Supporting Information

1. Chemicals

Cholic acid, deoxycholic acid, lithocholic acid, propargyl bromide, bromoacetyl bromide and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were purchased from Alfa Aesar. Other chemicals were purchased from Beijing Chemical Company and were analytically pure. The solvents used were all freshly distilled.

2. Characterization

NMR spectra were recorded at 300 MHz for protons on JOEL JNM-ECA 300 spectrometers. Chemical shifts (δ) are given in ppm relative to TMS (δ = 0.0). Data Reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), integration, coupling constant and identification. Electrospray ionization mass spectrometry (ESI-MS) was measured on Bruker ESQUIRE-LC spectrometer in positive mode. IR spectra were recorded on AVATAR 360 ESP FTS spectrophotometer with KBr pellets. Differential scanning calorimeter (DSC) experiments were carried out on a DSC821^e (Mettler-Toledo Co., Switzerland) equipped with the high-sensitivity sensor HSS7, which has a temperature precision of ±0.1 ℃ and a heat flow precision of ±0.01 mW. The heating rate was 1 ℃/min. The average molecular weights and polydispersity indices of all the samples were measured with a size exclusion chromatography (SEC) system equipped with a Waters 515 HPLC pump, three Waters Styragel columns (HT2, HT3, and HT4), a Rheodyne 7725i sampler, and a Waters 2414 refractive-index (RI) detector. Polystyrene standards were used to calibrate the SEC system. THF was used as the eluent at a flow rate of 1 mL/min at 35 ^{o}C.

3. Synthesis

Procedures for the synthesis of compound 1a

To a solution of cholic acid (25 mmol) in anhyd. DMF (60 mL) was added caesium carbonate (8.15 g, 25 mmol) at room temperature and stirred under an inert atmosphere. The mixture was stirred for 1 h before adding propargyl bromide (2.78 mL, 31.25 mmol). The reaction was monitored by TLC and after being stirred for 4 h, cold water (400 mL) was added, and the solution was acidified with 2 M $KHSO_4$. Extraction of the crude product was carried out with $CHCl_3$ (3×40 mL). The organic layer was washed with brine, dried with $MgSO_4$, filtered, and evaporated to dryness under reduced pressure. After recrystallization with $CHCl_3$ and petroleum ether, propargyl ester **1a** was isolated as white solid.

Propargyl 3α,7α,12α-trihydroxy-5β-cholan-24-oate **1a**

White solid, yield: 93%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.67 (s, 3H, 18-CH_3), 0.88 (s, 3H, 19-CH_3), 0.98 (d, 3H, 21-CH_3), 0.99 – 2.45 (m, 27H, steroid skeleton H), 2.49 (t, 1H, J = 2.1 Hz, terminal alkyne H), 3.43 (m, 1H, 3β-CH), 3.83 (m, 1H, 7β-CH), 3.95 (m, 1H, 12β-CH), 4.67 (d, 2H, J = 2.2 Hz, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.54, 14.27, 17.38, 22.53, 23.30, 26.35, 27.61, 28.22, 30.41, 30.86, 31.11, 34.77, 34.86, 35.32, 35.43, 39.55, 41.58, 41.64, 46.49, 47.03, 51.84, 60.48, 68.51, 71.92, 73.15, 74.84, 173.54; ESI-MS(+): *m/z* 469.1 $[M+Na]^+$.

Propargyl 3α, 12α-dihydroxy-5β-cholan-24-oate **1b**

White solid, yield: 95%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.66 (s, 3H, 18-CH_3), 0.89 (s, 3H, 19-CH_3), 0.96 (d, J = 6.18 Hz, 3H, 21-CH_3), 1.02 - 1.87 (m, 27H, steroid skeleton H), 2.29 (m, 1H, -CH_2COO-), 2.39 (m, 1H, -CH_2COO-), 2.46 (t, J = 2.58 Hz, 1H, -C≡CH), 3.59 (m, 1H, 3β-CH), 3.96 (s, 1H, 12β-CH), 4.66 (d, J = 2.40 Hz, 2H, -CH_2C≡CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.80, 17.34, 23.23, 23.72, 26.19, 27.20, 27.54, 28.74, 30.52,

30.80, 31.10, 33.70, 34.18, 36.17, 35.28, 36.09, 36.48, 42.13, 46.56, 47.33, 48.30, 51.85, 71.82, 73.17, 74.81, 77.89, 173.43; ESI-MS(+): *m/z* 453.1 $[M+Na]^+$.

Propargyl 3α-hydroxy-5β-cholan-24-oate **1c**

White solid, yield: 97%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.63 (s, 3H, 18-CH_3), 0.89 (s, 3H, 19-CH_3), 0.91 (d, J = 6.18 Hz, 3H, 21-CH_3), 0.95 - 1.80 (m, 27H, steroid skeleton H), 2.26 (m, 1H, -CH_2COO-), 2.39 (m, 1H, -CH_2COO-), 2.46 (t, J = 2.40 Hz, 1H, -C≡CH), 3.60 (m, 1H, 3β-CH), 4.66 (d, J = 2.40 H ‘z, 2H, -CH_2C≡CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.12, 18.33, 20.90, 23.46, 24.28, 26.50, 27.27, 28.27, 30.62, 30.90, 31.05, 34.65, 35.38, 35.92, 36.53, 40.25, 40.50, 42.18, 42.83, 51.84, 56.01, 56.57, 71.92, 74.78, 77.92, 173.50; ESI-MS(+): *m/z* 437.6 $[M+Na]^+$.

