

## Photochromic supramolecular photonic crystal based on host-guest interactions

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### 1. Materials

Tetraethoxysilane (TEOS), acrylamide (AAM, 99%), *N,N'*-methylenebisacrylamide (MBAAM,  $\geq 98\%$ ) and 2,6-Dimethoxyaniline (97%), obtained from Alfa Aesar. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%) and 3,5-Dimethoxyphenol (99%) were purchased from Arcos Organics. 6-Amino- $\beta$ -CD was purchased from Shandong Binzhou Zhiyuan Biotechnology Co., Ltd. Anhydrous ethanol, methanol, acetone, isopropanol, ethyl acetate, dimethyl sulfoxide, hydrofluoric acid,  $\text{NaHCO}_3$ , NaOH, sodium nitrite and other affiliated chemicals were all supplied by Beijing Chemical Industries. All of the solvents and chemicals used were of analytical quality and were used without further purification unless specified. Common glass slides (microscope slide, 76.2 mm, 25.4 mm, 1 mm) were purchased from Sail Brand (Shanghai, China). Polymethyl methacrylate (PMMA) slides (25 mm, 15 mm, 1mm) were from local suppliers.

### Characterization

Scanning electron microscope (SEM, model JEOL S4800) was used to characterize the morphology and microstructure of the silica microparticles and photonic films. Fiber spectrometer (AvaSpec-2048, Avantes) was used to measure optical Bragg diffractions of samples. NMR spectra was performed on a Bruker DPX-400 spectrometer operating at 400 MHz ( $^1\text{H}$ NMR), and was recorded by using DMSO- $d_6$  as solvent and tetramethylsilane (TMS) as an internal standard. High-resolution mass spectral analyses (HRMS) were measured using ESI (Q-Exactive) ionization.

### Measurement of Bragg diffraction

Optical Bragg diffraction of the  $\beta$ -CD-MAzo was measured by an optical fiber spectrometer. TA PLS-SXE300/300 (America) Xenon lamp as a solar simulator was used as the light source. The measured area (in circle shape) was approximately 2mm in diameter. These spectra were taken with light impinging perpendicular to the supramolecular hydrogel inverse

opal PCs.

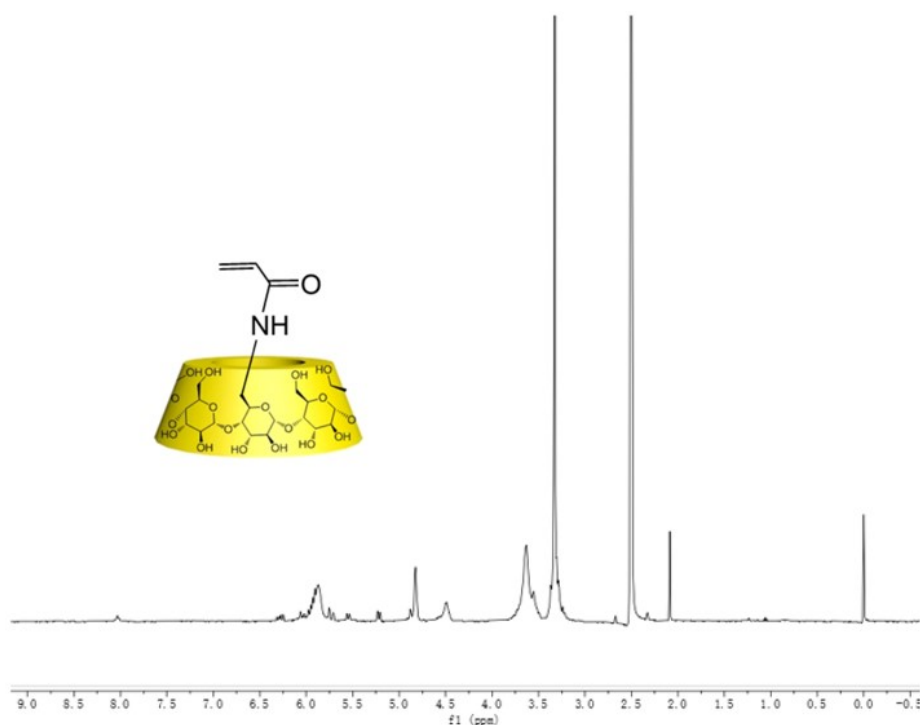
## 2. Formation of photonic crystal templates

The silica colloidal microspheres were synthesized by using an approach based on the Stöber method with certain modifications as follow.<sup>1</sup> In a typical preparation process, anhydrous ethanol (100 mL), deionized water (6 mL) and ammonia (4 mL) were mixed in a 250 mL flask and stirred gently with a magnetic stirrer at 35 °C in a water bath. Then TEOS (6 mL) was quickly added and the resulting reaction mixture was left overnight. The size of the silica particles can be tuned in the range of 180-360 nm by changing the reactant ratio or conditions. The monodispersed silica particles were obtained by centrifugation followed by rinsing 8 times using anhydrous ethanol to expunge the residues. The resulting product was then dispersed in anhydrous ethanol (volume concentration 0.5%). Common glass slides were cut to the same as the PMMA slides, and were treated with and immersed in a  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  mixture (7:3, v/v) for 24 h. All 5 mL vials for the formation of colloidal crystal templates were treated as well. The glass slide was well-cleaned by rinsing with deionized water and ethanol several times and dried with nitrogen. The silica colloidal microspheres were placed into 5 mL clean vials and a clean glass slide was placed vertically into each vial for photonic crystal growth. After complete volatilization of ethanol, photonic crystal templates were obtained. In this work, monodispersed silica spheres with a diameter of approximately 210-240 nm were used.

