Supporting Information

Facile fabrication of self-reporting micellar and vesicular structures based on etching-ion exchange strategy of photonic composite spheres of poly(ionic liquid)

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1. General

Commercially available reagents and solvents were used as purchased from the chemical suppliers. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer (JEOL, ECS-400). Electrospray ionization mass spectrometry (ESIMS) was measured on a mass spectrometer (Bruker, Esquire-LC). The optical microscopy images of spheres were recorded by an optical microscope (OLYMPUS, 51M) equipped with a CCD camera (OLYMPUS, UTV0.5XC-3). The reflection spectra and emission spectra of spheres was measured by a microscope equipped with a fiber optic spectrometer (Ocean Optics, USB2000+). The size and structure of nanoparticles and spheres were characterized using scanning electron microscope (SEM) (Hitachi, SU8010).

2. Preparation of opal SiO_2 template

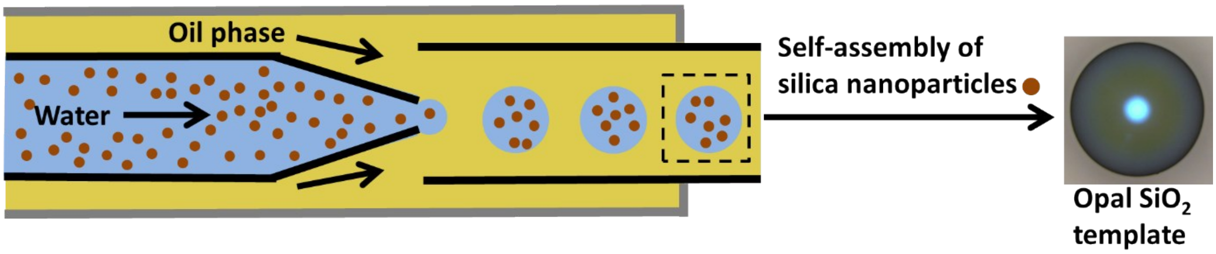

Figure S1. Schematic illustration of the preparation of the opal SiO_2 template. Firstly, monodisperse silica nanoparticles with a diameter from 190-300 nm were dispersed into aqueous solution and used as disperse phase. 50 cSt silicon oil was used as continuous phase. The aqueous droplets containing silica nanoparticles were allowed to evaporate water in a 60 °C oven for at least 12 hours to get opal SiO_2 template.

3. Synthesis of polymerizable ionic liquids

Ionic liquid 1-propyl-3-vinylimidazolium bromide (C_3vim-Br) was synthesized by 1-bromopropane and 1-vinylimidazole. In detail, 6 g 1-vinylimidazole and 10g 1-bromopropane were sealed into a pressure reactor. After heated at 60 °C for 12 hours, we got crude product with a yellow color. The crude product was washed with ethyl ether for 3 times and evaporate the residual solvent to get the 1-propyl-3-vinylimidazolium bromide.

Ionic liquid 1-propyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (C_3vim-Tf_2N) was synthesized by anion exchange. $LiTf_2N$ salt and 1-propyl-3-vinylimidazolium bromide aqueous solution was mixed with molar ratio of 1.2:1. The mixture was stirred for 12 hours at room temperature. The bottom layer of the mixture was crude product. The crude product was washed with water for 3 times to remove unreacted $LiTf_2N$ and get C_3vim-Tf_2N.

The crosslinker, 1,6-di(3-vinylimidazolium)hexane bromide ((C_3vim)$_2$-Br$_2$) was synthesized according to our previous work. Briefly, a mixture of 2 molar equivalents of 1-vinylimidazole and 1 molar equivalent of 1,6-dibromohexane was stirred at room temperature for 48 hours. The mixture was washed with ethyl ether three times to remove impurities.

^{1}H-NMR (C_3vim-Br, 300 MHz , DMSO): δ 9.48 (1H, s), 8.21 (1H, s), 7.93 (1H, s), 7.32 (1H, dd, J = 8.8 Hz, J = 15.6 Hz), 5.97 (1H, dd, J = 2.3 Hz, J = 15.7 Hz), 5.44 (1H, dd, J = 2.3 Hz, J = 8.7 Hz), 4.16 (2H, t, J = 7.1 Hz), 1.87-1.81 (2H, m), 0.88 (3H, t, J = 7.4 Hz).

