Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2022

Supporting Information

Switchable Lasers via Solvent Stimuli-Responsive Photonic Crystals

Bao-Xin Zhang, [a,b] *Feng Jin,*[*, a] *Xian-Zi Dong,* [a] *Jie Liu,* [a] *Mei-Ling Zheng*[*, a, b]

a. Laboratory of Organic NanoPhotonics and CAS Key Laboratory of Bio-Inspired Materials and Interfacial Science, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, No. 29, Zhongguancun East Road, Beijing, 100190, P. R. China
b. University of Chinese Academy of Sciences, Yanqihu Campus, Beijing, 101407, P. R. China

Correspondence and requests for materials should be addressed to F. Jin (jinfeng@mail.ipc.ac.cn) or M.-L. Zheng (zhengmeiling@mail.ipc.ac.cn).

Experimental Section

Materials. N-Isopropyl acrylamide (NIPAM) was purchased from Tokyo Chemical Industry Co., Ltd. Acrylic acid (AA), acetaldehyde solution (40 % solution in water), toluene, polyvinyl alcohol (PVA), polystyrene resin (PS) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. The supernatant of 40% acetaldehyde solution is denoted as the supernatant and used to redshift the stopband of the RPCs. Dipentaerythritol hexacrylate (DPE-6A) was purchased from Kyoeisha Chemical Co. Ltd., Japan. Benzil and 2-benzyl–2-(dimethylamino)-4-morpholinobutyrophenone were purchased from Sigma Aldrich (Shanghai) Trading Co., Ltd. 3-(Trimethoxysilyl) propyl methacrylate (KH-570) was purchased from Nanjing Chuangshi Chemical Co., Ltd. Tetrahydrofuran (THF), fluorescein sodium and coumarin 307 were purchased from J&K Chemical Co., Ltd. Rhodamine B was purchased from Tianjin Hengxing Chemical Reagent Co., Ltd. Ethanol, hydrogen peroxide (H_2O_2) and sulfuric acid (H_2SO_4) were purchased from Modern Oriental (Beijing) Technology Development Co., Ltd. The glass substrates were purchased from Yancheng Flying Boat Glass Co. Ltd. All of the chemicals are used without further purification.

Preparation of photoresist. During the preparation of photoresist, benzil (12 mg, 1.2 wt%, photoinitiator) and 2-benzyl–2-(dimethylamino)-4'-morpholinobutyrophenone (12 mg, 1.2 wt%, photosensitizer) were dissolved in AA (362 mg, 36.2 wt%, monomer) and NIPAm (354 mg, 35.4 wt%, monomer) in dark room at room temperature. Then DPE-6A (260 mg, 26 wt%, cross-linking agent) was added to the above solution and stirred for 4 h. The composition of the photoresist is shown in Table S2.

Fabrication of PS colloidal crystals. PS colloidal crystal templates were prepared by vertical deposition method.[1] Firstly, the glasses were cleaned by piranha solution, rinsed with deionized water, and dried. Secondly, the glass was vertically immersed in PS emulsion (0.21wt %) with the diameter of 280 nm and 380 nm in the oven, and heated at 65℃ for 72 hours.

Preparation of RPCs. We prepared RPCs by template method.[38] Firstly, the glass slides were cleaned and soaked in 5 wt% KH-570/toluene solution overnight. Then, the glasses were rinsed with anhydrous ethanol and dried. The KH-570 treated glass was used to cover PS colloidal crystal templates. Secondly, the photoresist is transported into the void of PS colloidal crystal template by capillary effect. Thirdly, photoresist was cured by a high-voltage Hg mercury lamp (power: 32.5 $mW \cdot cm^{-2}$, wavelength: 365 nm) irradiation via the photopolymerization. Then the sandwiched structure was separated. Finally, PS microspheres were removed by soaking in THF overnight to obtain the RPCs.

Preparation of dye doped Polymer films with different colors. We prepared dye doped polymer films with blue, green and red color, respectively. The preparation process and the components of dye doped polymer films are shown in supporting information, Figure S7, Table S1 and Table S3. (1) C-307/PS films (3 wt %) with blue color. Firstly, 0.2 g PS was added to 1 g THF to prepared PS/THF solution (1g, 20 wt %). Secondly, C-307 (6 mg) was added to the PS-THF solution. The solution was mixed thoroughly. The C-307/PS film was constructed by spin-coating C-307/THF solution at 1000 rad/min, and the evaporation of THF. (2) FSS/PVA films (3 wt %) with green color. Firstly, PVA-water solution (3 g, 10 wt %) was prepared by

resolving 0.3 g PVA in 3 g water at 80 ℃. Secondly, FSS (9 mg) was added to the PVA/water solution and mixed thoroughly. The green film was produced by spin-coating of FSS/PVA/water solution at 300 rad/min, and the evaporation of water. (3) RhB/photoresist films (4.8 wt %) with red color. Firstly, RhB (50 mg) was added to 1 g photoresist solution (Table S3). Secondly, two cleaned glasses and a paper was used to make a cavity. The RhB doped photoresist is transported into the gap of glasses by capillary effect. Thirdly, RhB doped photoresist was cured by UV lamp (320 W high-pressure Hg Arc lamp) irradiation. After photopolymerization, the sandwiched structure was separated to obtain the red RhB/ photoresist films.

Preparation of RPC resonators. The RPC resonators are constructed by sandwiching two RPCs with dye doped polymer film, as shown in Figure S16. To obtain the blue lasing emission, C-307/PS film and original RPC_{280nm} are employed to fabricate the RPC resonator (Figure S16A). Meanwhile, FSS/PVA film and original $RPC_{380\ nm}$ are used to construct the resonator for green lasing emission (Figure S16B). RhB/Photoresist film and the supernatant of 40 % acetaldehyde-treated $RPC_{380\ nm}$ are used to prepare for the resonator for red lasing emission (Figure S16C). Furthermore, the RPC resonator, which can produce tunable lasing emission from blue to green, is constructed by the RPC_{280nm}, C-307/PS film and FSS/PVA film as shown in Figure S16D. Figure S16E demonstrates the process of the fabrication of RPC resonator by RPC_{380nm}, FSS/PVA film and RhB/photoresist film to obtain switchable lasing emission from green to red.

