Supporting information

Solvent-Triggered Off-to-On Circular Polarization Activation via Scattering Modulation in Polymer-Based Chiral Photonic Particles for Encryption and Authentication

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Experimental Section

Materials

All solvents and materials were used as received without further purification unless otherwise stated. n-hexane (anhydrous, 98%) was purchased from Aladdin. chloroform (99.5%) was purchased from Sigma-Aldrich. Poly(vinyl alcohol) 1788 was purchased from Macklin. Ethanol (99.7%) and dichloromethane (99.5%) were purchased from Innochem. Toluene (99.5%) and Tetrahydrofuran

(99.5%) were purchased from Concord. Polymer precursor 2-methyl-1,4-phenylene bis(4-((6-(acryloyloxy) hexyl)oxy)benzoate) (C6M, 97%), cross-linking agent trimethylol propane triacrylate (TMPTA, 95%), and photoinitiator 2,2 dimethoxy-2-phenylacetophenone (I-651, 99%) were purchased from Merck. The nematic liquid crystal HTG135200 and chiral dopant S (or R)5011 (>98%) were provided by Jiangsu Hecheng Display Technology Co., Ltd. Cleaned glass slides were used for substrate in polymerization.

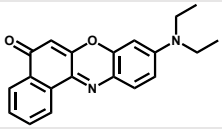
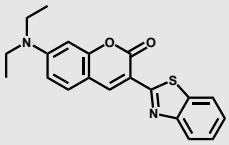
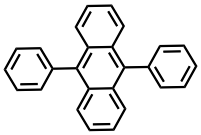
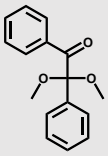
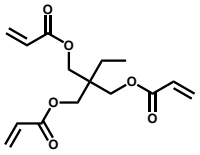
Characterizations.

UV–Vis absorption spectra were recorded on the Hitachi U-3900 spectrophotometer. Fluorescence spectra were recorded on the Spectrofluorometer Edinburgh FS5. CDR spectra were measured in transmittance mode using the powder measurement accessory of the JASCO J-1500 spectrophotometer, which includes an integrating sphere in a 90° optical path configuration. This accessory is provided as a standard component of the instrument, ensuring that the measurements follow the standard testing setup. The powdered samples were loaded into the standard sample holder located between the light source and the entrance of the integrating sphere. CPL spectra were measured on a JASCO CPL-200 spectrophotometer. TEM images were collected from a Tecnai G2 20 S-TWIN. TEM samples were obtained by ultramicrotoming resin-embedded samples using a Leica EM UC7. Microscopy images were collected on a Leica DM2700 M upright materials microscope. XRD spectra were recorded on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/Kα radiation (λ = 1.5406 Å). SEM images were obtained from a Hitachi S-4800 FE-SEM with an accelerating voltage of 10 kV. Size distribution was analyzed by ImageJ. Reduced scattering coefficient calculate program was

run in MATLAB. Reflectance spectra and ARMS was acquired using a Microscope Systems ARMS manufactured by Shanghai Ideaoptics Corporation, Shanghai, China.

Fabrication

LCs mixture: HTG135200 (100 wt%), R5011/S5011 (1.6 ~ 2.6 wt%), C6M (50 wt%), TMPTA (7 wt%), and I-651 (2.5 wt%) was blended with a 10 wt% PVA aqueous solution at a mass ratio of 1:30 (LCs mixture: PVA solution) under continuous stirring at 200 r/min for 30 minutes, forming a stable oil-in-water (O/W) emulsion. The emulsion was then cast onto glass slides and dried in an oven at 50 ℃. Subsequently, the dried samples were subjected to 365 nm UV irradiation for 30 minutes polymerization. Then, the PVA matrix and unpolymerized components were removed through successive water and hexane washes for 3 times, yielding chiral PhC particles.

