Dual Stimuli-Responsive, Rechargeable Micropumps *via* "Host–Guest" Interactions

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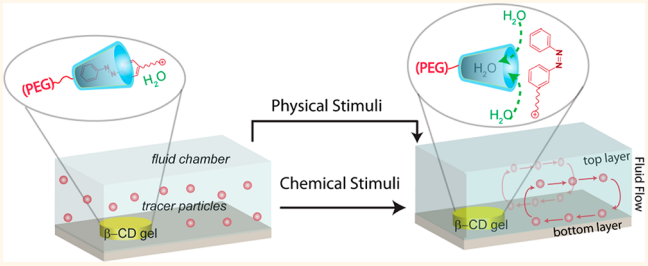
ABSTRACT We demonstrate a supramolecular approach to the fabrication of self-powered micropumps based on "host–guest" molecular recognition between α- and β-cyclodextrin and *trans*-azobenzene. Both hydrogels and surface coatings based on host–guest partners were used as scaffolds to devise the micropumps. These soft micropumps are dual stimuli-responsive and can be actuated either by light or by introducing guest molecules. Furthermore, the micropumps can be recharged through reversible host–guest interaction.



KEYWORDS: polymer microdevice · micropump · supramolecular · host–guest · cyclodextrin · azobenzene · drug delivery

Micropumps that respond to external stimuli and convert chemical energy into mechanical motion[1,2] offer considerable promise in microfluidics[3−6] and drug delivery applications.[7−10] Key attributes of these micropumps are their ability to regulate fluid flow and easy fabrication compared to traditional nonmechanical pumps.[11] Previously, our group[12−14] and others[15−17] demonstrated the fabrication of autonomous micropumps driven by chemical reactions in order to transport fluid over long distances.[18] Despite the impressive progress, these micropumps are fuel-specific and the lack of remote on/off switching limits their applications in microfluidics. More importantly, none of the current systems are rechargeable and are only good for one-time use. To extend the scope of self-powered micropumps, a rapid responsive system with easy recharge ability must be designed.

In our work, we employed the supramolecular approach as a versatile tool-kit to create microscale pump assemblies. Supramolecular interactions rely on reversible noncovalent attractions, such as hydrogen bonding and hydrophobic, electrostatic, and van der Waals forces. The inherent reversible and dynamic nature of supramolecular interactions allows the creation of responsive and rechargeable microdevices that can be actuated by external stimuli.[19−23]

Cyclodextrins (CDs) are well-known molecular "hosts" with defined structures and are capable of forming inclusion complexes with small "guest" molecules inside their hydrophobic cavities.[24−26] Among various guest molecules, azobenzene is well-studied and form a stable (1:1) "host–guest" inclusion complex with CDs in aqueous media.[27] Previous studies have shown that *trans*-azobenzene has higher binding affinity ($K_a \sim 770\ M^{-1}$) toward β-CD compared to the *cis*-isomer ($K_a \sim 280\ M^{-1}$). Thus, upon photoirradiation with UV light of 365 nm, *trans*-azobenzene isomerizes to *cis*-azobenzene and the host–guest assembly dissociates.

Fluid pumping through reversible and dynamic host–guest interactions[28] can be demonstrated with two possible experimental designs. The first involves the synthesis of a material with pendant CD host that releases free azobenzene guest; the second utilizes a material with a pendant azobenzene guest that discharges free host CD molecules. Herein, we demonstrate both approaches based on host–guest molecular recognition by using β-CD/*trans*-azobenzene[29] complex and α-CD/*trans*-azobenzene complex (see Supporting Information for synthesis and structure).[30] Both bulk hydrogels and surface

