

Supporting Information

Harnessing the photo-acidity of organic dyes for the development of ring-opening polymerization of lactones under visible light

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Photoreaction setup

The ROP were conducted in blue or purple photo-reactors (purchased from <http://www.geaochem.com/>), equipped with a fan for keeping at room temperature and six 1W LEDs beads dispersed inside the photo-reactor. The average power output from the reactor was $\sim 30 \text{ mW/cm}^2$ as recorded.

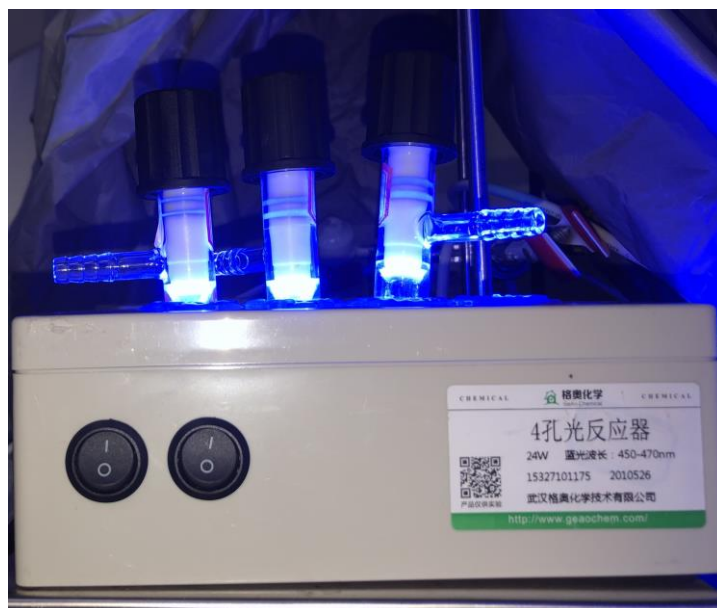


Fig. S1. Blue photo-reactors used in this work (λ 450-470 nm).



Fig. S2. Purple photo-reactors used in this work (λ 385-395 nm).



Fig. S3. Green photo-reactors used in this work (λ 490-530 nm).

Typical procedure for star type block polymer synthesis

In a glovebox, ϵ -caprolactone (ϵ -CL) (119.7 mg, 1.05 mmol, 35 equiv.) was added via a syringe in toluene ($[\delta\text{-VL}]_0 = 3.0 \text{ mol L}^{-1}$) in a Schlenk tube (after dried by flame for three times), trimethylol propane (4.0 mg, 30 μmol , 1 equiv.) was added in the system and bromocresol green (Dye **1**, 2.1 mg, 3.0 μmol , 0.1 equiv.) was weighed in a Schlenk tube. The solution was stirred and irradiated at 30 mW/cm² blue light reactor at room temperature. After 24 h, a little portion of the system was characterized by NMR and GPC (PCL, Conv. = 96%, $M_{n,\text{NMR}} = 3.900 \text{ kg/mol}$, $D = 1.08$), 50 equivalents of δ -VL were added to the ROP system. After another 36 hours, a portion of the ROP mixtures was syringed out and quenched with a few drops of triethylamine for checking the monomer conversion by ¹H NMR. The final product (PCL-*b*-PVL, $M_{n,\text{NMR}} = 8.9 \text{ kg/mol}$, $D = 1.10$) was obtained after precipitation using DCM as a good solvent and cold methanol as a poor solvent.

Typical procedure for the light “ON”/ “OFF” experiments

In a glovebox, δ -valerolactone (δ -VL) (150.0 mg, 1.5 mmol, 50 equiv.) was added via a syringe in DCM ($[\delta\text{-VL}]_0 = 0.5 \text{ mol L}^{-1}$) in a Schlenk tube (after dried by flame for three times), 3-phenyl-1-propanol (PPA, 4.1 mg, 30 μmol , 1 equiv.) was added in the system and bromocresol green (Dye **1**, 2.1 mg, 3 μmol , 0.1 equiv.) was weighed in a Schlenk tube. The solution was stirred and irradiated with the 30 mW/cm² blue LED reactor at room temperature for 9h. Upon removing the blue light, a little portion of the system was characterized by ¹H NMR for checking the monomer conversion. During the dark period of 14 hours, the monomer conversion was followed by ¹H NMR. Then, the ROP system was placed under the irradiation of blue light again for another 10 hours and the end up monomer conversion was also determined by ¹H NMR.

