## Supporting Information

# Monodisperse and size-regulable nanoparticles by polymerization-induced self-assembly for printable colloidal photonic crystals

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## **Experimental section**

## 1. Chemicals

Poly(ethylene glycol) methyl ether (mPEG<sub>45</sub>-OH;  $M_{average} \approx 2000$  g/mol, Aldrich), randomly methylated- $\beta$ -cyclodextrin (MCD;  $M_n = 1303$  g/mol, rate of substitution is 57.1% calculated from  $M_n$ , Bidepharm, 99.9%), 2,2'-azobis(2-methylpropionamide) dihydrochloride (VA-056; J&K, 98%), 2,3,4,5,6-pentafluorostyrene (PFS; Energy Chemical, 98%), oxalyl chloride (Macklin, 98%), fluorescein PEG thiol (FITC; 1000 Da, Aladdin, 95%), 2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl] propanoic acid (TTC) were synthesized according to the previously published procedures.<sup>1</sup>

## 2. Characterization

### 2.1 Nuclear Magnetic Resonance (NMR)

JEOL JNM-ECZ400S spectrometer (400 MHz) and JEOL JNM-ECA 400 spectrometer (400 MHz) was used to record <sup>1</sup>H NMR spectra. JEOL JNM-ECZ400S spectrometer (376 MHz) was used to record <sup>19</sup>F NMR spectra. The solvents include CDCl<sub>3</sub>, acetone-d<sub>6</sub>, and CDCl<sub>3</sub>/trichlorotrifluoroethane (1:1 v/v).

### 2.2 Size Exclusion Chromatography (SEC)

The number-average molecular weight, weight-average molecular weight, and polydispersity of polymers were characterized by a Waters 1515 Gel permeation chromatography (GPC) instrument with THF (with 2% v/v triethylamine) as eluent at 35 °C. The flow rate was 1.0 mL/min. A series of narrow distribution linear polystyrene ( $M_p$  from 580 to 2580000 g/mol) was used for calibration.

## 2.3 Dynamic Light Scattering (DLS)/ Electrophoresis Light Scattering

The hydrodynamic diameter of nanoparticles was measured by dynamic light scattering (DLS). Malvern Zetasizer Nano ZS90 recorded the DLS curves of nanoparticles with a He-Ne laser (633 nm) at 25 °C. The scattering light at 90° was detected. Before the DLS measurement, all the dispersions were diluted. The zeta potential of nanoparticles is determined by electrophoresis light scattering using the same instrument at 25 °C.

#### 2.4 Transmission Electron Microscope (TEM)

Hitachi H-7650B transmission electron microscope (TEM, acceleration voltage at 80 kV) was used to investigate the morphology of nanoparticles. Before the TEM measurements, all the dispersions were diluted. In a typical preparation of the sample, the diluted dispersion of nanoparticles (10  $\mu$ L) was dropped onto a carbon-coated copper grid. The excess dispersion was blotted by an airlaid paper (Kimtech Science, Kimwipes) after 1 min. The copper grids were dried at room temperature overnight before the test. The TEM images of nanoparticles have been analyzed by ImageJ software. We took the Feret diameter as the particle diameter, after screening the particles with area larger than 30000 nm<sup>2</sup> and circularity between 0.80 and 1.00 to plot the statistical histograms (a circularity of 1.00 indicates that the particle is a perfect circle).

#### 2.5 Scanning Electron Microscope (SEM)

Hitachi SU-8010 scanning electron microscope (SEM, acceleration voltage at 10 kV) was used to demonstrate the morphology of nanoparticles and the microscopic arrays self-assembled by nanoparticles. Before the SEM measurements, all the dispersions were diluted. In a typical preparation of the nanoparticle sample, the diluted dispersion of nanoparticles was dropped onto a clean silicon wafer and heated at 60 °C until dry. For the SEM characterization of printed photonic patterns, the paper samples

were cut to about 1\*1 cm<sup>2</sup>. The surfaces were all sprayed with platinum before the test.