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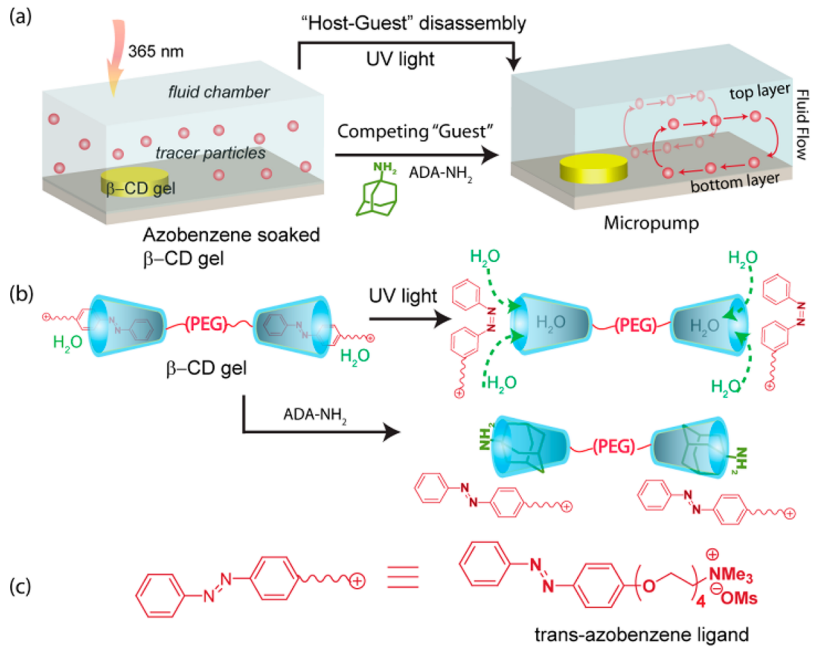

Figure 1. (a) Schematic representation of dual responsive micropump; β-CD-PEG micropump initiates fluid flow either by photo or chemical stimuli. (b) Schematic view of fluid motion originating from host–guest assembly/disassembly. (c) Chemical structure of *trans*-azobenzene guest molecule used for the micropump.

coatings based on host–guest partners were used as scaffolds to devise the micropumps. We also show that reversible disassembly/assembly of the host–guest complex can be utilized to recharge micropumps which allows them to be used multiple times.

RESULTS AND DISCUSSION

To demonstrate the feasibility of light-responsive supramolecular pumps, we synthesized β-cyclodextrin polyethyleneglycol (β-CD-PEG) gel as the host and water-soluble *trans*-azobenzene derivative as the complementary guest. The host–guest assembly was achieved by incubation of β-CD-PEG gel in an aqueous solution of *trans*-azobenzene. Excess and physically trapped guests were removed by dialysis of the gel for 3 days, and the subsequent host–guest assembly was confirmed by characteristic absorbance of azobenzene at 345–350 nm (see Supporting Information, Figure S1). To show the pumping behavior, a small piece of host–guest inclusion gel (β-CD-PEG/*trans*-azobenzene) was placed on a glass slide and covered by an imaging chamber. Next, sulfate latex particles (0.08% w/v; 2 μm in diameter) suspended in deionized water were injected as tracers into the chamber to monitor the fluid flow pattern around the gel, and the chamber was sealed with tape. The tracer particles showed an inward motion toward the gel edge (see Supporting Information, video S1) when the gel was irradiated with UV light, indicating an inward fluid flow (Figure 1). The motion of the tracer particles stopped immediately after the UV source was turned off and resumed on UV reillumination. This on/off cycle can be repeated multiple times over a long period of time until all the host–guest complexes in the gel dissociate (see Supporting Information, video S2). Since the fluid flow was observed in a closed system, a reverse drift of tracer particles was observed at an upper plane (viewed 500–700 μm above the glass surface), due to fluid continuity (see Supporting Information, video S3). We considered the tracers' velocity as fluid pumping velocity, and it was calculated to be 2.4 ± 0.2 μm/s. The self-assembly of tracer particles was observed at the bottom layer around the gel edge when the gel was illuminated by UV light in a closed chamber over an extended period (Figure 2a–d), indicating that the micropump is capable of continuous pumping for a long time (>15 min). In addition, we compared the pumping speed at 0, 5, and 10 min time intervals. The fluid velocity remained almost constant during this period ($\sim$2.2 μm/s), consistent with a zero-order photochemical reaction. As expected, pumping stops when all the host molecules are expelled after prolonged exposure. To validate our experimental results, two control experiments were performed: (i) the host (β-CD-PEG) gel only was placed inside the chamber and exposed to UV light (see Supporting Information, video S4); (ii) the host–guest inclusion gel was placed inside the chamber and exposed to visible light. In both cases, no directed motion of tracer particles was observed, which confirmed that the disassembly of the host–guest complex plays a pivotal role in fluid pumping. To verify any possible role of electrophoresis in particle motion, we conducted the experiment in the presence of high salt concentration since electrophoretic motion is sharply attenuated by increasing ionic conductivity of the fluid.[31] In this case, the gel was soaked with