### 3. Synthesis of inverse opal hydrogel film of $\beta$ -CD-MAzo gels.

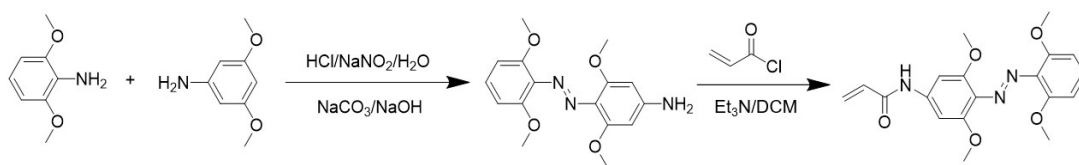
#### (1) Preparation of the monomer: $\beta$ -CD-AAm.<sup>2</sup>

6-Amino- $\beta$ -CD (1.02 g, 0.90 mmol) was dissolved in 75 mL of  $\text{NaHCO}_3$  (aq., 0.75 g) and pH of the solution was adjusted around 10 with aqueous NaOH. Acryloyl chloride (150  $\mu\text{L}$ , 1.8 mmol) was added to the solution of 6-amino- $\beta$ -CD in an ice bath, and stirred for 6 hours. After evaporation to around 15 mL remaining, it was poured into acetone (500 mL). The obtained crude product was collected by centrifugation, and purified by the following method. The white solid was dissolved in the mixture of methanol and  $\text{H}_2\text{O}$  (3:1, 20 mL), and precipitated in acetone (300 mL) before being dried in a vacuum oven overnight. The crude product was purified by a mixture of isopropanol/ethyl acetate/ $\text{H}_2\text{O}$  (7:7:4). Yield: 59%.  $^1\text{H}$ -NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  = 8.03 (brs, 1H), 6.32 (dd, 1H), 6.12 (d, 1H), 6.04-5.57 (d, 1H and m, 15H), 4.89-4.74 (m, 7H), 4.58-4.39 (m, 6H), 3.81-3.25 (m, overlaps with HOD). (ESI-MS):  $m/z$  = 1210.4  $[\text{M}^+\text{Na}]^+$ .



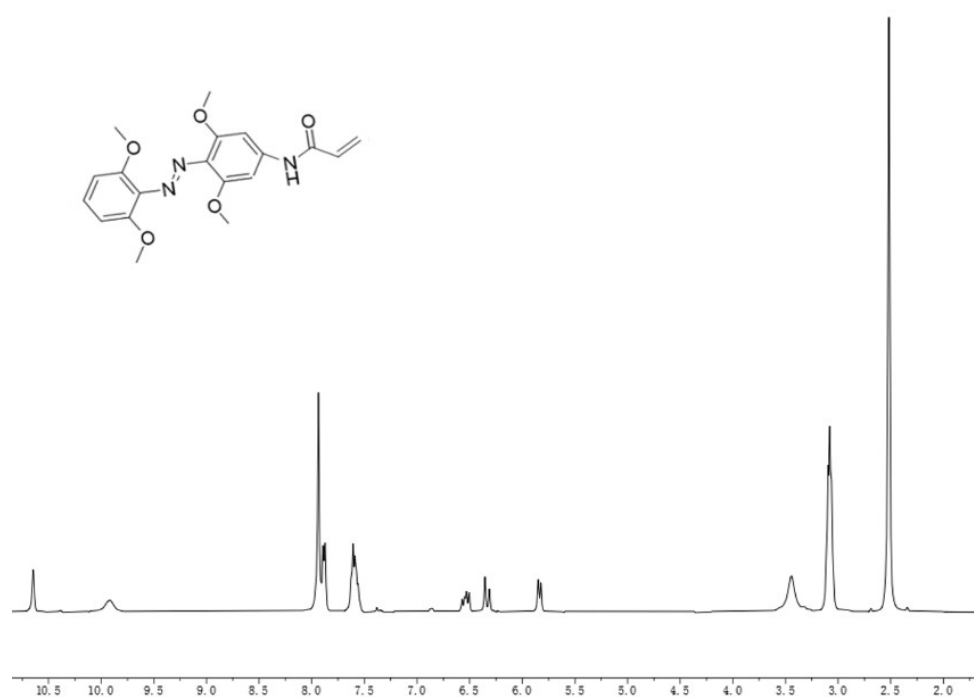
**Figure S1.**  $^1\text{H}$ -NMR (250 MHz,  $\text{D}_2\text{O}$ , 298K) spectra of  $\beta$ -CD-AAm.

