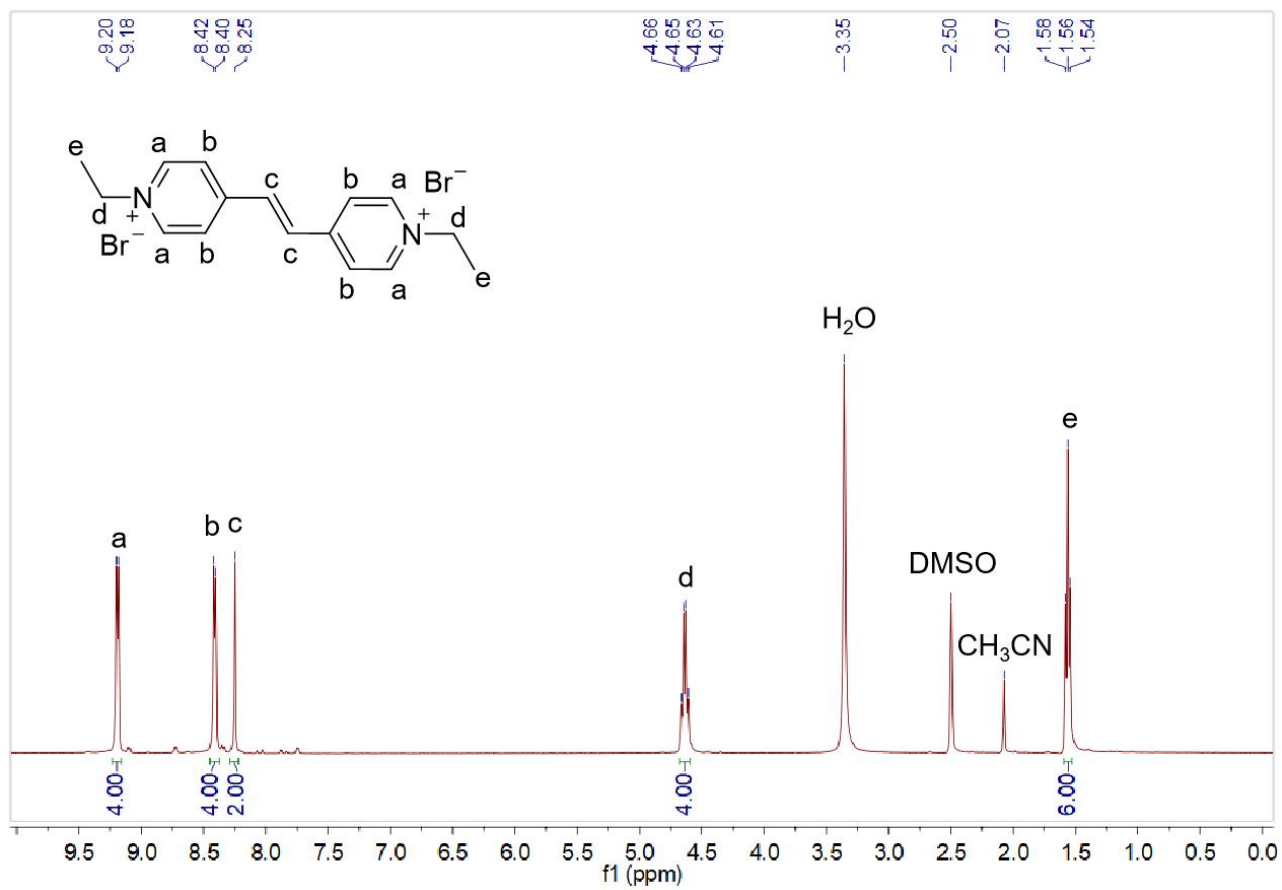
**Scheme S1** *In situ* synthesis of the conjugated viologen ionic radical polyacetylene (VIRP-3) by  $K_2CO_3$ -involved quaternization-induced spontaneous polymerization (QISP) reaction between 4,4'-bipyridine (Bpy) and propargyl bromide (PGB) in  $CH_3CN$  at 100 °C for 24 h.



**Scheme S2** Synthesis of the ethyl-tethered 1,2-bis(4-pyridyl)ethylene-based ionic liquid monomer (BPE-IL) by the quaternization reaction in  $CH_3CN$  at 100 °C for 48 h.



**Scheme S3** A proposed polymerization mechanism for the synthesis of VIRP-1 and VIRP-2.



**Fig. S1**  $^1\text{H}$  NMR of BPE-IL in the solvent of  $\text{DMSO-d}_6$ .



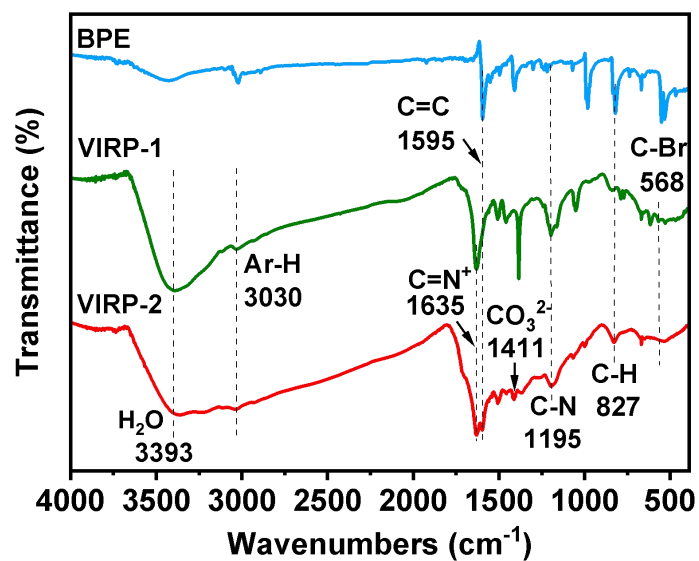


Fig. S2 FTIR spectra of BPE, VIRP-1 and VIRP-2.