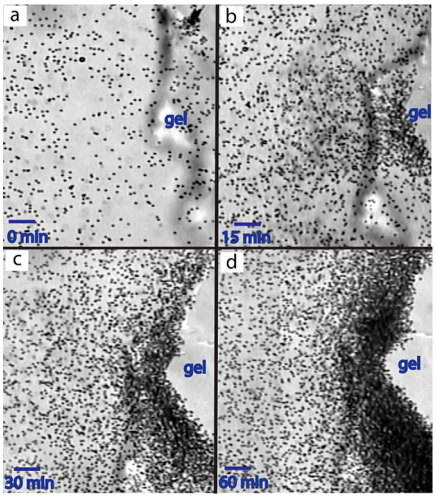

Figure 2. Optical microscopy images of tracer particle assembly at the bottom of the gel edge. The gel was irradiated with UV light of 365 nm, and snapshots were recorded after (a) 0 min, (b) 15 min, (c) 30 min, and (d) 1 h. This assembly clearly depicts the inward motion of the tracer particles under UV illumination. The black dots represent latex tracer particles. The scale bars are 50 μm.

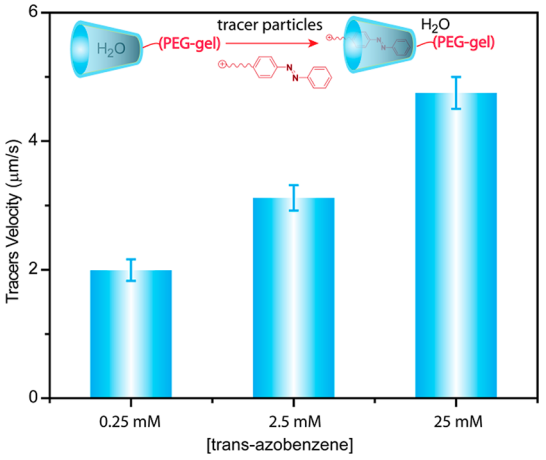

Figure 3. Plot showing increase in tracer velocity with increasing concentration of *trans*-azobenzene during host–guest inclusion complex formation.

trans-azobenzene in the presence of 100 mM NaCl solution, and sulfate latex tracer particles (in 100 mM NaCl) were injected into the chamber. An inward motion of tracer particles was still observed with only a slight decrease in velocity (2.1 $\pm$ 0.3 μm/s), which might be due to a small viscosity increase of the solution with increasing salt concentration (see Supporting Information, video S5). Moreover, the velocities of the tracer particles were independent of the zeta-potential of the underlying substrate (glass *vs* polystyrene) (see Supporting Information, Figure S3), suggesting that electro-osmosis is not a dominant mechanism for the observed fluid flow.[32]

Upon UV irradiation, *trans*-azobenzene undergoes photochemical isomerization to *cis*-azobenzene, which dissociated from the β-CD cavity. One possible mechanism for the observed fluid flow involves changes in local fluid density due to host–guest disassembly. On inverting the experimental setup, such that the gel is on top of the chamber, the direction of fluid flow reverses. The tracers now moved outward from the gel when monitored close to the glass surface. It can be hypothesized that release of *cis*-azobenzene reduces the local fluid density around the gel. The less dense fluid rises above the gel, thereby driving the flow inward close to the surface. In the inverted setup, the less dense fluid extends along the glass surface on which the gel sits, pushing the fluid outward. In another possibility, the release of guest molecules from the β-CD cavity with concomitant incorporation of water molecules into the cavity may be responsible for creating an inward fluid flux in the surrounding environment. In aqueous solution, the slightly apolar cyclodextrin cavity is occupied by polar water molecules. Crystal structures show that, at full hydration, the cavity of β-CD accommodates 11 water molecules, a similar number expected to be displaced upon association of the guest molecule.[33]

We also examined the fluid flow during the inclusion complex formation upon the addition of *trans*-azobenzene to vacant host β-CD-PEG. As anticipated, the movement of tracer particles reversed, moving away from the gel (viewed close to glass surface in the normal setup) (see Supporting Information, video S6). Furthermore, as shown in Figure 3, the pumping velocity increased with increasing *trans*-azobenzene concentration and reached an average velocity of 5 μm/s at 25 mM of azobenzene.