^{1}H-NMR (C_3vim-Tf$_2$N, 400 MHz, DMSO): δ 9.52 (1H, s), 8.21 (1H, s), 7.94 (1H, s), 7.30 (1H, dd, J = 8.8 Hz, J = 15.6 Hz), 5.96 (1H, dd, J = 2.3 Hz, J = 15.7 Hz), 5.43 (1H, dd, J = 2.3 Hz, J = 8.7 Hz), 4.17 (2H, t, J = 7.1 Hz), 1.91-1.79 (2H, m), 0.88 (3H, t, J = 7.4 Hz). ^{13}C-NMR(C_3vim-Tf$_2$N, 400 MHz, DMSO): δ 135.83, 129.38, 123.73, 121.09, 119.70, 118.95, 109.10, 51.27, 23.07, 10.82. MS: calcd. For C_3vim$^+$(m/z)$^+$: 137; found: 137.107.

^{1}H-NMR ((C_3vim)$_2$-Br$_2$, 400MHz, DMSO): δ 9.72 (2H, s), 8.26 (2H, s), 8.01 (2H, s), 7.34 (2H, dd, J=8.8 Hz, J=15.7 Hz), 6.00 (2H, dd, J=2.3 Hz, J=15.6 Hz), 5.42 (2H, dd, J=2.3 Hz, J=8.8 Hz), 4.23 (4H, t, J=7.2 Hz), 1.82-1.87 (4H, m), 1.31 (4H, t, J=6.8 Hz).

4. Inverse opal structure

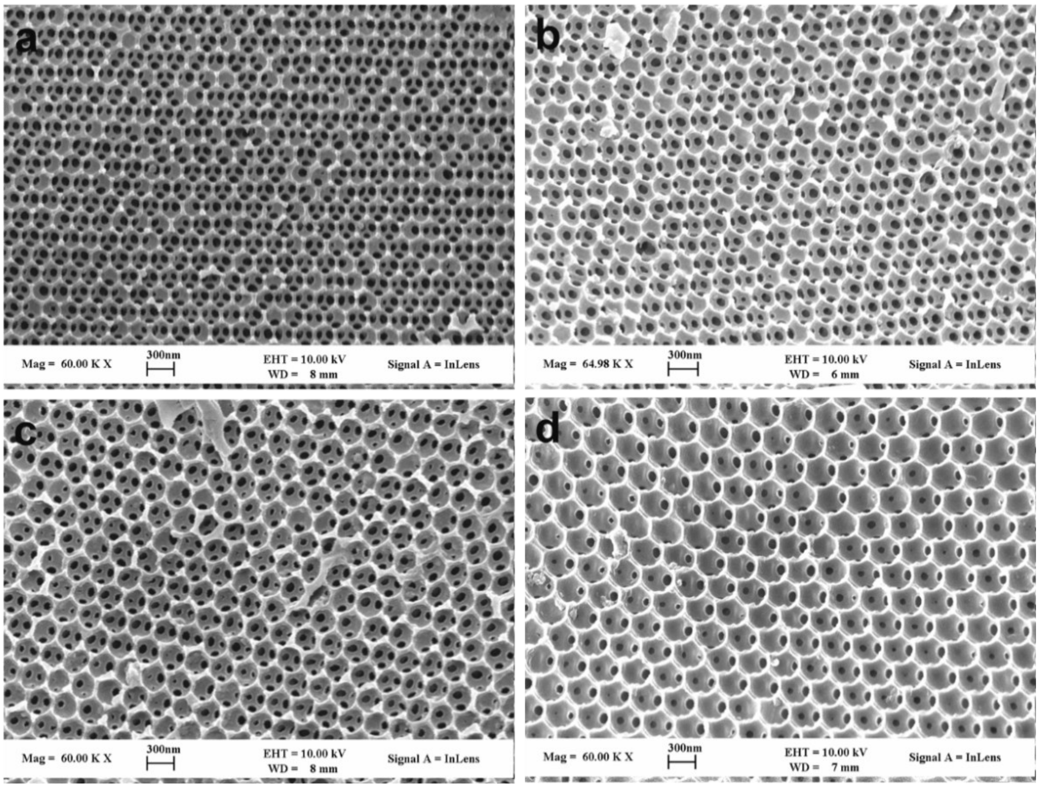

Figure S2. SEM images showing the inverse opal polyILs shell prepared by different SiO$_2$ nanoparticles.