## (2) Preparation of the monomer: MAzo<sup>3</sup>

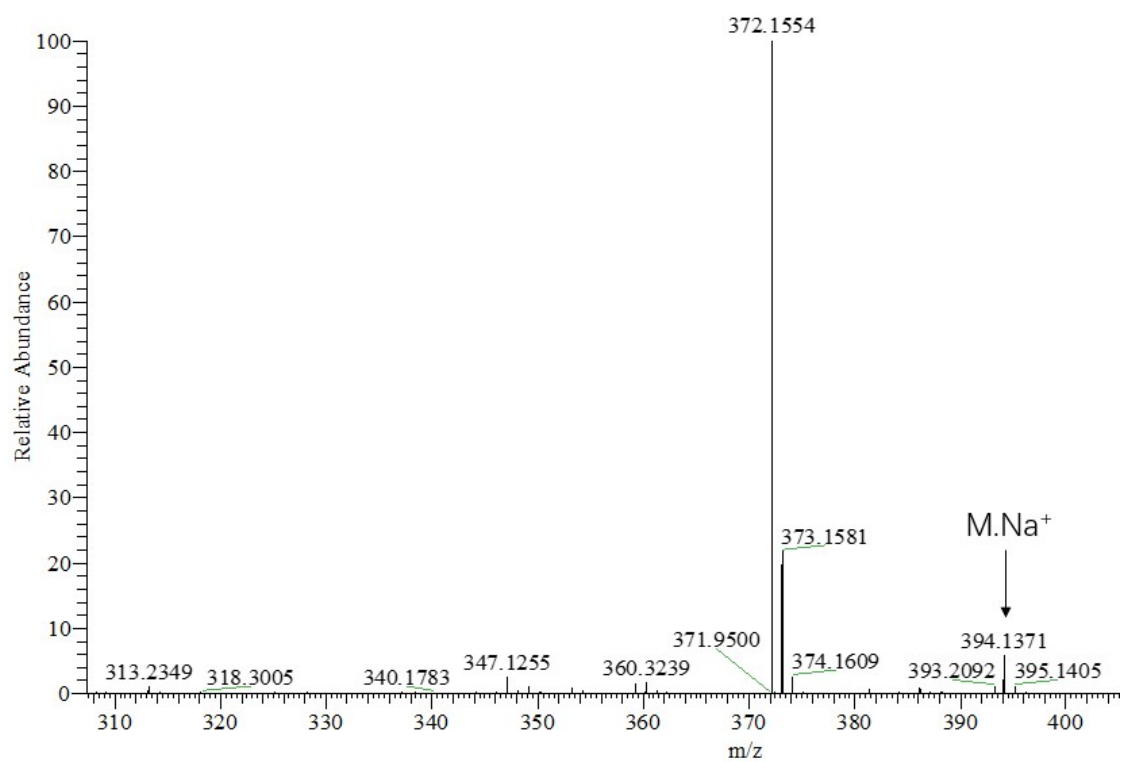


**Scheme S1.** Synthetic route of MAzo.

2,6-Dimethoxyaniline (58.8 mmol) was mixed with hydrochloric acid (7.2 mL, 30%) in a round bottomed flask and cooled to 0 °C. Aqueous solution of sodium nitrite (64.1 mmol, 20 mL) was added quickly to the solution of 2,6-Dimethoxyaniline. Meanwhile, aqueous solution of 3,5-dimethoxyphenol (58.8 mmol) and sodium hydroxide (4.2g, 20 mL) was added dropwise at 0 °C. The mixture was stirred for 24 h, then acidified to pH 6, and stirred for an additional 3 h. The precipitate was cooled with ice, filtered, and washed with ice cold deionized water (100 mL). The orange powder was dried overnight in a vacuum oven. Yield: 31%, HPLC≥95%. The above product (14.2 mmol) was mixed with triethylamine (28.3mmol) and anhydrous THF, added into a 100 ml round bottomed flask below 10°C. After acryloyl chloride (1.28 mmol) was added dropwise, the reaction system stirred for 24 h to complete the reaction. The orange powder was then dried overnight in a vacuum oven. Yield: 86%, HPLC≥97%.