Measurements. The UV-Vis spectra were taken by Shimadzu UV-2550 photospectrometer. The photoluminescence (PL) spectra were obtained by using a Hitachi F-4500 fluorescence spectrometer. The reflection spectra were obtained by the FT-IR Spectrometer (VERTEX 70v FT-IR Spectrometer, Bruker) equipped with microscope (Hyperion 1000, Bruker). The solvent response of the RPCs to the supernatant of 40 % acetaldehyde and THF are evaluated by measuring the reflection spectra after exposure to the

supernatant of 40 % acetaldehyde and THF. The SEM images were recorded by a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Photo-pumped emission spectra were obtained by using an excitation beam produced by nanosecond pulsed laser (Nd: YAG, 8 ns, 10 Hz, Spectrum Physics) with OPO at 355, 460 and 532 nm, respectively. The emission spectra were measured by a home-made measurement equipment with SD 2000 fiber optic spectrometer (Figure S17). The mass spectra were measured by gas chromatograph-Mass spectrometer (Shimadzu, GCMS-QP2020 NX, Japan). The ^{1}H NMR spectra were taken by nuclear magnetic resonance spectrometer (Bruker, Advance-400). All the measurements are carried out at room temperature.

Supporting Figures

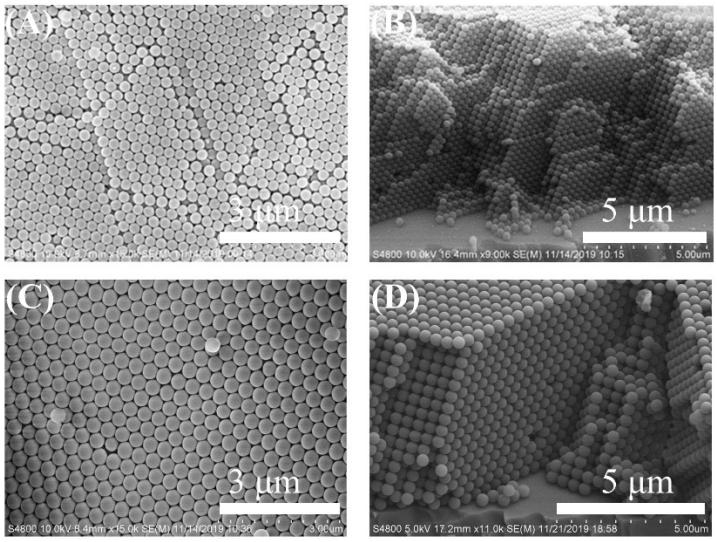


Figure S1. SEM images of PS colloidal crystal templates used to construct RPCs. SEM images of 280 nm PS colloidal crystal template at (A) top view, and (B) side view. SEM images of 380 nm PS colloidal crystal template at (C) top view, and (D) side view

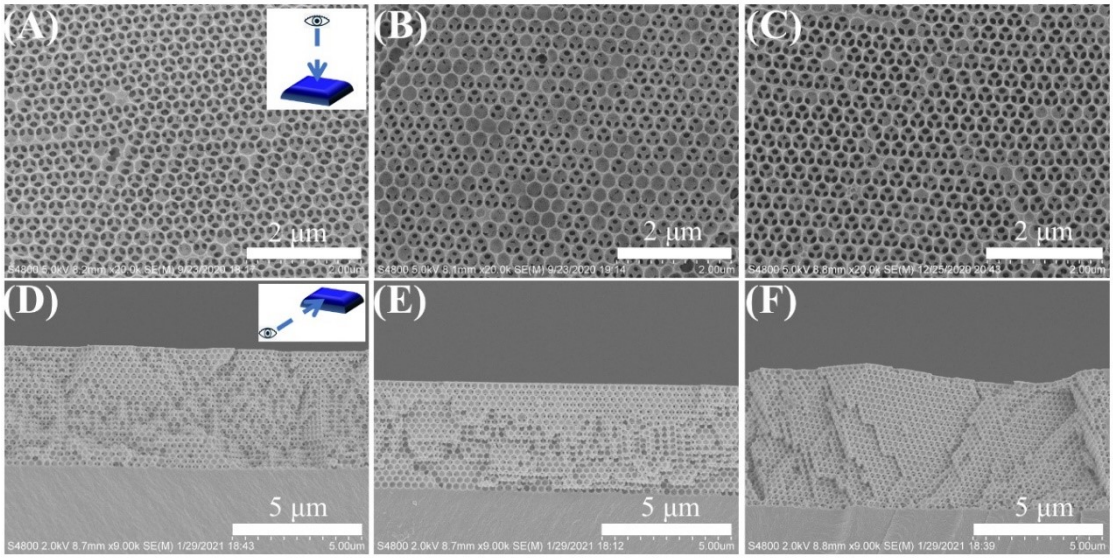


Figure S2. SEM images of RPC_{280nm} with the treatment of the supernatant of 40 % acetaldehyde and THF. Top view SEM images of (A) original, (B) the supernatant of 40 % acetaldehyde-treated, and (C) THF-treated RPC_{280nm}. The inset is a schematic diagram of the viewing angle. Cross-sectional view SEM images of (D) original, (E) the supernatant of 40 % acetaldehyde-treated, and (F) THF-treated RPC_{280nm}. The insets are schematic diagram of the viewing angle of the SEM images