5. Fluorescence distribution

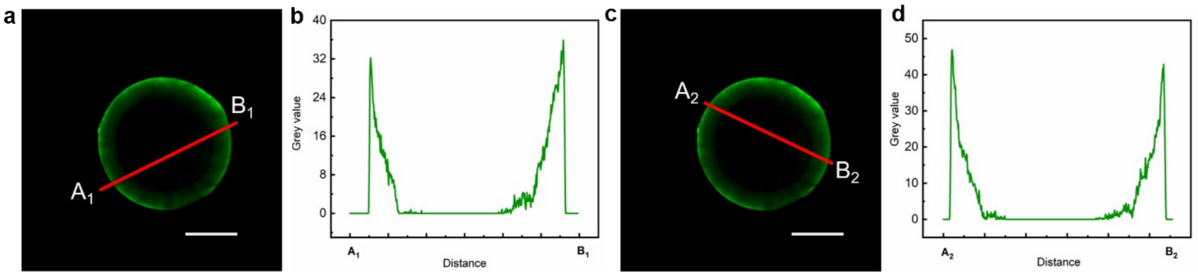

Figure S3. Fluorescent intensity distribution of the anisotropic photonic compartment. (a, c) confocal laser scanning microscope (CLSM) image of the same anisotropic photonic compartment. (b, d) Fluorescent intensity of anisotropic compartment (b corresponds to line A_1B_1 and d corresponds to line A_2B_2). Scale bars are 150 μm.

6. Self-reporting optical signal of MPCs in oil mixtures

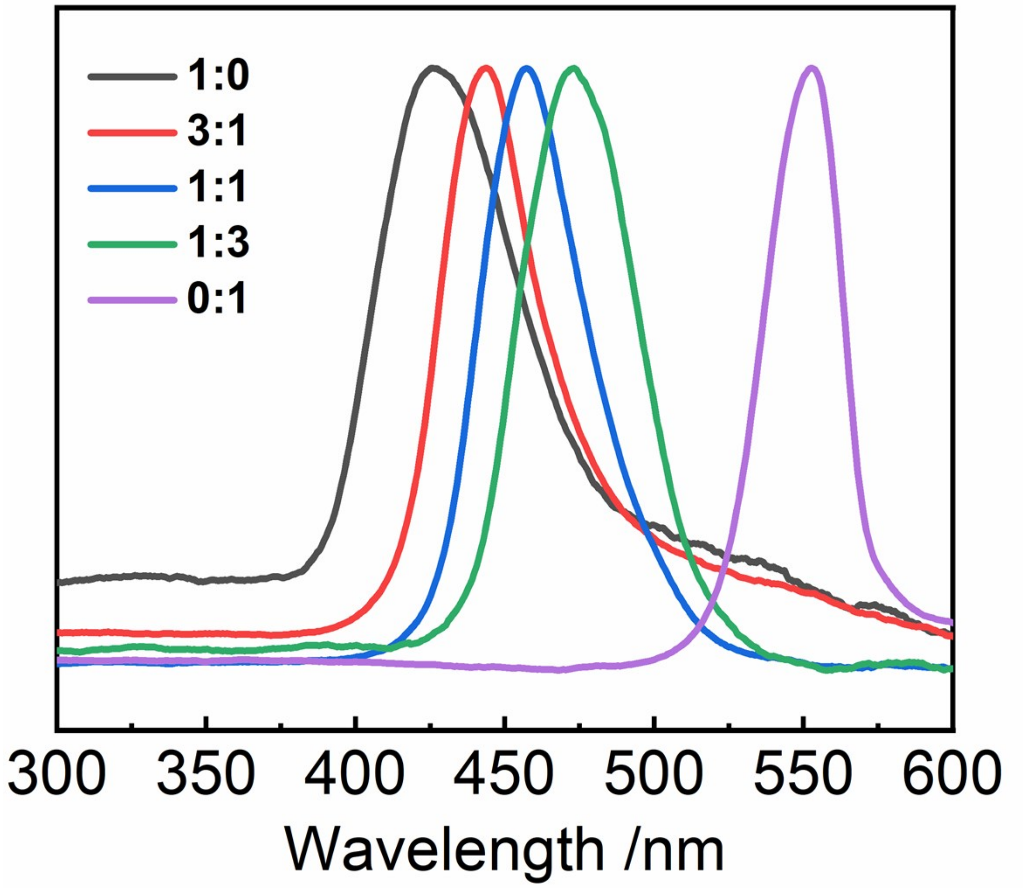

Figure S4. Optical responses of the MPCs after the absorption of oil mixtures. The molar ratio of hexane and dichloromethane were shown in the plot.