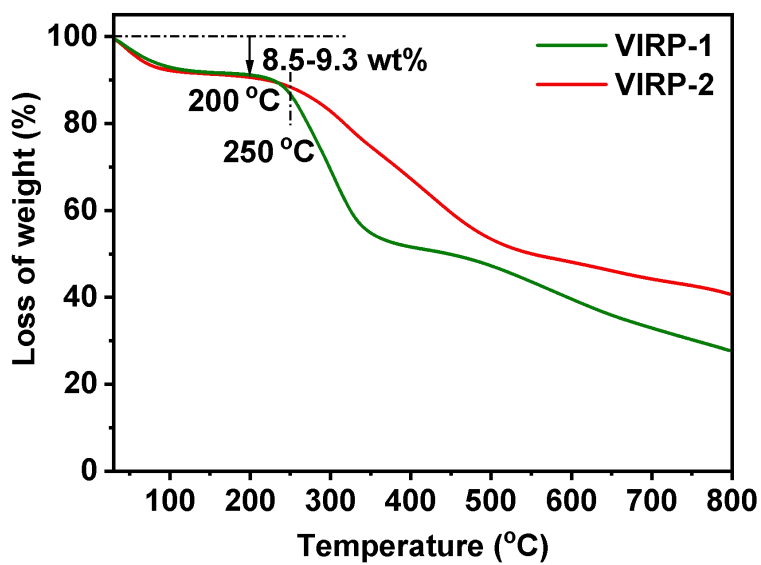


Fig. S3 Thermogravimetric analysis (TGA) curves of VIRP-1 and VIRP-2.



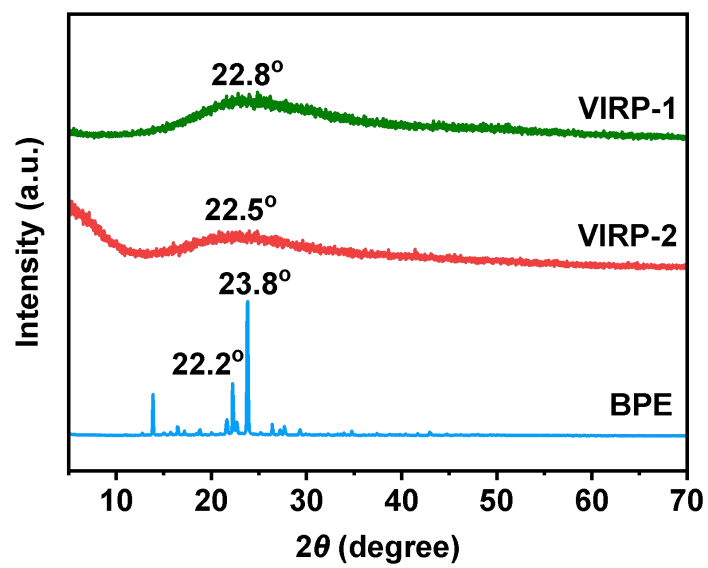


Fig. S6 XRD patterns of VIRP-1, VIRP-2 and BPE.

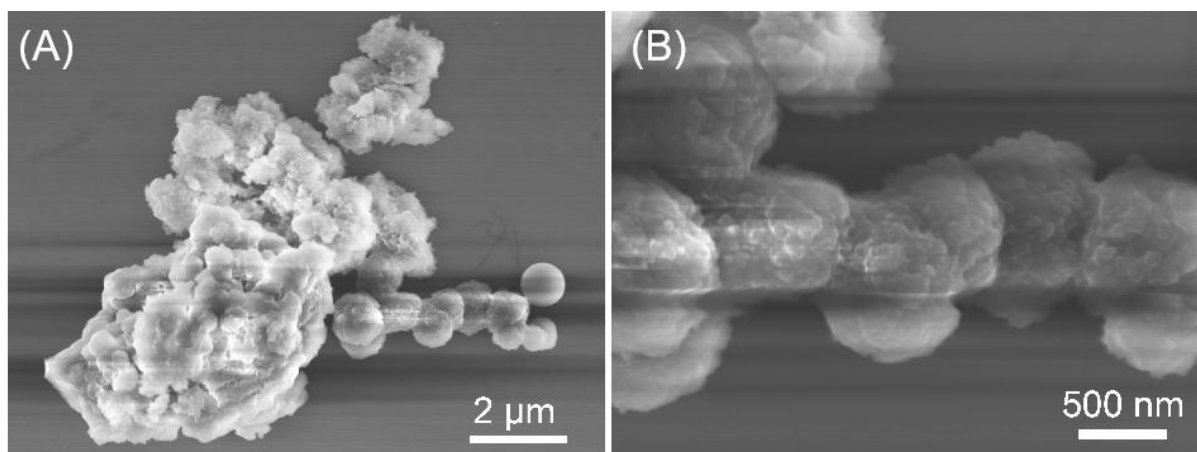
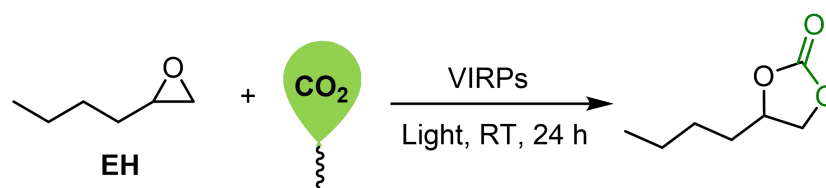
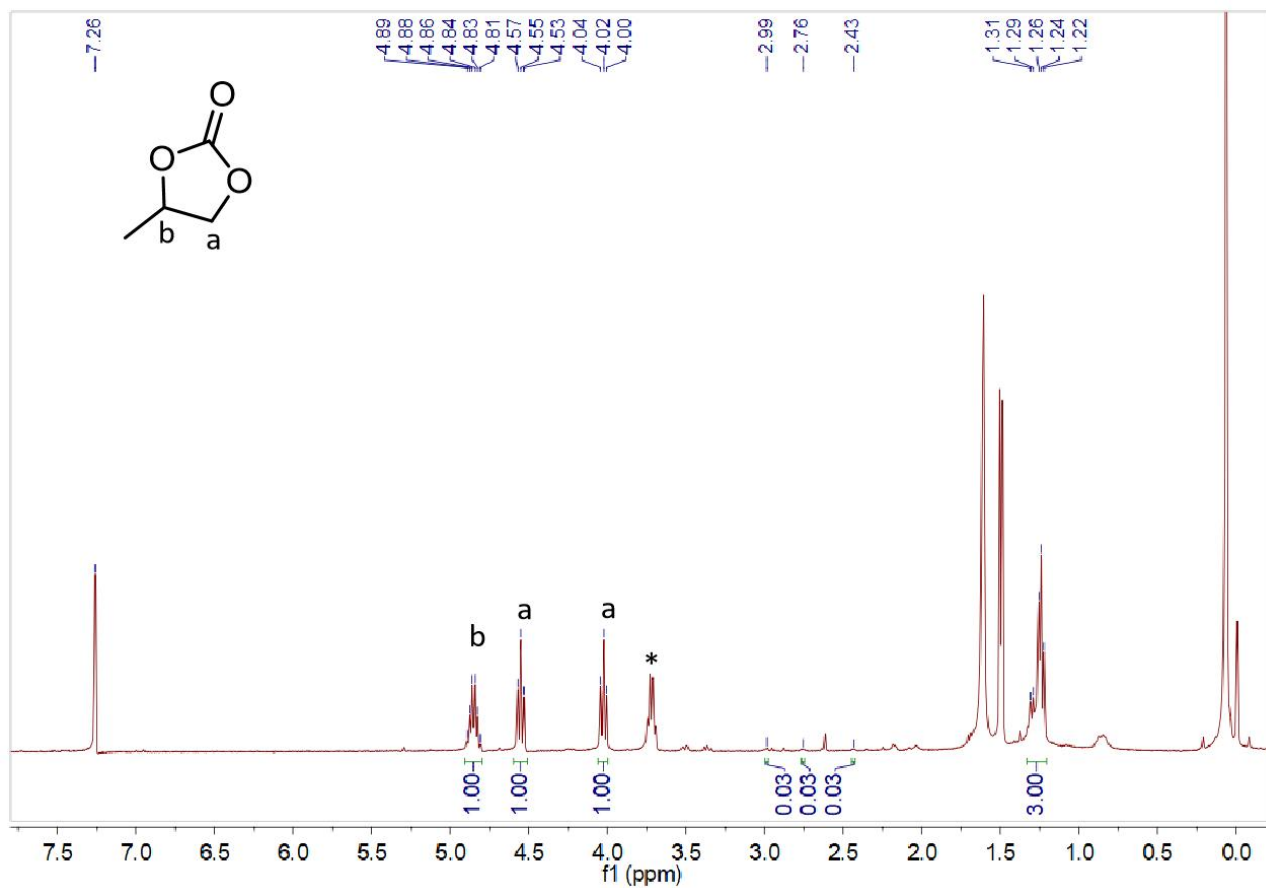


