Supporting Information

Clickable Inverse Opal: A Useful Platform for Fabrication of Stimuli-Responsive Photonic Materials

1. Experiment part

1.1 Materials:
Tetrabutylammonium hexafluorophosphate was obtained from Fluka. 6-bromo-1-hexanol, ferrocenecarboxylic acid, cholic acid and 2-(trimethylsilyl)ethynyl were purchased from Sigma Company and were used without further purification. Other materials and solvents were received from Beijing Chemicals Company.

1.2 Characterization:
Common glass slide were cut into 50×20 mm and immersed in H₂SO₄/H₂O₂ (7:3) mixture for 12 h, following rinsing with deionized water in ultrasonic bath for three times and then dried for use. ¹H NMR spectra were obtained by a JEOLJNMECS 300NMR spectrometer. Morphology and microstructure of silica colloidal crystals and photonic hydrogel films were observed by a Hitachi S-6700 field emission scanning electron microscope. Optical Bragg diffractions were checked by an Olympus BX51M fiber optic spectrophotometer coupled to an optical microscope. The photopolymerization was performed using a UV light (FUSI Electric ST3) with 16 W. Electrochemical behavior of photonic hydrogel films were studied with a PG310 (HEKA Electronic, Dr.Schulz GmbH) electrochemical potentials station in acetonitrile in the presence of Bu₄NPF₆ (0.2M) as supporting electrolyte. A platinum electrode (diameter 10 mm) enwrapped with Teflon and a platinum wire (diameter 0.1 mm) were used as the working electrode and the counter electrode, respectively. The potentials were measured against an Ag reference electrode.
1.3 Synthesis of functional monomer and functional molecules:

1. **Reaction 1**
   
   \[
   \text{CH}_2=\text{CHCOOH} + \text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{DCC, DMAP}} \text{CH}_2=\text{CHCOO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaN}_3} \text{CH}_2=\text{CHCOO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3
   \]
   
   Dry THF, r.t.

2. **Reaction 2**
   
   \[
   \text{HCl} \cdot \text{N} - \text{C}_6\text{H}_4\text{Br} + \text{Si} = \xrightarrow{\text{Pd(PPh}_3)_4, \text{CuI}} \text{N} - \text{C}_6\text{H}_4\text{Si}= \xrightarrow{\text{KOH}} \text{N} - \text{C}_6\text{H}_4\text{Si} \xrightarrow{\text{THF, r.t.}} \text{N} = \text{C}_6\text{H}_4\text{Si}
   \]
   
   Et_3N, DMF, 40

3. **Reaction 3**
   
   \[
   \text{Fc} \text{COOH} + \text{H}_2\text{N} \text{CH} = \text{CH}_2 \xrightarrow{\text{DCC, DMAP}} \text{Fc} \text{CO} \text{N} \text{CH} = \text{CH}_2
   \]
   
   CH_2Cl_2, r.t.

4. **Reaction 4**
   
   \[
   \text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{Br} \text{CH} = \text{CH}_2 \xrightarrow{\text{Cs}_2\text{CO}_3} \text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCH} = \text{CH}_2
   \]
   
   DMF, r.t.

**Figure S1.** Synthesis of functional monomer and functional molecules
1. Synthesis of 6-azidohexyl acrylate

A mixture of acrylic acid (1g, 1mol), 6-bromo-1-hexanol (3g, 1.2mol), N, N'-dicyclohexyl carbodiimide (DCC 3.15 g, 1.1 mol), and 4-dimethylaminopyridine (DMAP 1.7 g, 1 mol) in anhydrous CH₂Cl₂ (150 mL) was stirred at room temperature for 24 h. After the reaction mixture filtrated, the organic layer was washed with 4% hydrochloric acid, saturated aqueous sodium bicarbonate and brine, respectively. And then the product was dried by anhydrous magnesium sulfate, filtered and evaporated in vacuum. The last residue was purified by flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether=1/30) to afford 6-bromohexylacrylate as a pale yellow liquid with a yield of 40% for the next step. ¹H NMR (300 MHz, CDCl₃): δ 6.38-6.43 (d, 1H, J=15Hz, CH₂=CH-), 6.08-6.17 (dd, 1H, J=9Hz, J=15Hz, CH₂=CH-), 5.81-5.84 (d, 1H, J=9Hz, CH₂=CH-), 4.14-4.18 (t, 2H, -CH₂-O-), 3.39-3.44 (t, 2H, -CH₂-Br-), 1.85-1.90 (m, 2H, -CH₂-), 1.67-1.72 (m, 2H, -CH₂-), 1.43-1.47 (m, 4H, -CH₂-); ¹³C NMR (75 MHz, CDCl₃): δ 165.5, 129.8, 127.8, 63.6, 32.9, 31.9, 27.9, 27.0, 24.4; IR (KBr), 2962 cm⁻¹, 2876 cm⁻¹, 1727 cm⁻¹, 1630 cm⁻¹; MS(ESI): 235.1 (M⁺).