A reviewer has suggested the possibility of pumping arising from differences in osmotic pressure upon release and uptake of host molecules in the gel. This appears unlikely because (i) the gel is permeable to both water and the host molecules and (ii) similar fluid pumping was also observed when the pump was fabricated in the form of a surface coating rather than a gel, as described later in detail.

Another important aspect of host–guest chemistry is that the functional motifs can be engineered to assemble or disassemble in response to a range of triggers. Thus, in addition to photochemical actuation, the microdevice can be triggered chemically by introducing competing guest molecules. Among known guests, adamantane (ADA) is almost exactly accommodated by the cavity of β-CD and forms a very stable inclusion complex with an association constant of $K_a \sim 5 \times 10^4\ M^{-1}$ at room temperature. In our experiment, *trans*-azobenzene-soaked gel was treated with 1-adamantylamine hydrochloride (ADA-NH_2·HCl) in the presence of tracer particles. As a result, the existing host–guest assembly was disrupted and β-CD formed a new inclusion complex with ADA-NH_2·HCl due to its higher binding affinity. In this case, an inward motion of tracer particles toward gel was observed (see Supporting Information, video S7), and the pumping response

increased as a function of ADA-NH_2·HCl concentration (Figure 4). On the contrary, an ADA-NH_2·HCl-soaked gel did not show pumping in the presence of 100 mM *trans*-azobenzene (see Supporting Information, video S8) because the latter guest cannot displace ADA-NH_2·HCl. As with *trans*-azobenzene, the fluid flow was also examined during complex formation between vacant host β-CD-PEG and ADA-NH_2·HCl. An outward motion of the tracer particles was observed (see Supporting Information, video S9 and Figure S4).

To further validate our concept, we performed a complementary experiment by synthesizing a different hydrogel bearing a *trans*-azobenzene moiety (azo-gel) and used α-cyclodextrin molecules to form the host–guest complex (azo-gel/α-CD). No active pumping was observed with azo-gel/α-CD in the absence of UV radiation since the *trans*-azobenzene/α-cyclodextrin complex is stable under ambient light. However, when this system was exposed to UV light, *trans*-azobenzene

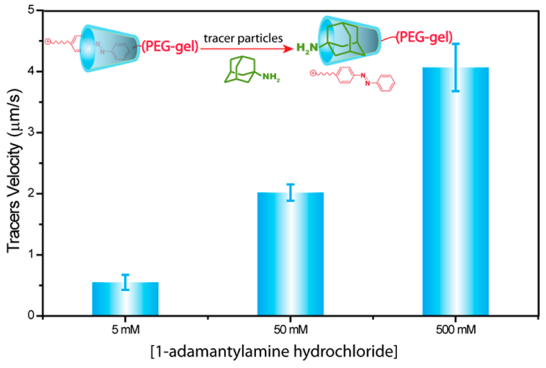

Figure 4. Plot showing tracer velocities in the presence of a competing guest, 1-adamantylamine hydrochloride (ADA-NH_2·HCl). ADA-NH_2·HCl replaces the existing guest (*trans*-azobenzene) due to its higher binding affinity with the host. The velocity increases with increasing concentration of the ADA-NH_2·HCl.

isomerized to the *cis*-isomer and the α-CD molecules were expelled from the polymer chains. An inward movement of tracer particles toward the azo-gel was observed with a velocity of 3.8 ± 0.7 μm/s (see Supporting Information, video S10). The motion of the tracer particles stopped immediately when UV light was turned off and resumed on UV reillumination. This experiment was also performed under a high ionic strength medium (100 mM NaCl), and the motion of the tracers was still observed, again ruling out an electrophoretic mechanism.

