Supplementary Information

Materials and instrumentation

Tetracycline hydrochloride was purchased from Alfa Aesar (Fig. S1a). Glycine (Fig. S1b), copper acetate, styrene, sodium dodecyl sulfonate, ammonium persulfate, acrylamide, acrylic acid, acetic acid, *N*, *N*'-methylene bisacrylamide, sodium acetate and other affiliated chemicals were all from local suppliers.

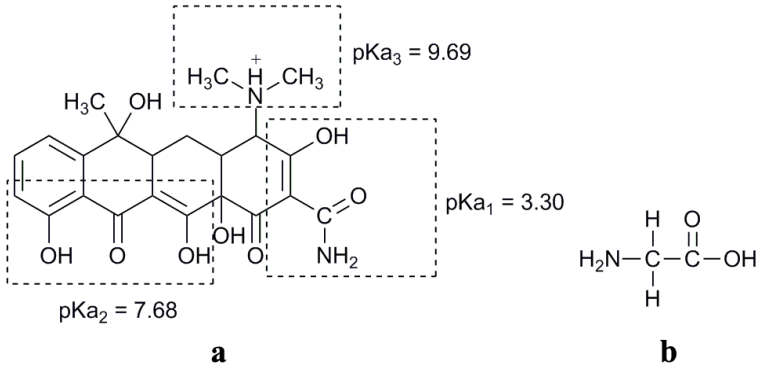

Fig. S1 Structures of (a) tetracycline and (b) glycine.

Styrene and acrylic acid was vacuum distilled to remove inhibitors prior to use, and other solvents and chemicals were of reagent quality and were used without further purification unless specially mentioned.

All buffer solutions were prepared by 0.2 M acetic acid solution and 0.2 M sodium acetate solution when used. pH values from pH 3 to pH 6 were adjusted by adding additional 0.2 M acetic acid solution or 0.2 M sodium acetate solution. Copper(II) and glycine standard solutions were prepared by dissolving a certain amount of copper acetate and glycine in the corresponding pH buffer solution, and then diluted to the required concentrations.

Surface structure of photonic crystal template and tetracycline-immobilized

hydrogel photonic crystals (HPC) were observed through a scanning electron microscopy (Nova NanoSEM 430, FEI) operating at 5 kV. The diffractive wavelength was measured by using a 380-1050 nm fiber optic spectrometer (JKHQ-D1, Tianjin, China). The pH value was measured via pH meter (FE20K, Mettler Toledo).

Preparation of monodispersed polystyrene colloids

The monodispersed polystyrene colloids were synthesized by emulsion polymerization. Briefly, 100 mL deionized water was poured into a four-neck flask equipped with a stirrer, an argon supplying pipe and a condenser. Then 0.120 g sodium dodecyl sulfonate and 0.25 g ammonium persulfate were added under the stirring and argon atmosphere. The four-neck flask was heated up to 50 ^{o}C in a water bath and then the water solution was deoxygenated by bubbling with argon for 1 hour. 25 mL treated styrene was added into the flask at a rate of one dropper per 4 seconds and then the temperature was increased to 75 ^{o}C. The reaction was allowed to reflux for 12 hours before it was terminated.

Self-assembly of polystyrene photonic crystal template

Photonic crystal template was self-assembled from the obtained 210 nm monodispersed polystyrene colloids by using the vertical deposition method. The polystyrene colloids in deionized water with a concentration of 1: 15 (*v*/*v*) were placed into clean containers, which were laid in a 45 °C water bath for 2-3 days. Following the solvent was completely evaporated, photonic crystal template of close-packed face-centered cubic (fcc) was obtained.

Fabrication of tetracycline-immobilized HPC

The immobilization of tetracycline within photonic crystal structures was along with the polymerization procedure of polyacrylamide. After an optimization, tetracycline-immobilized HPC was fabricated as below: 42 mmol (62 mol%) acrylamide and 24 mmol (36 mol%) acrylic acid as monomers were mixed with 0.021 mmol (0.04 mol%) tetracycline in 4 mL deionized water, and then 0.6 mmol (0.9 mol%) N, N'-methylene bisacrylamide as cross-linker and 0.4 mmol (0.6 mol%) ammonium persulfate as initiator were added into this solution. Following a sufficient homogenization, the mixture was infiltrated into the obtained polystyrene photonic crystal templates by using a capillary-attraction-induced method until the interstitial space among the close-packed spheres was filled with the solution via the capillary effects. After thermal polymerization in an oven at 55 °C for less than 6 hours, the opal structure of tetracycline-immobilized HPC film with a highly-ordered array was obtained.

Measurement of optical responses

All the responses were studied by monitoring the diffractive wavelength changes of the HPC film. The diffractive wavelength of HPC film to external chemicals were measured in buffer solutions by using a 380-1050 nm fiber optic spectrometer (JKHQ-D1, Tianjin, China) at the vertical direction. The fiber optic spectrometer is convenient to fix a same measurement location on the film by focusing the incident light on one dot. And always maximum diffraction peak is observed in our experiments. Before each spectral scan, the pH of all solutions was checked. In all cases, HPC film was soaked in 10 mL buffer solutions of various chemicals for 10

minutes at room temperature until it reached a swelling equilibrium. After one detecting, the film was soaked again in a 0.1 M hydrochloric acid solution for 2 minutes and then rinsed thoroughly with deionized water to recover the blank state for the next detection. For a series of measurements, the detection followed the sequence from low to high concentrations to eliminate interference.