Fig. S7 (A, B) SEM images of the polymer VIRP-2.

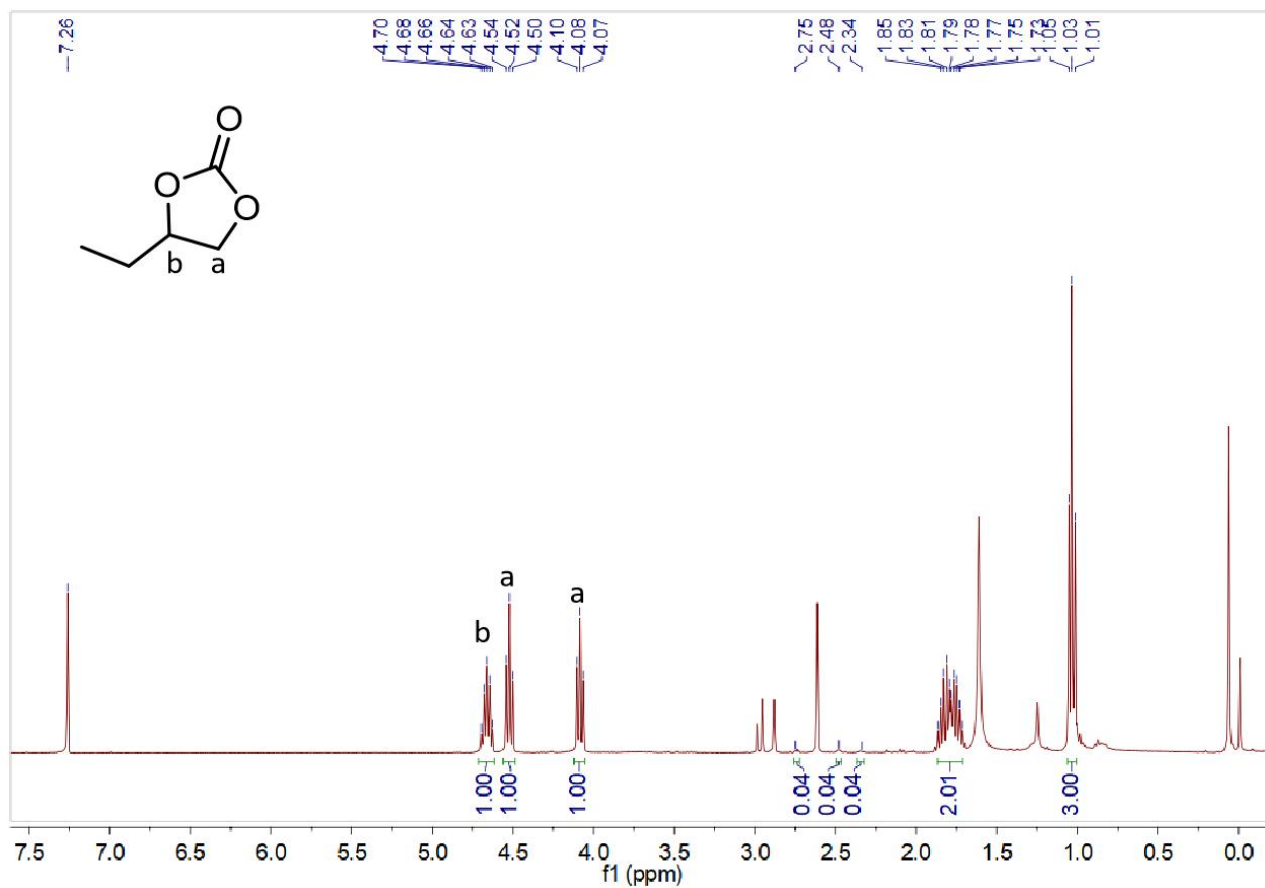
**Table S3** Photocatalytic CO<sub>2</sub> cycloaddition with 1,2-epoxyhexane over different catalysts.<sup>a</sup>

| Entry | Catalysts                                   | Light sources      | Yield (%) <sup>c</sup> | Selectivity (%) <sup>c</sup> |
|-------|---|--------------------|------------------------|------------------------------|
| 1     | VIRP-1                                      | Blue LEDs          | 17                     | 99                           |
| 2     | VIRP-2                                      | Blue LEDs          | 69                     | 99                           |
| 3     | VIRP-3                                      | Blue LEDs          | 51                     | 99                           |
| 4     | VIRP-1                                      | Room natural light | 6                      | 99                           |
| 5     | VIRP-2                                      | Room natural light | 35                     | 99                           |
| 6     | VIRP-3                                      | Room natural light | 34                     | 99                           |
| 7     | VIRP-2                                      | In dark            | 12                     | 99                           |
| 8     | BPE-IL <sup>b</sup>                         | Blue LEDs          | trace                  | -                            |
| 9     | BPE <sup>b</sup>                            | Blue LEDs          | trace                  | -                            |
| 10    | K <sub>2</sub> CO <sub>3</sub> <sup>b</sup> | Blue LEDs          | trace                  | -                            |

