Electronic Supporting Information

Inhibited/Enhanced Fluorescence of Embedded Fluorescent Defects by Manipulation of Spontaneous Emission Based on Photonic Stopband

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Experimental.

Materials: SCR 500 is a commercial photoresist, which is purchased from Japan Synthetic Rubber Co. Ltd.. Allyl-fluorescein (Allyl-FL) was synthesized according to our previous report.[1] Methyl methacrylate (MMA, AR), methanol (CH_3OH, AR), styrene (St, AR), sodium dodecyl benzene sulfonate (SDBS, AR), acrylic acid (AA, AR), sodium bicarbonate ($NaHCO_3$, AR), ammonium persulphate (APS, AR), sulphuric acid (H_2SO_4, AR) and potassium dichromate ($K_2Cr_2O_7$, AR) were purchased from Beijing Chemical Reagent Company. St, MMA, and AA were purified by distillation under induced pressure and stored in refrigerator before use. All other reagents were used without purification.

Preparation of the CCs: The CCs were prepared by self-assembly of monodisperse latex microspheres. First, monodisperse latex microspheres of Poly(styrene-methylmethacrylate-acrylic acid) (Poly(St-MMA-AA)) with different diameters were synthesized according to our previous procedure.[2] The resultant latex microspheres with a hydrophobic Poly(St) core and a hydrophilic Poly(MMA-PAA) shell were used directly without purification. Second, CCs were fabricated on a glass slide by a vertical deposition method using 0.2 wt % Poly(St-MMA-AA) colloidal suspensions. The self-assembly process was carried out in a temperature and humidity chamber (KCL2000, Tokyo Rikakikai Co. LTD) with a constant temperature of 60 ℃ and a relative humility of 60 % for 36 h. The glass slides were pre-treated with a chromic acid solution to ensure clean surfaces. Finally, CCs were prepared by self-assembly of the Poly(St-MMA-AA) microspheres with diameters of 210 nm, 220 nm, and 240 nm, respectively. The self-assembled CCs were sintered to 85 ℃ for 30 min to improve the stability, and then used to fabricate the embedded fluorescent features.

Preparation of allyl-FL doped photoresist: Allyl-FL doped photoresist was prepared by mixing SCR 500 (1.0070 g) and ally-FL (0.0101 g) in a dark room. After agitation overnight in a dark room, a transparent orange photoresist was obtained. The allyl-FL doped photoresist was kept in the dark room before two-photon polymerization. For comparison, allyl-FL doped polymer film was obtained by photopolymerization of the

allyl-FL doped SCR500 under UV irradiation using a high-voltage mercury lamp (Power: 32.5 mW/cm^2, wavelength range: 300-400 nm).

Incorporation of embedded defects in CCs via TPP: Embedded defects were fabricated via TPP by employing a mode-locked Ti: Sapphire laser (Tsunami, Spectra-Physics), which was tightly focused by an oil-immersion objective lens (N.A. = 1.45, 100 ×, Olympus). To demonstrate the ability to precisely incorporate defects inside CCs with different thickness, rectangular microstructures were fabricated with 3/4 inside the CC, while the other 1/4 suspended on the edge of the CC. Planar defects (50μm x50μm x1μm) were constructed inside CCs with the same position of the rectangular microstructures to characterize the defect mode. Embedded fluorescent rectangules and character "A" were fabricated inside the CCs with different photonic stopbands to explore the fluorescent images.

Characterization: Absorption and fluorescence (FL) spectra were collected using a Shimadzu UV-2550 spectrometer and Hitachi F-4500 fluorescence spectrometer, respectively. Scanning electron microscope (SEM) images were obtained with a field emission SEM (JEOL 6700F, Japan). The reflectance spectra of the CCs were measured employing a Hitachi U-4100 spectrometer. In order to explore the photonic stopband effect of the CCs on the FL spectra, FL spectra of allyl-FL doped CCs were measured by infiltrating allyl-FL in the CCs with different photonic stopbands. Optical transmission and reflection spectra of the embedded defects were eavulated by using Fourier transform infrared spectroscopy (FTIR, Bruker). A confocal laser scanning microscope (FV1000-IX 81, Olympus) was used to investigate the fluorescent images of the embedded features.

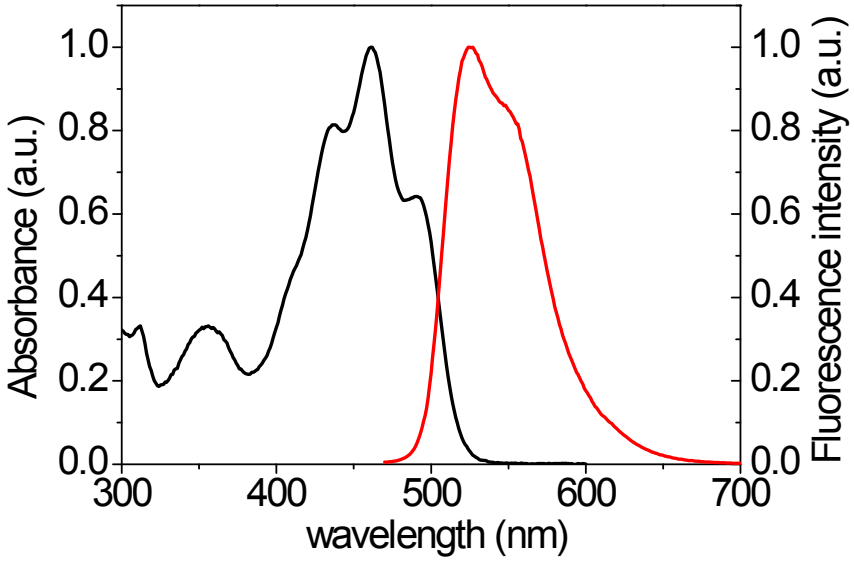

Fig. S1 Absorption (black) and fluorescence (red) spectra of $1x10^{-5}$ M allyl-Fluorescein chloroform solution.

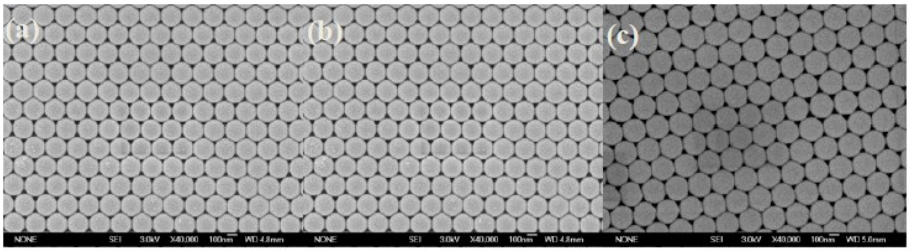

Fig. S2 SEM images of the CCs assembled with (a) 210, (b) 220, and (c) 240 nm Poly(St-MMA-AA) microspheres, respectively.

References

[1] C. F. Li, F. Jin, X. Z. Dong, W. Q. Chen and X. M. Duan, *J. Lumin.*, 2007, **127**, 321–326.

[2] J. X. Wang, Y. Q. Wen, H. L. Ge, Z. W. Sun, Y. M. Zheng, Y. L. Song and L. Jiang, *Macromol. Chem. Phys.*, 2006, **207**, 596-604.