Electronic Supplementary Material (ESI) for Polymer Chemistry.

Visible light-regulated organocatalytic ring-opening polymerization of lactones by harnessing excited state acidity

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Supplementary Information

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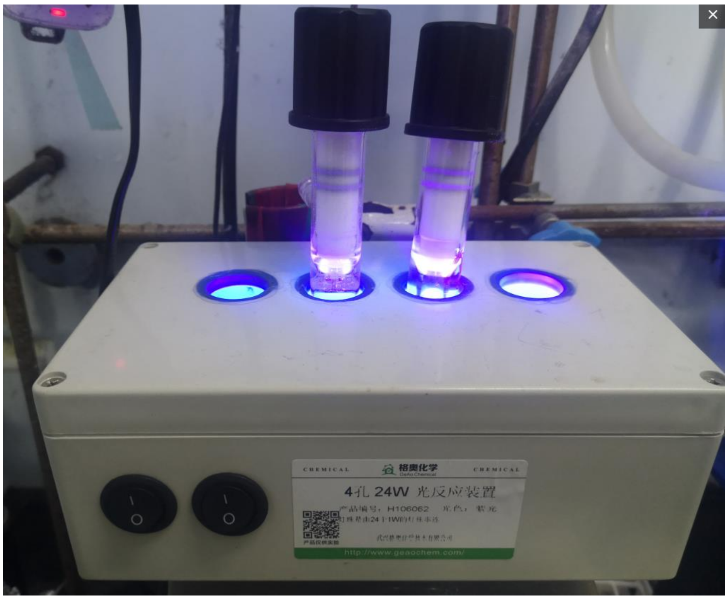
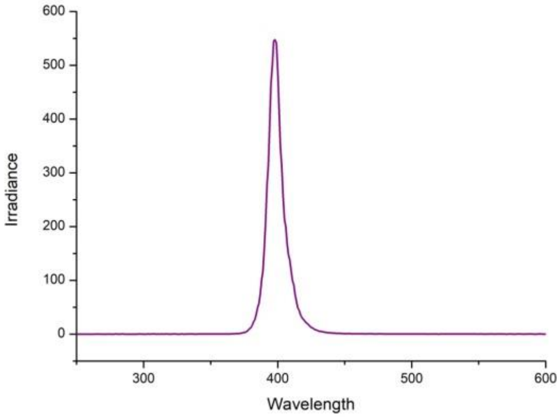
Photoreaction Setup:

All manipulations for the visible light-mediated ROP of lactones were set up in a 10 mL Schlenk Tubes (unless otherwise noted) under an inert Argon (Argon) atmosphere using glove-box techniques. The reactions were conducted in photo-reactors (purchased from http://www.geaochem.com/), which comprisea fan for cooling(approximately room temperature) andsix 1W blue LEDs beads for each place. The average power output of the photo-reactor was recorded at 30 mW/cm^2. The emission spectra of the purple LEDs were recorded on an Ocean Optics HR4000CG-UVNIR spectrometer. The spectra was normalised to 1.0 at the maximum (400 nm).





Typical procedure for chain extension experiments

In glovebox, δ-valerolactone (δ-VL) (0.15 g, 1.5 mmol, 50 equiv.) was dissolved in DCM ($[\delta\text{-VL}]_0$ = 3.0 mol L^{-1}) added in a Schlenk tube (flame dried three times), 3-phenyl-1-propanol (PPA, 4.1 µL, 30 µmol, 1 equiv.) was added using a syringe and 1-hydroxypyrene (PyOH, 6.5 mg, 30 µmol, 1 equiv.) was then added. The mixtures were stirred and irradiated at purple light reactor (6 W) at room temperature. After 12 h, samples were taken out for GPC and NMR analysis (conv. = 87%, $M_{\mathrm{n,NMR}}$ = 5000, $Đ$ = 1.08), another 50 equivalents of δ-VL was added and the reaction mixtures were exposed to purple light again for further 12h, Then the polymerization was quenched by the addition of Amberlyst A21. Before the addition of the Amberlyst A21, a portion of the polymerization mixtures was syringed out and quenched with triethylamine for determining the monomer conversion by ^{1}H NMR. The obtained polymers were purified by re-precipitation using CH_2Cl_2 as the good solvent and cold methanol as the poor solvent, the desired PVL-*b*-PVL with $M_{\mathrm{n,NMR}}$ = 10100, $Đ$ = 1.11 (Figure 3A).