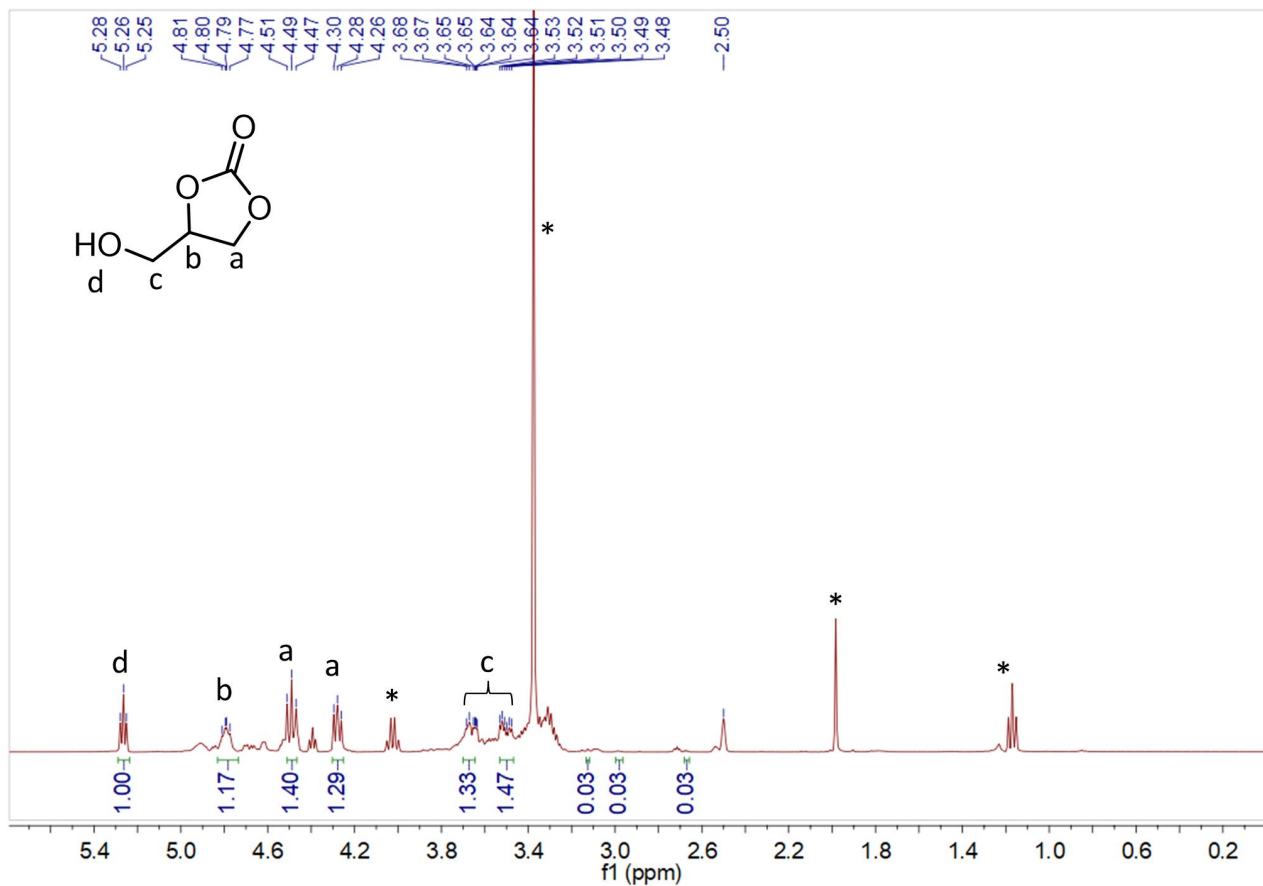
<sup>[a]</sup> Reaction conditions: 1,2-epoxyhexane (1 mmol), CO<sub>2</sub> balloon (0.1 MPa), the catalyst (30 mg, 5 mol% based on the BPE content), blue LEDs (8 W), at room temperature (RT) for 24 h. <sup>[b]</sup> The dosages of BPE-IL, BPE and K<sub>2</sub>CO<sub>3</sub> were 14, 17 and 6 mg based on the BPE content (3.10 mmol g<sup>-1</sup>) in VIRP-2. <sup>[c]</sup> Yield and selectivity of the product were determined from <sup>1</sup>H NMR spectra.