Procedures for the synthesis of compound 2a

To a solution of propargyl cholate **1a** (15 mM) and dry K_2CO_3 (4.15 mg, 30 mM) in 50 mL dry dichloromethane bromoacetyl bromide (1.6 mL, 18.4 mM) in 10 mL dry dichloromethane was added drop wise at 0 ℃. The reaction mixture was allowed to stir at r. t. for c.a. 24 h. The crude mixture was filtered through a short column of silica gel to remove the insoluble material. The filtrate was extracted with 10% critic acid and brine, dried over anhydrous $MgSO_4$. The crude organic material was purified by silica gel column chromatograph to afford target molecular.

Propargyl 3α-bromoacetoxy-7α,12α-dihydroxy-5β-cholan-24-oate **2a**

Yellow waxy solid, yield: 62%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70 (s, 3H, 18-CH_3), 0.91 (s, 3H, 19-CH_3), 0.98 (d, 3H, 21-CH_3), 2.48 (t, 1H, J = 2.1 Hz, terminal alkyne H), 3.79 (s, 2H, $BrCH_2CO$), 3.87 (br, 1H, 7β-CH), 4.00 (br, 1H, 12β-CH), 4.67 (m, 3H, 3β-CH, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.50, 17.31, 22.43, 23.12, 26.38, 26.45, 26.64, 27.41, 28.32, 30.67, 30.94, 34.31, 34.64, 34.72, 34.79, 35.07, 39.46, 41.13, 41.97, 46.52, 47.19, 51.77, 68.20, 72.88, 74.72, 77.76, 166.80, 173.31; ESI-MS (+): *m/z* 590.8 $[M+Na]^+$.

Propargyl 3α-bromoacetoxy 12α-hydroxy-5β-cholan-24-oate **2b**

Yellow waxy solid, yield: 60%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.68 (s, 3H, 18-CH_3), 0.92 (s, 3H, 19-CH_3), 0.97 (d, J = 5.52 Hz, 3H, 21-CH_3), 1.02 - 1.97 (m, 27H, steroid skeleton H), 2.31 (m, 1H, -CH_2COO-), 2.40 (m, 1H, -CH_2COO-), 2.46 (s, 1H, -C≡CH), 3.79 (s, 2H, $BrCH_2$COO-), 3.99 (s, 1H, 12β-CH), 4.67 (s, 2H, -OCH_2C≡CH), 4.78 (m, 1H, 3β-CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.83, 17.42, 23.16, 23.67, 26.08, 26.17, 26.35, 26.52, 26.99, 27.50, 28.80, 30.81, 31.08, 31.94, 33.75, 34.20, 34.84, 35.08, 36.05, 41.93, 46.59, 47.46, 48.34, 51.88, 74.82, 76.59, 77.31, 77.90, 166.91, 173.40; ESI-MS (+): *m/z* 575.4 $[M+Na]^+$.

Propargyl 3α- bromoacetoxy -5β-cholan-24-oate **2c**

White solid, yield: 95%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.64 (s, 3H, 18-CH_3), 0.90 (s, 3H, 19-CH_3), 0.93 (d, J = 2.07 Hz, 3H, 21-CH_3), 1.02 - 1.97 (m, 27H, steroid skeleton H), 2.26 (m, 1H, -CH_2COO-), 2.40 (m, 1H, -CH_2COO-), 2.46 (t, J = 2.58 Hz, 1H, -C≡CH), 3.80 (s, 2H, $BrCH_2$COO-), 3.99 (s, 1H, 12β-CH), 4.67 (d, J = 2.40 Hz, 2H, -OCH_2C≡CH), 4.77 (m, 1H, 3β-CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.13, 18.35, 20.92, 23.37, 24.26, 26.38, 26.51, 27.07, 28.27, 30.92, 31.07, 32.02, 34.67, 35.01, 35.39, 35.87, 40.19, 40.51, 41.98, 42.84, 51.85, 56.07, 56.54, 74.78, 77.92, 166.87, 173.47; ESI-MS (+): *m/z* 558.5 $[M+Na]^+$.

Procedures for the synthesis of compound 3a

To a solution of 3-bromoacetoxy propargyl cholate **2a** (8.4 mM) in 60 mL dry DMF was added NaN_3 (0.87 g, 13.5 mM). The mixture was heated at 60 ℃ for c.a. 3 h until 3-bromoacetoxy propargyl cholate disappeared. The

mixture was poured into 100 mL cool water, extracted with ethyl acetate and brine, dried over anhydrous $MgSO_4$. The crude organic material was purified by silica gel column chromatograph to afford **5a** as white solid.