7. Contact angel of different solvents on poly(C_3vim-Tf_2N) membrane

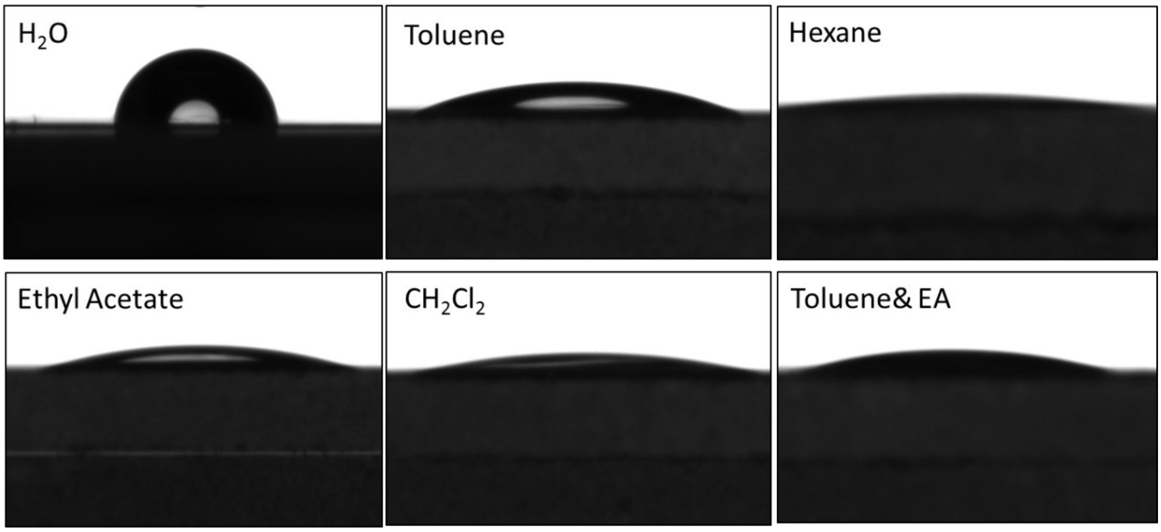

Figure S5. Contact angle of different solvents on the poly(C_3vim-Tf_2N): water (85.2°); toluene (20.7°); hexane (9°); ethyl acetate (16.3°); dichloromethane (15.9°); mixture of toluene and ethyl acetate(1:1 v/v, 19.3°).

8. Structure of photonic spheres after drying out

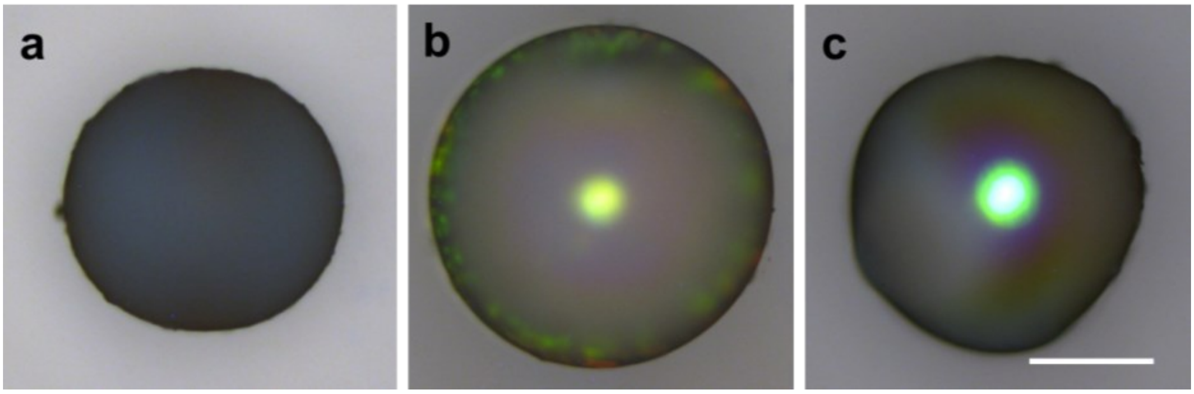

Figure S6 Optical microscopy images showing the structure of photonic spheres after drying out. (a) Br^- as counter anion. (b) Tf_2N^- as counter anion. (c) Inverse micellar photonic compartment. Scale bar is 100 μm.