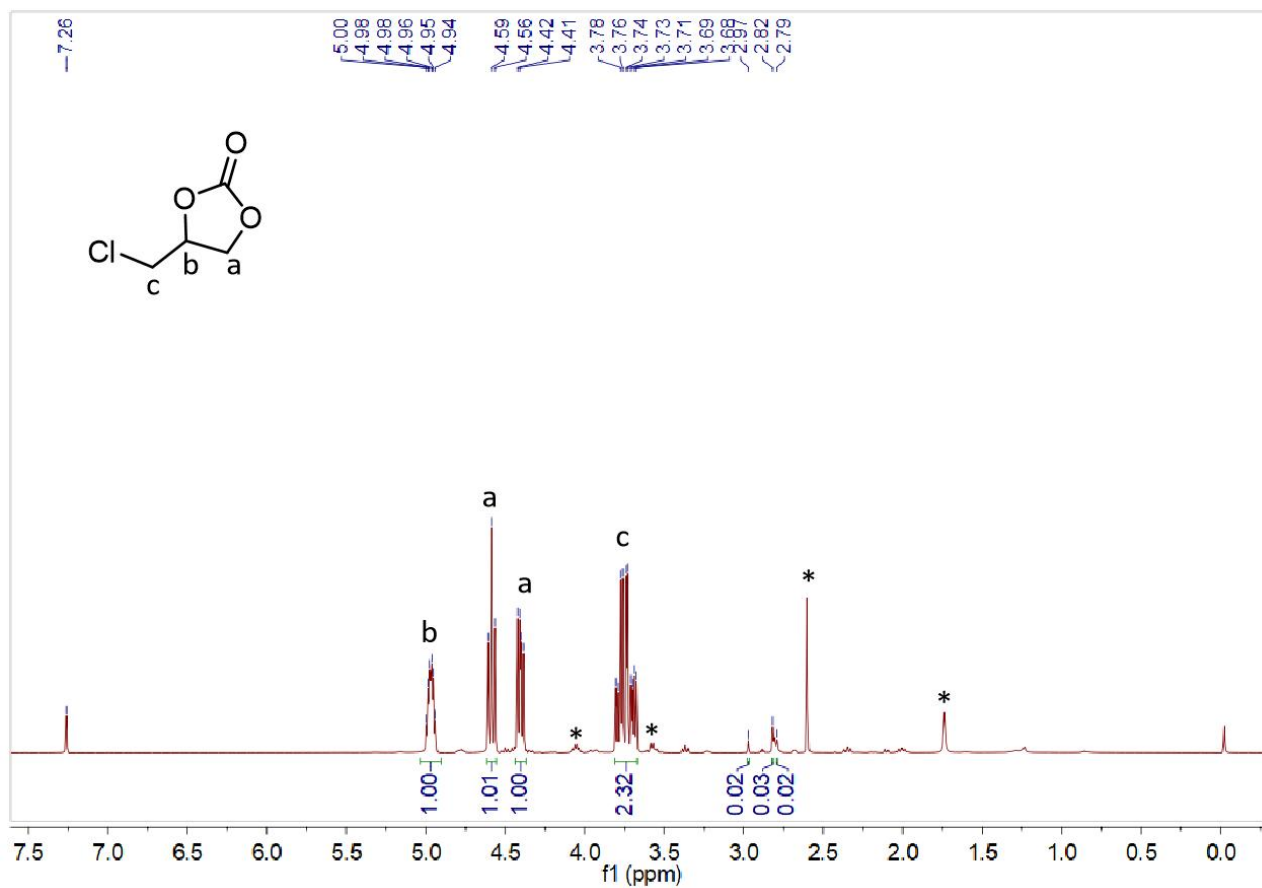
**Fig. S8** <sup>1</sup>H NMR spectrum of 4-methyl-1,3-dioxolan-2-one (400 MHz, CDCl<sub>3</sub>):  $\delta$ =4.89~4.81 (1H, CH), 4.57~4.53 (1H, CH<sub>2</sub>), 4.04~4.00 (1H, CH<sub>2</sub>) and 1.31~1.22 ppm (3H, CH<sub>3</sub>). \* represents the residual solvent THF from the catalyst. Reaction conditions: blue LEDs (8 W), room temperature, 24 h, yield of 97%.



**Fig. S9** <sup>1</sup>H NMR spectrum of 4-ethyl-1,3-dioxolan-2-one (400 MHz, CDCl<sub>3</sub>):  $\delta$ =4.70~4.63 (1H, CH<sub>2</sub>), 4.54~4.50 (1H, CH<sub>2</sub>), 4.10~4.07 (1H, CH<sub>2</sub>), 1.85~1.73 (2H, CH<sub>2</sub>) and 1.05~1.021 ppm (3H, CH<sub>3</sub>). Reaction conditions: blue LEDs (8 W), room temperature, 24 h, yield of 96%.

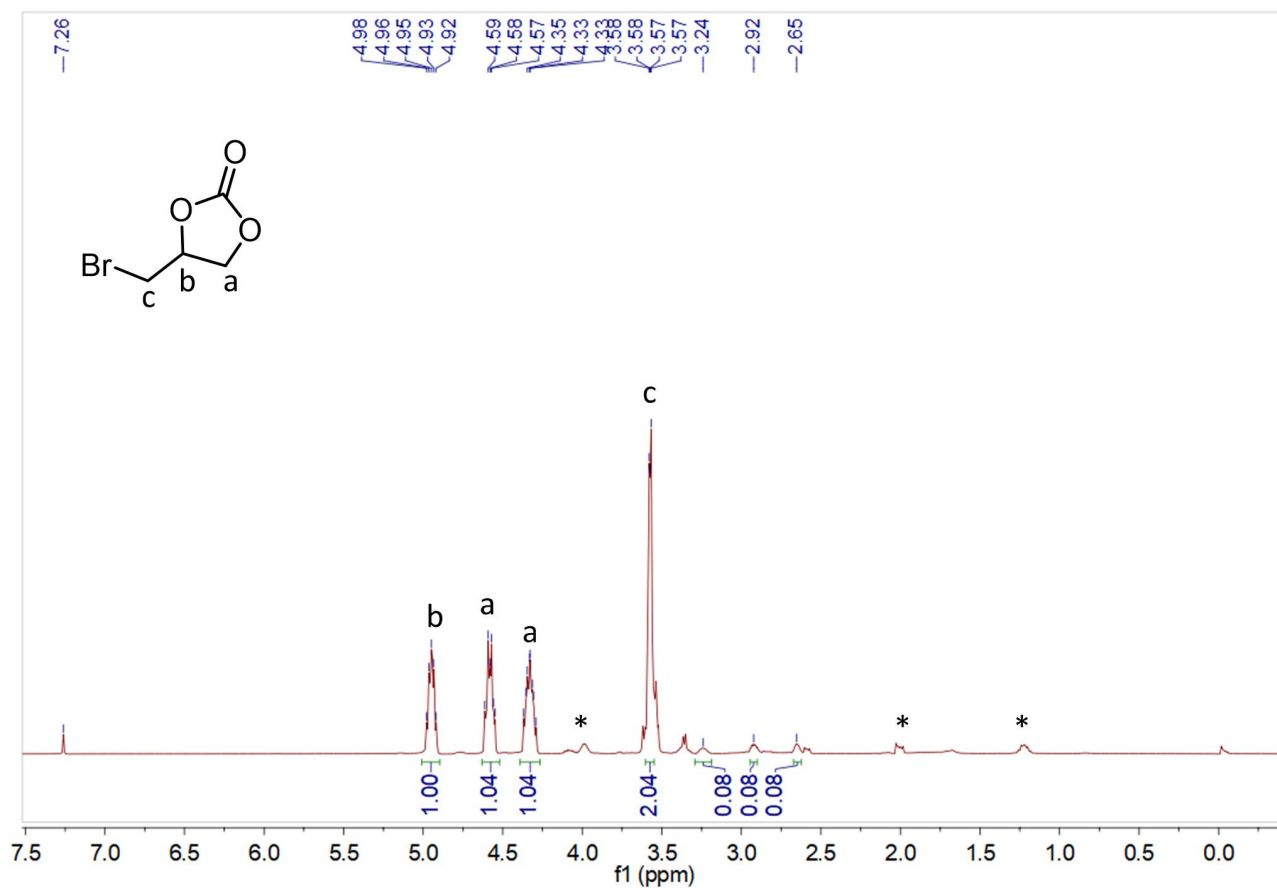


**Fig. S10** <sup>1</sup>H NMR spectrum of 4-(hydroxymethyl)-1,3-dioxolan-2-one (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ =5.28~5.25 (1H, OH), 4.81~4.79 (1H, OCH), 4.51~4.47 (1H, CH<sub>2</sub>O), 4.30~4.26 (1H, CH<sub>2</sub>O), 3.68~3.64 (1H, CH<sub>2</sub>OH) and 3.53~3.48 ppm (1H, CH<sub>2</sub>OH). \* represents the residual solvent ethyl acetate and water. Reaction conditions: blue LEDs (8 W), room temperature, 24 h, yield of 97%.