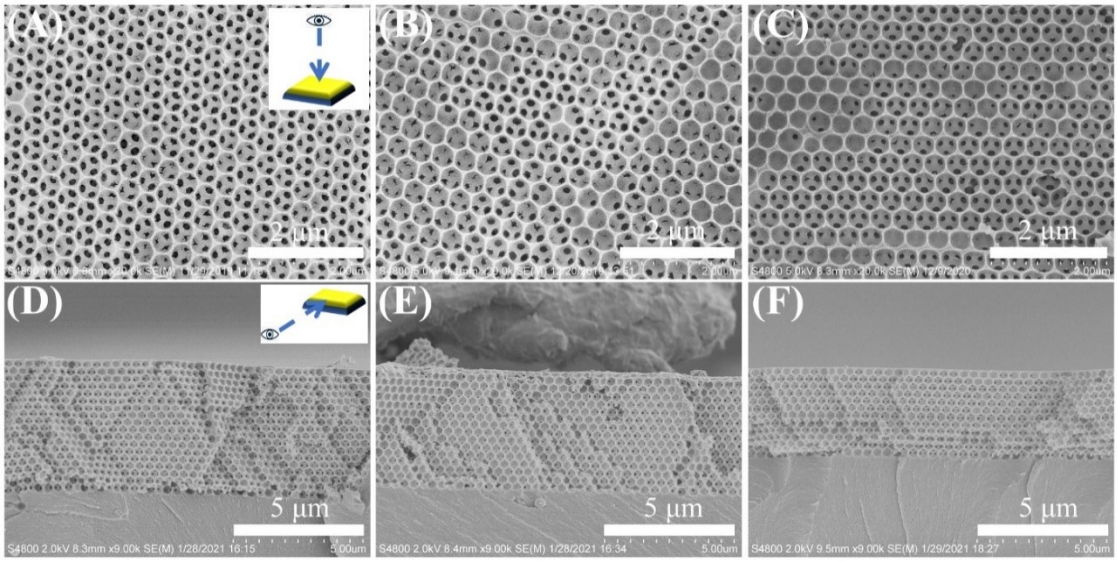


Figure S3. SEM images of RPC_{380nm} with the treatment of the supernatant of 40 % acetaldehyde and THF. Top view SEM image of (A) original (B) the supernatant of 40 % acetaldehyde-treated (C) THF-treated RPC_{380nm}. The inset is a schematic diagram of the viewing angle. Cross-

sectional view SEM image of (D) original (E) the supernatant of 40 % acetaldehyde-treated (F) THF-treated RPC_{380nm}. The insets are a schematic diagram of the viewing angle of the SEM images

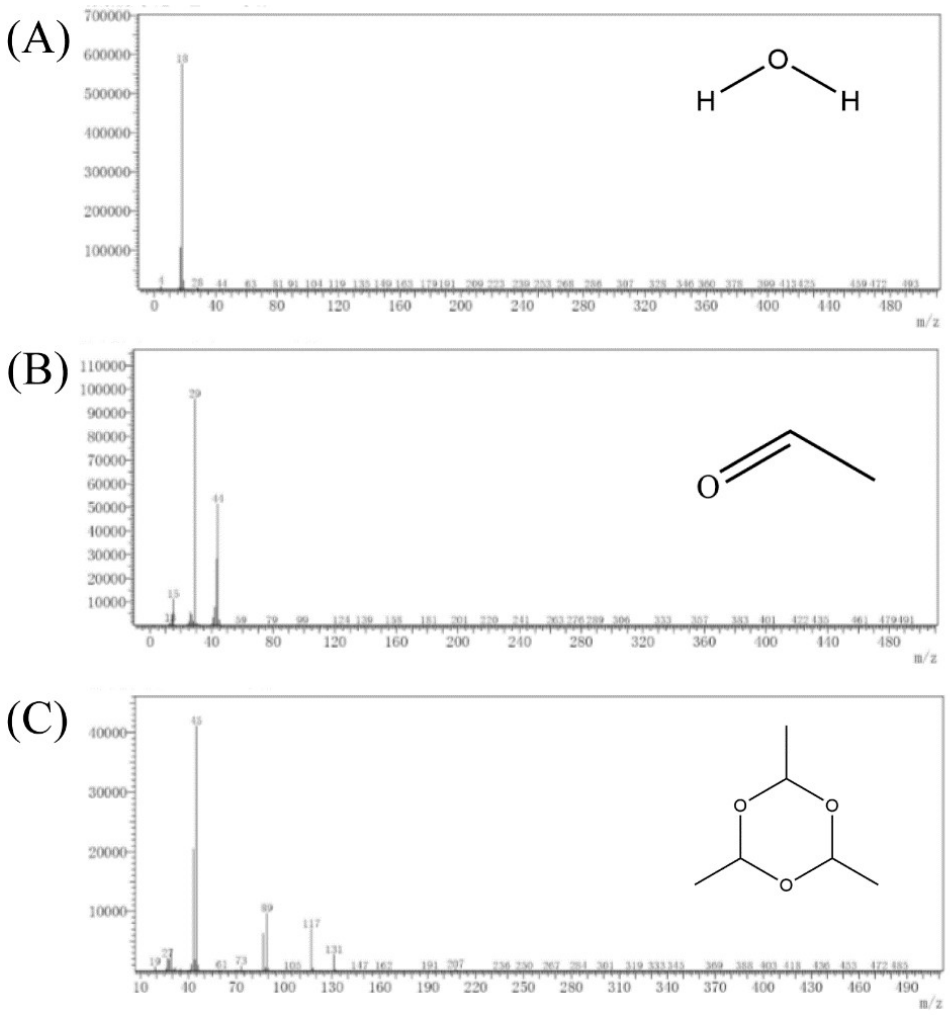


Figure S4. Mass spectra of Gas Chromatography-Mass Spectrometer of supernatant of 40 % acetaldehyde solution. (A) The spectrum at low-boiling point. (B, C) The spectra at low-boiling point

Mass spectra of Gas Chromatography-Mass Spectrometer of supernatant of 40 % acetaldehyde are shown in Figure S4. By comparison with the standard spectrum, the composition of the supernatant of 40 % acetaldehyde was determined to be water, acetaldehyde and paraldehyde.

