

Supporting Information

A Supramolecular Photonic Crystal Hydrogel Based on Host-Guest Interaction for Organic Molecules Recognition

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1. Formation of photonic crystal templates

The silica colloidal microspheres were synthesized by using an approach based on the Stöber method with certain modifications as follow.^[1] In a typical preparation process, anhydrous ethanol (100 mL), deionized water (6 mL) and ammonia (4 mL) were mixed in a 250 mL flask and stirred gently with a magnetic stirrer at 35 °C in a water bath. Then TEOS (6 mL) was quickly added and the resulting reaction mixture was left overnight. The size of the silica particles can be tuned in the range of 180-360 nm by changing the reactant ratio or conditions. The monodispersed silica particles were obtained by centrifugation followed by rinsing 8 times using anhydrous ethanol to expunge the residues. The resulting product was then dispersed in anhydrous ethanol (Volume concentration 0.5%). Common glass slides were cut to the same as the PMMA slides, and were treated with and immersed in a H₂SO₄/H₂O₂ mixture (7:3, v/v) for 24 h. All 5 mL vials for the formation of colloidal crystal templates were treated as well. The glass slide was well-cleaned by rinsing with deionized water and ethanol several times and dried with nitrogen. The silica colloidal microspheres were placed into 5 mL clean vials and a clean glass slide was placed vertically into each vial for photonic crystal growth. After complete volatilization of ethanol, photonic crystal templates were obtained. In this work, monodispersed silica spheres with a diameter of approximately 195 nm and 190 nm were used.

2.FT-IR spectra

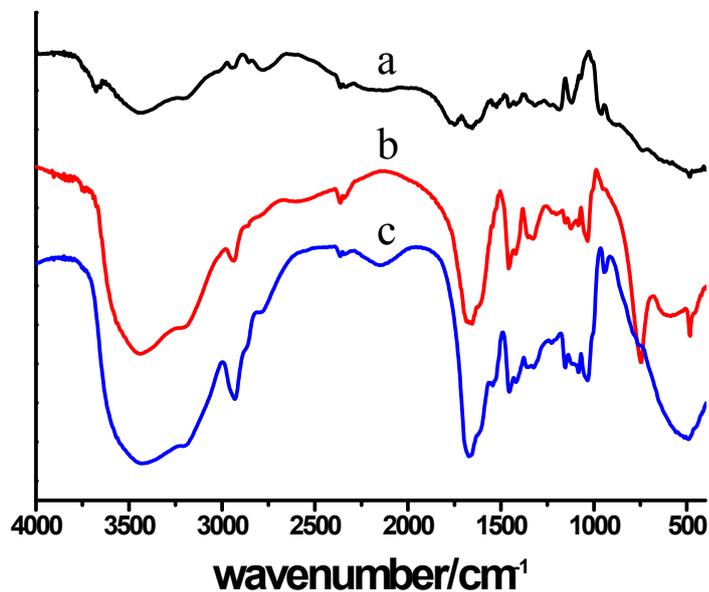


Fig S1. FT-IR spectra of (a) PAAm gel; (b) PAAm- β -CD gel (5, 5); (c) PAAm- β -CD-*t*-Bu gel (5, 5).

PAAm gel (5): 3431, 3198 cm^{-1} (O-H stretching vibration, N-H asymmetric stretching vibration, and N-H symmetric stretching vibration), 2939 cm^{-1} (methylene C-H stretching vibration), 1658 cm^{-1} (C=O stretching vibration, N-H bending vibration).

PAAm- β -CD gel (5, 5): 3437, 3198 cm^{-1} (O-H stretching vibration, N-H asymmetric stretching vibration, and N-H symmetric stretching vibration), 2933 cm^{-1} (methylene C-H stretching vibration), 1665 cm^{-1} (C=O stretching vibration, N-H bending vibration).

PAAm- β -CD-*t*-Bu gel (5, 5): 3437, 3198 cm^{-1} (O-H stretching vibration, N-H asymmetric stretching vibration, and N-H symmetric stretching vibration), 2933 cm^{-1} (methylene C-H stretching vibration), 1671 cm^{-1} (C=O stretching vibration, N-H bending vibration).