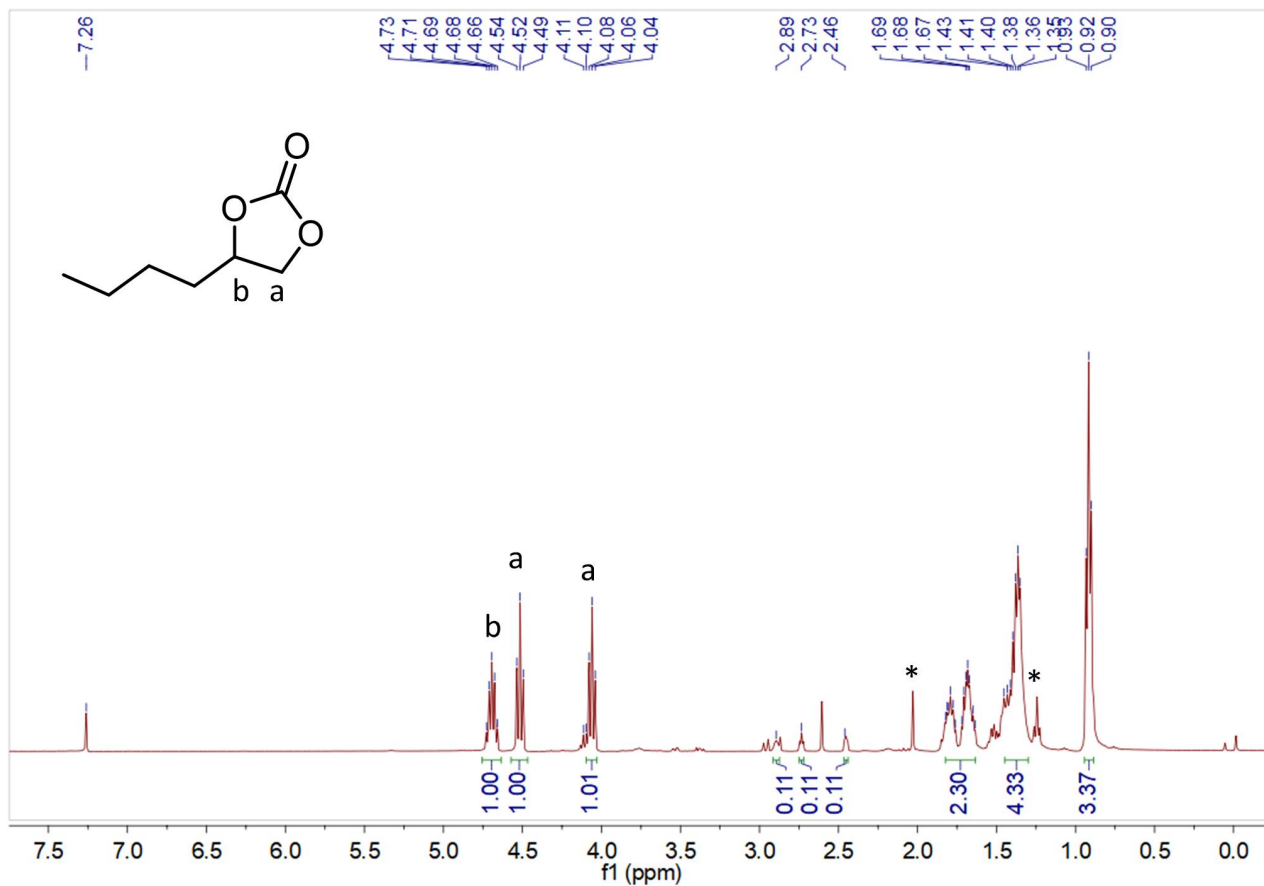


**Fig. S11** <sup>1</sup>H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (400 MHz, CDCl<sub>3</sub>):  $\delta$ =5.00~4.94 (1H, CH), 4.59~4.56 (1H, CH<sub>2</sub>), 4.42~4.41 (1H, CH<sub>2</sub>) and 3.78~3.68 ppm (2H, CH<sub>2</sub>). \* represents the residual solvent ethyl acetate. Reaction conditions: blue LEDs (8 W), room temperature, 24 h, yield of 98%.





**Fig. S12**  $^1\text{H}$  NMR spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =4.98~4.92 (1H, CH), 4.59~4.57 (1H,  $\text{CH}_2$ ), 4.35~4.33 (1H,  $\text{CH}_2$ ) and 3.58~3.57 ppm (2H,  $\text{CH}_2$ ). \* represents the residual solvent ethyl acetate. Reaction conditions: blue LEDs (8 W), room temperature, 24 h, yield of 93%.



**Fig. S13** <sup>1</sup>H NMR spectrum of 4-butyl-1,3-dioxolan-2-one (400 MHz, CDCl<sub>3</sub>):  $\delta$ =4.73~4.66 (1H, CH<sub>2</sub>), 4.54~4.49 (1H, CH<sub>2</sub>), 4.11~4.04 (1H, CH<sub>2</sub>), 1.69~1.67 (2H, CH<sub>2</sub>), 1.43~1.35 (4H, CH<sub>2</sub>) and 0.93~0.90 ppm (3H, CH<sub>3</sub>). \* represents the residual solvent ethyl acetate. Reaction conditions: blue LEDs (8 W), room temperature, 48 h, yield of 90%.