Typical procedure for block polymer synthesis

In glovebox, ε-caprolactone (ε-CL) (0.17 g, 1.5 mmol, 50 equiv.) was dissolved in DCM ($[\varepsilon\text{-CL}]_0$ = 3.0 mol L-1) added in a Schlenk tube (flame dried three times), 3-phenyl-1-propanol (PPA, 4.1 µL, 30 µmol, 1 equiv.) was added using a syringe and 1-hydroxypyrene (PyOH, 6.5 mg, 30 µmol, 1 equiv.) was then added. The mixtures were stirred and irradiated at purple light reactor (6 W) at room temperature. After 24 h, samples were taken out for GPC and NMR analysis (conv. = 95%, $M_{\mathrm{n,NMR}}$ = 5900, $Đ$ = 1.08), another 50 equivalents of δ-VL(0.15 g, 1.5 mmol) was added and the reaction mixtures were exposed to purple light again for further 12h, Then the polymerization was quenched by the addition of Amberlyst A21. Before the addition of the Amberlyst A21, a portion of the polymerization mixtures was syringed out and quenched with triethylamine for determining the monomer conversion by ^{1}H NMR. The obtained polymers were purified by re-precipitation using CH_2Cl_2 as the good solvent and cold methanol as the poor solvent, giving the di-block polymer PCL-*b*-PVL ($M_{\mathrm{n,NMR}}$ = 12000, $Đ$ = 1.10) (Figure 3B).

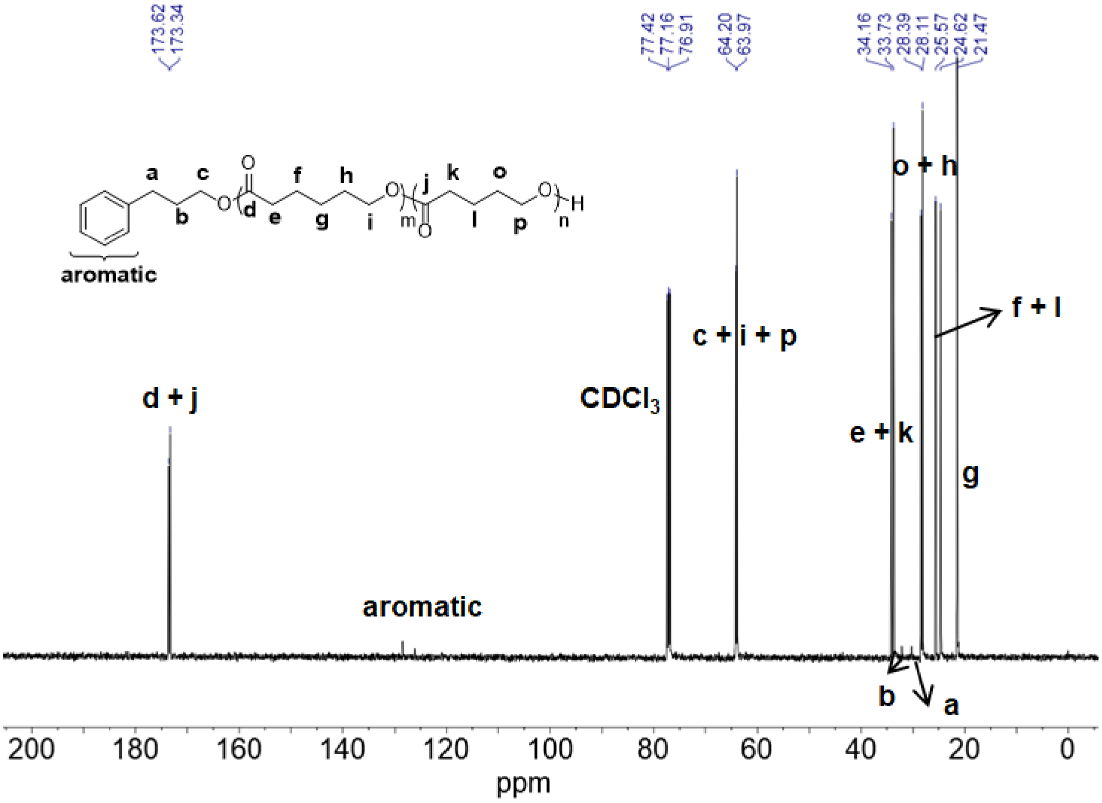
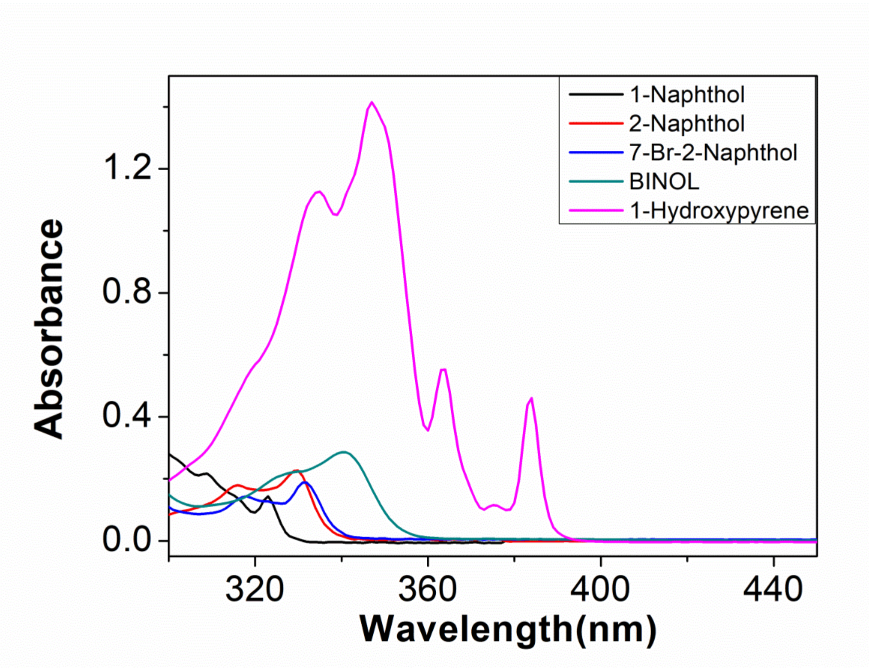