Name	Chemical Structure	Synonyms
PVA		Poly(vinyl alcohol)
NR		Nile Blue A oxazone
C6		3-(2-Benzothiazolyl)-N,N-diethylumbelliferylamine
DPA		9,10-Diphenylanthracene
I-651		2,2-Dimethoxy-2 phenylacetonphenone
TMPTA		1,1,1-Trimethylolpropane Triacrylate

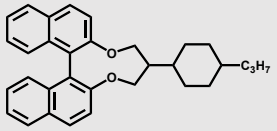
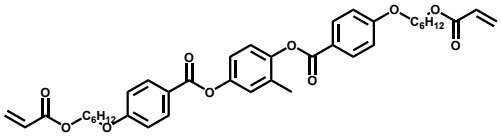
R5011/ S5011		(13bR)-5,6-Dihydro-5-(trans-4-propylcyclohexyl)-4H- dinaphtho[2,1-:1',2'- h][1,5]dioxonin
C6M		2-methyyl-1,4-phenylene bis(4- ((6 - (acryloyloxy)hexyl)oxy)benzoat e))
HTG 135200	Commercial Nematic Liquid Crystal hybrid	

Table S1 Chemical structures of water phase, dye fluorescence, crosslinking agent, chiral dopant, photoinitiator, reactive monomers, and LCs

Application of the Mie theory

Here we employ Mie theory to model the scattering of light in our case. The scattering anisotropy factor g and the scattering coefficient μ_s can be described as follows:

$$g = \frac{4}{k^2 \sigma_s} \sum_{n=1}^{\infty} \left[\frac{n(n+2)}{n+1} \mathrm{Re}\left(a_n a_{n+1}^{*} + b_n b_{n+1}^{*} \right) + \frac{2n+1}{n(n+1)} \mathrm{Re}\left(a_n b_n^{*} \right) \right]$$

$$\mu_s = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2)$$

Coefficients a_n and b_n are given by

$$a_n = \frac{\psi_n(\alpha)\psi_n'(\beta) - m\psi_n'(\alpha)\psi_n(\beta)}{\xi_n(\alpha)\psi_n'(\beta) - m\xi_n'(\alpha)\psi_n(\beta)}$$

$$b_n = \frac{m\psi_n(\alpha)\psi_n'(\beta) - \psi_n'(\alpha)\psi_n(\beta)}{m\xi_n(\alpha)\psi_n'(\beta) - \xi_n'(\alpha)\psi_n(\beta)}$$

where superscript prime denotes first-order differentiation and size parameter β is defined by

$$\beta = m\alpha = kma = \frac{2\pi ma}{\lambda}$$

m is the ratio of the particle refractive index np to the medium refractive index nm.

The Riccati-Bessel functions are defined by

$$\psi_n(x) = xj_n(x), \xi_n(x) = xh_n^{(1)}(x)$$

$$j_n(x) = \sqrt{\frac{\pi}{2x}} J_{n+\frac{1}{2}}(x)$$

$$h_n^{(1)}(x) = \sqrt{\frac{\pi}{2x}} H^{(1)}_{n+\frac{1}{2}}(x)$$

$J_{n+\frac{1}{2}}(x)$ and $H^{(1)}_{n+\frac{1}{2}}(x)$ are the Bessel function of the first kind and the Hankel function, respectively, of half-odd integer order.

The relationship between the reduced scattering coefficient μ'_s and the relative refractive index can be calculated by combining the following equations. It can be observed that this conforms to the general law of Mie scattering: as the refractive index of the solvent increases, the refractive indices match, and the scattering intensity gradually decreases.

$$\mu'_s = \mu_s(1 - g)$$

To simplify the calculation, we approximate the particles as spherical particles with a diameter of 10 μm, ignoring their size distribution. The wavelengths are set to 450 nm, 550 nm, and 650 nm, and the particle refractive index is taken as 1.54, without considering the effects of solvent penetration.