Propargyl 3α-azidoacetoxy-7α,12α-dihydroxy-5β-cholan-24-oate **3a**

White solid, yield: 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70 (s, 3H, 18-CH_3), 0.92 (s, 3H, 19-CH_3), 0.98 (d, 3H, 21-CH_3), 2.48 (t, 1H, J = 2.1 Hz, terminal alkyne H), 3.82 (s, 2H, $BrCH_2CO$), 3.86 (br, 1H, 7β-CH), 3.99 (br, 1H, 12β-CH), 4.68 (m, 3H, 3β-CH, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.47, 17.27, 22.38, 23.09, 26.56, 28.25, 30.64, 30.92, 34.31, 34.61, 34.70, 34.95, 35.07, 39.42, 41.13, 41.89, 46.49, 47.17, 50.47, 51.74, 68.18, 72.87, 74.71, 76.24, 167.84, 173.29; ESI-MS (+): *m/z* 553.1 $[M+Na]^+$.

Propargyl 3α-azidoacetoxy 12α-hydroxy-5β-cholan-24-oate **3b**

White solid, yield: 72%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.68 (s, 3H, 18-CH_3), 0.93 (s, 3H, 19-CH_3), 0.98 (d, J = 5.85 Hz, 3H, 21-CH_3), 0.99 - 1.94 (m, 27H, steroid skeleton H), 2.31 (m, 1H, -CH_2COO-), 2.39 (m, 1H, -CH_2COO-), 2.46 (t, J = 2.40 Hz, 1H, -C≡CH), 3.83 (s, 2H, N_3CH_2COO-), 3.99 (s, 1H, 12β-CH), 4.67 (d, J = 2.43 Hz, 2H, -CH_2C≡CH), 4.83 (m, 1H, 3β-CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.83, 17.42, 23.15, 23.66, 26.08, 26.54, 26.98, 27.50, 28.80, 30.81, 31.08, 32.15, 33.75, 34.19, 34.85, 35.07, 36.05, 41.95, 46.59, 47.48, 48.35, 50.64, 51.87, 73.18, 74.80, 76.35, 77.90, 167.93, 173.38; ESI-MS (+): *m/z* 536.4 $[M+Na]^+$.

Propargyl 3α-azidoacetoxy 5β-cholan-24-oate **3c**

White solid, yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.64 (s, 3H, 18-CH_3), 0.90 (s, 3H, 19-CH_3), 0.93 (d, J = 3.09 Hz, 3H, 21-CH_3), 1.03 - 1.97 (m, 27H, steroid skeleton H), 2.26 (m, 1H, -CH_2COO-), 2.40 (m, 1H, -CH_2COO-), 2.46 (t, J = 2.40 Hz, 1H, -C≡CH), 3.83 (s, 2H, $BrCH_2$COO-), 4.67 (d, J = 2.40 Hz, 2H, -OCH_2C≡CH), 4.83 (m, 1H, 3β-CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.13, 18.34, 20.92, 23.37, 24.25, 26.38, 26.67, 27.06, 28.26, 30.92, 31.06, 32.23, 34.67, 35.02, 35.38, 35.87, 40.19, 40.53, 41.99, 42.83, 50.67, 51.85, 56.06, 56.54, 74.78, 77.91, 166.88, 173.47; ESI-MS (+): *m/z* 520.4 $[M+Na]^+$.

Procedures for the synthesis of poly(bile acid)s

Temperature programming was designed for the synthesis of poly(bile acid)s. The vial filled with **3a**, **3b** or **3c** was placed in pipe purnace. Under N_2 protection, the three compounds were heated to initiate Huisgen polyaddition in the solid state.

CA-P

IR (KBr): *v*=3463 (w), 2941 (s), 2869 (s), 1744 (vs) cm^{-1}; ^{1}H NMR (300 MH_Z, DMSO, 25°C-d_6, TMS): δ=0.56 (s, 6H, 18-CH_3), 0.82 (s, 6H, 19-CH_3), 0.90 (s, 6H, 21-CH_3), 1.16-2.49 (m, 48H, steroidal skeleton H), 3.61 (s, 2H, 12α-OH), 3.77 (s, 2H, 7α-OH), 4.14 (s, 4H, 12β-CH, 7β-CH), 4.54 (br, s, 2H, 3β-CH), 5.16 (br, 8H, triazole-1-CH_2), 5.39 (br, 8H, triazole-4-CH_2), 7.78 (s, 1H, triazole-4-H), 8.12 (s, 2H, triazole-5-H).

DCA-P

IR (KBr): *v*=3464 (w), 2941 (s), 2870 (s), 1745 (vs) cm^{-1}; ^{1}H NMR (300 MH_Z, $CDCl_3$&CD_3OD-d_4 (v/v)=7:3, 25°C, TMS): δ=0.68 (s, 6H, 18-CH_3), 0.95 (br, 6H, 19-CH_3), 0.98 (br, 6H, 21-CH_3), 1.05-2.42 (m, 48H, steroidal skeleton H), 3.98 (s, 2H, 12β-CH), 4.84 (br, s, 2H, 3β-CH), 5.22 (br, 8H, triazole-1-CH_2), 5.33 (br, 8H, triazole-4-CH_2), 7.76 (s, 1H, triazole-4-H), 7.90 (s, 2H, triazole-5-H).