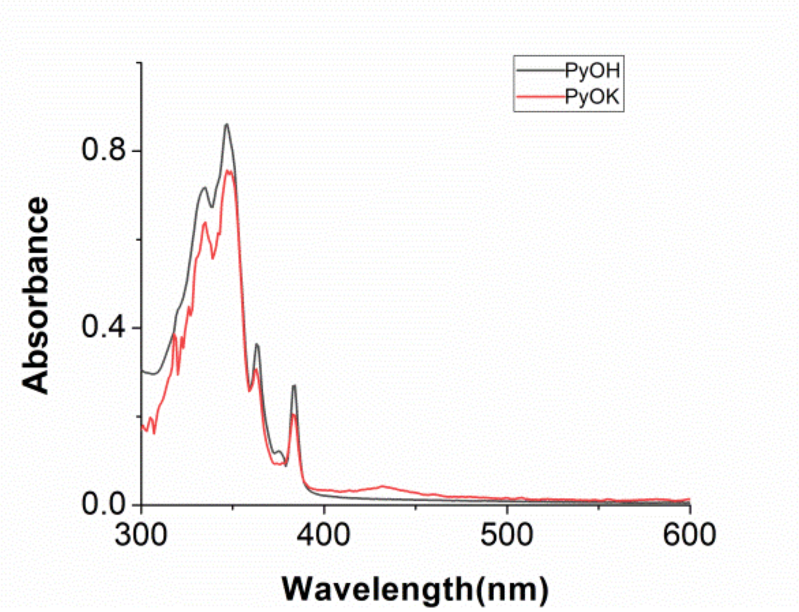
Fig. S1 ^{13}C NMR spectra of PCL-*b*-PVL

Typical procedure for the light "ON"/"OFF" experiments

In glovebox, δ-valerolactone (δ-VL) (0.30 g, 3.0 mmol, 100 equiv.) was dissolved in DCM ([δ-VL]0= 1.0 mol L-1) added in a Schlenk tube (flame dried three times), 3-phenyl-1-propanol (PPA)(4.1 µL, 30 µmol, 1 equiv.) was added using a syringe and 1-hydroxypyrene (PyOH) (6.5 mg, 30 µmol, 1 equiv.) was then added. The mixtures were stirred and irradiated at purple light reactor (6 W) at room temperature ("ON") for 4 h followed by removal of blue light ("OFF") for 4 h. The "ON"/ "OFF" process was repeated for several times. Samples were withdrawn at predetermined time interval for NMR analysis.