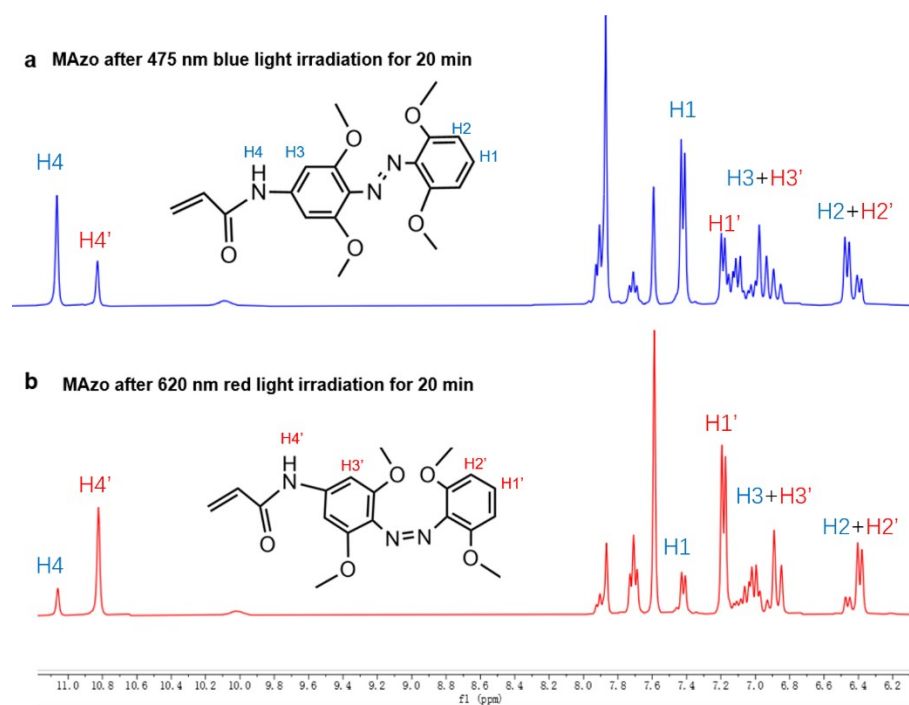


**Figure S2.** <sup>1</sup>H-NMR (250 MHz, D<sub>2</sub>O, 298K) spectrum of MAzo

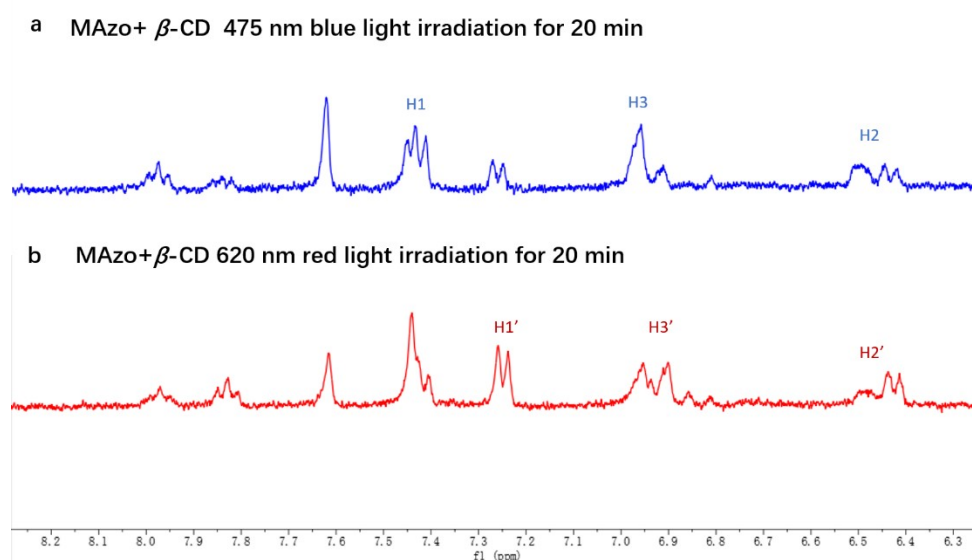


**Figure S3.** ESI-MS Spectrum of MAzo

### 3) Photoisomerization of MAzo and host-guest interactions between MAzo and $\beta$ -CD

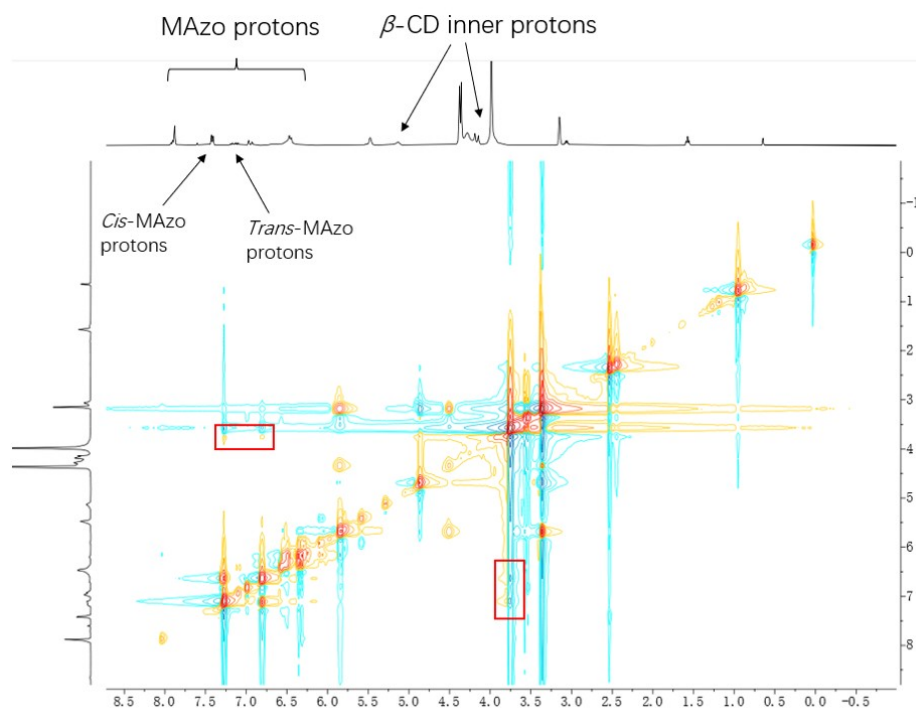


**Figure S4.** <sup>1</sup>H-NMR (250 MHz, DMSO-d<sub>6</sub>, 298K) spectra of MAzo: (a) After 475 nm blue light irradiation for 20 min; (b) After 620 nm red light irradiation for 20 min. Photoisomerization of MAzo can be induced by blue and red light.