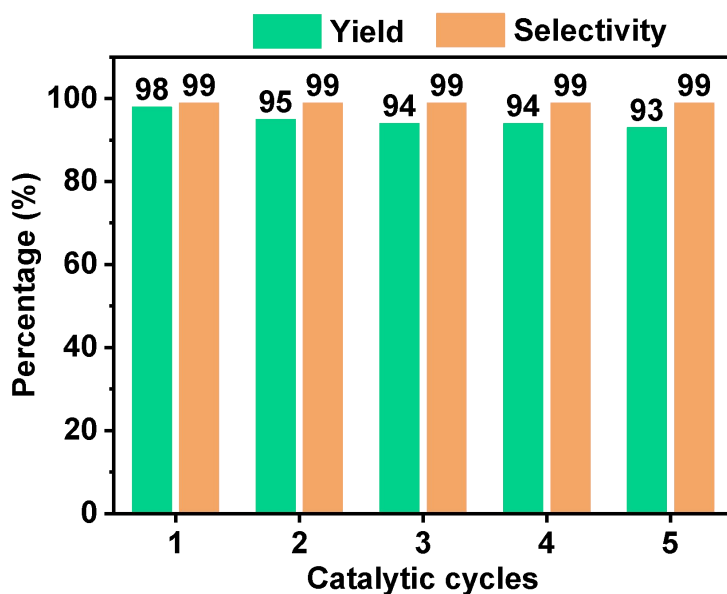
**Table S4** Comparisons of catalytic performances in the photocatalytic CO<sub>2</sub> cycloaddition with epoxides over different metal/metal-free heterogeneous catalysts combined with the cocatalyst TBAB.

| Entry | Catalysts                                 | Reaction conditions  | Yield (%) | Ref. |
|-------|---|--|-----------|------|
| 1     | MOF1                                      | Epichlorohydrin (10 mmol), catalyst (cat. 0.5 mol%), TBAB (2.5 mol%), CO <sub>2</sub> (0.1 MPa), room temperature (RT), LED light (18 × 3 W), 24 h | 100       | S1   |
| 2     | PCN-224(Mg)                               | Epichlorohydrin (20 mmol), cat. (0.025 mol%), TBAB (1 mol%), CO <sub>2</sub> (1 atm), RT, LED light (3 × 30 W), 6 h                                | 99        | S2   |
| 3     | SNNU-97-InV                               | Epichlorohydrin (20 mmol), cat. (0.12 mol%), TBAB (3 mol%), CO <sub>2</sub> (0.8 MPa), RT, 300W Xe lamp, 24 h                                      | 94.9      | S3   |
| 4     | IHEP-9                                    | Epichlorohydrin (1 mmol), cat. (0.5 mol%), TBAB (5 mol%), CO <sub>2</sub> (0.1 MPa), RT, 6500 K compact fluorescent lamp (45 W), RT, 12 h          | 99        | S4   |
| 5     | Bi-PCN-224                                | 1,2-Epoxypropane (4.5 mmol), cat. (30 mg), TBAB (0.5 mmol), CO <sub>2</sub> (1 bar), RT, 300 W xenon lamp, 6 h                                     | 99        | S5   |
| 6     | Mg-MOF-74                                 | Epibromohydrin (0.58 mmol), cat. (10 mg), TBAB (0.06 mmol), DMF (2 mL), CO <sub>2</sub> (1 bar), 25 °C, 400 W xenon lamp, 12 h                     | 97        | S6   |
| 7     | Zn@MA-POP                                 | Epichlorohydrin (0.5 mL), cat. (30 mg), TBAB (0.160 g), CO <sub>2</sub> (1 bar), 40 °C, 250 W xenon lamp, 8 h                                      | 74        | S7   |
| 8     | Py-POP                                    | Epoxides (4 mmol), cat. (10 mg), TBAB (0.5 mmol), anhydrous ZnCl <sub>2</sub> (10 wt %), 250 W Xe lamp, room temperature, 10 h                     | 94        | S8   |
| 9     | Co@BiPy-POP                               | Epichlorohydrin (0.5 mL), cat. (30 mg), TBAB (160 mg), CO <sub>2</sub> (0.1 MPa), RT, blue LED lamp, 10 h  | 96        | S9   |
| 10    | Cs@Ti <sub>7</sub> Cr <sub>14</sub>       | 1,2-Epoxyhexane (3 mmol), cat. (16.7 μmol), TBAB (0.5 mmol), CO <sub>2</sub> (1 bar), 50 °C, simulated sunlight, 8 h                               | 99        | S10  |
| 11    | Ti <sub>18</sub> Bi <sub>4</sub> catalyst | 1,2-Epoxyhexane (3 mmol), cat. (20 μmol), TBAB (0.5 mmol), CO <sub>2</sub> (1 atm), 293 K, 300 W xenon lamp, 14 h                                  | 99        | S11  |