1-naphthol, 7-Bromo-2-naphthol, (BINOL) and PyOH in DCM (5× 10^{-5} M)



PyOH and PyOK in DCM (3× 10^{-5} M)

Fig. S2. **UV-Vis spectra of 1-naphthol, 7-Bromo-2-naphthol, BINOL, PyOH and PyOK**

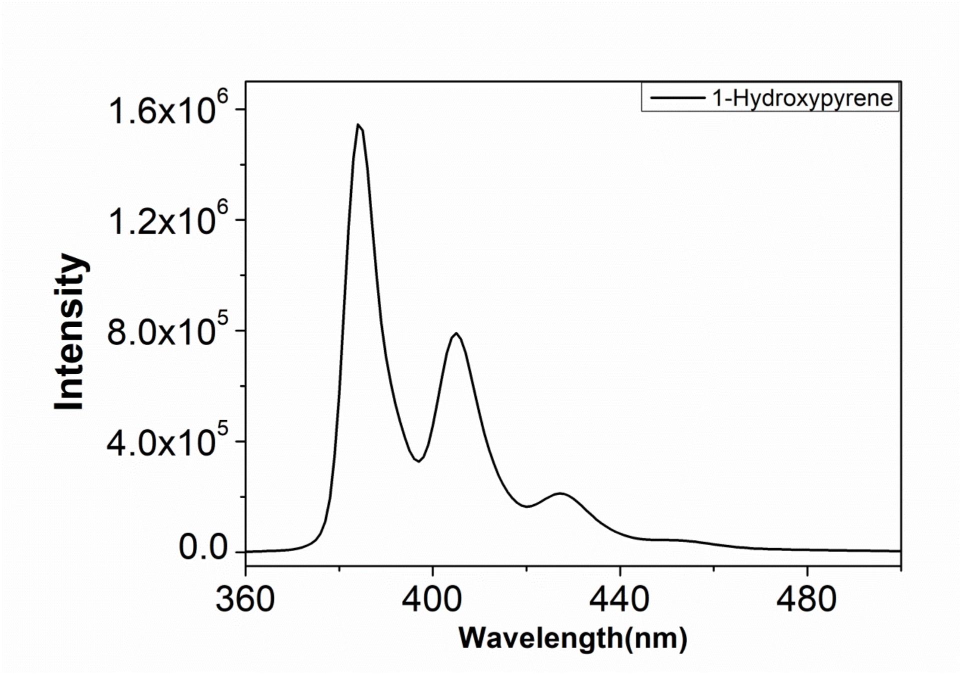


Fig. S3. Emission spectra of 1-hydroxypyrene (PyOH) in DCM

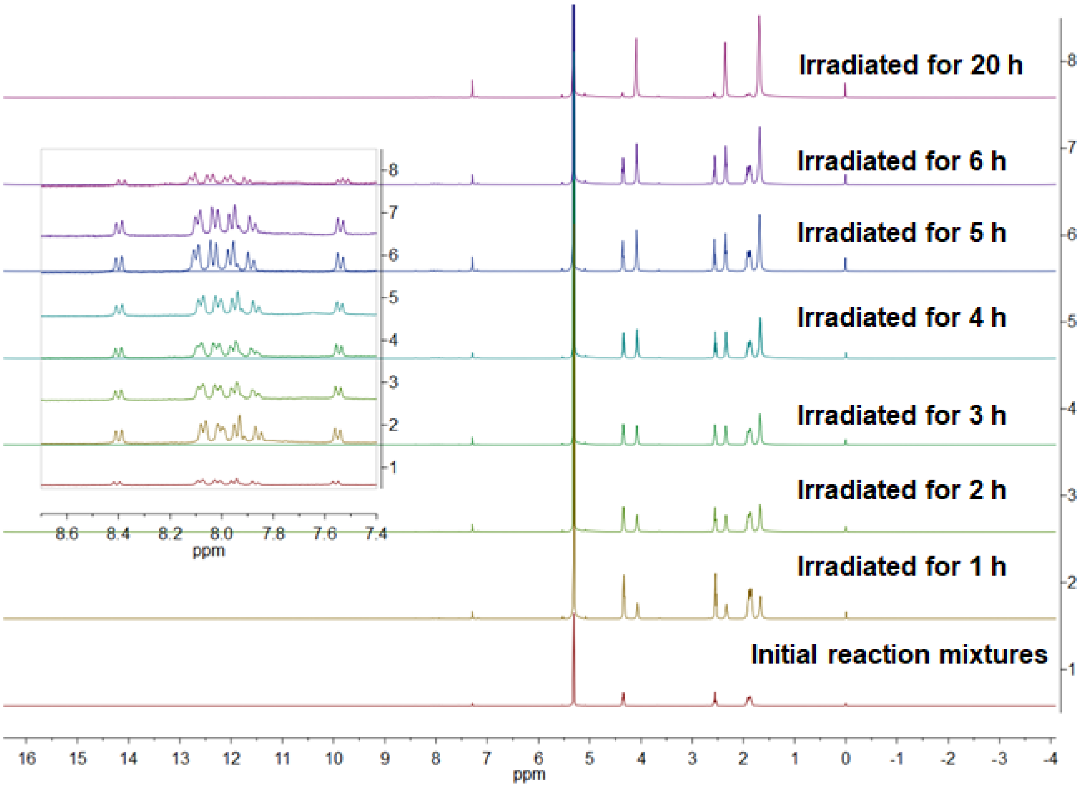
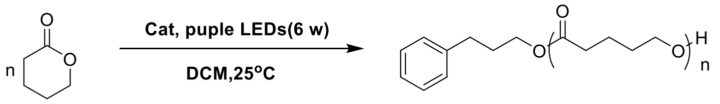