LCA-P

IR (KBr): ν=3150 (w), 2941 (s), 2871 (s), 1747 (vs) cm^{-1}; ^1H NMR (300 MH_Z, $CDCl_3$, 25°C, TMS): δ=0.59(s, 6H, 18-CH_3), 0.85-0.89 (m, 12H, 19-CH_3, 21-CH_3), 1.03-2.35 (m, 48H, steroidal skeleton H), 4.78 (br, s, 2H, 3β-CH), 5.11 (br, 8H, triazole-1-CH_2), 5.19 (br, 8H, triazole-4-CH_2), 7.69 (s, 1H, triazole-4-H), 7.72 (s, 2H, triazole-5-H).

4. Preparation for Silica Colloidal Crystal Templates

The glass slides were immersed in H_2SO_4/H_2O_2 overnight, rinsed via deionized water and dehydrous ethanol respectively and then dried for use. The PMMA slides used for photonic film support were cleaned via dehydrous ethanol before use.

The monodispersed silica nanoparticles were synthesized based on the Stöber method. 4 mL tetraethoxylsilane, 150 mL ethanol and over 20 mL ammonia were blended in a flask with stir. After ca. 4 hours, the mixture were operated by centrifuge and washed via dehydrous ethanol for several times. The size of silica could be controlled by alteration of ammonia quantity. The vertical deposition was employed to self-assemble photonic crystals, that is to say, glass slide was vertically inserted vial in which silica was dispersed by dehydrous ethanol. After entire volatilization of ethanol, the silica photonic crystals templates were obtained.

5. Fabrication for Photonic Hydrogels with different bile acid derivatives

The solution of bile acid derivative was infiltrated into silica photonic crystals templates until the templates became transparent completely. After evaporating solvent in oven at 80℃ and etching silica nanoparticles with dilute HF, the photonic hydrogels were obtained.

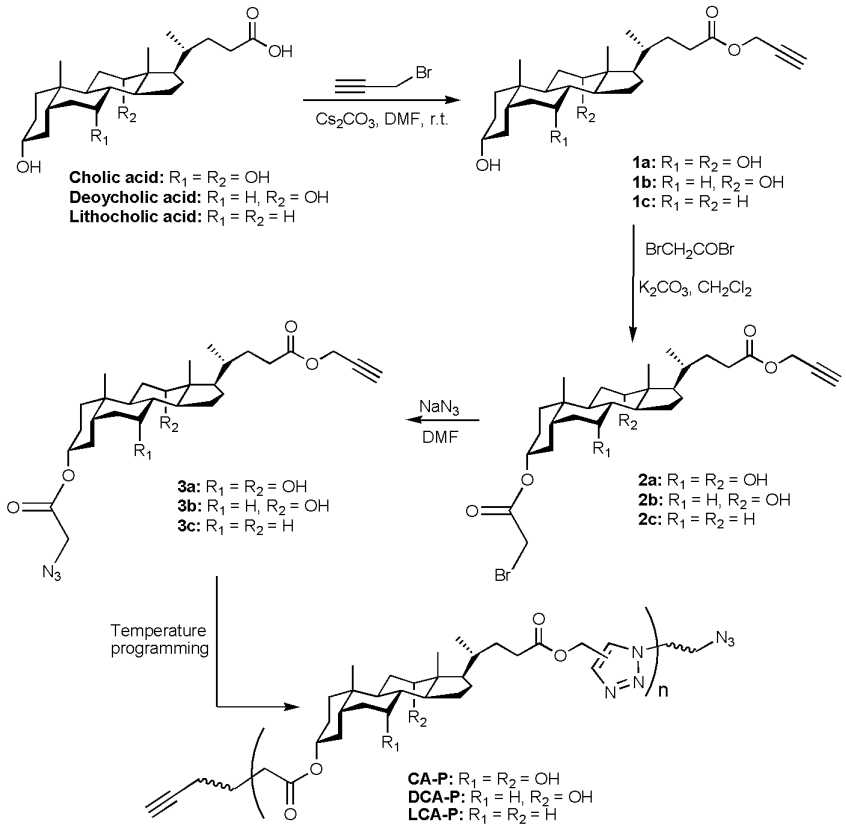

Figure S1. Synthsis of bile acid derivatives bearing a terminal azide and alkyne groups at opposite ends of steroidal core and the formation of triazole group linked poly(bile acid)s (**CA-P**, **DCA-P** and **LCA-P**).