Responses of tetracycline-immobilized HPC to aluminium(III) and zinc(II)

In the formation of tetracycline binary complex procedure, aluminium(III) and zinc(II) were also investigated by measuring their responses in terms of 0.04 mol% immobilized tetracycline. Under the same conditions of copper(II), the tetracycline-immobilized HPC was immersed in 10 mL 10^{-5} M aluminium(III) and zinc(II) solution (pH 5.5), respectively, to observe the maximum diffraction peak. As shown in Fig. S2, it is indicated that aluminum(III) and zinc(II) resulted in much smaller responses to tetracycline-immobilized HPC compared to copper(II) under the same conditions.

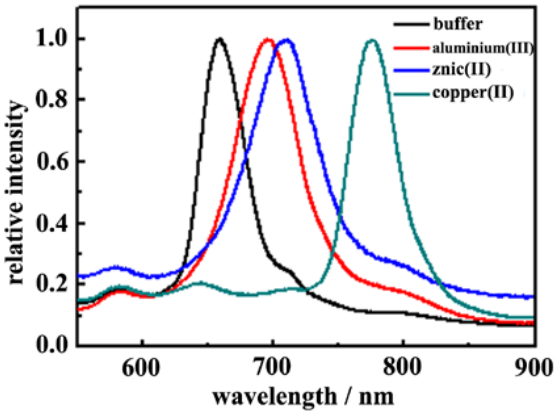

Fig. S2 Responses of tetracycline-immobilized HPC to aluminium(III) and zinc(II) compared to copper(II) under the same conditions.

Effect of ionic strength

Effect of ionic strength on the formation of tetracycline-copper(II) complex was experimentally examined in response to 10^{-5} M copper(II) solution which contained 0, 10^{-5} M, 10^{-4} M, 10^{-3} M, 0.01 M, 0.1 M and 1.0 M KNO_3. With KNO_3 concentration increasing from 0 to 1.0 M in 10^{-5} M copper(II) buffer solution, the diffraction peak of tetracycline-immobilized HPC shifted slightly (Fig. S3). It was demonstrated that the effect of ionic strength on the formation of tetracycline-copper(II) complex was neglectable.

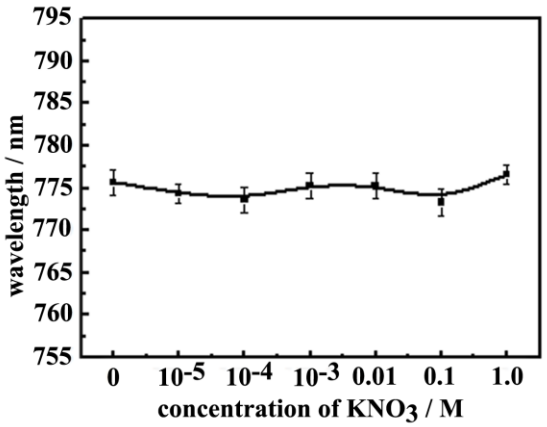

Fig. S3 Effect of ionic strength on the formation of tetracycline-copper(II) complex in presence of 10^{-5} M copper(II).

Recoverability

The tetracycline-immobilized HPC film was firstly soaked in buffer solution (pH 5.5) to form a stable blank state, and then immersed in a 10 mL 10^{-5} M copper(II) buffer solution to create the binary system. Here, an red-shift from 660 nm to 776 nm occurred in presence of copper(II). Following that, the tetracycline-copper(II) film fixed at 10^{-5} M copper(II) was taken out from the copper(II) solution and immersed in a 10 mL 10^{-8} M glycine solution to construct the ternary system. At this time, the diffractive wavelength had a subsequent red-shift from 776 nm to 815 nm in the

presence of glycine. Finally, the film was throughly washed with 0.1 M hydrochloric acid and deionized water successively, the diffractive wavelength then shifted back to the original blank state. As shown in Fig. S4, the diffraction response of tetracycline-immobilized HPC film was not affected over five cycles, and it can be easily recovered.

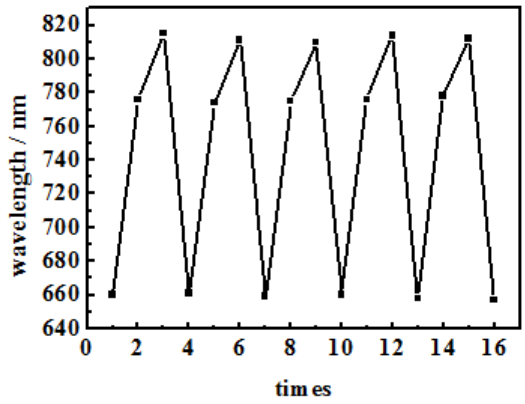

Fig. S4 Diffraction response of tetracycline-immobilized HPC film over five cycles.