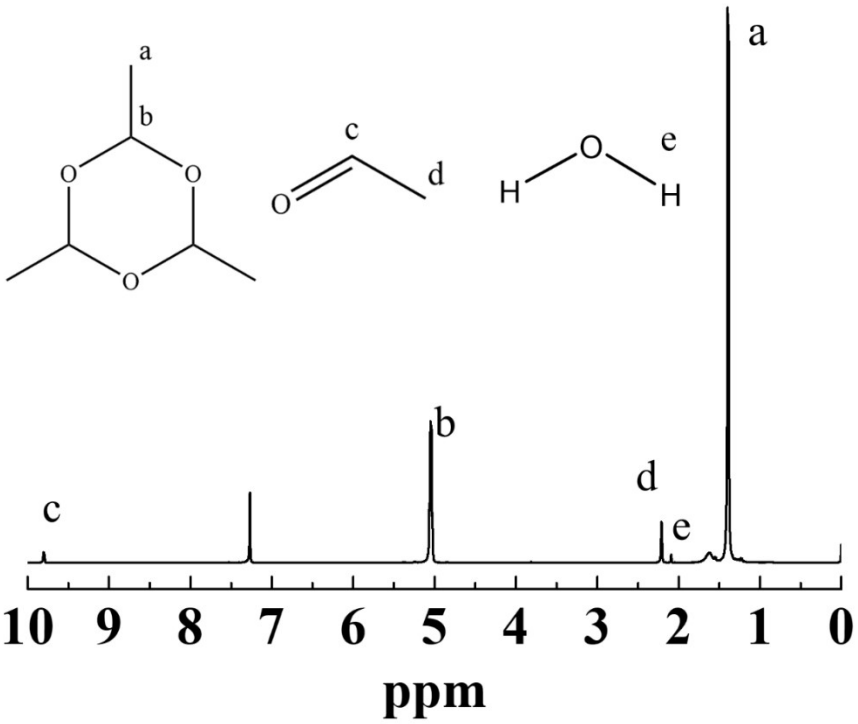


Figure S5. The ^{1}H NMR spectrum of supernatant of 40 % acetaldehyde solution

The ^{1}H NMR spectrum of supernatant of 40 % acetaldehyde solution is shown in Figure S5. The ^{1}H NMR spectrum confirms that the ingredient and content of supernatant of 40 % acetaldehyde solution are acetaldehyde: paraldehyde: water (wt %: wt %: wt %) = 1: 16.53: 0.73.

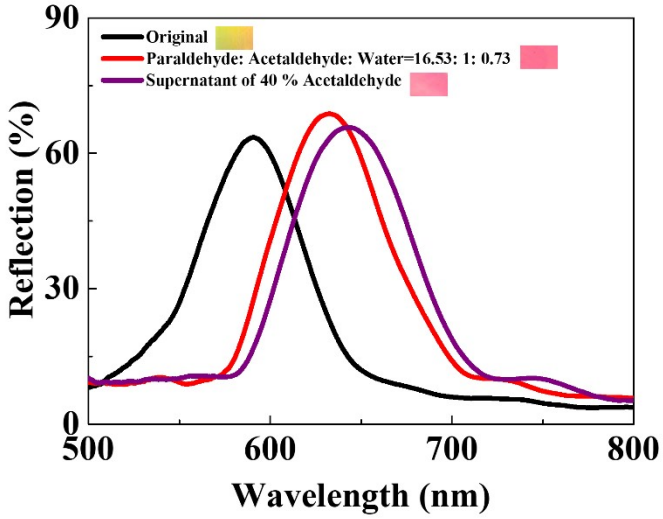


Figure S6. The reflection spectra of RPC_{380nm} under different treatment. The insets are photos of the RPC_{380nm} at corresponsive state

The composition and content about supernatant of 40 % acetaldehyde solution was obtained by Mass spectra of Gas Chromatography-Mass Spectrometer and ^{1}H NMR. To further verify the constituent, the simulated solution of $m_{acetaldehyde}$: $m_{paraldehyde}$: m_{water} = 1: 16.53: 0.73 has been prepared. The stopband redshift of simulated solution treated RPC_{380nm} is similar to that of the supernatant of 40 % acetaldehyde treated RPC_{380nm}, as shown in Figure S6. Therefore, the effective constituent of the supernatant of 40 % acetaldehyde is $m_{acetaldehyde}$: $m_{paraldehyde}$: m_{water} = 1: 16.53: 0.73.

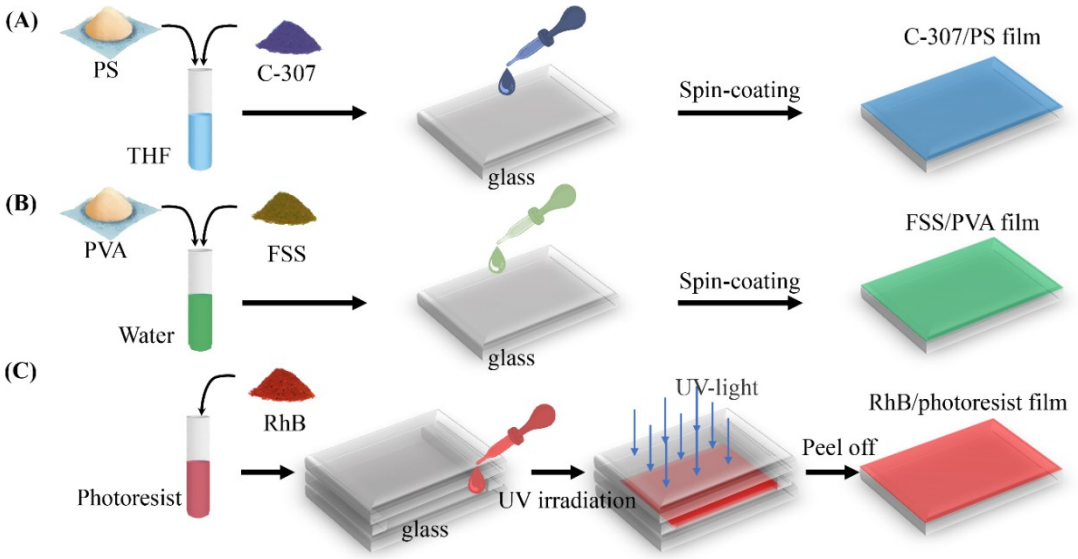


Figure S7. Schematic diagram of the preparation of dye doped polymer films with different colors. The process of fabricating (A) C-307/PS film, (B) FSS/PVA film, and (C) RhB/photoresist film