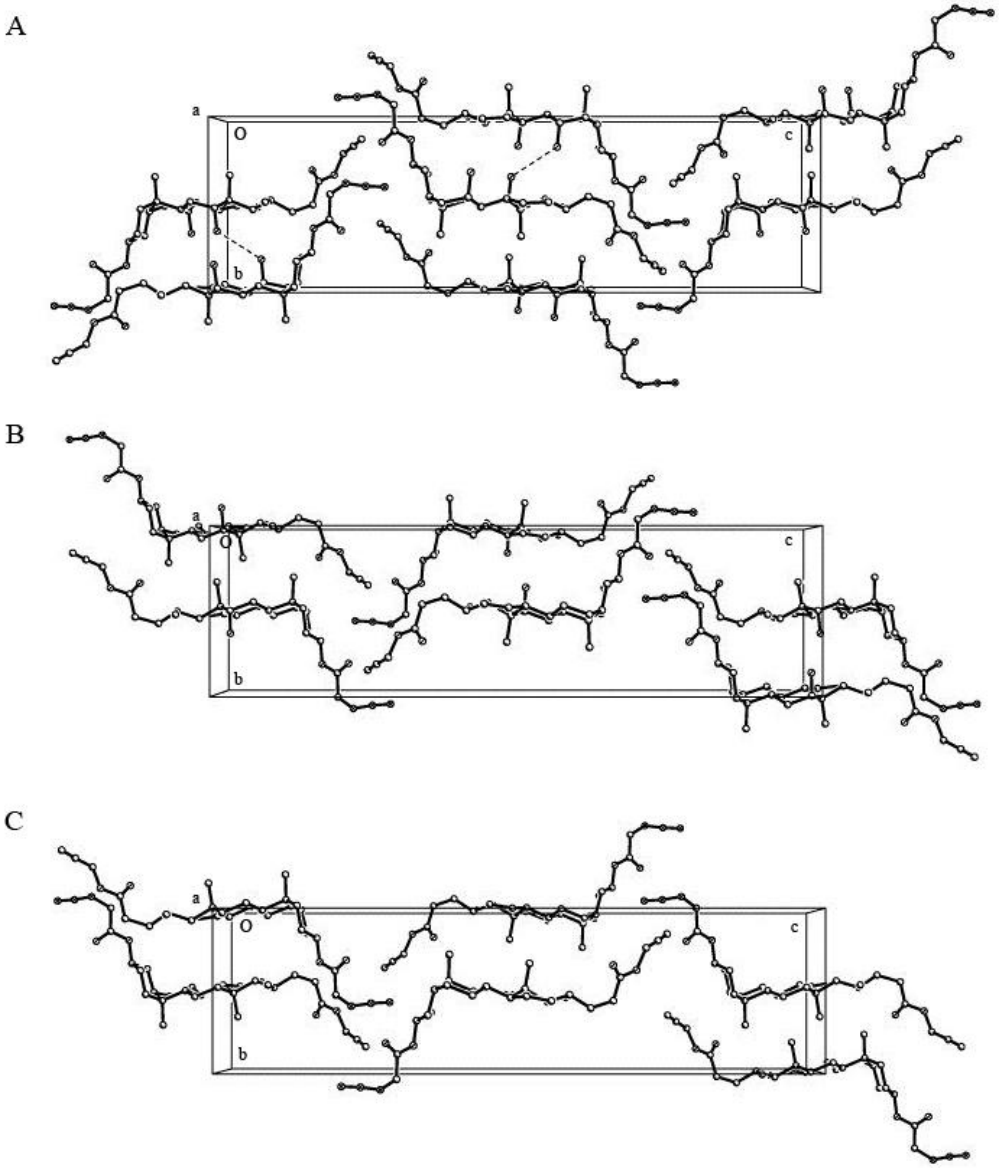

Figure S2. Single crystals structure of **3a** (**A**), **3b** (**B**) and **3c** (**C**).

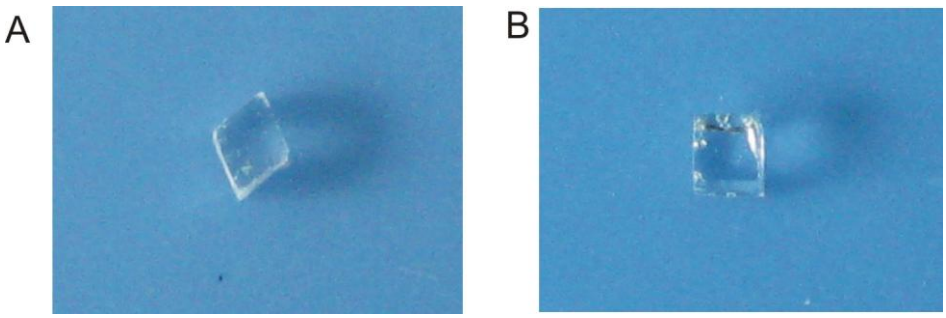

Figure S3 Morphologies of bile acid crystal before (A) and after (B) thermally induced polymerization