Polymerization in the dark or under blue LEDs

Table S1 Visible light-regulated ROP of lactones by using organic dyes molecules as catalysts.^a

Ph-CH₂-CH₂-CH₂-OH + O=C1OCCCCO1 $\xrightarrow[\text{DCM, r.t.}]{\text{visible light (Dye)}}$ Ph-CH₂-CH₂-CH₂-O-(O=C1OCCCCO1)_n-H

Bromocresol green (Dye 1)

Fluorescein (Dye 2)

Eosin Y (Dye 3)

Erythrosin B (Dye 4)

Rhodamine 6G (Dye 5)

Rhodamine B (Dye 6)

Isatin (Dye 7)

Pigment red 122 (Dye 8)

Entry	Dye	λ (nm) ^b	Conv.	$M_{n,theo}$ (kg/mol) ^c	$M_{n,NMR}$ (kg/mol)	\bar{D} ^d
1	Dye 1	460	90%	4.6	4.5	1.10
2	Dye 1	/ ^e	/	/	/	/
3	Dye 2	460	88%	4.5	4.5	1.09
4	Dye 2	/	2%	0.2	0.2	/
5	Dye 3	460	4%	0.3	0.3	/
6	Dye 3	/	< 1%	/	/	/
7	Dye 4	460	5%	0.4	0.3	/
8	Dye 4	/	< 1%	/	/	/
9	Dye 5	460	< 1%	/	/	/
10	Dye 5	/	< 1%	/	/	/
11	Dye 6	460	< 1%	/	/	/
12	Dye 6	/	< 1%	/	/	/
13	Dye 7	460	< 1%	/	/	/
14	Dye 7	/	< 1%	/	/	/
15	Dye 8	460	< 1%	/	/	/
16	Dye 8	/	< 1%	/	/	/

^a $[M]_0/[I]_0/[Dye]_0 = [\delta-VL]_0/[PPA]_0/[Dye]_0 = 50:1:0.1$, light irradiation for 24 hours, $[M]_0 = 3 \text{ mol L}^{-1}$, Conv. and $M_{n,NMR}$ were determined by ¹H NMR; ^b The wavelength of visible light from LEDs reactor (6 W). ^c $M_{n,theo} = [M]_0/[I]_0 \times MW_{[M]} \times \text{Conv.} + MW_{[I]}$, where $MW_{[M]}$ and $MW_{[I]}$ represent the molar mass of monomer and the molar mass of initiator, respectively; ^d Determined by GPC using polystyrene standards; ^e In the dark.

Polymerization kinetics of the ring-opening polymerization of ϵ -caprolactone driven by dyes as Photoacid.

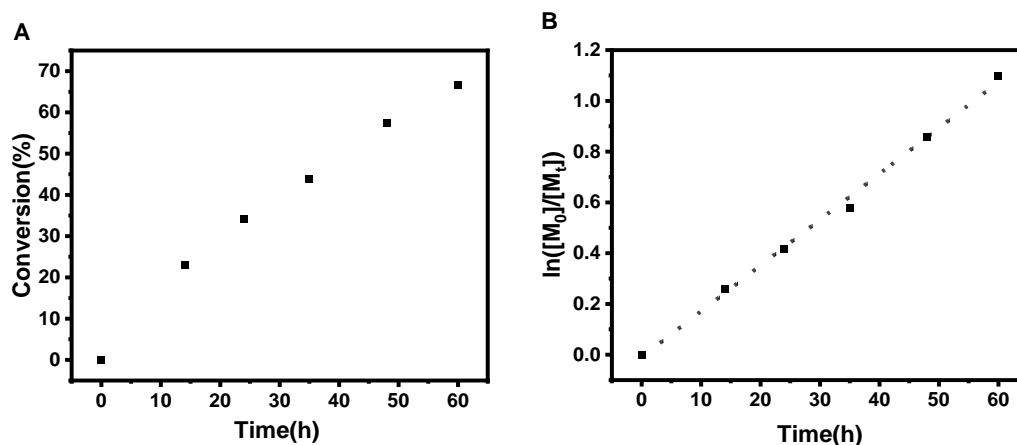
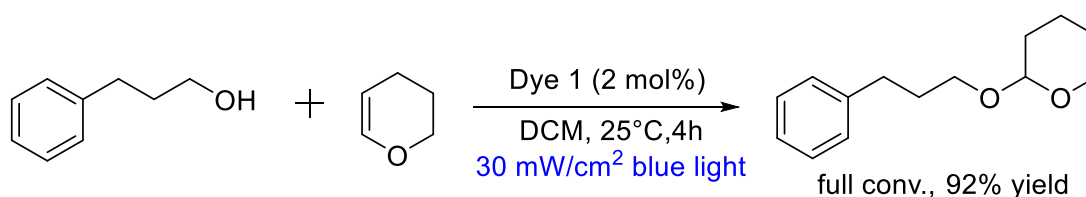


Fig. S4. Kinetic plots for the polymerization of ϵ -caprolactone with $[\epsilon\text{-CL}]_0 / [\text{PPA}]_0 / [\text{Dye } 1]_0$ at the ratio of 50/1/0.1 at room temperature. (A) Monomer conversion at different times. (B) $\ln([M]_0/[M]_t)$ versus time.

