Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Valveless flow reversal by pH responsive supramolecular micropump

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1. Experimental Section

1.1 Materials

β-Cyclodextrin (β-CD), Hexamethylene diisocyanate (HDMI), and dibutyltin dilaurate (DBTDL) were purchased from TCI chemicals. Benzimidazole and Sulfate latex particles (5µm in diameter) were purchased ed from Sigma-Aldrich. Dimethyl Formamide (DMF), hydrochloric acid, and sodium hydroxide were obtained from Merck. DC/GEN/184 SYLGARD (PDMS Elastomer KIT) was purchased from Kevin Electrochem. Millipore water (18.2 MΩ•cm at 25 °C) was used in all experiments.

1.2 Characterization

The synthesized β-CD-PEG gel was characterized by FTIR using Thermo Scientific. Isothermal titration Calorimetric measurements were carried by Malvern MicroCal PEAQ-ITC. The UV-vis spectrophotometer (UV-2600 ultraviolet-visible spectrophotometer SHIMADZU) was used to measure the absorption of the host-guest complexation. Videos were recorded using an inverted optical microscope (OLYMPUS IX73) with a X-Cite 120 LED Boost, via a 10X objective (CPLN10XPH), excitation light was focused on the sample. Emission light was captured by the objective, passed through interference filters, and eventually recorded at 15 frames per second by a high resolution colored cooled camera (DP74). Using this DP74 camera connected to an optical microscope, videos were recorded. For each experiment, 30 tracer particles were monitored for a time interval of 15 seconds using the Tracker software (Motion Analysis Software) to calculate the fluid-pumping velocity.

2. Synthesis of β-cyclodextrin-polyethylene glycol (β-CD-PEG) gel

The β-CD-PEG- gel was prepared according to the reported method.[1] The gel was prepared in two steps. First, two solutions of PEG and HDMI in DMF in a molar ratio of 1:2 are allowed to react in a two-neck round bottom flask initially purged with dry N_2 at 55 °C. The reactor contains 0.01 wt % of the catalyst (DBTDL) compared to the total weight of the reagents and the overall concentration of reagents is 25 wt %. The product is poly(ethylene glycol) chains where terminal hydroxyl groups were substituted by isocyanate groups by an end-capped method in which each molecule of HDMI utilizes one of its two isocyanate groups to react with the hydroxyl group of PEG through the formation of a urethane group. The first step of the resulting reaction is shown in Scheme 1 (a). Second, the solution of β-CD in dimethylformamide (16.5 wt %) was added into the flask for 60 minutes to achieve the desired composition in the gel. After keeping the system in agitation for 30 minutes, the reactive mixture was transferred to the test tube, capped with septa under N_2 maintained at75 °C for 7 days. The resulting reaction is described in Scheme 2 (b).

After that the gel was collected and washed repeatedly, first with DMF and then with DI water, at room temperature, to remove water-soluble β-CD until less than 1 ppm monomer was found in the wash solution. Synthesized gel has been characterized by FTIR. It can be noted that the gel spectrum reveals the presence of bands at 1094 cm^{-1} and 1031 cm^{-1}, corresponding to PEG and β-CD. Amide I (1700 cm^{-1}) and amide II (1561 cm^{-1}), which confirm the chemical structure, are two simple bands corresponding to the existence of urethane groups as shown in figure S2.