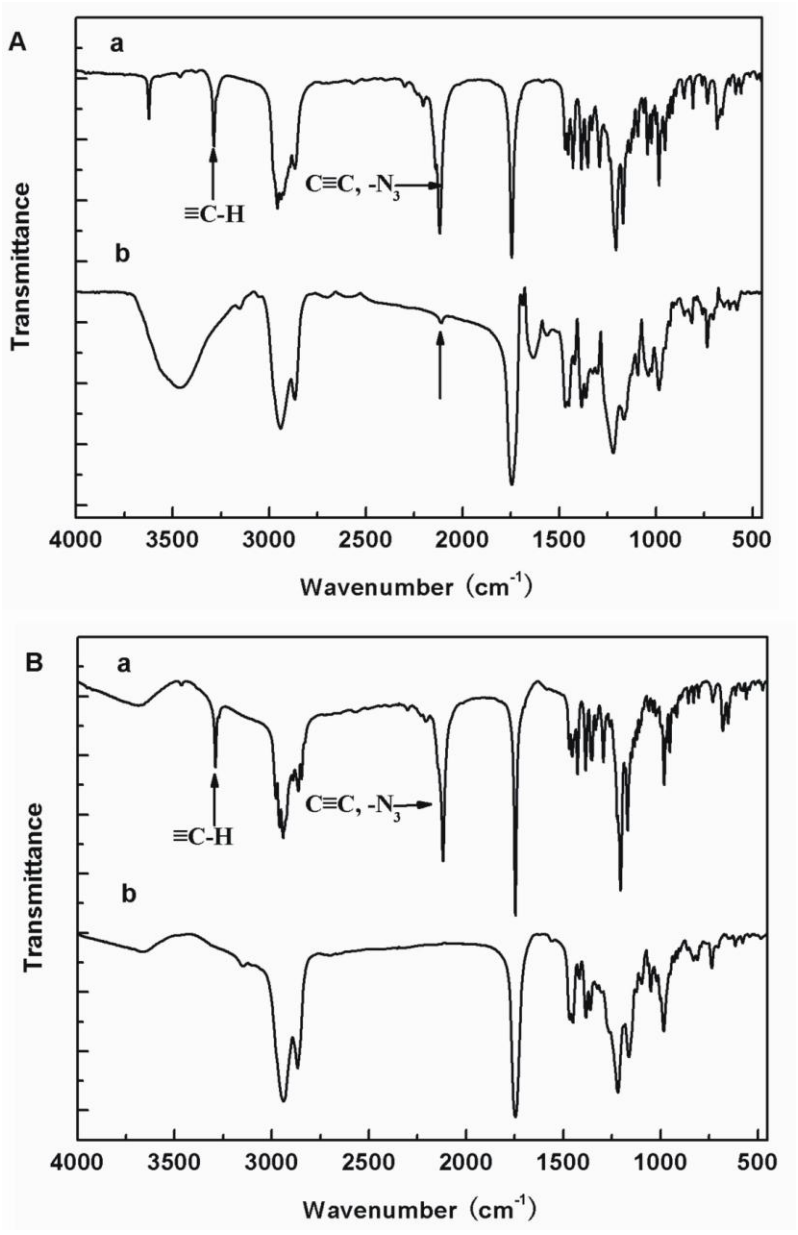

Figure S4. IR spectra of **3b** (**A(a)**), **DCA-P (A(b)), 3c (B(a)), LCA-P (B(b)).**