### 2.6 Optical Characterization

The reflection spectra were measured by an optical spectrometer (Ocean Optics, USB2000+) combined with a metallurgical microscope (Olympus, BX51M). The angle-dependent reflection spectra are acquired by angle resolution spectrograph (R1 Macroscopic Angle Resolution Spectrograph. Shanghai Ideaoptics Corporation). The measurements were made in reflection mode with the incident angle varying from  $0^{\circ}$  to  $60^{\circ}$ .

### 2.7 Digital Photographs

All of the photographs and movies were taken by a digital camera (Sony, ILCE-7M3).

#### 2.8 Infrared & Fluorescence Spectra

The Fourier-transform infrared (FT-IR) spectra were collected in attenuated total reflection (ATR) mode by a PerkinElmer Spectrum 100 FT-IR Spectrometer. The fluorescence spectra were collected by a Shimadzu RF-6000 Spectro fluorophotometer equipped with quartz cuvettes.

## 3. Synthesis and polymerization

#### 3.1 Synthesis of macro chain transfer agents PEG<sub>45</sub>-TTC

Oxalyl chloride (1.29 mL, 15 mmol), TTC (3.6 g, 10 mmol), and dichloromethane (DCM, 50 mL) were added into a dry round-bottom flask and stirring at room temperature. The reaction was stopped when the gas did not generate, and then solvent and excess oxalyl chloride were removed by rotary evaporation. Then mPEG<sub>45</sub>-OH (5 g, 2.5 mmol) and DCM (50 mL) were added, and the mixture was stirred at room temperature for 24 h. After concentration, the mixture was precipitated in diethyl ether. The product was collected after centrifugation and dried in vacuum oven at room temperature.

### 3.2 Polymerization of PEG-b-PPFS (PPFS<sub>x</sub>)

In a typical polymerization of  $PEG_{45}$ -*b*-PPFS<sub>500</sub> with solid content of 15% w/w, PFS (5.82 g, 30 mmol), PEG<sub>45</sub>-TTC (141.6 mg, 0.06 mmol), MCD (19.55 g, 15 mmol), and VA-056 (4.9 mg, 0.018 mmol) were weighted into a certain amount of water (32.98 g, 32.98 mL) in a 100 mL dry round-bottom flask. After 30 min of deoxygenation by argon and stirring process, the polymerization was started at 60 °C. The polymerization was typically run for 12 h to achieve the quantitative monomer conversion. The milky products were undergoing dialysis (3000 Da) to remove free MCD, and were then freeze-dried for the <sup>1</sup>H\<sup>19</sup>F NMR and SEC characterization. The feed of PFS was depend on the target degree of polymerization, and the detailed feeds of polymerization are available in Table S1 for other DP. MCD are not involved in calculations of solid content.

No.	PFS / g	PEG <sub>45</sub> -TTC / mg	VA-056 / mg	MCD / g	H <sub>2</sub> O / g
PPFS <sub>200</sub>	5.82	354.0	12.2	19.55	32.98
PPFS <sub>300</sub>	5.82	236.0	8.1	19.55	32.98
PPFS <sub>400</sub>	5.82	177.0	6.1	19.55	32.98
PPFS <sub>500</sub>	5.82	141.6	4.9	19.55	32.98

Table S1. Detail feeds of PISA formulations

#### 3.3 Post-modification of PPFS<sub>x</sub>

The PPFS<sub>500</sub> dispersion (7.5% w/w, 0.27 g) was add into buffer (pH 13) in a 5 mL tube and stirred for 15 min at room temperature. The buffer was configured according to previously published procedures<sup>2</sup>:

NaOH solution (0.4 mol/L, 0.45 mL), NaCl solution (5.86 g/L, 0.70 mL), and glycine solution (7.52 g/L, 0.70 mL). The FITC (1000 Da, 25 mg) was then added and the tube was sealed and purged with argon for 30 min in an ice bath. The tube was then placed in a pre-heated oil bath at 50 °C. The reaction was kept for 48 h. After the reaction, the dispersion was dialyzed (3000 Da) to remove free FITC until the outer dialysate was almost colorless. Part of the dispersion was freeze-dried for ATR-IR characterization.