9. SiO_2-etching process for the preparation of photonic capsule

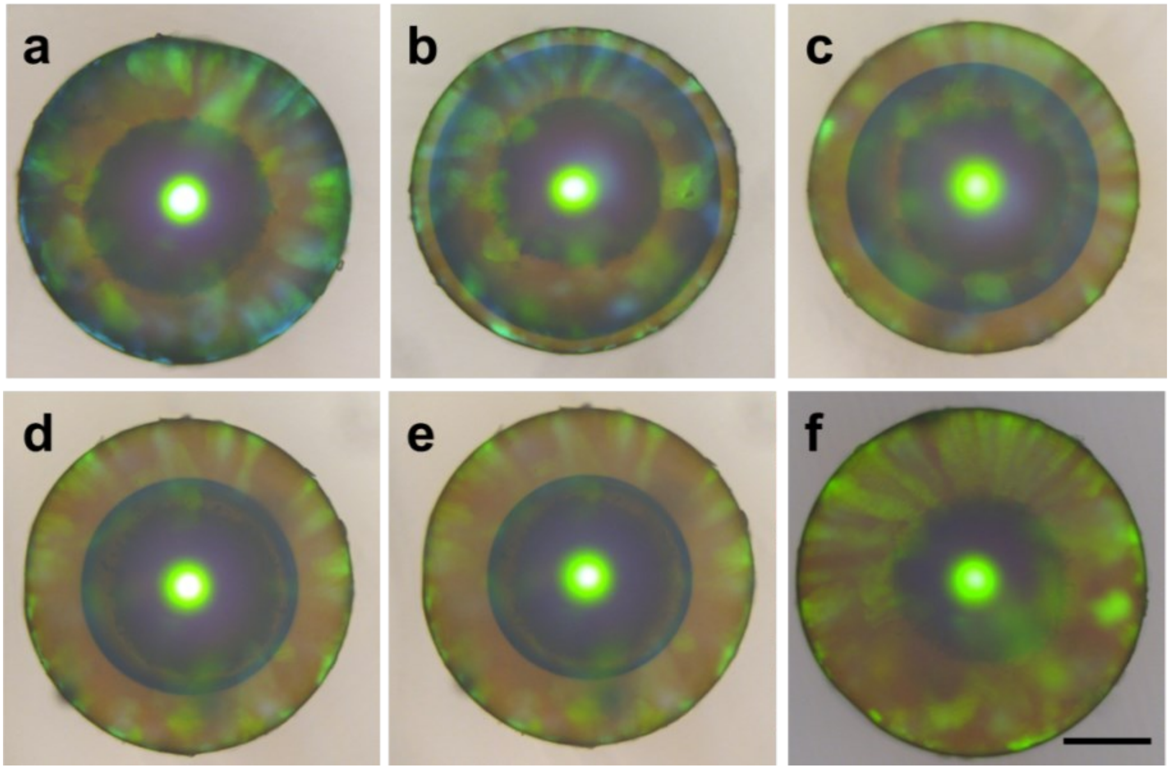

Figure S7. (a-f) optical microscope images showing the SiO_2-etching process for the preparation of vesicular photonic compartment. The images were not taken from the same photonic sphere. Scale bar is 100 μm.