Acetalization reactions under blue Light by using Dye 1 as photocatalyst



Furthermore, we tried a small molecule synthesis reaction by using Dye 1 (2 mol%) as the photoacid catalyst under blue light irradiation. The reaction between 3-phenyl-1-propanol and 3,4-dihydropyran reached a full conversion after irradiation for 4 h. The target product, 3-phenylpropyl tetrahydropyranyl ether, was isolated in 92% yield by column and characterized by ¹H NMR (Figure S4). This reaction is a classic acetalization reaction which is a typical type of reaction catalyzed by acid, suggesting acid species

was generated with Dye 1 under irradiation of blue light.

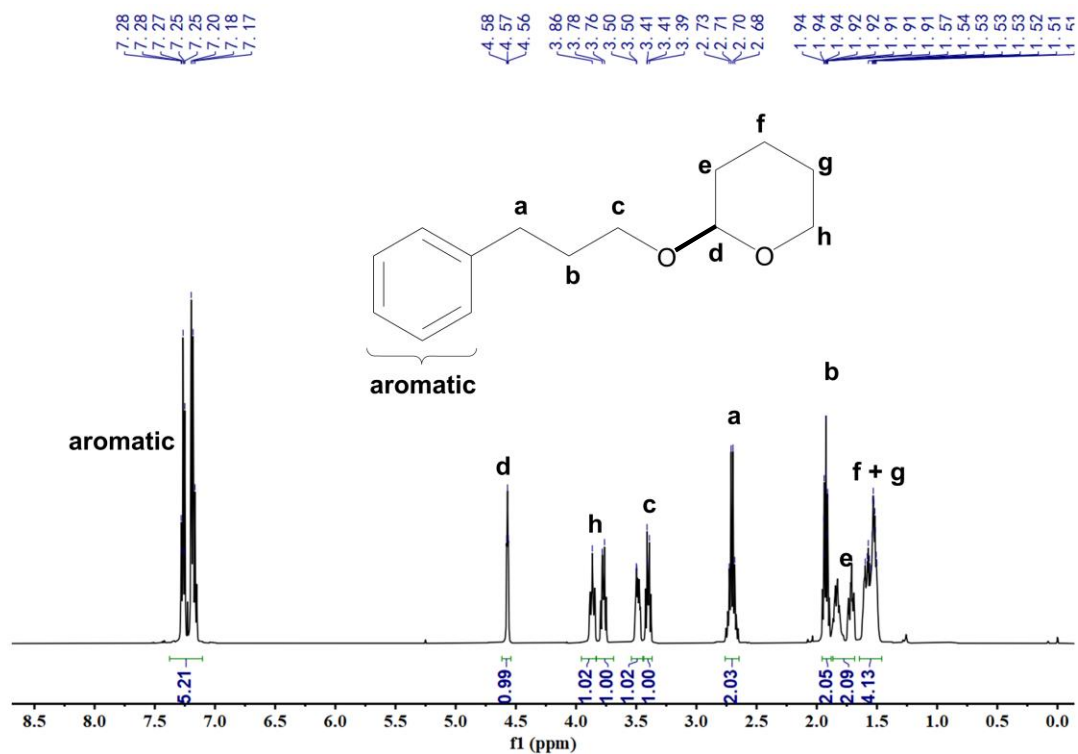


Fig. S5. ¹H NMR analysis for acetalization product.

The pH change of the solution of Dye 1 before and after irradiation

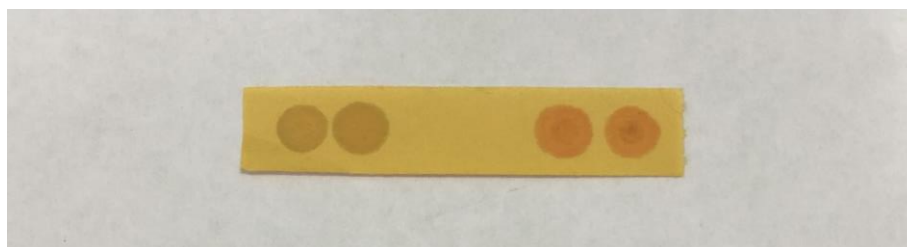


Fig. S6. The pH change of Dye 1 in DCM ([Dye 1] = 6 mmol L⁻¹) before (left) and after (right) blue light irradiation for 3 hours.