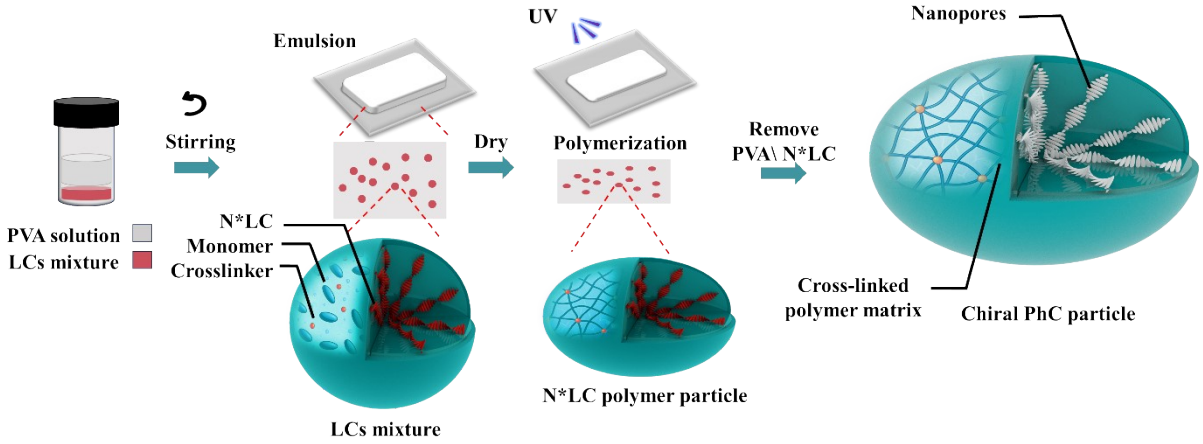


Figure S1. Scheme illustration of the fabrication process of chiral PhC particles

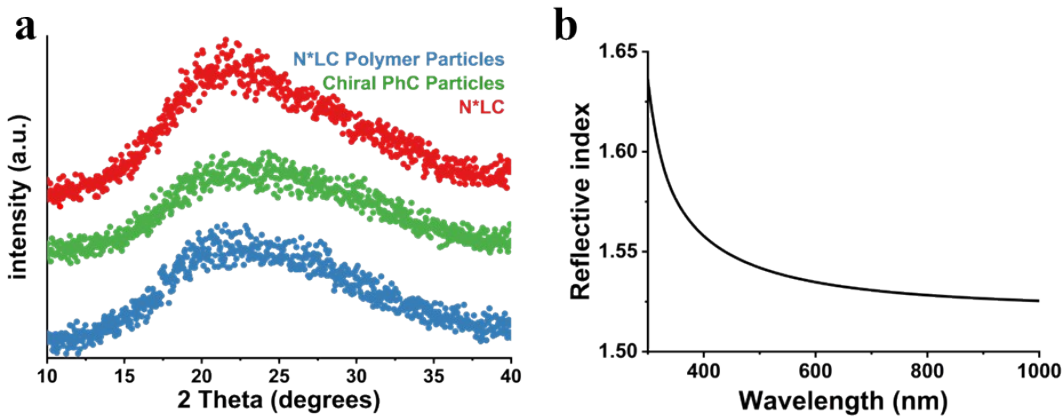


Figure S2. (a) XRD patterns of N*LC, N*LC polymer particles and chiral PhC particles. (b) Material refractive index of C6M polymer.