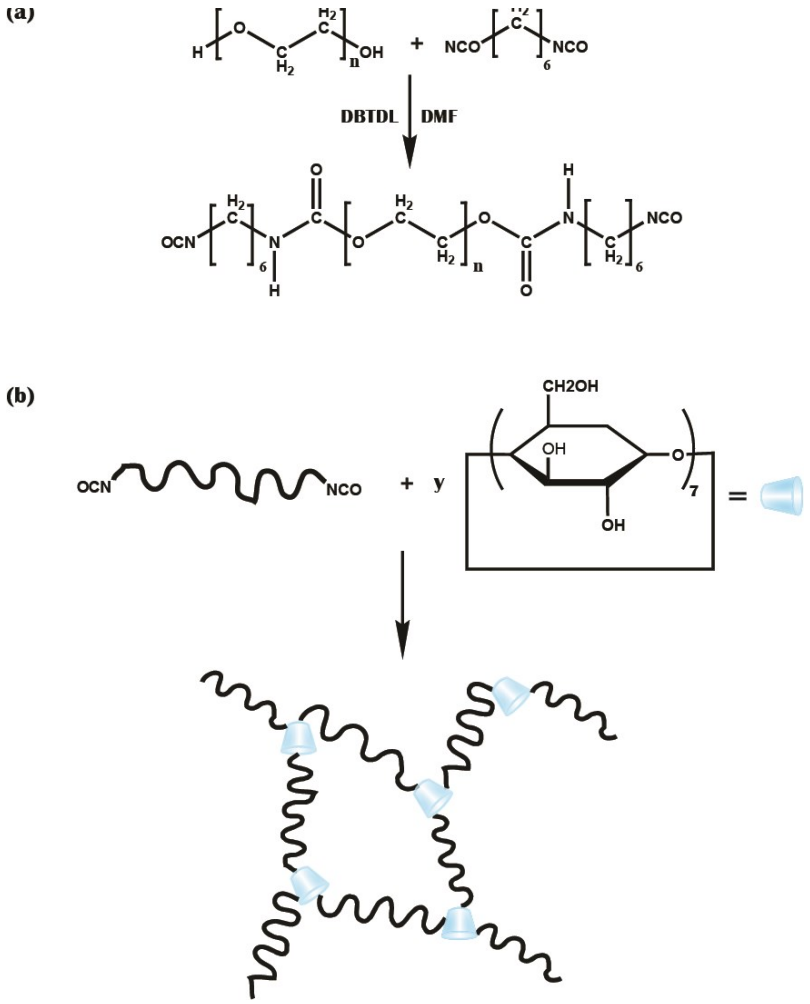

Figure S1. (a) End-capping process of PEG with HDMI. (b) Reaction among the end-capped PEG with isocyanate groups and the β-CD, together with an idealized outline of the structure of the gel.