Fig. S4. ^{1}H NMR spectra of the reaction mixtures at different irradiated time

The effect of PyOK or AcONa on the polymerization

For comparison, PyOK was used in place of PyOH in the photocatalyzed ROP of δ-VL at a ratio of [δ-VL]$_0$/[PPA]$_0$/[Cat]$_0$=50/1/1 under the standard polymerization conditions. After irradiated under purple light for the same time, the monomer conversion up to 92% was achieved when PyOH used as catalyst, while no polymerization was observed when PyOK was used as a catalyst. Moreover, stirred the reaction mixture in dark also no polymerization was observed with either PyOH or PyOK. Furthermore, a weak inorganic base CH_3COONa also utilized as additive in the ROP of δ-VL, when the ratio of CH_3COONa/PyOH=2/1， the reaction mixture exposed to light for 12 h and the monomer conversion was lower than 5 %. When increasing the ratio of CH3COONa/PyOH to 4/1, almost no polymerization occurred under the same condition. These results indicated that PyOH in its acidic form is crucial to promote the ROP of lactones, and a strong photoacid is formed (at least stronger than acetic acid) upon irradiation under purple light.

Table S1. ROP of δ-VL in the presence of base.



Entry	$[M]_0/[I]_0/[Cat]_0$	Cat.	t	CH_3CO2Na	Conv/%
1	50/1/1	**PyOK**	12 h	/	0
2	50/1/1	**PyOH**	12 h	/	92%
3	50/1/1	**PyOK**	12 h in dark	/	0
4	50/1/1	**PyOH**	12 h	2 equiv	<3
5	50/1/1	**PyOH**	12 h	4 equiv	<1