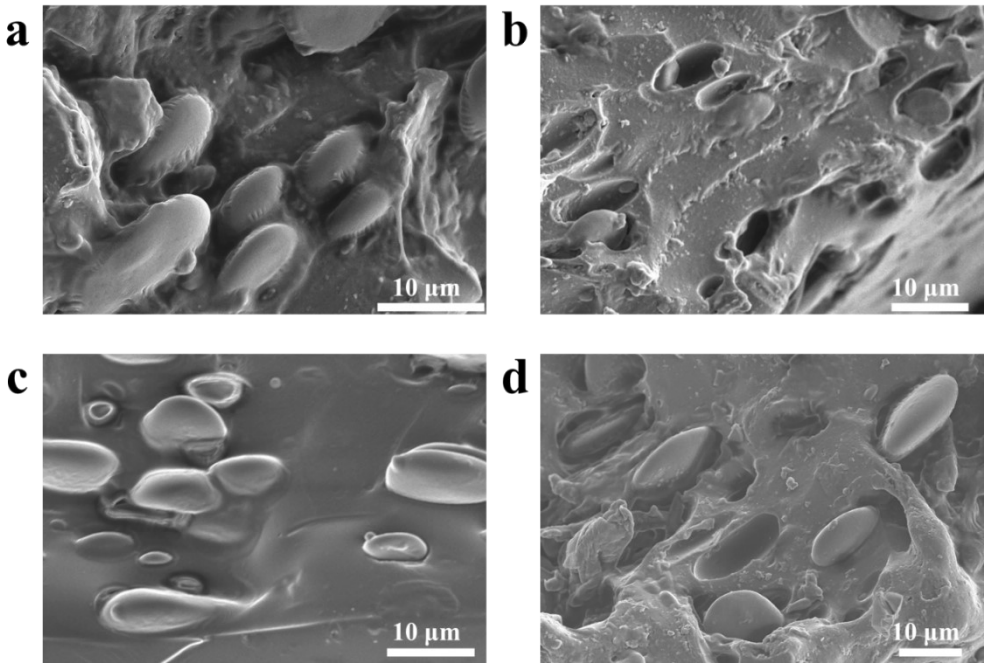


Figure S3. SEM images of ellipsoidal N*LC polymer particles in PVA

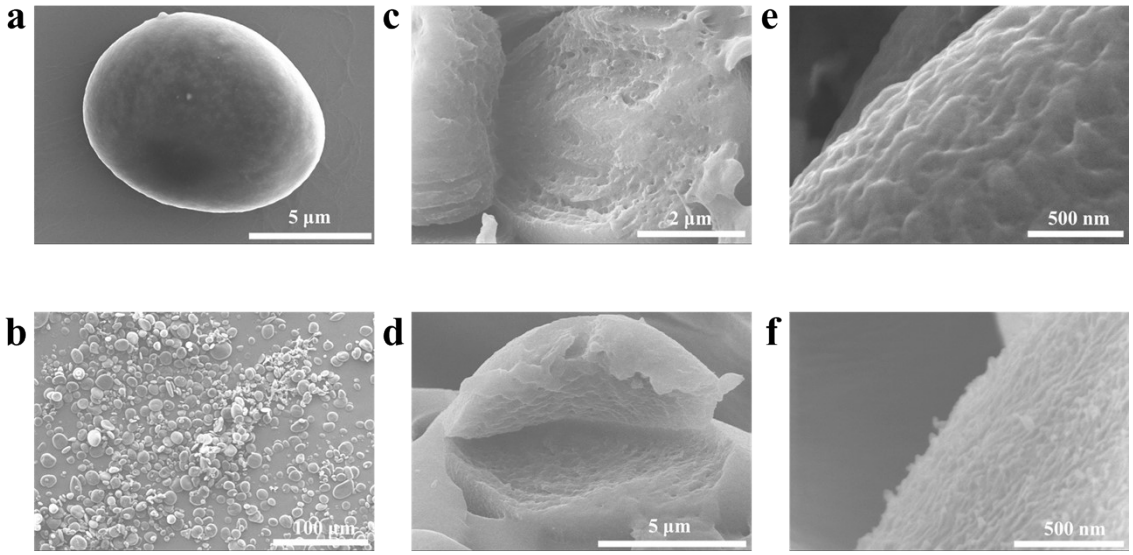


Figure S4. SEM images of (a, b) morphology of chiral PhC particles; (c, d) internal concentric ellipsoidal structure of CPCPs; (e) surface of chiral PhC particles; (f) surface of chiral PhC particles embedded in resin.

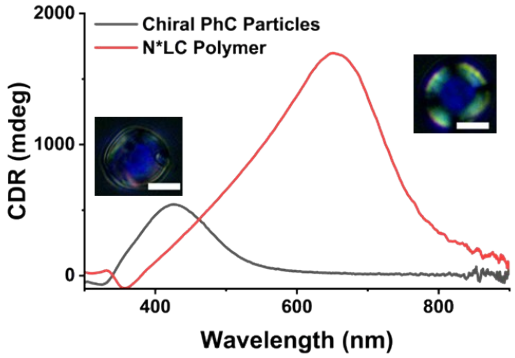


Figure S5. CDR spectra of the N*LC polymer before and after removal of liquid crystals(Chiral PhC Particles). Insets: POM images of the N*LC polymer (right) and the resulting chiral PhC particles after LCs removal (left).