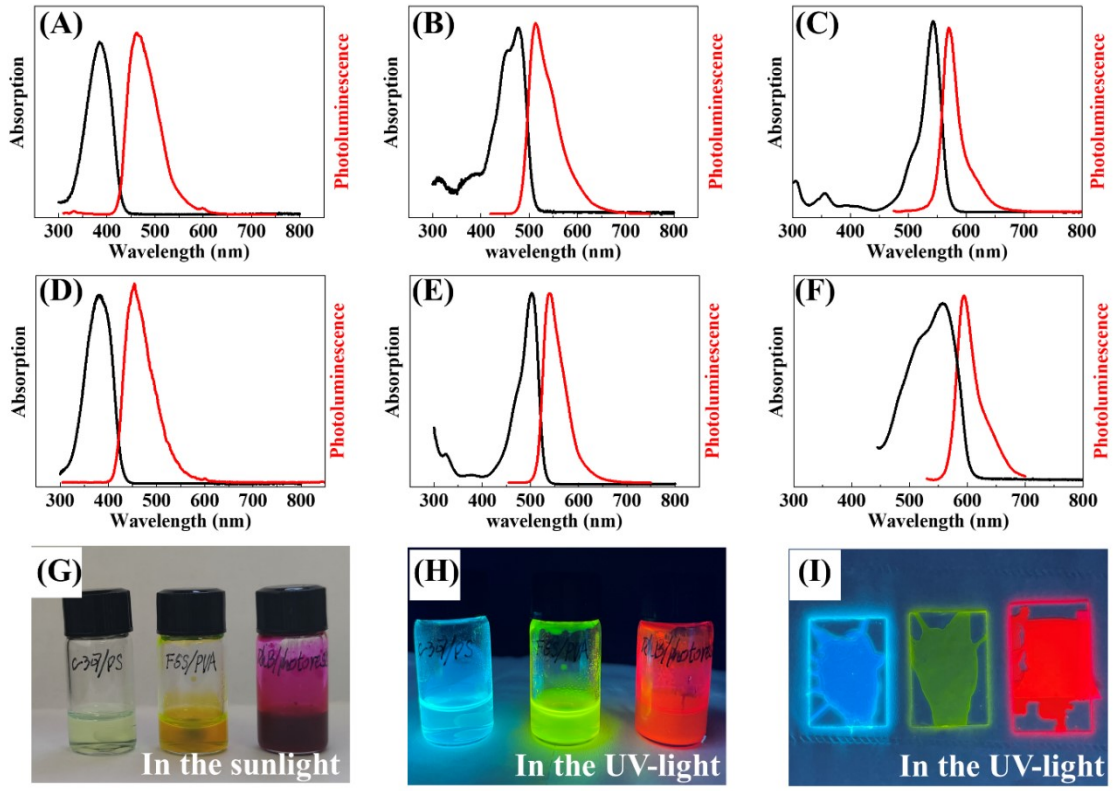


Figure S8. UV absorption, PL spectra and photos of dye solution, dye doped polymer solution and dye doped polymer films. The UV absorption and PL spectra of (A) $1x10^{-5}$ M C-307/THF solution, (B) $1x10^{-5}$ M FSS/water solution, (C) $1x10^{-5}$ M RhB/ethanol solution, (D) C-307/PS film (3 wt %), (E) FSS/PVA film (3 wt %), and (F) RhB/photoresist film (4.8 wt %). The photos of (G) C-307/PS-THF (3 wt %), FSS/PVA-water (3 wt %) and RhB/photoresist (4.8 wt %) solution under the sunlight. The photos of (H) C-307/PS-THF (3 wt %), FSS/PVA-water (3 wt %) and RhB/photoresist (4.8 wt %) solution under the UV light. The photos of (I) C-307/PS (3 wt %), FSS/PVA (3 wt %) and RhB/photoresist (4.8 wt %) films under the UV light

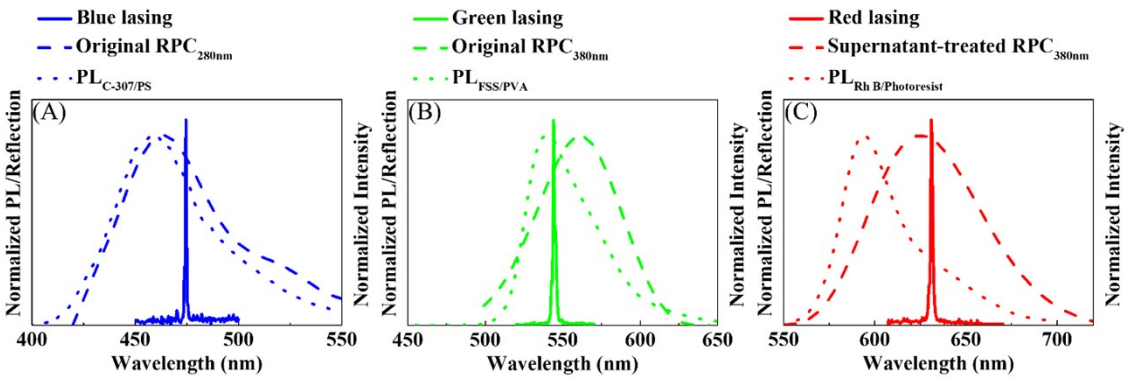


Figure S9. Photoluminescence, reflectance and emission spectra of the RPC resonators with blue, green and red colors, respectively. Photoluminescence, reflectance and emission spectra of the RPC resonators constructed by (A) C-307/PS film and RPC_{280nm}, (B) FSS/PVA film and RPC_{380nm}, (C) RhB/photoresist film and the supernatant of 40 % acetaldehyde-treated RPC_{380nm}

Figure S9 shows photoluminescence, reflectance and emission spectra of the RPC resonators with blue, green and red colors, respectively. It can be seen that the lasing emission is always located at the overlapping wavelength of the stopband of RPCs and the PL of dye doped films. As shown in Figure S9A, the stopband of original RPC_{280nm} matches the PL peak of C-307/PS film, which leads to the blue lasing emission at 475 nm. Figure S9B exhibits the green lasing emission at 544 nm due to the match of RPC_{380nm} and the PL peak of FSS/PVA film. Figure S9C displays the red lasing emission at 631 nm occurred by the overlapping of the supernatant of 40 % acetaldehyde-treated RPC_{380nm} and PL peak of RhB/photoresist film.