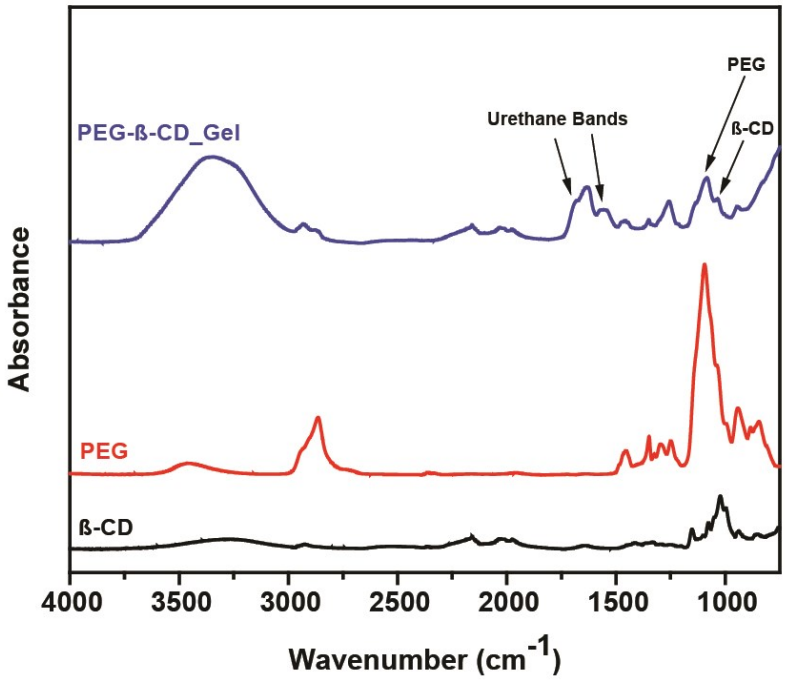

Figure S2. FTIR Spectra of PEG, β-CD, and a β-CD-PEG gel

3. Isothermal Titration Calorimetry

The thermodynamic parameters of cyclodextrin/benzimidazole molecular recognition were measured in aqueous at pH 7.4 using the Malvern MicroCal PEAQ-ITC at 25.0 °C (298.15 K). The ITC experiment included 39 consecutive 0.5 µL injections of BzI solution (10.0 mM) with the use of a syringe into the calorimeter sample cell containing β-cyclodextrin (200 µM) at an interval of 150s with the constant rate of 750 rpm. Control experiment involved similar injections into an aqueous solution under same conditions at 25.0 °C. Benzimidazole titration into an aqueous β-cyclodextrin solution resulted in an exothermic isotherm, which fitted to a 1:1 complexation model after heat of dilution corrections.

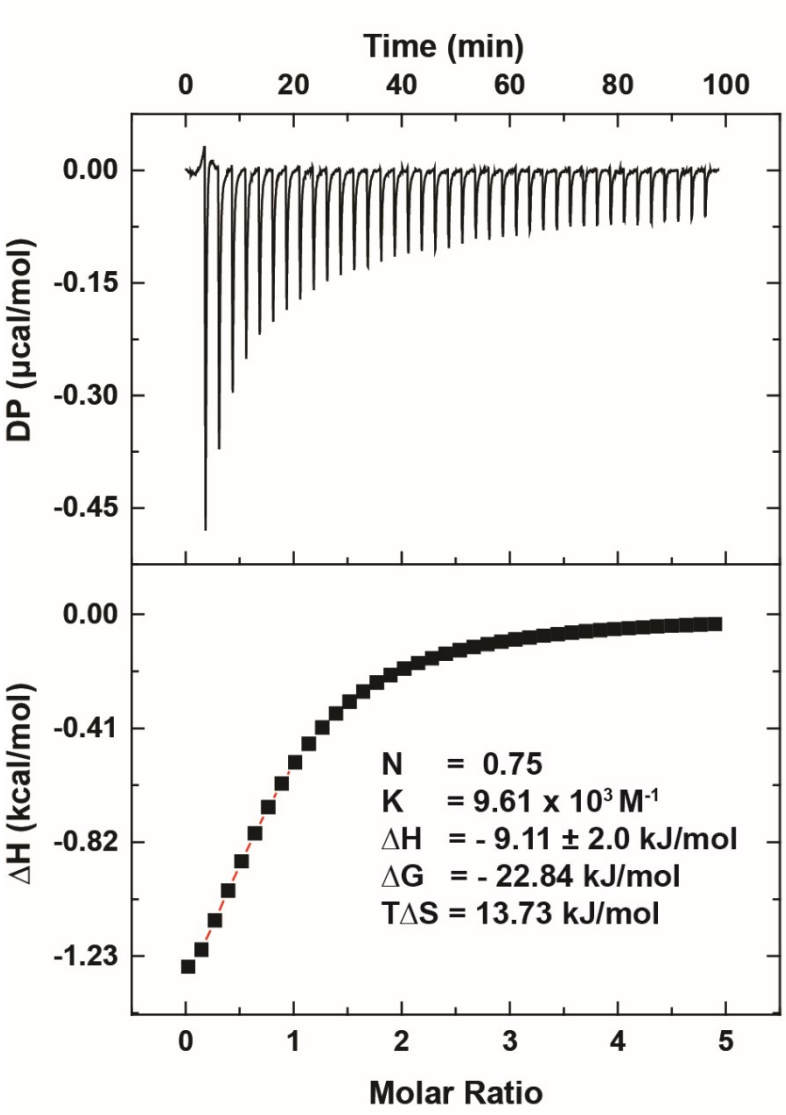

Figure S3. Isothermal Titration Calorimetry (ITC) isotherm of BzI (10mM) with β-CD (200 µM) at 25°C.

4. UV-Vis Study of BzI soaked β-CD gel

A small piece of "host" gel was soaked in an aqueous solution for 12 hours and then dialyzed for 24 hours to remove any loosely bound “guest” molecules. To measure the absorbance of “host-guest” assembled gel, a small piece of the gel was placed between two quartz slides and the absorbance of the gel demonstrated a characteristic absorption of benzimidazole as shown in the figure S3. No characteristic absorption was observed for “host” gel only.