UV-Vis spectrum of organic dyes

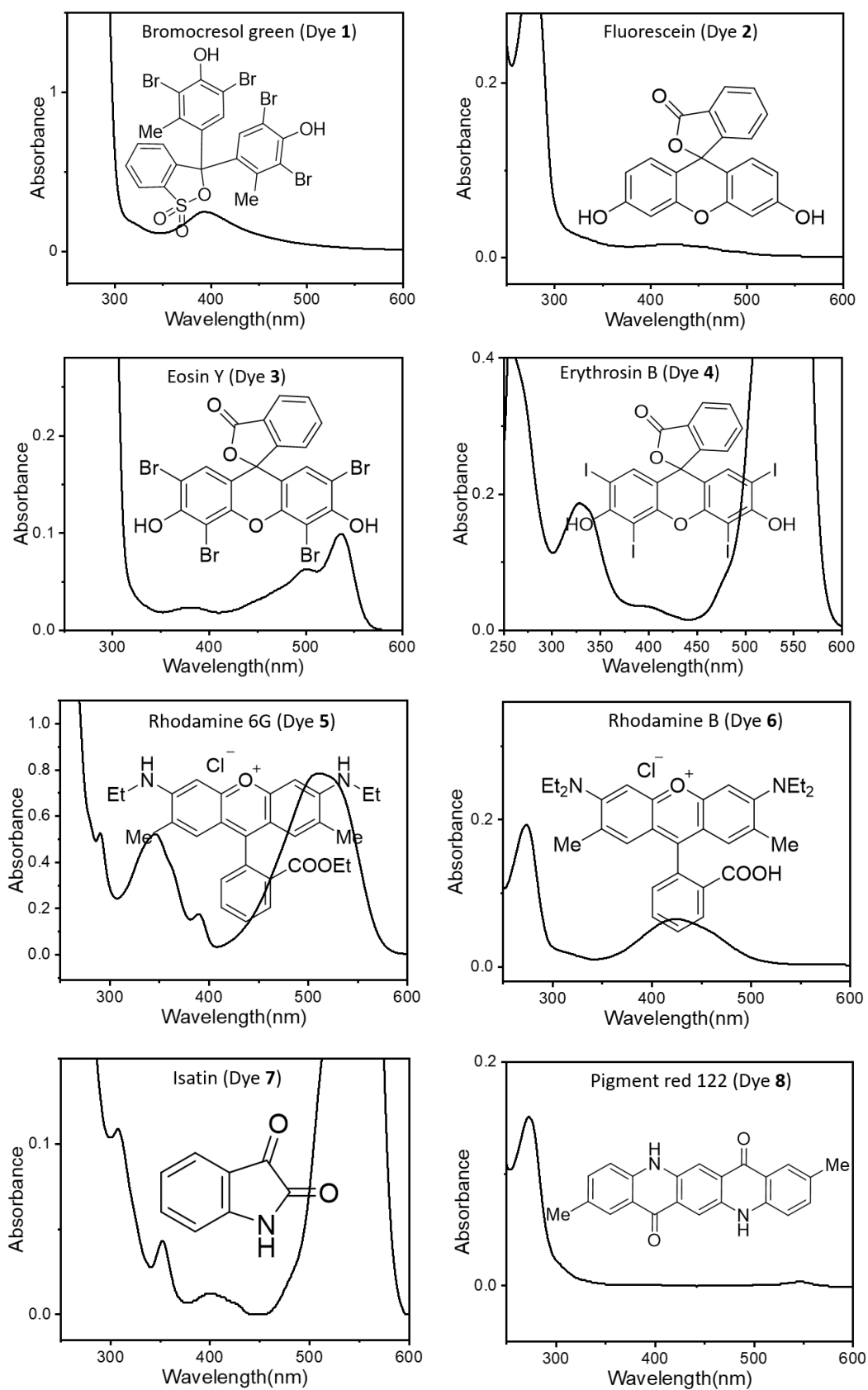


Fig. S7. The UV-Vis spectra of organic dyes in DCM (Dye 4 was measured in DMSO, in some cases, ring-opened forms could also contribute to the observed absorption)