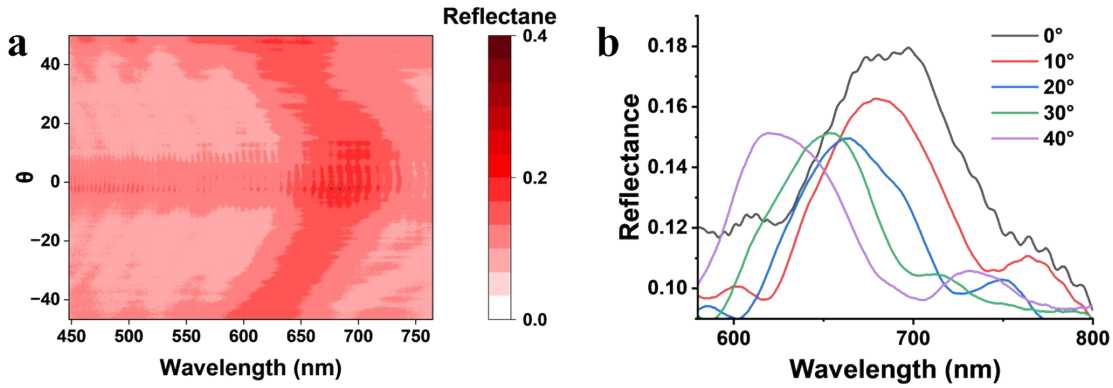


Figure S6. (a) ARMS of chiral PhC particle. (b) Selected reflectance spectra at representative incident angles, extracted from (a)

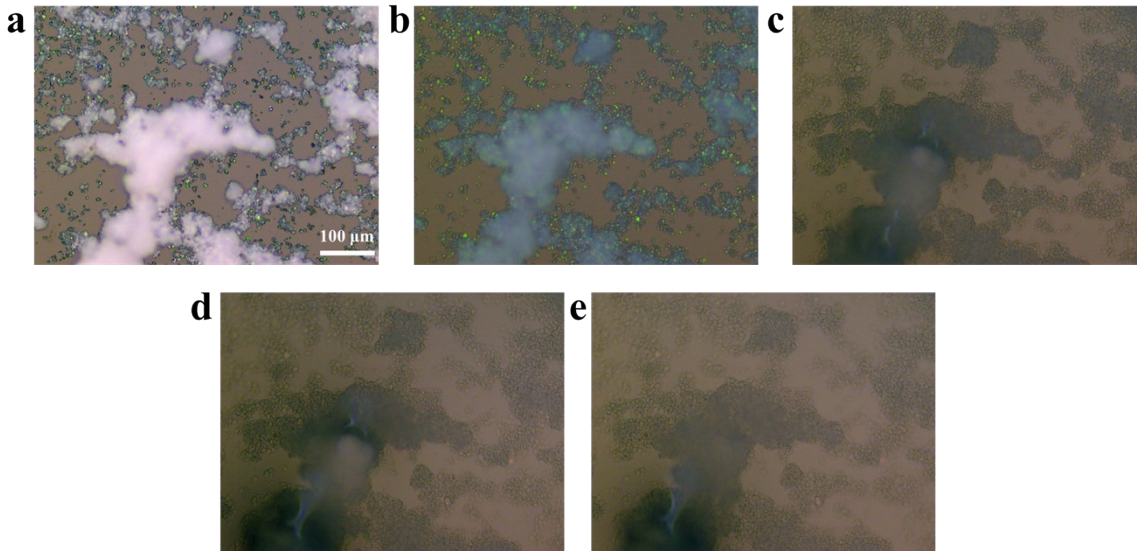


Figure S7. Reflection microscopy images of chiral PhC particles in (a) dry state, and immersed in (b) ethanol, (c) tetrahydrofuran, (d) dichloromethane, and (e) chloroform.

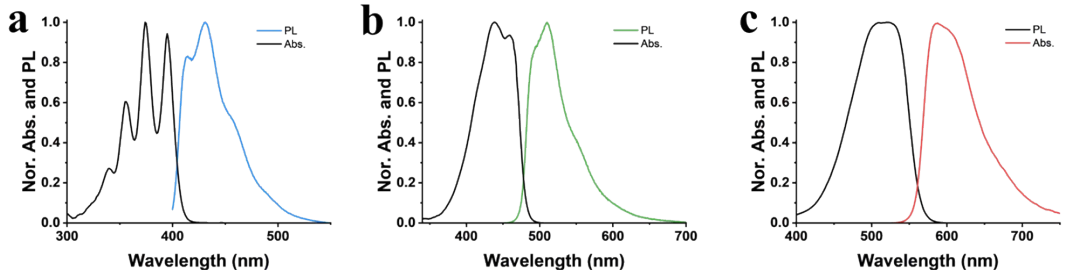


Figure S8. Photoluminescence (PL) and UV–vis absorption spectra of (a) DPA, (b) C6, and (c) NR, all measured in toluene solution at a concentration of 0.1 mg/mL. PL spectra were recorded with an excitation wavelength of 360 nm.