3. 2D ROESY NMR

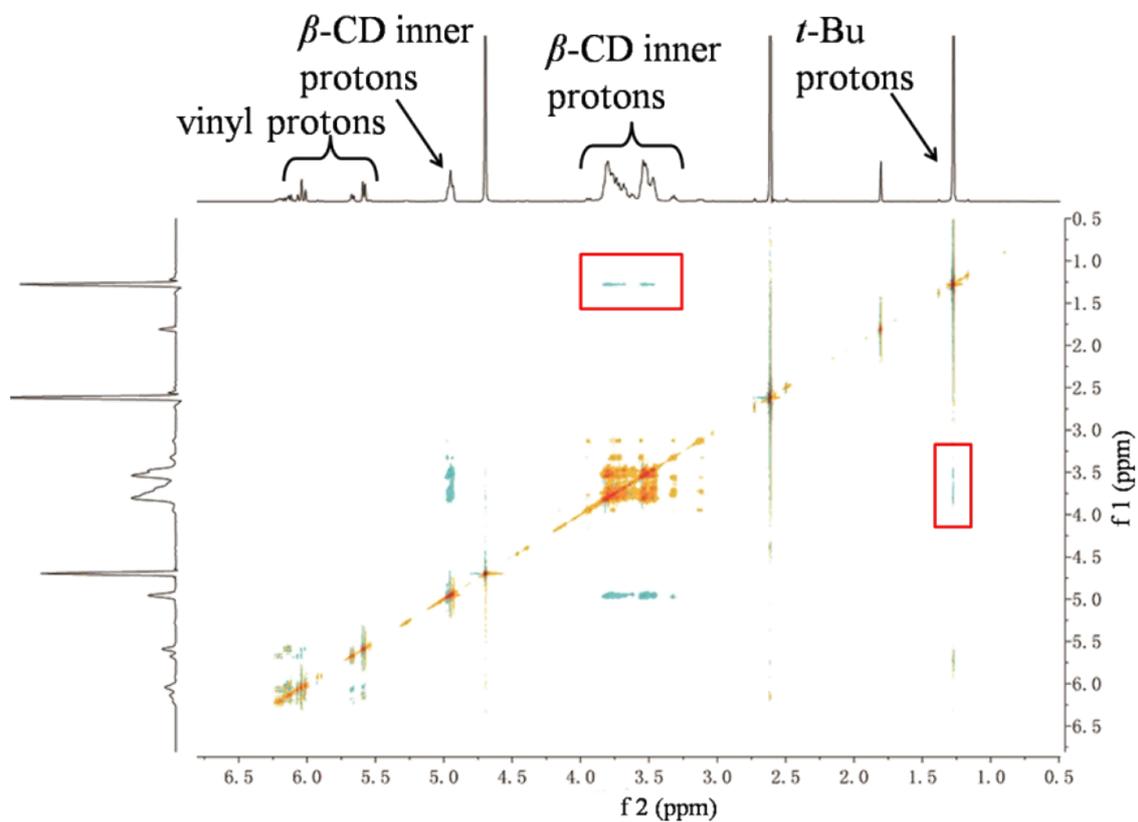


Fig S2. 2D ROESY NMR spectrum and proposed structure of the inclusion complex for a mixture of β -CDAAm and *t*-BuAAm ($D_2O/DMSO-d_6(95/5, v/v)$, 600 MHz, 30 °C). The red rectangles in the spectrum highlight the correlation peaks between the protons of *t*-Bu and the protons of β -CD.