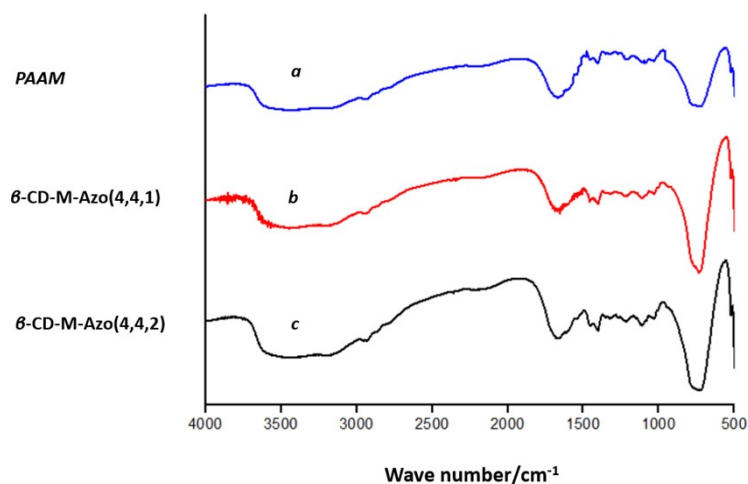
**Figure S5.** <sup>1</sup>H-NMR (250 MHz, D<sub>2</sub>O, 298K) spectra of a mixture of MAzo and  $\beta$ -CD (D<sub>2</sub>O): (a) After 475 nm blue light irradiation for 20 min; (b) After 620 nm red light irradiation for 20 min. The light can induce the photoisomerization of MAzo in the presence of  $\beta$ -CD.

## 2D ROESY NMR of MAzo and $\beta$ -CD



**Figure S6.** 2D ROESY NMR spectrum and proposed structure of the inclusion complex for a mixture of  $\beta$ -CDAAm and MAzo (DMSO- $d_6$ ), 600 MHz, 30 °C). The red rectangles in the spectrum highlight the correlation peaks between the protons of MAzo and the protons of  $\beta$ -CD.

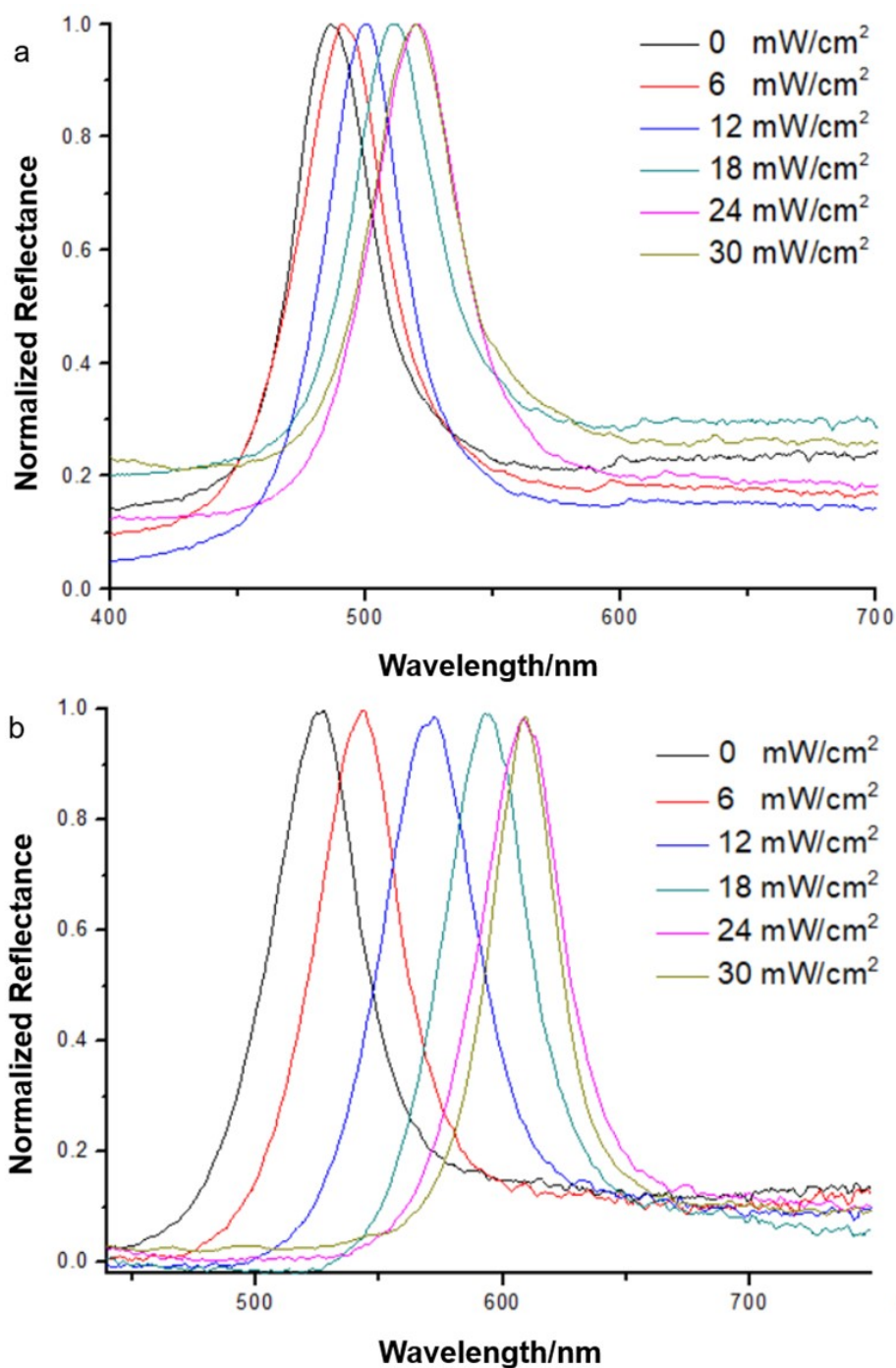
Host monomer ( $\beta$ -CD-AAm), guest monomer (MAzo) and the cross-linker *N,N'*-methylenebis (acrylamide) (MBAAm) were added in DMSO, (total monomer concentration: 2.00 M), and the feeding ratio of each monomer is as follows: AAm: (100–2x–y) mol%,  $\beta$ -CD-AAm: x mol%, MAzo: x mol% and MBAAm: y mol%. The resulting solution was ultrasonicate for 2 h. Then the homogeneous mixture was degassed with nitrogen for 5 mins to remove the dissolved oxygen. After this, main chain radical initiator AIBN (15 mg/mL) was added. The solution was infiltrated into the photonic crystal template which was covered with PMMA slide in a Petri dish. The radical polymerization was performed at 50 °C for 10 h. The photonic templates were frozen in a 3D network of polymer. Afterward the film was immersed in 2% HF aqueous solution to remove the SiO<sub>2</sub>. The dissociative inverse opal photonic crystal polymer was formed and rinsed thoroughly with deionized water several times. Finally, the resulting polymer was immersed in deionized water at room temperature to reach a swelling equilibrium and then was ready for use.