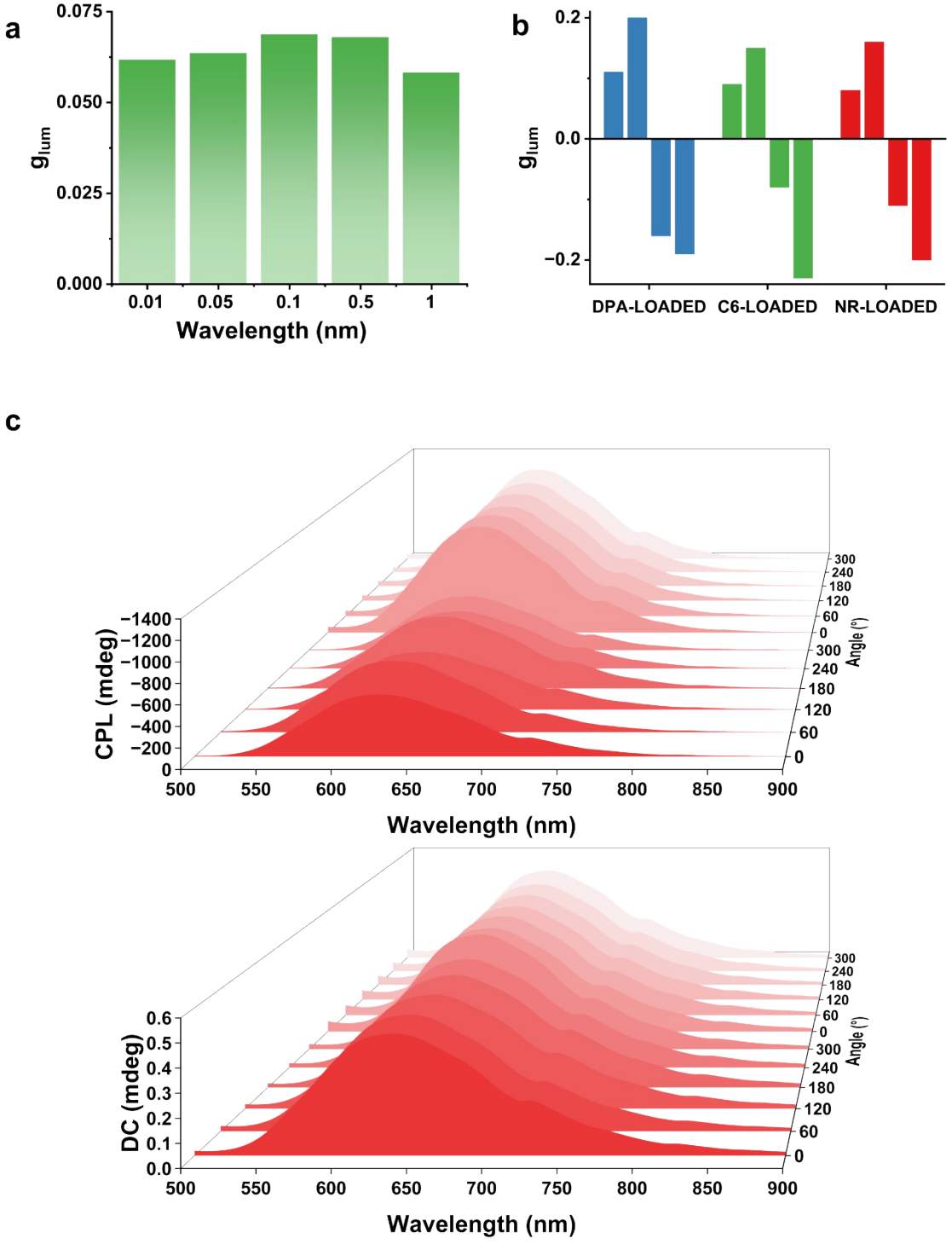


Figure S9. Luminescence dissymmetry factor of dye-loaded chiral PhC particles under varying conditions. (a) glum of chiral PhC particles -C6 at different concentrations after 6 h immersion. (b) glum of chiral PhC particles loaded with different dyes from Figure 4 (d–f), measured in dry state and in

aqueous environment. (c) CPL spectra of NR-loaded S-chiral PhC particles dry and in water at different angles.