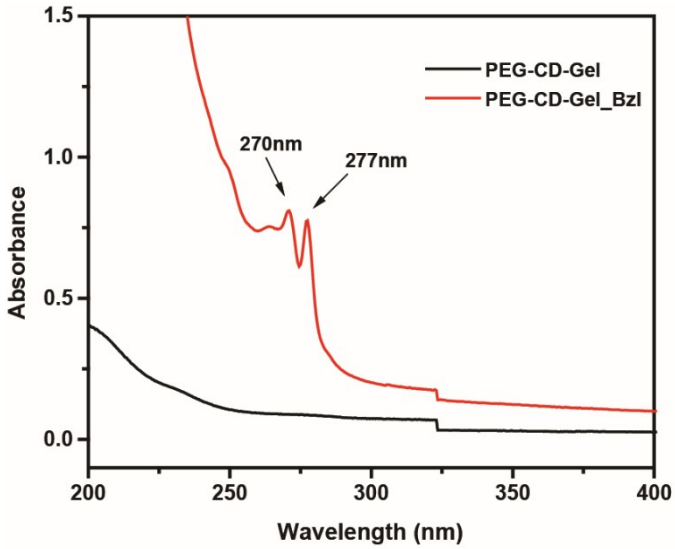

Figure S4. Absorption spectra of β-CD-PEG gel pre-assembled with BzI

5. Release of BzI from β-CD-PEG gel at different pH.

A small piece of gel pre-assembled with BzI was placed inside a cuvette. Upon addition of acidic aqueous solution (pH 3) to the cuvette, the dissociation of BzI from β-CD cavity occurred and the release was monitored by measuring the absorbance of BzI. It is observed that the rate of release id higher at lower pH as shown in figure S5.

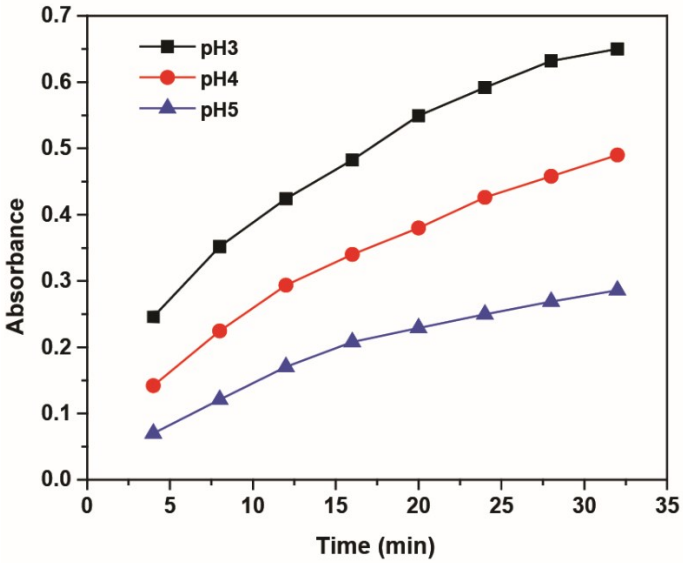

Figure S5. Absorption spectra of β-CD-PEG gel pre-assembled with Bzi on addition of acidic water at pH3, pH4, and pH5.

6. Heat measurement during "host-guest" disassembly by ITC.

For the disassembly of β-CD/BzI complex, the solution of acidic water (pH3) in the syringe was titrated into the pre-assembled β-CD/BzI solution in the calorimetric cell involved 19 sequential 2µl injections. It resulted into an endothermic isotherm.