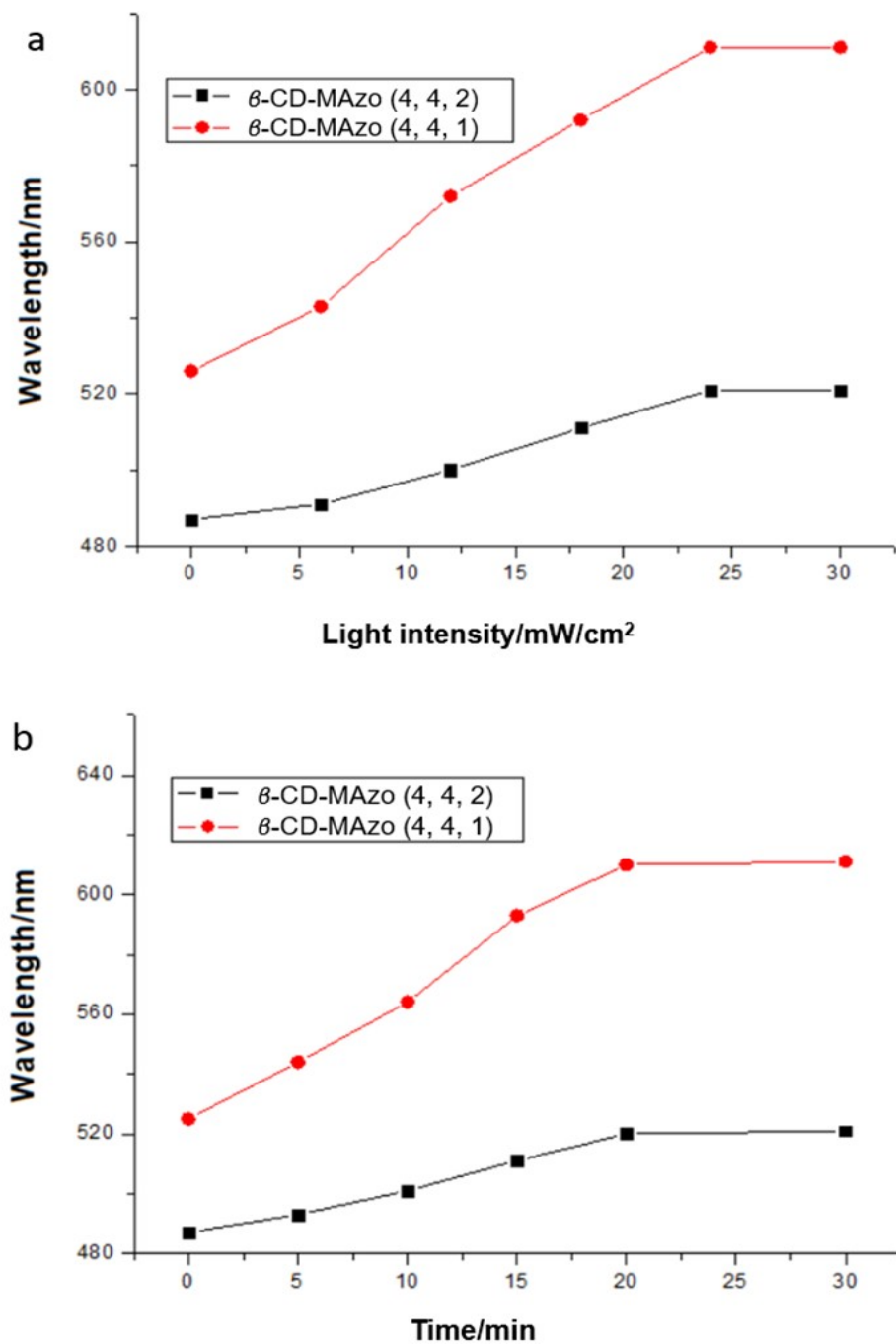
**Figure S7.** FT-IR spectra of (a) PAAm gel, (b)  $\beta$ -CD-MAzo gel (4, 4, 1) and (c)  $\beta$ -CD-MAzo (4, 4, 2) gel