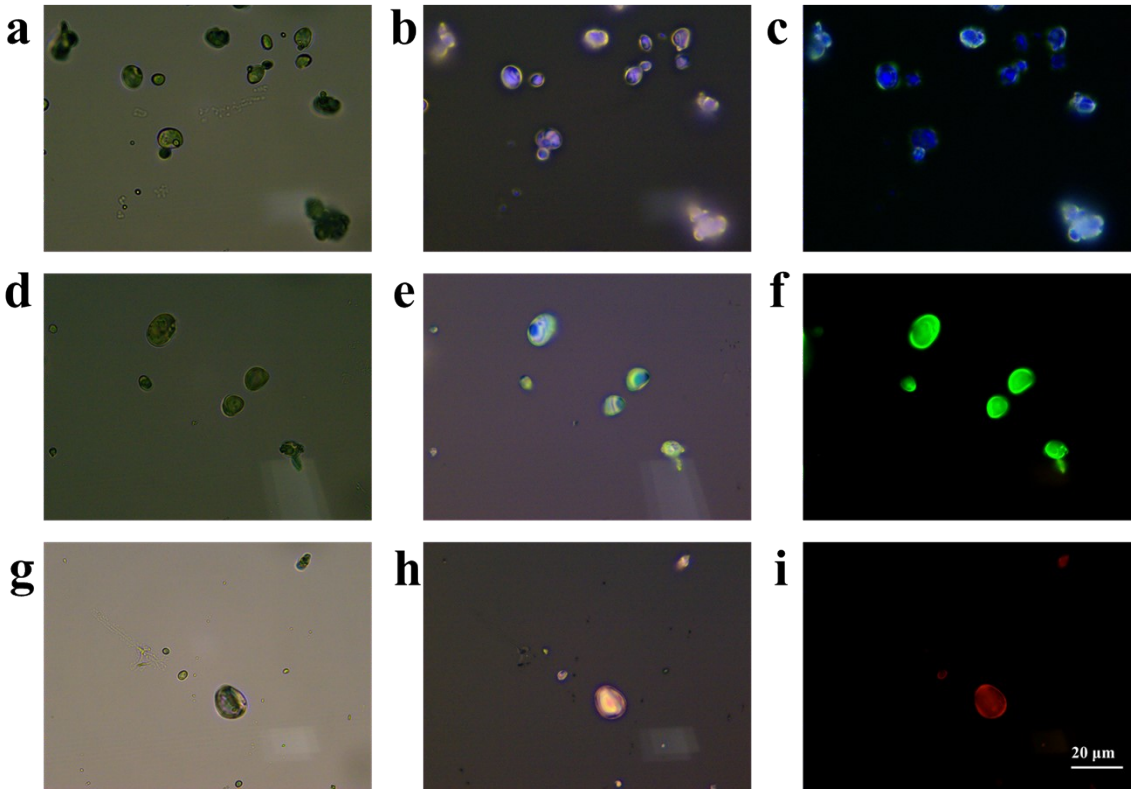


Figure S10. Microscopy images of dye-loaded chiral PhC particles with distinct photonic bandgaps. (a, d, g) Bright-field transmission images. (b, e, h) Reflectance images. (c, f, i) Fluorescence microscopy images.