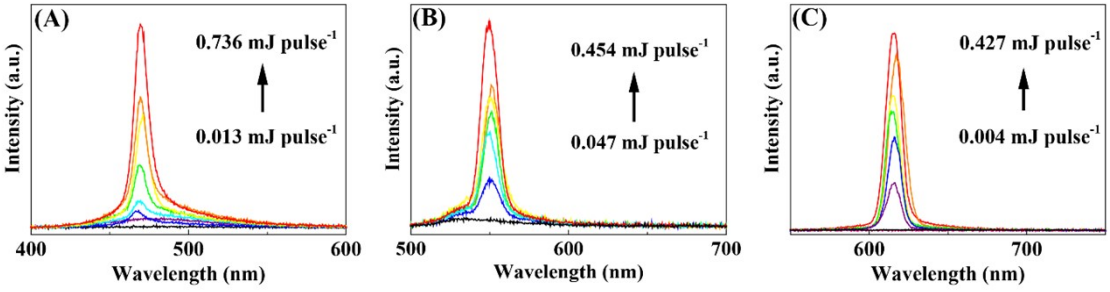


Figure S10. Emission spectra of dye doped polymer films under Nd: YAG laser excitation. (A) Emission spectra of C-307/PS film (3 wt %) under 355 nm laser excitation. (B) Emission spectra of FSS/PVA film (3 wt %) under 460 nm laser excitation. (C) Emission spectra of RhB/photoresist film (4.8 wt %) under 532 nm laser excitation

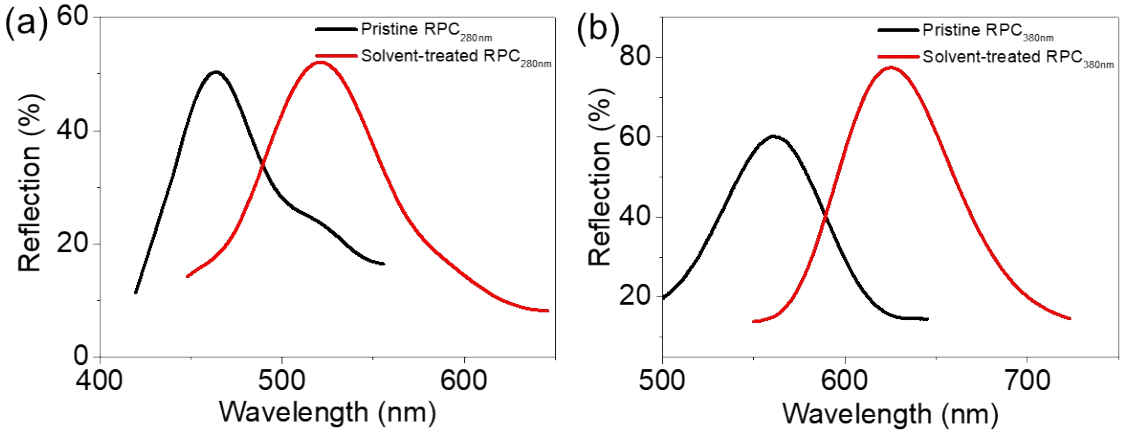


Figure S11. Reflection spectra of (A) RPC_{280nm} and (B) RPC_{380nm} before (black) and after (red) the treatment of supernatant of 40 % acetaldehyde

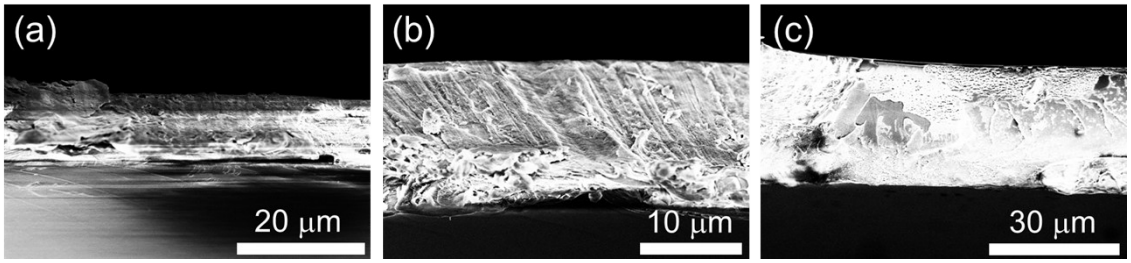


Figure S12. SEM images of the dye doped polymer films for (a) C-307/PS film, (b) FSS/PVA film, and (c) RhB/Photoresist film