A mixture of NaN₃ (0.6g, 9.2mmol) and 6-bromohexylacrylate (0.94g, 4mmol) in dry DMF 20ml was stirred at 45 for 10h. On completion of the reaction, the mixture was poured onto crashed ice and extracted with diethyl ether. The organic phase was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue obtained was purified by flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether=1/30) to give the desired 6-azidohexyl acrylate as a pale yellow liquid with a yield of 50%. ¹H NMR (300 MHz, CDCl₃): δ 6.38-6.43 (d, 1H, J=15Hz, CH₂=CH-), 6.08-6.17 (dd, 1H, J=9Hz, J=15Hz, CH₂=CH-), 5.81-5.84 (d, 1H, J=9Hz, CH₂=CH-), 4.14-4.18 (t, 2H, -CH₂-O-), 3.25-3.29 (t, 2H, -CH₂-N₃-), 1.55-1.71 (m, 4H, -CH₂-), 1.42-1.44 (m, 4H, -CH₂-); ¹³C NMR (75 MHz, CDCl₃): δ 166.7, 126.7, 124.5, 63.8, 50.6, 27.9, 27.7, 25.6, 24.8; IR (KBr), 2950 cm⁻¹, 2851 cm⁻¹, 1719 cm⁻¹, 1630 cm⁻¹ (azide asymmetric stretch), 1632 cm⁻¹; MS(ESI): 197.1 (M⁺).

2. Synthesis of 4-ethynylpyridine¹

4-(2-(trimethylsilyl)ethyl)pyridine: 4-bromo-pyridine hydrochloride (1.0g, 5.14
mmol, 1.0 eq.) and 2-(trimethylsilyl)ethynyl (1.3 ml, 9.26 mmol, 1.8 eq.) were suspended in a well degassed solution of 50 ml DMF and 5 ml triethylamine. It was degassed for another 20 minutes. Pd(PPh3)₄ (300 mg, 0.26 mmol, 5 mol%) and CuI (95 mg, 0.51 mmol, 10 mol%) were added. It was stirred for 24 hours at 40°C. The reaction mixture was filtrated over silica gel, washed with DMF, and extracted with diethyl ether. The organic phase was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue obtained was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to give a yellowish liquid with a yield of 70%. The reaction was performed in absence of light. ¹H NMR (300 MHz, CDCl₃): 8.38-8.39 (2H, d, J= 5.1 Hz, -CH-CH-); 7.12-7.13 (2H, d, J = 5.1Hz, CH-CH-); 0.1 (9H, s, -Si(CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 150.4, 131.8, 126.4, 102.7, 100.5, 0.4; MS (ESI): 175.5 (M⁺).

4-(ethynyl)pyridine :
4-(2-(trimethylsilyl)ethynyl)pyridine (516 mg, 2.94 mmol, 1.0 eq.) was dissolved in 20 ml THF. 6 ml 1M KOH-solution (6 mmol, 2 eq.) in THF was added. The reaction mixture was stirred for 12 hour at room temperature and was then evaporated, dissolved in CH₂Cl₂, absorbed on silica gel, evaporated and chromatographed in the dark (petroleum ether/ethyl acetate=1:1) to give 4-(ethynyl)pyridine as a light sensitive white solid with a yield of 90%. ¹H NMR (300 MHz, CDCl₃): 8.59-8.61 (2H, d, J= 6 Hz, -CH-CH-); 7.35-7.37 (2H, d, J = 6Hz, -CH-CH-); 3.31 (1H, s, terminal alkyne H). IR (KBr), 2929 cm⁻¹, 2100 cm⁻¹, 1598 cm⁻¹, 1545 cm⁻¹; ¹³C NMR (75 MHz, CDCl₃): δ 149.9, 130.4, 126.2, 82.0, 81.0; MS(ESI): 103 (M⁺).