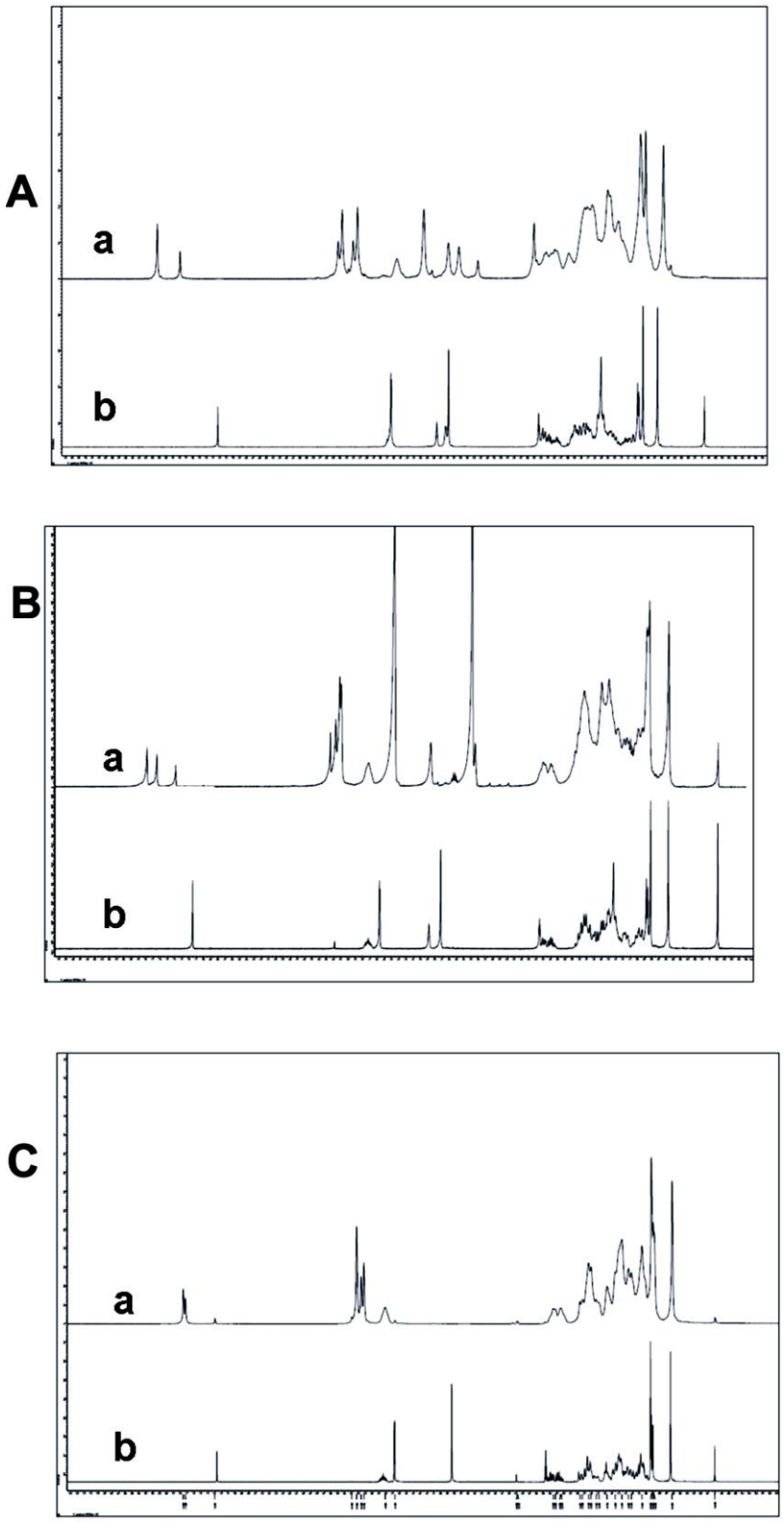

Figure S5. ^{1}H NMR spectra of **CA-P** (**A**(**a**)) in DMSO-d_6, **3a (A(b))** in $CDCl_3$, **DCA-P (B**(**a**)**)** in $CDCl_3$&CD_3OD-d_4, **3b (B**(**b**)**)** in $CDCl_3$, **LCA-P** (**C**(**a**)) in $CDCl_3$ and **3c (C**(**b**)**)** in $CDCl_3$.

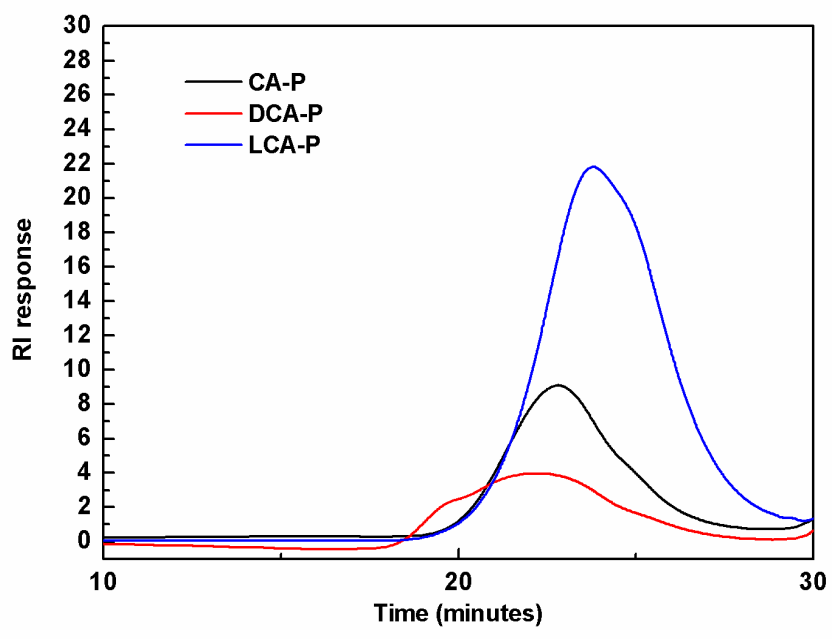

Figure S6. GPC spectra of poly(bile acid)s and GPC results.