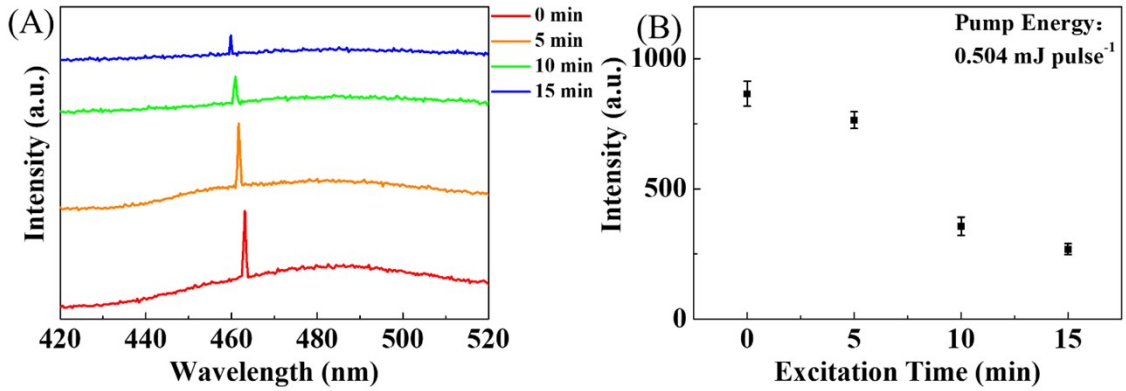


Figure S13. Emission spectra of RPC resonator constructed by C-307/PS film and RPC_{280nm}. (A) Emission spectra of RPC resonator under different laser irradiation time. (B) Emission intensity of resonator with different irradiation time

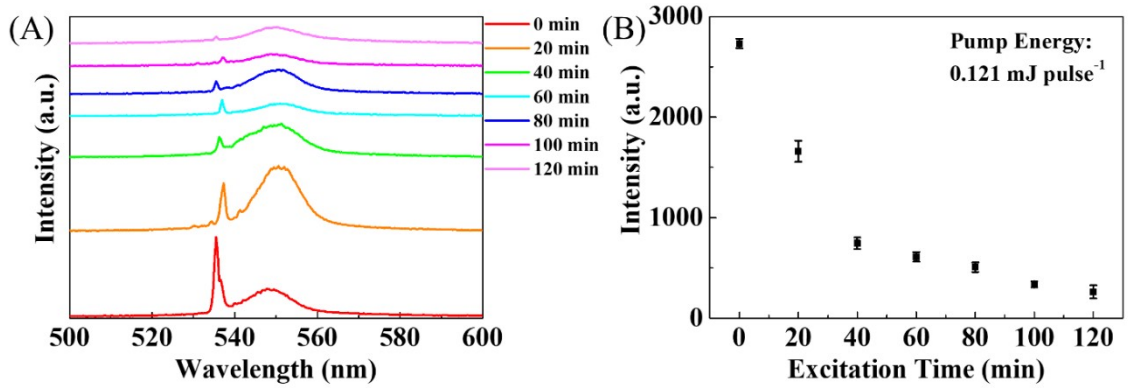


Figure S14. Emission spectra of RPC resonator constructed by FSS/PVA film and RPC_{380nm}. (A) Emission spectra of RPC resonator under different laser irradiation time. (B) Emission intensity of resonator with different irradiation time

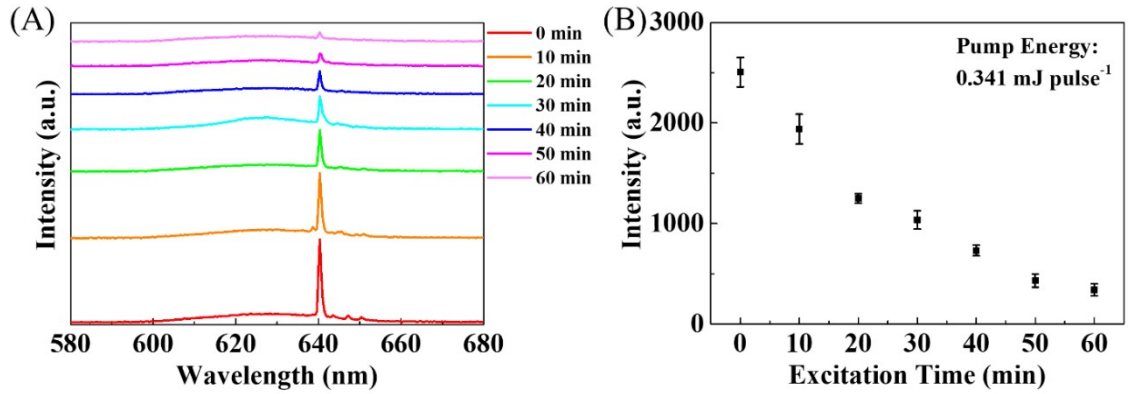


Figure S15. Emission spectra of RPC resonator constructed by RhB/photoresist film and the supernatant of 40 % acetaldehyde-treated RPC_{380nm}. (A) Emission spectra of RPC resonator under different laser irradiation time. (B) Emission intensity of resonator with different irradiation time