#### 4. Control experiment

##### (1) Irradiation intensity



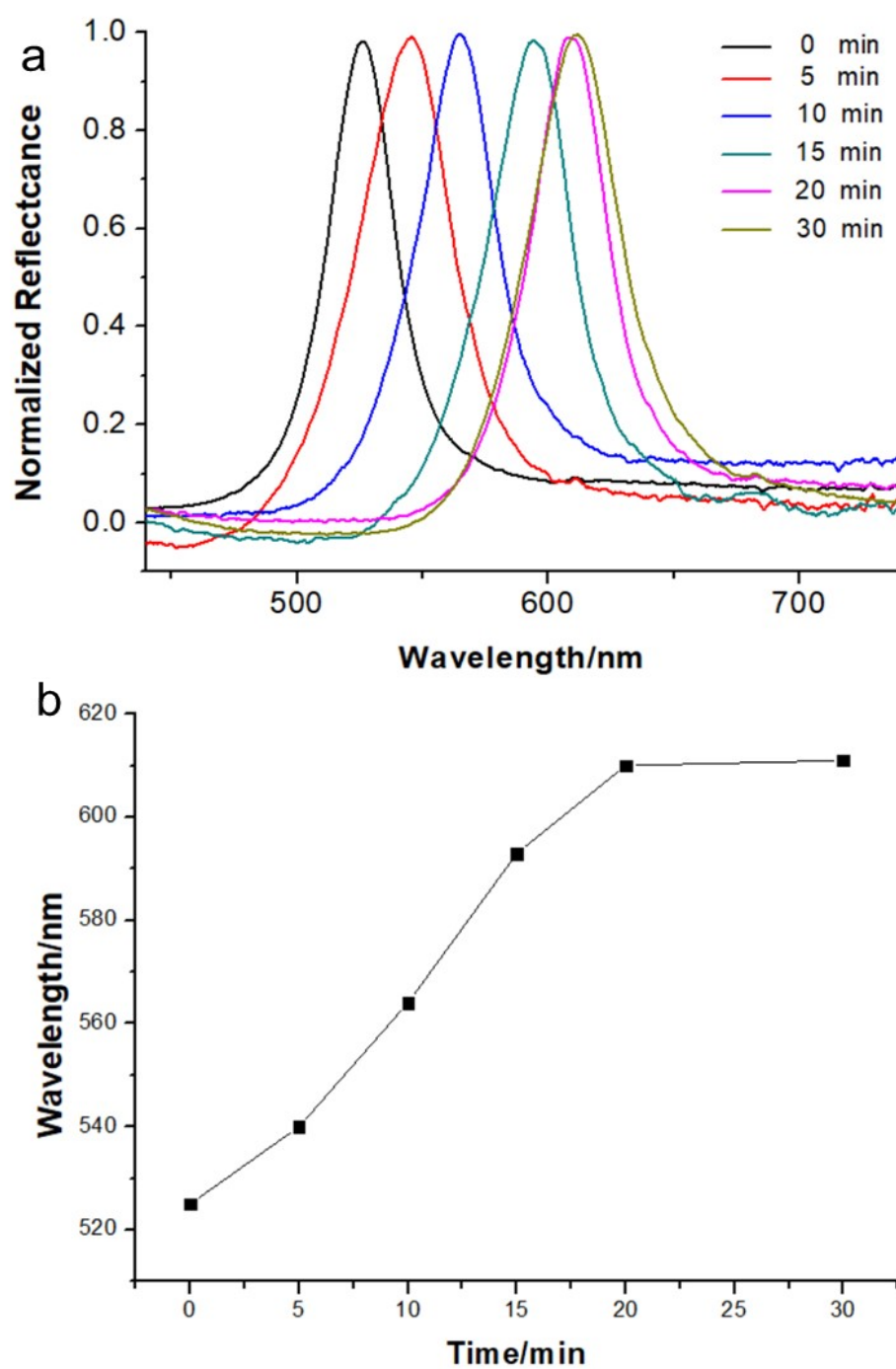
**Figure S8.** (a) Bragg diffraction of the  $\beta$ -CD-MAzo (4, 4, 2) with red light irradiation for 5 min and irradiation intensity increased from 0 to 30 mW/cm<sup>2</sup>. (b) Bragg diffraction of the  $\beta$ -CD-MAzo (4, 4, 1) with red light irradiation for 5 min and irradiation intensity increased from 0 to 30 mW/cm<sup>2</sup>.



**Figure S9.** (a) Bragg peak shift of the inverse opal hydrogel with red light irradiation intensity increased from 0 to 30 mW/cm<sup>2</sup>: mole percentage of the cross-linker MBAAm at 1 mol% (red line) and 2 mol% (black line). (b) Bragg peak shift of the inverse opal hydrogel with red light irradiation time increased from 0 to 30 minutes: mole percentage of the cross-linker MBAAm at 1 mol% (red line) and 2 mol% (black line).