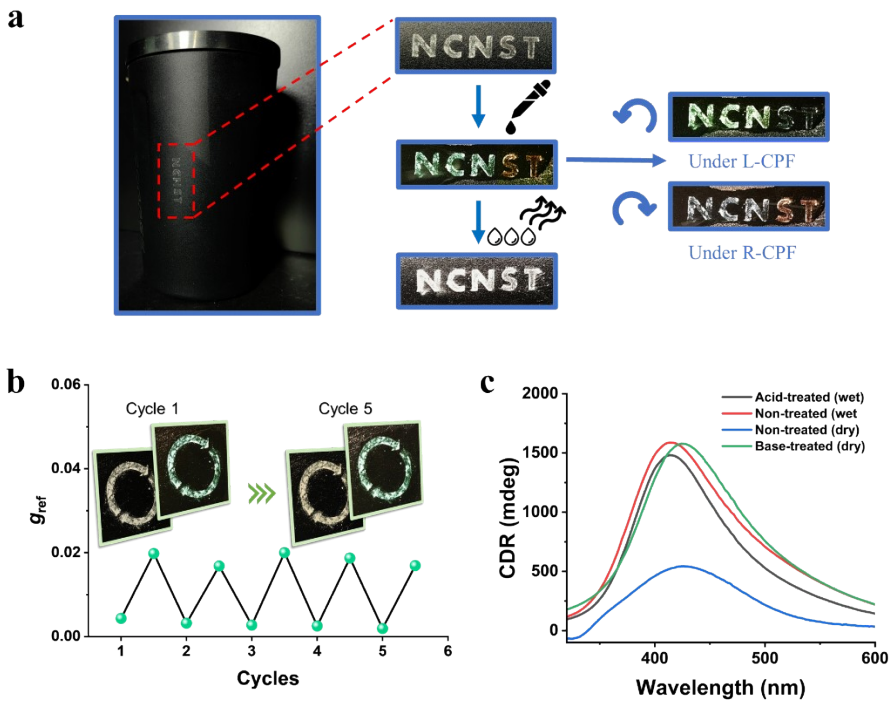


Figure S11. (a) Photonic tag on a cup with an initially white "NCNST" pattern revealed by ethanol and re-concealed upon evaporation. (b) g_{ref} recyclability over five cycles; insets show visual appearance at cycles 1 and 5. (c) CDR spectra of chiral PhC particles under different chemical treatment conditions to evaluate durability. Samples were measured in four states: acid-treated (wet), non-treated (wet), non-treated (dry), and base-treated (dry).

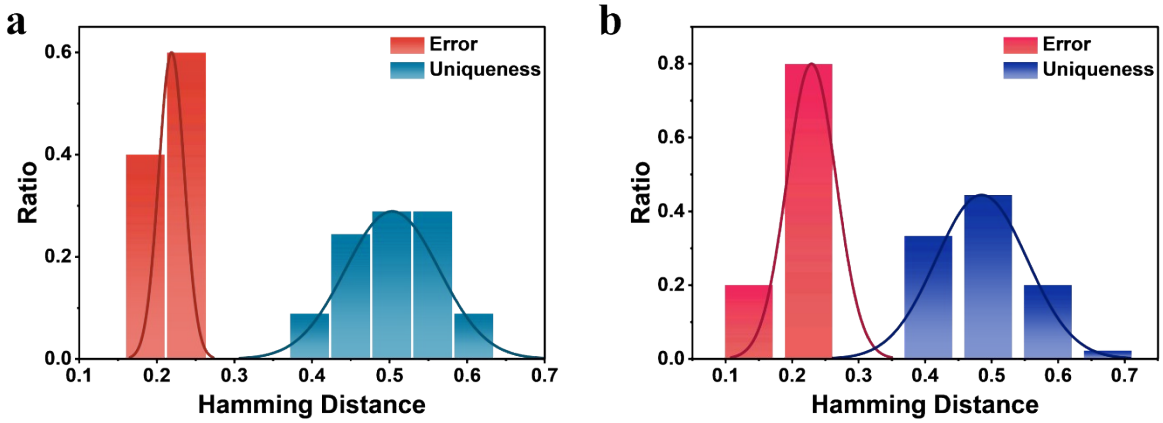


Figure S12. (a) Uniqueness and bit error rate spectra of Keys L and (b)R.

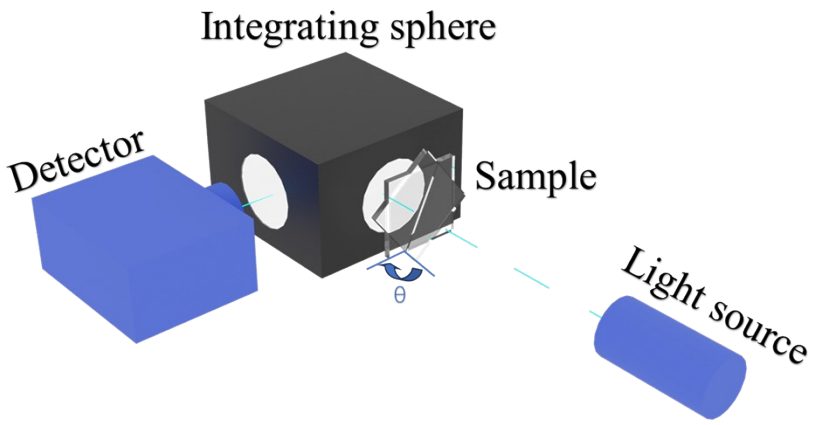


Figure S13. Measurement setup for CDR. Powder measurement accessory of the Jasco J-1500, which includes an integrating sphere in a 90° optical path configuration.