4. Effect of Crosslinker proportion

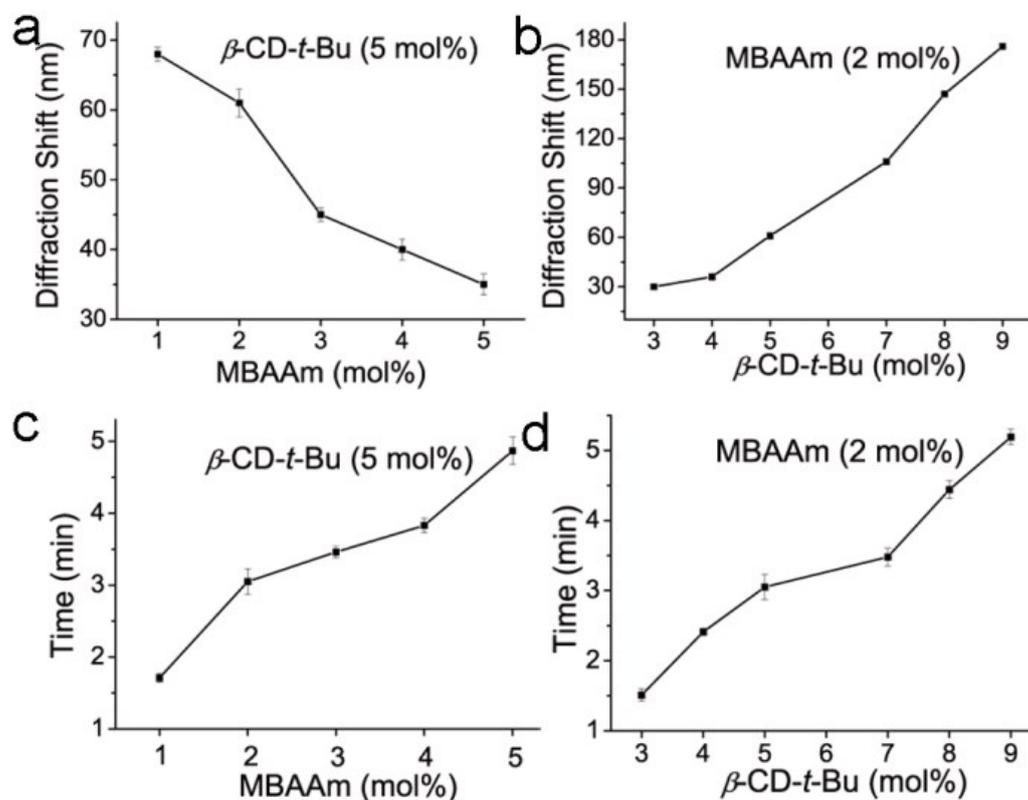


Fig. S3 Bragg peak shift of the inverse opal hydrogel vs. mole percentage of the cross-linker MBAAm at 5 mol% of the host-guest pair (a). Bragg peak shift of the inverse opal hydrogel vs. mole percentage of the host-guest pair at 2 mol% of the cross-linker MBAAm (b). Responding time of the inverse opal hydrogel vs. mole percentage of the cross-linker MBAAm at 5 mol% of the host-guest pair (c). Responding time of the inverse opal hydrogel vs. mole percentage of the host-guest pair at 2 mol% of the cross-linker MBAAm.

5. control experiment

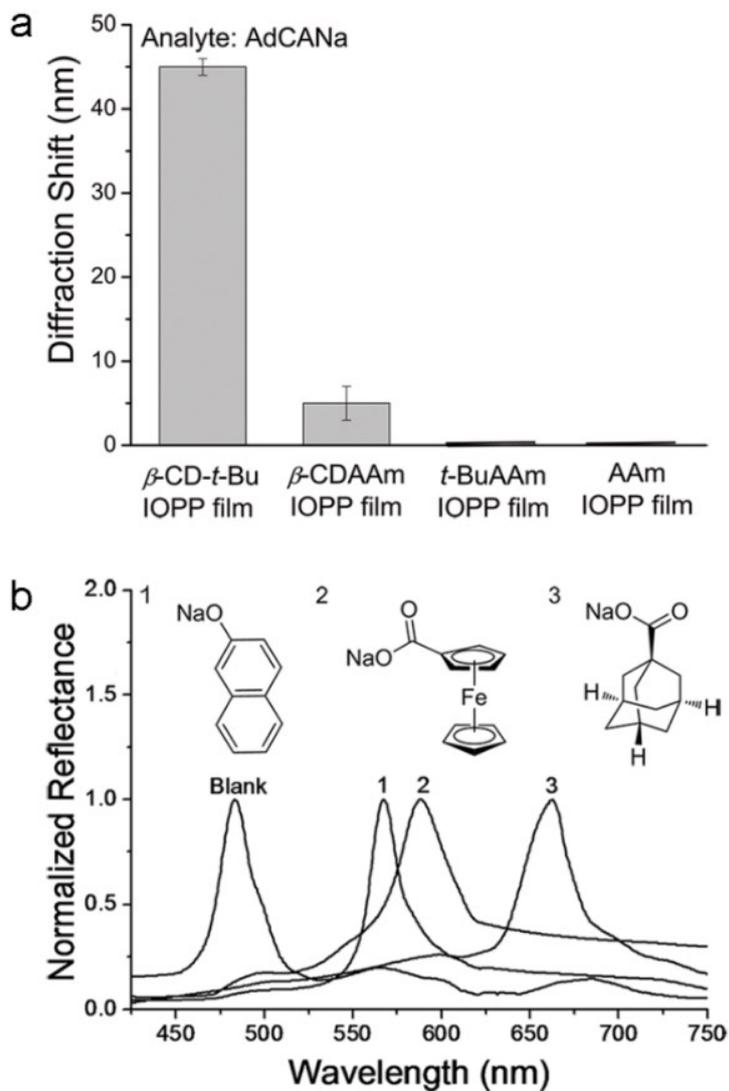


Figure S4. Bragg peak shift of different hydrogel samples (a). Optical response of the β -CD-*t*-Bu hydrogel (9, 2) to the competitive guest molecules (molecule 1, 2 and 3) with different association constants with the host β -CD (b).