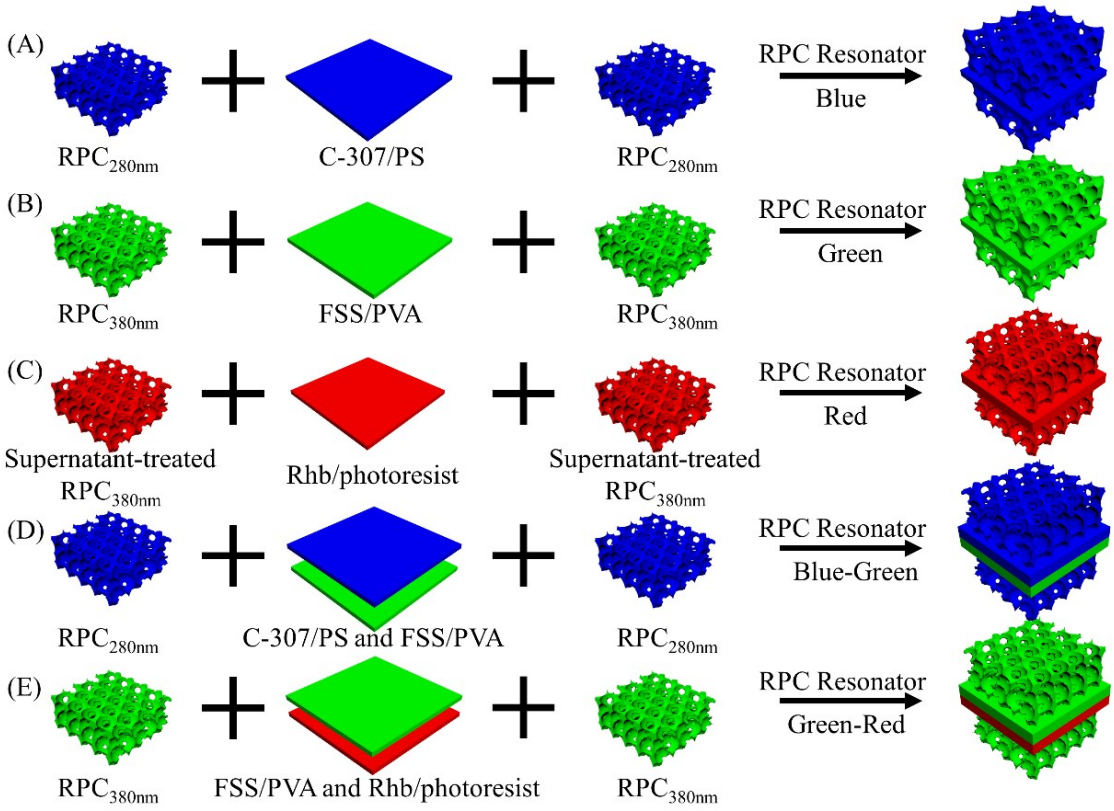


Figure S16. Schematic diagram of fabricating the RPC resonators. (A) Schematic diagram of fabricating the RPC resonator by original RPC_{280nm} and C-307/PS film to achieve single-wavelength lasing emission with blue color. (B) Schematic diagram of preparing the RPC resonator by RPC_{380nm} and FSS/PVA film to obtained single-wavelength lasing emission with green color. (C) Schematic diagram of constructing the RPC resonator by supernatant-treated RPC_{380nm} and RhB/photoresist film to obtained single-wavelength lasing emission with red color. (D) Schematic diagram of fabricating the RPC resonator by RPC_{280nm}, C-307/PS film and FSS/PVA film to achieve switchable lasing emission between blue and green color. (E) Schematic diagram of preparing the RPC resonator by RPC_{380nm}, FSS/PVA film and RhB/photoresist film to obtain switchable lasing emission between green and red color

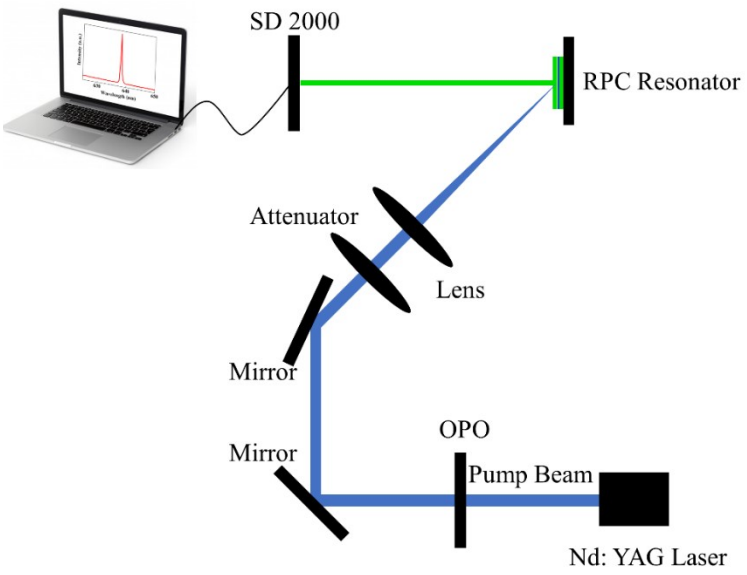


Figure S17. Schematic diagram of the home-made measurement equipment for the emission spectra under the pulsed Nd: YAG laser irradiation

As shown in Figure S17, photo-pumped emission spectra were obtained by using an excitation beam produced by nanosecond pulsed laser (Nd: YAG, 8 ns, 10 Hz, Spectrum Physics) with OPO at 355, 460 and 532 nm. The lasing emission spectra was measured by a home-made measurement equipment with SD 2000 fiber optic spectrometer. All the measurements are carried out at room temperature.

Table S1. Components of the dye-polymer solution for constructing polymer film

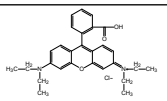
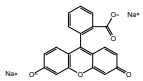
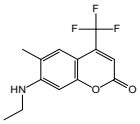
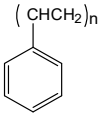
Polymer film	Dye	Formula	Polymer	Formula	Solvent	Formula
Red	Rhodamine B		Photoresist	Table S3	-	-
Green	Fluorescein sodium		PVA		Water	
Blue	Coumarin 307		PS		THF	

Table S2. Components of the photoresist for constructing responsive photonic crystals

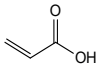
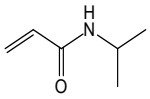
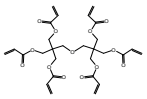
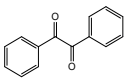
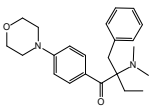
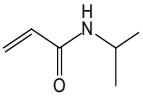
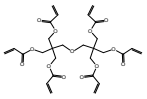
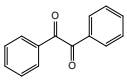
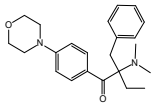
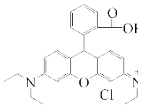
Material	AA	NIPAm	DPE-6A	Benzil	Photosensitizer
Formula					
Weight percentage [%]	36.2	35.4	26	1.2	1.2

Table S3. Components of the photoresist for constructing RhB doped polymer film

Material	AA	NIPAm	DPE-6A	Benzil	Photosensitizer	RhB
Formula						
Weight percentage [%]	24.9	24.3	43.8	1.1	1.1	4.8

Reference

[1] P. Jiang, J. F. Bertone, K. S. Hwang, V. L. Colvin, *Chem. Mat.* **1999**, 11, 2132.