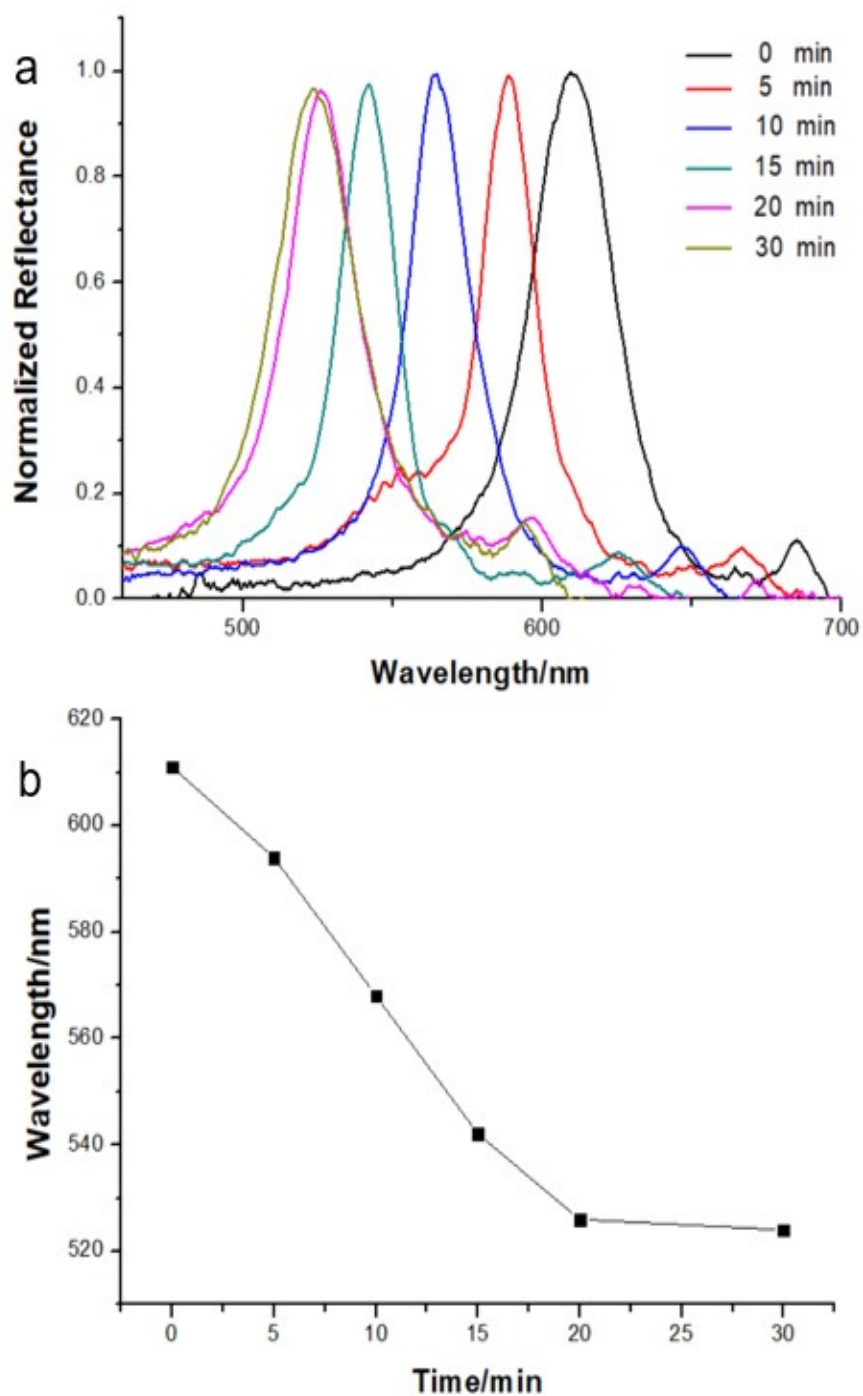
## (2) Red/Blue shift

Red-shift



**Figure S10.** Bragg diffraction of the  $\beta$ -CD-MAZo (4, 4, 1) hydrogel PC with red light irradiation time increased from 0 to 30 minutes with red light irradiation intensity fixed to 12 mW/cm<sup>2</sup>.

# Blue-shift



**Figure S11.** Bragg diffraction of the  $\beta$ -CD-MAZo (4, 4, 1) hydrogel PC with blue light irradiation time increased from 0 to 30 minutes with blue light irradiation intensity fixed to 12 mW/cm<sup>2</sup>.

## Notes and references

- 1 P. Jiang, J. F. Bertone, K. S. Hwang, and V. L. Colvin, *Chem. Mater.* 1999, **11**, 2132-2140.
- 2 M. Nakahata, Y. Takashima, H. Yamaguchi, A. Harada, *Nat. Commun.* 2011, **2**, 511.
- 3 P. Weis, D. Wang, S. Wu. *Macromolecules*, 2016, **4**, 6368-6373.
- 4 K. Miyamae, M. Nakahata, Y. Takashima, A. Harada, *Angew. Chem. Int. Ed.* 2015, **54**, 8984-8987.