## 4. Fabrication of photonic crystals

After dialysis of PISA products, we determined the mass fraction of the nanoparticle dispersion via freeze-drying. Subsequently, the dispersions were diluted to a suitable concentration, e.g., 4% w/w. Quantitative dispersions (generally 5  $\mu$ L, but 2.5  $\mu$ L for glass substrate) were dropped onto the substrates (including quartz, glass, silicon wafers, aluminum foil, and PTFE) using a pipette, and the solvent (water) was evaporated on a hot plate at 60 °C. The quartz sheets used in Figure 3 were pre-treated: sequentially ultrasonic-cleaning in methanol and deionized water for 20 min.

## 5. Printing of structural color patterns

### 5.1 Large-area printing

The ink consists entirely of dialyzed dispersion of nanoparticles, without other additives. In a typical large-area printing process, the diluted ink (4% w/w) was dropped onto the paper substrate with a suitable amount according to the area to be printed. Subsequently, the ink is applied to the area to be printed at an even rate with a Mayer rod (20  $\mu$ m). Discard excess ink and heat the printed portion to rapidly evaporate the moisture. Subsequently, the structural color patterns are obtained.

#### 5.2 Printing of designed patterns

The mask is made by pasting the PTFE film with skeletonized patterns on aluminum foil that fits the size of the paper substrate. The area of the aluminum foil is slightly larger than the paper substrate to facilitate fixing the mask to the substrate. In the printing process, the paper substrate is covered by the mask and only the part under the skeletonized pattern is exposed. Other printing steps are the same as for large-area printing. After the printing, the excess ink is carefully removed from the mask. The mask is removed till the pattern remains dry after the heating process, in order to avoid damaging the pattern.

## **Additional results**



Figure S1. Represent of <sup>1</sup>H NMR spectra of PEG<sub>45</sub>-TTC. (Solvent: CDCl<sub>3</sub>)



**Figure S2.** Represent of <sup>1</sup>H NMR spectra of PEG-*b*-PPFS. (Solvent:  $CDCl_3/1, 1, 2$ -trichlorotrifluoroethane, 1:1 v/v, the solutions were set overnight; the PEG peaks are truncated.)



Figure S3. Represent of <sup>19</sup>F NMR spectra of PEG-*b*-PPFS. (Solvent: acetone-d<sub>6</sub>)



Figure S4. SEC curves of PEG-*b*-PPFS and PEG-TTC

No.	<b>DP</b> target	MCD-to-PFS ratio	<i>c</i> (PFS) <sup>a</sup> / % w/w	$D_h$ / nm	PDI
1	100	2	5	168.9	0.043
2	200	2	5	185.8	0.050
3	150	1	10	179.1	0.013
4	200	1	10	180.9	0.051
5	250	1	10	183.4	0.015
6	300	1	15	184.7	0.007
7	375	1	15	211.1	0.002
8	400	0.5	25	254.8	0.034

Table S2. DLS Results of other additional PISA formulations

<sup>a</sup> Concentration of monomer (PFS) =  $m(PFS)/[m(PFS)+m(H_2O)]$ 

Table S3. NMR & SEC results of PEG-b-PPFS

	<b>DP</b> target	<b>DP</b> <sub>NMR</sub> <sup>a</sup>	$M_n$ / g·mol <sup>-1</sup>	$M_w$ / g·mol <sup>-1</sup>	Ð
PPFS <sub>200</sub>	200	223	$7.11*10^4$	9.50*10 <sup>4</sup>	1.34
PPFS <sub>300</sub>	300	247	1.01*10 <sup>5</sup>	1.49*10 <sup>5</sup>	1.48
PPFS <sub>400</sub>	400	403	$1.07*10^{5}$	$1.60*10^5$	1.50
PPFS <sub>500</sub>	500	474	1.44*10 <sup>5</sup>	$2.21*10^{5}$	1.53
PEG <sub>45</sub> -TTC	/	/	2.96*10 <sup>3</sup>	3.23*10 <sup>3</sup>	1.09

<sup>a</sup> Calculated due to the <sup>1</sup>H NMR integral results



**Figure S5.** Digital photographs of dispersion of PEG-*b*-PPFS nanoparticles as example. A) Aqueous dispersion of colloids (PPFS<sub>300</sub>), B) iridescent opal formed by the natural deposition of colloids (PPFS<sub>500</sub>).