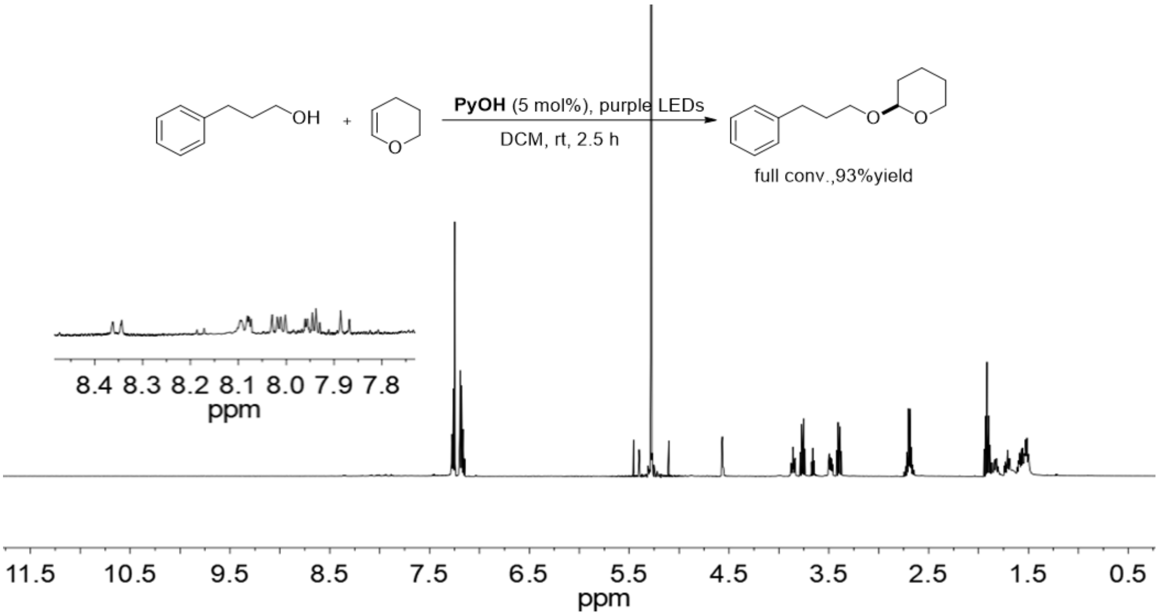


Fig. S5. ^{1}H NMR spectra of the reaction media of photoinduced acetalization