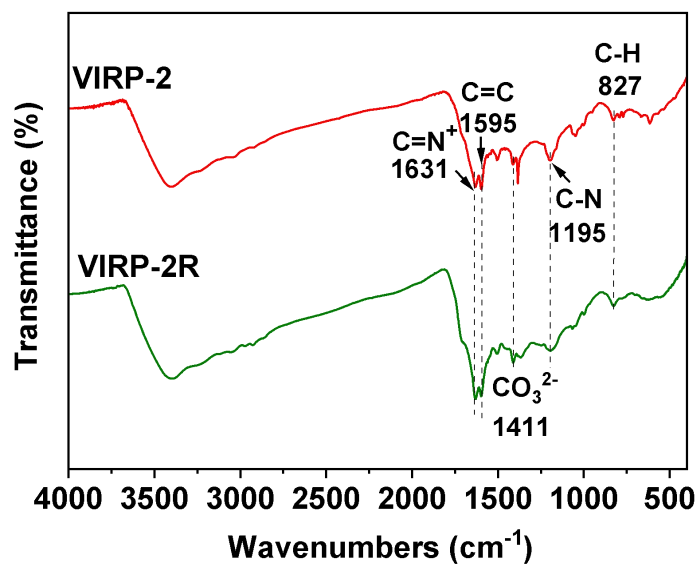
|    |                |  |      |                  |
|----|----------------|--|------|------------------|
| 12 | Al-N-C         | Epibromohydrin (0.67 mmol), cat. (20 mg), TBAB (21 mg),<br>DMF (2 mL), CO <sub>2</sub> (1 bar), 62 °C, 400 W Xe lamp, 9 h                              | 95   | S12              |
| 13 | CPT-2          | Epichlorohydrin (1 mmol), cat. (100 mg), TBAB (0.1 mmol), CH <sub>3</sub> CN + MeOH (15 mL), CO <sub>2</sub> (1 atm), 25 °C,<br>white LED (20 W), 24 h | 94   | S13              |
| 14 | SiWCo@GO-PEI   | Epichlorohydrin (2 mL), cat. (10 mg), TBAB (322 mg),<br>CO <sub>2</sub> (1 bar), 75 °C, 808 nm laser, 4 h  | 98.9 | S14              |
| 15 | ZNC-800        | 1,2-Epoxypropane (20 mmol), cat. (20 mg), TBAB (0.1 mmol), CO <sub>2</sub> (0.1 MPa), RT, 1000 mW cm <sup>-2</sup> full-spectrum<br>irradiation, 20 h  | 98.2 | S15              |
| 16 | ZnO/NCO-L      | Epichlorohydrin (1 mmol), cat. (50 mg), TBAB (0.2 mmol),<br>CH <sub>3</sub> CN (2 mL), CO <sub>2</sub> (0.1 MPa), 70 °C, 300 W Xe lamp,<br>24 h        | 94   | S16              |
| 17 | Zn SA-NC       | Epichlorohydrin (0.15 mmol), cat. (20 mg), TBAB (0.1 mmol), DMF (1 mL), CO <sub>2</sub> (1 bar), 65 °C, 300 W Xe lamp,<br>16 h                         | 99   | S17              |
| 18 | TpPa-1         | 1,2-Epoxypropane (0.2 mmol), cat. (5 mg), TBAB (5 mol%), ACN (5 mL), CO <sub>2</sub> (1 atm), 25 °C, blue LED<br>(20 W), 8 h                           | 86   | S18              |
| 19 | OH-P[5]-on-COF | Epichlorohydrin (0.25 mmol), cat. (1.5 mg), TBAB (0.0125 mmol), CO <sub>2</sub> (0.1 MPa), 20 °C, full spectrum LED lamp, 3 h                          | 99   | S19              |
| 20 | VIRP-2         | 1,2-Epoxypropane (1 mmol), cat. (30 mg), CO <sub>2</sub> balloon<br>(0.1 MPa), RT, blue LEDs (8 W), 24 h   | 97   | <b>This work</b> |
| 21 | VIRP-2         | Epichlorohydrin (1 mmol), cat. (50 mg), CO <sub>2</sub> balloon<br>(0.1 MPa), RT, blue LEDs (8 W), 24 h  | 98   | <b>This work</b> |
| 22 | VIRP-2         | 1,2-Epoxyhexane (1 mmol), cat. (60 mg), CO <sub>2</sub> balloon<br>(0.1 MPa), RT, blue LEDs (8 W), 48 h  | 90   | <b>This work</b> |

**Table S5** Comparisons of catalytic performances in the photocatalytic CO<sub>2</sub> cycloaddition with epoxides over different heterogeneous catalysts without using the cocatalyst TBAB.

| Entry | Catalysts                               | Reaction conditions   | Yield (%) | Ref.             |
|-------|---|---|-----------|------------------|
| 1     | COF-PI-2                                | Epibromohydrin (11.6 mmol), cat. (1 mol%), CO <sub>2</sub> (1 atm), the initial temperature is 25 °C, 500 W xenon lamp, 24 h                                      | 99        | S20              |
| 2     | Ni-BNCNTs@HMPs-NH <sub>2</sub>          | Epibromohydrin (10 mmol), cat. (20 mg), CO <sub>2</sub> (1 atm), 74.2 °C, 300 W Xe lamp, 12 h   | 99        | S21              |
| 3     | T2-PIL                                  | Glycidyl phenyl ether, cat., CO <sub>2</sub> (0.1 MPa), 79 °C, 300 W xenon lamp, 12 h   | 83.5      | S22              |
| 4     | Br-CN-1-550                             | Epichlorohydrin (0.15 mmol), cat. (30 mg), DMF (1.5 mL), CO <sub>2</sub> balloon (0.1 MPa), DMF (1.5 mL), 300 mW·cm <sup>-2</sup> full-spectrum irradiation, 10 h | 90        | S23              |
| 5     | PV <sub>2</sub> W <sub>10</sub> @EB-TFP | Epichlorohydrin (1 mmol), cat. (20 mg), DMF (2 mL), CO <sub>2</sub> (0.1 MPa), DMF (1.5 mL), 300W Xe lamp, 74.2 °C, 4 h   | 97.6      | S24              |
| 6     | VIRP-2                                  | Epichlorohydrin (1 mmol), cat. (50 mg), CO <sub>2</sub> balloon (0.1 MPa), RT, blue LEDs (8 W), 24 h  | 98        | <b>This work</b> |
| 7     | VIRP-2                                  | Epibromohydrin (1 mmol), cat. (50 mg), CO <sub>2</sub> balloon (0.1 MPa), RT, blue LEDs (8W), 24 h  | 93        | <b>This work</b> |



**Fig. S15** A five-cycle assessment in the catalytic reusability of VIRP-2 for the photocatalytic CO<sub>2</sub> conversion with epichlorohydrin. Reaction conditions: epichlorohydrin (1 mmol), CO<sub>2</sub> balloon (0.1 MPa), the catalyst VIRP-2 (50 mg), blue LEDs (8 W), room temperature, 24 h.



**Fig. S16** FTIR of the fresh catalyst VIRP-2 and the recovered catalyst VIRP-2R.

**Table S6** Quenching experiments to assess the role of photogenerated  $e^-$  and  $h^+$  over the photocatalyst VIRP-2.

| Entry | Quenchers                      | Role                | Yield (%) <sup>b</sup> | Selectivity (%) <sup>b</sup> |
|-------|--------------------------------|---------------------|------------------------|------------------------------|
| 1     | -                              | Standard conditions | 98                     | 99                           |
| 2     | <i>p</i> -BQ <sup>c</sup>      | Electron scavenger  | 2                      | 99                           |
| 3     | AgNO <sub>3</sub> <sup>d</sup> | Electron scavenger  | 24                     | 99                           |
| 4     | Methanol <sup>e</sup>          | Hole scavenger      | 63                     | 99                           |
| 5     | Isopropanol <sup>f</sup>       | Hole scavenger      | 46                     | 99                           |

<sup>[a]</sup> Reaction conditions: epichlorohydrin (1 mmol), CO<sub>2</sub> balloon (0.1 MPa), the catalyst VIRP-2 (50 mg), blue LEDs (8W), room temperature, 24 h. <sup>b</sup> Yield and selectivity of the cyclic carbonate determined by <sup>1</sup>H NMR analyses. <sup>c</sup> *p*-BQ, *p*-benzoquinone, 0.5 mmol. <sup>d</sup> AgNO<sub>3</sub>, 0.5 mmol. <sup>e</sup> Methanol, 0.5 mmol. <sup>f</sup> Isopropanol (IPA), 0.5 mmol.

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