3. Synthesis of N-(2-Propargyl)amidoferrocene²
N,N’-Dicyclohexylcarbodiimide (DCC, 3g,15mmol) and N,N-dimethylaminopyridine (DMAP, 0.12 g, 1mmol) were added to ferroacenecarboxylic acid (2.3g, 10mmol) in CH₂Cl₂ (30 mL).The resultant mixture was stirred for 10 min and then, propargylamine (0.55 g,10 mmol) was added. After stirring for 12 h, the solvent was removed by evaporation and the residue was dissolved in ethyl acetate. The organic layer was washed with aqueous 4%HCl and saturated aqueous NaHCO₃ several times. The resultant organic layer was dried (MgSO₄), and concentrated to dryness. The residue was subjected to
puriﬁcation by silica gel column chromatography (petroleum ether/ethyl acetate = 1:2)) to give N-(2-propargyl)amidoferrocene as a yellow powder with a yield of 40% after evaporation. \(^1\)H NMR (300 MHz, CDCl\(_3\)): 5.81 (br s, 1H, -NH), 4.69 (s, 2H, -C\(_5\)H\(_4\)), 4.37 (s, 2H, -C\(_5\)H\(_4\)), 4.24 (s, 5H, -C\(_5\)H\(_5\)), 4.18 (m, 2H, -CH\(_2\)-), 2.28 (s, 1H, terminal alkyne H); IR(KBr) 1620 cm\(^{-1}\), 1545 cm\(^{-1}\), 829 cm\(^{-1}\); MS(ESI): 267 (M\(^+\)).

4. Synthesis of bile acid derivative:

To a solution of bile acid (25 mmol) in anhydrous 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 was isolated as white solid with a yield of 90%. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 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\(_2\) ); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 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; IR(KBr) 3390 cm\(^{-1}\), 2939 cm\(^{-1}\), 2120 cm\(^{-1}\), 1740 cm\(^{-1}\); MS(ESI): 469.1 [M+Na\(^+\)].

1.4 Formation of colloidal-crystal templates:

The highly uniform silica colloidal microspheres were synthesized by using an approach based on the Stöber method\(^3\). In a typical preparation, TEOS (4mL) and anhydrous ethanol (180 mL) were mixed in a 250-mL flask and stirred with a magnetic beater. Then, ammonia (17mL) was slowly added and the resulting reaction mixture was left overnight. After centrifugation and dispersion with anhydrous ethanol had been repeated four or five times to expunge residues, the monodispersed silica particles were obtained and fully dispersed in anhydrous ethanol (weight concentration ca. 1–4%), which were allotted into 7-mL clean vials for the formation of colloidal-crystal templates.
A clean glass slide was vertically placed into each vial for colloidal-crystal growth. After complete volatilization of ethanol, silica colloidal-crystal templates were formed on both sides of each glass slide.

1.5 Fabrication of the free-standing film:

![Figure S2. Fabrication of the free-standing film](image)

6-azidohexyl acrylate (0.2 g, 1 mmol), MAA (0.1 g, 1 mmol), and EGDMA (0.2 g, 1 mmol) were mixed in a mixed solvent of 1 g methanol and 1 g chloroform under ultrasonic for 5 min. After adding 0.05 mM AIBN and degassing by nitrogen for 10 min, the homogeneous monomer mixture was dropped onto silica arrays. Once the colloidal crystals became transparent, indicating successful infiltration, excess precursors were removed by covering a clean glass slide (50 mm × 20 mm × 1.5 mm), and the remaining mixture was photopolymerized in an ice bath under an UV light at 365 nm for 40 min. The sandwich was immersed into 1% hydrofluoric acid for 2 h to separate double slides and fully etch the silica colloid. After washed by an amount of deionized water, the photonic free-standing film was ready for functionalization.

1.6 Modification of clickable inverse opal via click reaction:

4-(ethynyl)pyridine (0.05 g), CuSO₄·5H₂O (0.05 g), and sodium ascorbate (0.1 g) were solubilized in 3 mL of deionized water/THF (V:V=2:1). A piece of film was placed into the solution and incubated for 24 h at 50°C. After the reaction, the sample was rinsed with water/THF several times to remove physically adsorbed, unreacted reaction residue and kept in deionized water. Maintaining the same reaction conditions of 4-(ethylnyl)pyridine except for replacing the 4-(ethylnyl)pyridine with N-(2-Propargyl)amidoferrocene and bile acid derivative resulted in electroactive and bioactive films.
Figure S3. (a) CVs of N-(2-Propargyl)amidoferrocene and N-(2-Propargyl)-amidoferrocene modified film at 50 mVs\(^{-1}\) in acetonitrile in the presence of Bu\(_4\)NPF\(_6\) (0.2 M).

IR spectra of the clickable film post-modified by bile acid molecule:

Figure S4. IR spectra of the film before click reaction (b), after click reaction (a) and bile acid molecule (c)

References
1  Sergio Grunder, Roman Huber, Marcel Mayor, et al. J. Org. Chem. 2007, 72, 8337-8344
2  Teruaki Hasegawa, a Mariko Umeda, Seiji Shinkai et al. Carbohydrate Research,
2006, 341, 35–40
3 W. Stoeber, A. Fink, E. Bohn, J. Colloid Interface Sci. 1968, 26, 62.