Table S1 GPC data of the synthesized poly(bile acid)s

Polymer	*Mn* ($\times 10^3$)	*Mw* ($\times 10^3$)	*Mz* ($\times 10^3$)	Polydispersity
CA-P	113.0	172.0	222.0	1.53
DCA-P	111.0	178.0	233.0	1.60
LCA-P	70.0	120.0	175.0	1.71

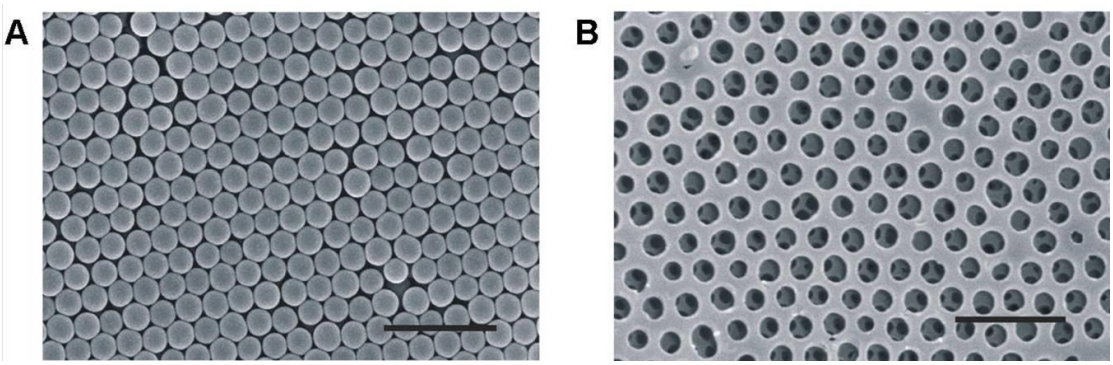

Figure S7 SEM images of the colloidal silica template (C) and a DCA-P based inverse opal structure (D). The bar inserted is equal to 1 μm.

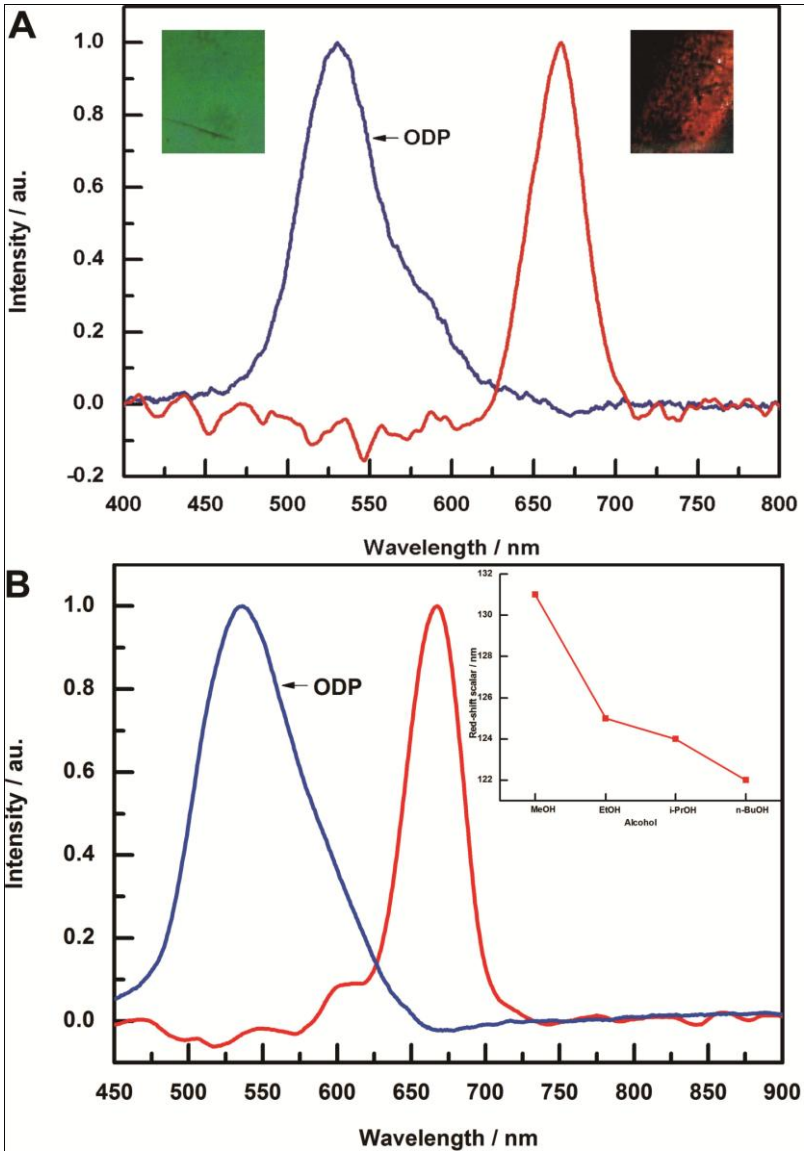

Figure S8. UV/Vis spectra of the photonic **DCA-P** film and its response to polar and nonpolar solvents: (A) upon exposure to CCl_4; (B) upon exposure to methanol. Inset in A is the accompanying color change. Inset in B is the diffraction-shift of the film upon exposure to different alcohols (methanol, ethanol, propanol and butanol).

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References

1 (a) J. E. Gautrot and X. X. Zhu, *Chem. Commun.* 2008, 1674; (b) J. E. Gautrot and X. X. Zhu, *Macromolecules* 2009, **42**, 7324.
2 D. Braga and F. Grepioni, *Angew. Chem. Int. Ed.* 2004, **43**, 4002