10. EDS for Au nanoparticles doped vesicular photonic compartments

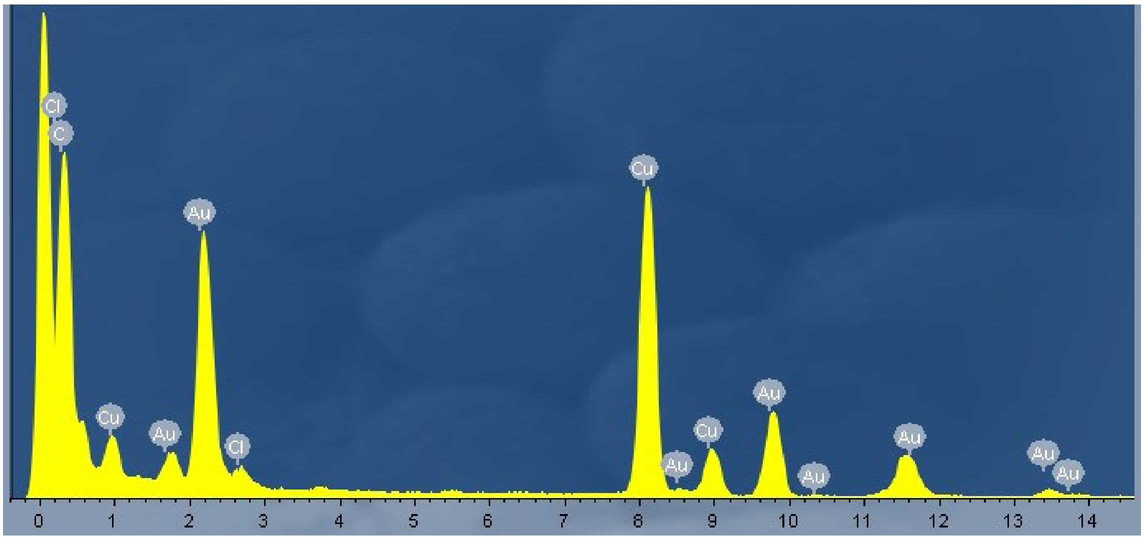

Figure S8. Energy dispersive spectroscopy of Au nanoparticle doped vesicular photonic compartments. Weight percent of Au is 13.21%.

11. Physical model

The total free-energy change associated with the liquid front having descended from the top of the pore down to an azimuthal angle, φ, is given by:

$$\Delta G = \gamma_{\mathrm{lg}} \pi R^2 [(\sin^2 \varphi - \sin^2 \varphi_0) - 2(\cos\theta_c)(\cos\varphi_0 - \cos\varphi)]$$

An energy barrier (a metastable nonwetting state) exists when

$$\left.\frac{d\Delta G}{d\varphi}\right|_{\varphi=\varphi_0} > 0$$

$$\frac{d\Delta G}{d\varphi} = 2\gamma_{\mathrm{lg}} \pi R(\sin\varphi)(\cos\varphi - \cos\theta_c)$$

This occur when

$$\theta_c > \varphi_0$$

12.Robust property of vesicular photonic compartments (VPCs) and functionalized VPCs