Figure S6. Zeta potential of PPFS<sub>x</sub> colloids.



Figure S7. DLS curves of PEG-*b*-PPFS after 6 months of storage.



**Figure S8.** (A) Photographs of unmodified PPFS<sub>500</sub> (left) and FITC modified PPFS<sub>500</sub> (right) under normal light (above) and 365 nm UV light (bottom). (B) The fluorescent spectra of FITC modified (red) and unmodified (blue) PPFS<sub>500</sub> (excited wavelength 365 nm, the dispersion was diluted to approximately 0.002% w/w) (C) FT-IR spectra of FITC modified (red) and unmodified (blue) PPFS<sub>500</sub>. The post-modification steps are mentioned in experimental section 3.3.



**Figure S9.** SEM images of colloidal arrays in larger micrometer scales: (A) PPFS<sub>200</sub>, (B) PPFS<sub>300</sub>, (C) PPFS<sub>400</sub>, and (D) PPFS<sub>500</sub>. The insert images show the corresponding FFT patterns.



**Figure S10.** The angle resolution reflection curves (normalized) of (A) PPFS<sub>200</sub>, (B) PPFS<sub>300</sub>, (C) PPFS<sub>400</sub>, and (D) PPFS<sub>500</sub>-based photonic crystals.



**Figure S11.** Additional SEM images of printed photonic patterns: (A) blue, (B) green, (C) yellow, and (D) red printed patterns.



**Figure S12.** Supplemental illustration of the viewing angles  $\theta$  in Figure 5A.

A spatial Cartesian coordinate system was be established to demonstrate the observation of angledependent structural color patterns. The central point of the pattern was designated as the origin, denoted as **0**. The **xOy** plane was defined by the substrate, while the normal direction extended along the *z* axis. The light source and the camera were in the **xOz** plane, and the position of the light source remained fixed. For the line of sight (camera), the angle of inclination (complementary angle of  $\theta$ ) was set to 90° ( $\theta = 0^{\circ}$ ), 75° ( $\theta = 15^{\circ}$ ), 60° ( $\theta = 30^{\circ}$ ), 45° ( $\theta = 45^{\circ}$ ), and 30° ( $\theta = 60^{\circ}$ ), respectively.



Figure S13. Reflectance spectra of the printed pattern measured after cycles of immersion and drying.

We tested the water resistance of the printed pattern. The pattern was immersed in deionized water and kept for 1 min. Then, the removed patterned was heated to evaporate the water. Since the reflectance of photonic patterns is low in the immersed state, we only measured the reflection curves after drying the patterns. The reflection peaks of the photonic pattern did not shift significantly after 5 immersion-drying recycle process.



**Figure S14.** (A) The result of solvent evaporation-induced colloidal self-assembly using protosomatic dispersion (top view, from left to right: PPFS<sub>200</sub>, PPFS<sub>300</sub>, PPFS<sub>400</sub>, and PPFS<sub>500</sub>), and (B) the comparison of undialyzed droplets (left) with dialyzed droplets (right) for solvent evaporation-induced colloidal self-assembly (main view).



**Figure S15.** Comparison of printing results with different photonic ink concentrations. (A) 0.5% w/w, (B) 1% w/w, (C) 2% w/w, and (D) 4% w/w.



Figure S16. The printing results using protosomatic dispersion (PPFS<sub>500</sub>).

## **Movie captions**

Movie 1. Solvent evaporation-induced colloidal self-assembly to form CPCs on silicon wafer as an example.

Movie 2. Angle-dependent blueshift test of the printed structural color pattern.

Movie 3. Water-responsive redshift test of the printed structural color pattern.

## References

1. J. T. Lai, D. Filla, R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.

2. H. Turgut, A. C. Schmidt, P. Wadhwani, A. Welle. R. Müller, G. Delaittre, *Polym. Chem.*, 2017, **8**, 1288-1293