Finally, we examined the possibility that the observed pumping was due to expansion/contraction of the gels resulting from host–guest interactions.[34] We designed our host/guest micropump in the form of a polymer coating grafted on a glass slide (Figure 5). Polymer coating with pendant *trans*-azobenzene moieties, covalently bonded to the glass, formed a host–guest complex with α-CD. When this host–guest polymer coating was subjected to UV radiation, α-CD molecules were released from the cavities. The tracer particles moved toward the polymer coating (velocity, 1.8 ± 0.6 μm/s), suggesting an inward fluid flow. The motion of tracer particles stopped immediately when UV light was turned off (see Supporting Information, video S11). On inverting the experimental device, similar to the gel setup, the direction of fluid flow relative to the glass surface reversed, again suggesting the possibility of a density-driven mechanism for fluid pumping. That the micropump can also operate in the form of a coating suggests that the exact form of the pump is irrelevant to the working mechanism.

The unique feature of the present micropump system, compared to its predecessors, is its ability to recharge after use because host–guest interaction is a fully reversible physical phenomenon. In principle, the system can be recharged in two ways: (a) the β-CD

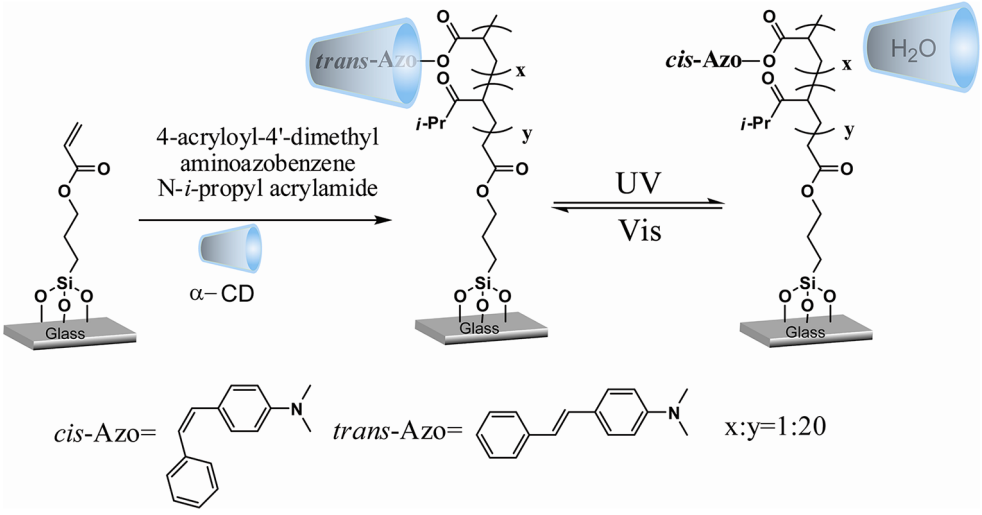

Figure 5. Scheme for the fabrication of surface-anchored azobenzene coating and reversible assembly/disassembly of azobenzene/α-CD complex.

gel is removed from the original solution, which contains released *cis*-azobenzene molecules, and soaked in a fresh *trans*-azobenzene solution to refill the cavity of β-CD; (b) the β-CD gel is left in the original solution, which contains released *cis*-azobenzene molecules. The released *cis*-azobenzene molecules will isomerize back to *trans*-azobenzene, which in turn, will recombine with β-CD gel, thereby recharging the pump. The second method was chosen to demonstrate the rechargeable ability. Initially, β-CD-PEG/*trans*-azobenzene complex was incubated with water in a closed chamber and exposed to a high-power UV lamp to achieve a complete dissociation of the host molecules (until no further pumping was observed). The released *cis*-azobenzene molecules were then allowed to isomerize back to *trans*-azobenzene in visible light and recaptured by the β-CD-PEG gel. Finally, the solution was discarded, and the re-formed β-CD-PEG/*trans*-azobenzene complex was washed extensively to remove any free *trans*-azobenzene. The recharged β-CD-PEG/*trans*-azobenzene complex was then sealed in a new chamber with fresh tracer particles in an aqueous solution and observed under a microscope. The pumping velocity of the recharged system was only slightly lower than the initial velocity (1.6 $\pm$ 0.6 μm/s).