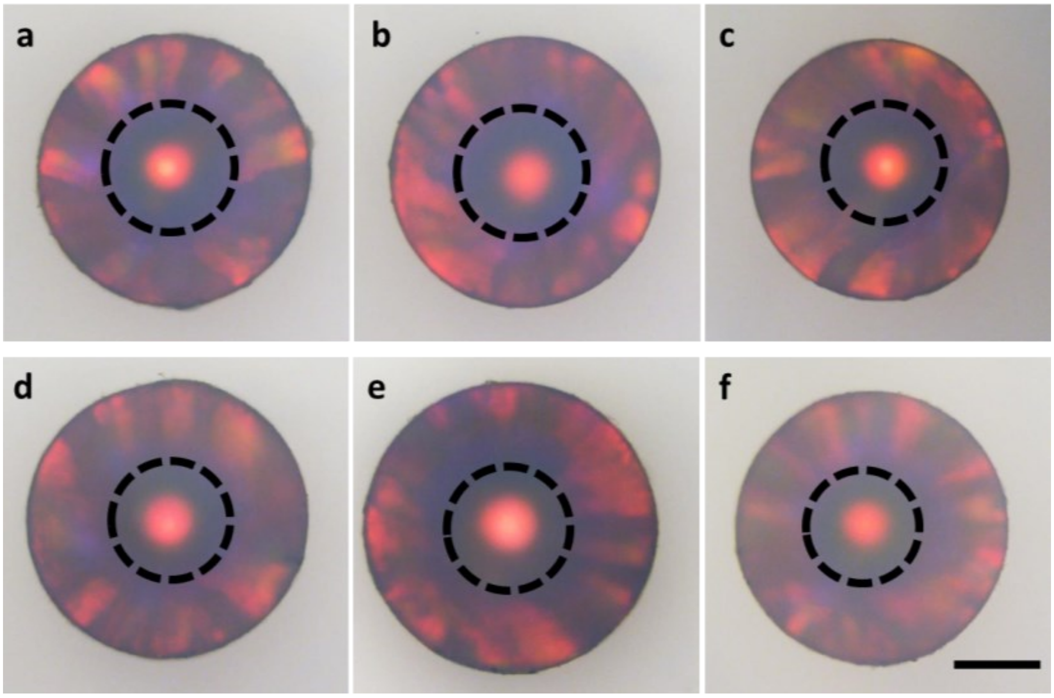

Figure S9 Optical microscopy images showing hydrophilic VPCs (a) and the hydrophilic VPCs after the treatment of 60°C for one hour (b) or immersing in organic solvent (ethanol) for one hour (c). Optical microscopy images showing magnetic VPCs (d, functionalized by $FeCl_3$) and the magnetic VPCs after the treatment of 60°C for one hour (e) or immersing in organic solvent (ethanol) for one hour (f). The dashed black circles indicate the boundary of the shell. Scale bar is 100 μm.

13. Asymmetric vesicular photonic compartments

Vesicular photonic compartments (VPCs) with asymmetric shell were prepared by using anisotropic photonic composites. The SiO_2 template in the outer shell of the VPCs was selectively etched by HF solution to expose the poly(C_3vim-Br). Then the photonic spheres were immersed into $LiTf_2N$ solution overnight. Subsequently removing the SiO_2 template afforded the asymmetric vesicular photonic compartments.

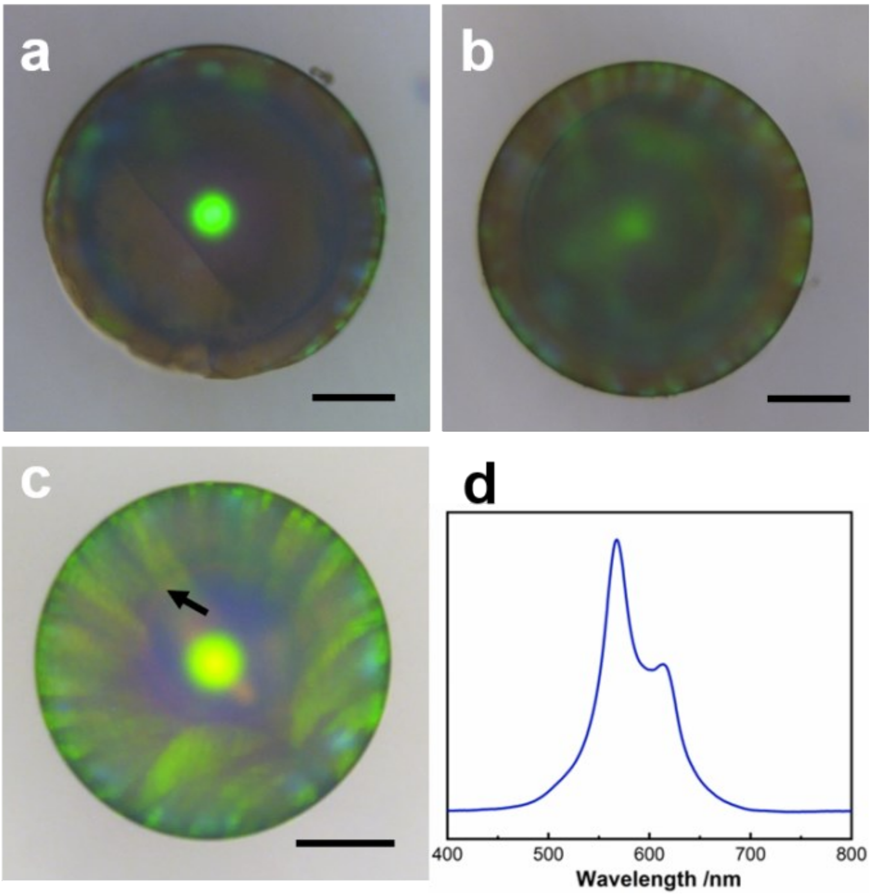

Figure S10 (a-b) Optical microscopy images showing the VPCs with asymmetric shells. (a) and (b) corresponds to the VPCs shown in Figure 10. Optical microscopy image (c) and reflection UV/Vis spectrum (d) showing the anisotropic photonic composite sphere used to prepare VPC. Scale bars are 100 μm.