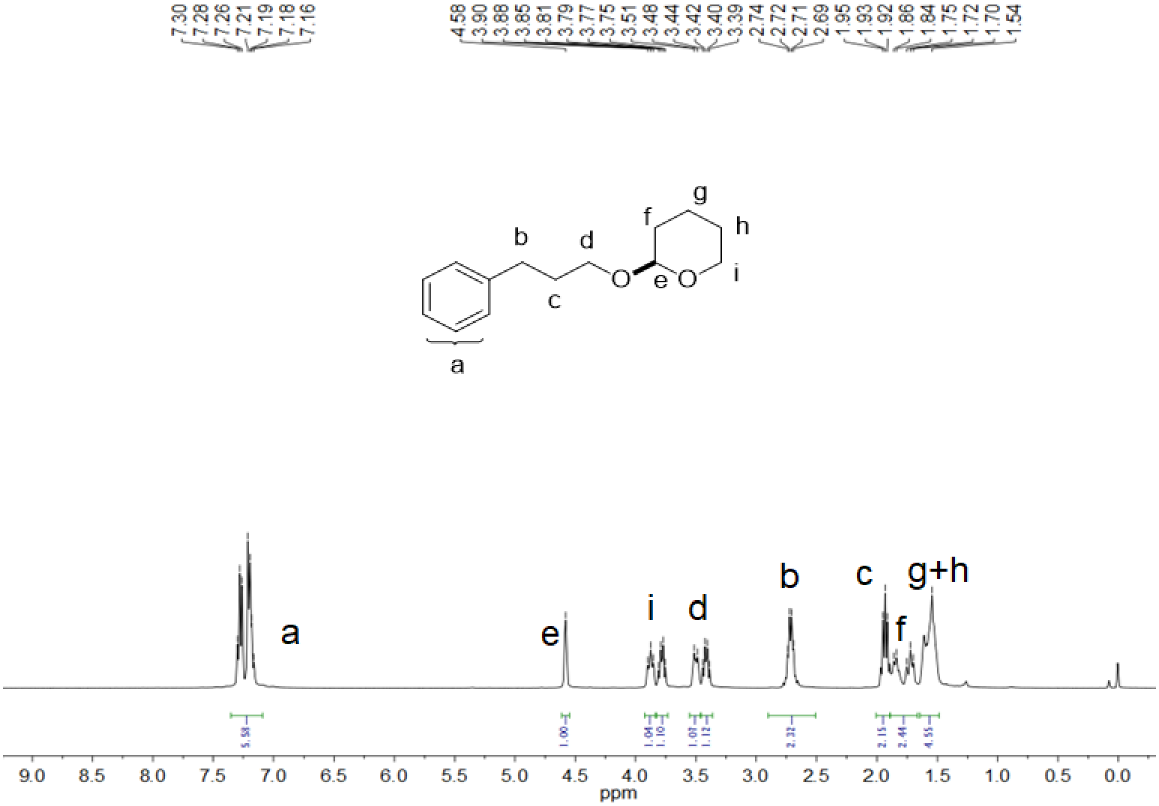
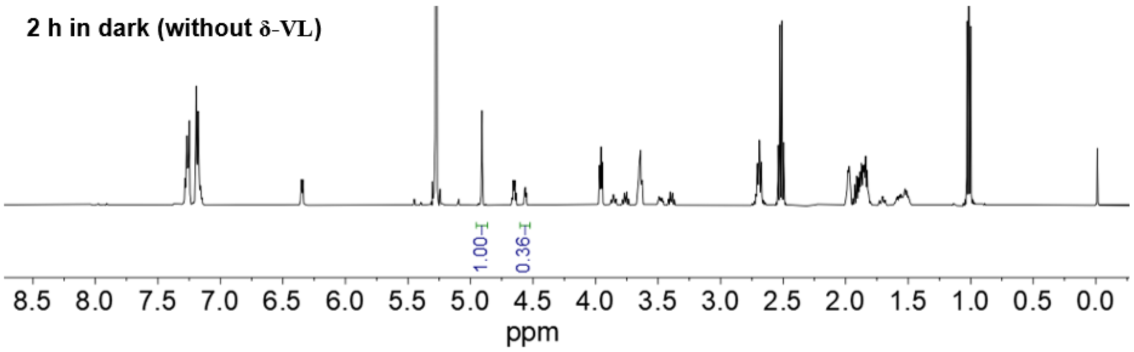
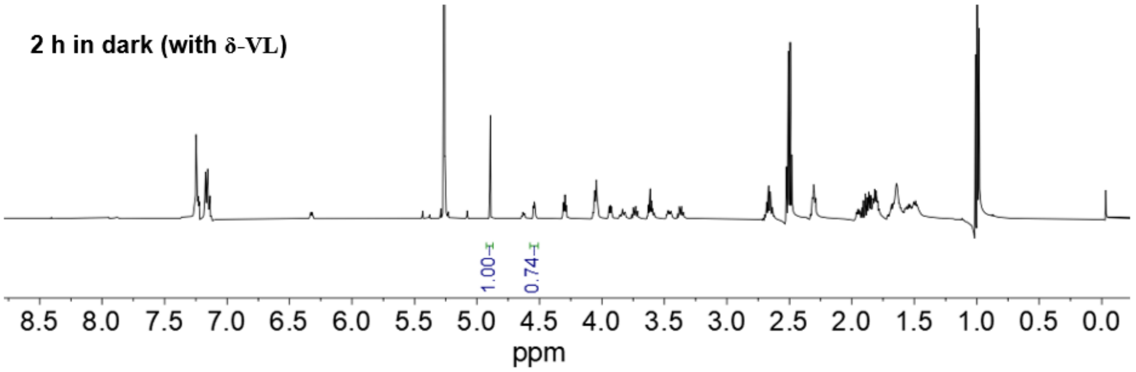