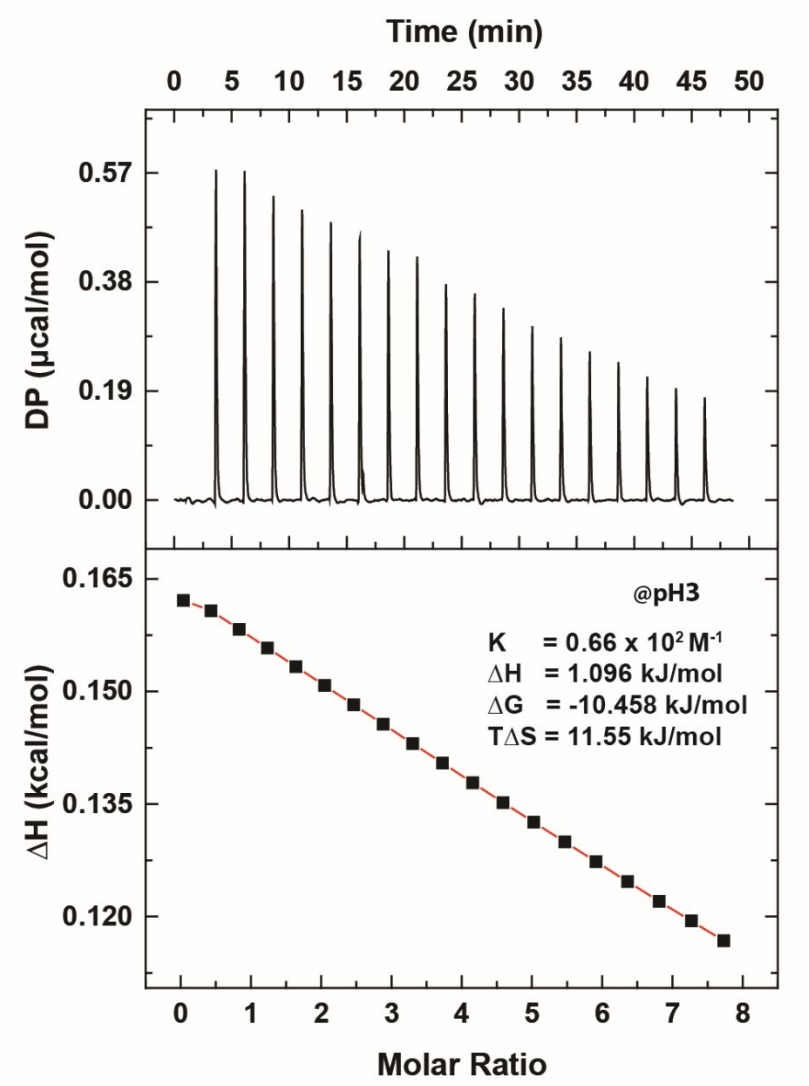

Figure S6. Isothermal Titration Calorimetry (ITC) isotherm of β-CD (150 µM) pre-soaked with BzI (50mM) at 25°C.

7. Estimation of tracer velocity during disassembly of “host-guest” complex at different pH.

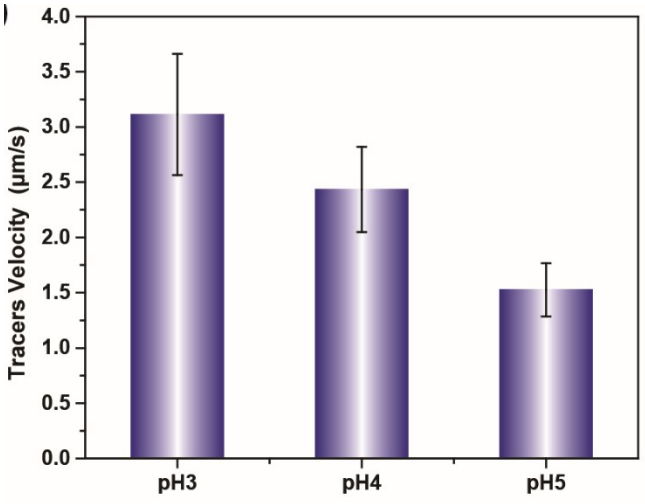

Figure S7. Tracer velocity with varying pH in presence of β-CD-PEG/Bzi complexed gel at 20 mM.

References

1 L. C. Cesteros, C. A. Ramírez, A. Peciña and I. Katime, *J. Appl. Polym. Sci.,* 2006, **102**, 1162–1166.