6. The recoverability of inverse opal hydrogel film of β -CD-*t*-Bu gels.

Fig. S5 presents the recoverability of the IOPP films which were tested by immersing into deionized water, the whole process was accomplished in 18, 15, 90, 180 and 240 minutes, respectively, for β -CD-*t*-Bu (4, 2), β -CD-*t*-Bu (5, 2), β -CD-*t*-Bu (7, 2), β -CD-*t*-Bu (8, 2) and β -CD-*t*-Bu (9, 2).

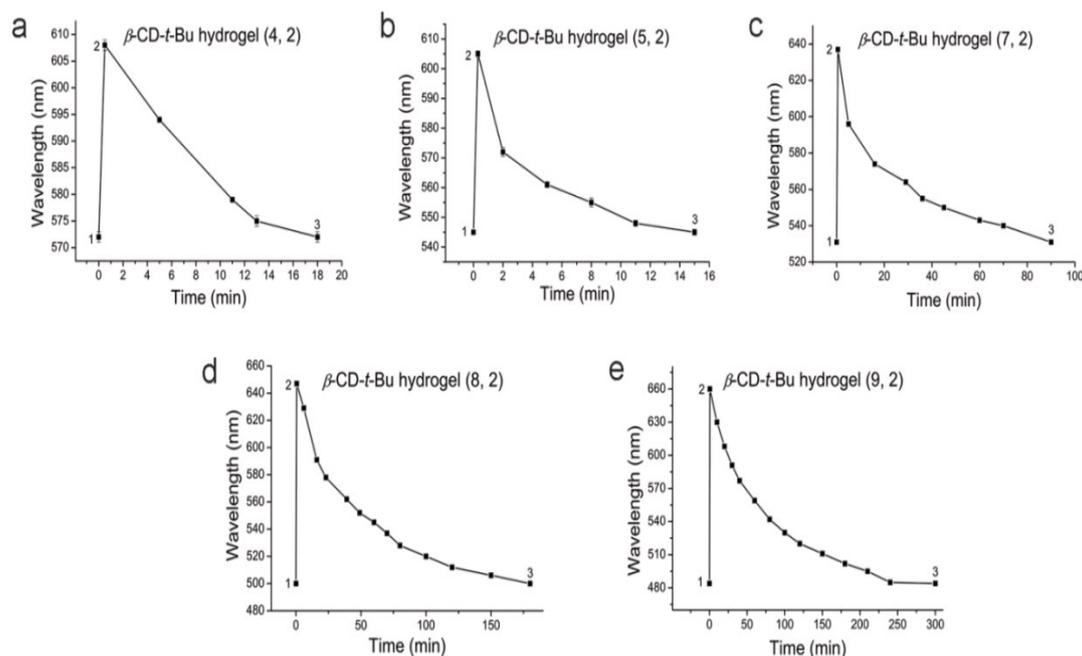


Fig S5. Recoverability of the inverse opal hydrogel film β -CD-*t*-Bu (4, 2) (a), β -CD-*t*-Bu (5, 2) (b), β -CD-*t*-Bu (7, 2) (c), β -CD-*t*-Bu (8, 2) (d) and β -CD-*t*-Bu (9, 2) (e). 1-2: addition of AdCANA, 2-3: immersing the hydrogel film in deionized water.

Table 1. Optical response of β -CD-*t*-Bu hydrogel (9, 2) to the competitive guest molecules (molecule 1, 2 and 3).

Target molecule	Sodium β -naphthol (Molecule 1)	Sodium ferrocenecarboxylate (Molecule 2)	AdCANA (Molecule 3)
Association constant with β -CD (M^{-1})	500	2000	35000
Time to reach the largest red-shift (min)	20	3.0	0.5
The largest red-shift (nm)	81 \pm 1	102 \pm 2	176 \pm 1

REFERENCES

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- [2] M. Nakahata, Y. Takashima, H. Yamaguchi, A. Harada, *Nat. Commun.* **2011**, *2*, 511.
- [3] K. Miyamae, M. Nakahata, Y. Takashima, A. Harada, *Angew. Chem. Int. Ed.* **2015**, *54*, 8984-8987.