Fig. S6. ^{1}H NMR spectra of the acetalization product

Effect of polymerization on the photoinduced acetalization reaction.

The photoinduced acetalization with δ-VL present was conducted at a [δ-VL]$_0$/[PPA]$_0$/[PyOH]$_0$ ratio of 50/1/1. δ-VL (0.150 g, 1.5 mmol), PyOH (6.5 mg, 60 μmol), PPA (4.1 mg, 30 μmol) and DCM (0.35 mL) were added into a flame-dried Schlenk tube in glovebox, and the tube was then exposed to the irradiation of purple LEDs. After 6 h, a sample was syringed out for ^{1}H NMR analysis (quenched with Et_3N, conversion of δ-VL was 74%). Then, the reaction was placed in dark, and dihydropyran (84 mg, 1.0 mmol), PPA (136 mg, 1 mmol) and dibromomethane (87 mg, 0.5 mmol, used as internal standard) were added. Samples were syringed out for NMR analysis (quenched with Et_3N) at specified time. After stirred for 2 h in dark, the conversion of dihydropyran was determined to be 75%, while the conversion of the reaction without δ-VL added in the beginning was 36% only.


2 h in dark (without δ-VL)


2 h in dark (with δ-VL)

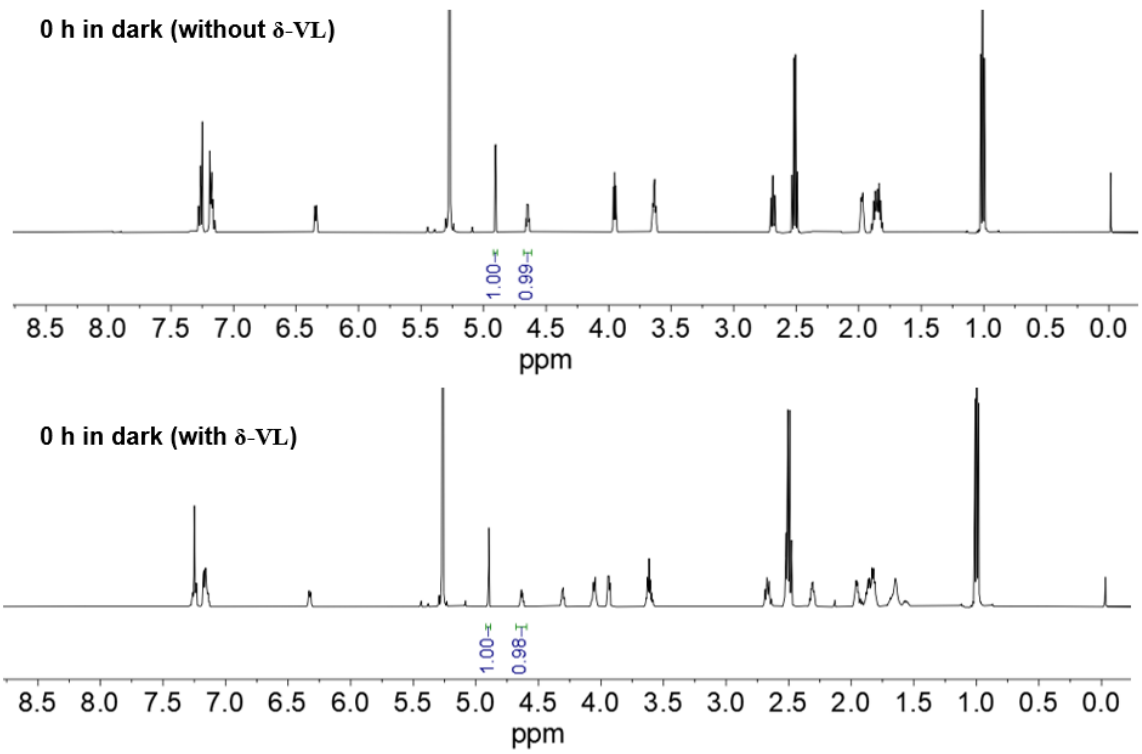


Fig. S7. ^{1}H NMR analysis of the acetalization with or without δ-VL present

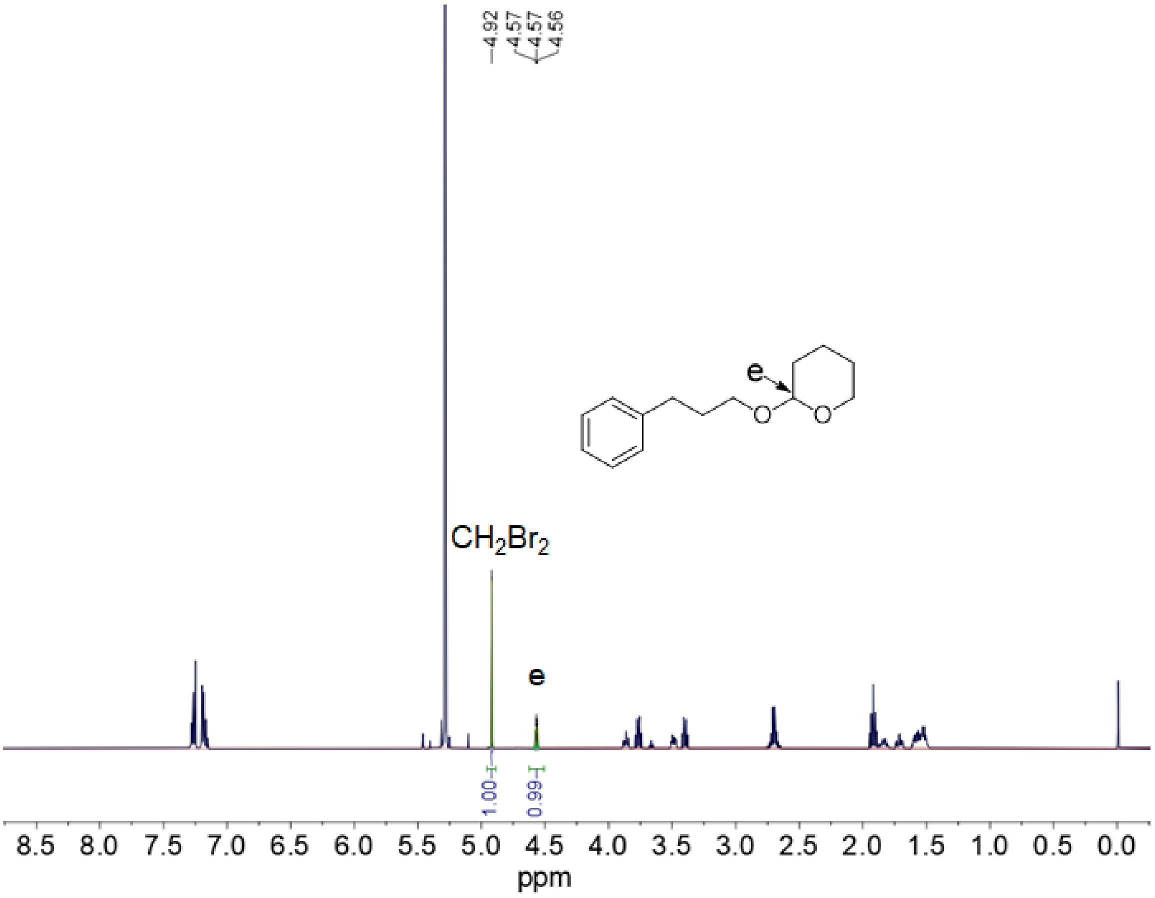


Fig. S8. ^{1}**H NMR analysis of the yield of acetalization when dibromomethane used as internal standard (an example)**