CONCLUSION

We have devised novel multi-stimuli-responsive micropumps using host–guest molecular recognition. Under UV light, fluid flow occurs through host–guest disassembly. Parallel to the photochemical pumping, fluid flow can also be turned on by adding a chemical stimulus (resulting in supramolecular host–guest binding). This rechargeable system provides a unique opportunity to fine-tune the pump response to each stimulus independently. Furthermore, the work provides a proof-of-concept demonstration of pumps whose pumping velocity is controlled by both the presence and concentration of specific analytes. Most importantly, the system can be recharged *via* reversible host–guest interaction. The inherent reversible and dynamic nature of supramolecular interactions considerably expands the repertoire of responsive microdevices that can be actuated by external stimuli.

METHODS

Synthesis of *trans*-Azobenzene Ligand (Guest) and 4-Acrylate-4′-dimethylaminoazobenzene. See Supporting Information for details.

Synthesis of β-CD-PEG Gel (Host). The syntheses of β-CD-PEG gel (host) and *trans*-azobenzene ligand (guest) were achieved following a literature reported procedure.[29] Poly(ethylene glycol) (PEG), hexamethylene diisocyanate (HDMI), dibutyltin dilaurate (DBTDL), and DMF (dimethylformamide) were purchased from Aldrich, and β-CD was purchased from TCI Organics. The preparation of the gels was carried out in two steps in a single vessel. First, two solutions of PEG and HDMI in DMF (molar ratio, 1:2) were mixed in a three-neck flask and heated at 55 °C under an inert atmosphere. Then 0.01 wt % of catalyst (DBTDL, with respect to the total weight of the reagents) was added to the vessel, and the mixture was allowed to react for 30 min. In the next step, a solution of β-CD in DMF (PEG/β-CD = 4:1) was slowly injected into the reaction mixture over a duration of 30 min. The reaction was allowed to proceed for 5–7 days, and the temperature was maintained at 55 °C during the course of the reaction. After gel formation, the reaction mixture was washed and extracted multiple times with DMF and dialyzed for 1 week to remove excess β-CD. See Supporting Information for a detailed reaction scheme.

Synthesis of Azo-gel (Host). *N*-Isopropyl acrylamide (565 mg), 4-acrylate-4′-dimethylaminoazobenzene (77 mg), and *N*,*N*′-methylenebisacrylamide (16 mg) were dissolved in 3 mL of DMSO/H_2O (v/v, 2/1). Ammonium persulfate (radical initiator, 20 mg) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (accelerator, 7 mg) were added to initiate radical polymerization. The reaction was allowed to proceed overnight. Azo-gel was then soaked in methanol at 50 °C to remove unreacted reagents and DMSO. The methanol was replaced every 6 h until it became colorless, indicating the removal of all unreacted 4-acrylate-4′-dimethylaminoazobenzene. The gel was transferred to water and dialyzed for 2–3 days.

Host–Guest Inclusion Complex Formation. A small piece of β-CD-PEG gel or azo-gel (approximately 1 mm^3) was incubated overnight in aqueous solution of *trans*-azobenzene or α-cyclodextrin solution, respectively (100 mg/mL). Later, the gel was dialyzed for 3 days prior to use.

Fabrication of Azo Coating (Host). *N*-Isopropyl acrylamide (565 mg) and 4-acrylate-4′-dimethylaminoazobenzene (77 mg) were dissolved in 3 mL of DMSO/H_2O (v/v, 2/1). Ammonium persulfate (radical initiator, 20 mg) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (accelerator, 7 mg) were added to initiate radical polymerization. The reaction mixture was injected into a patterned gasket attached to a vinyl-functionalized glass slide (see Supporting Information for the glass functionalization step). The reaction was allowed to proceed overnight. The azo coating was then soaked in methanol at 50 °C to remove unreacted reagents and DMSO. The methanol was changed every 6 h until it became colorless, indicating the removal of all unreacted 4-acrylate-4′-dimethylaminoazobenzene. The coating was soaked in α-CD solution (100 mg/mL) for 2 days and washed extensively to remove any free α-CD molecules.

Photoregulated Micropumps. β-CD-PEG gel or azo-gel was cut into a small cube and put on a glass slide. Azo coating was used directly. We placed an imaging chamber (EMS, 20 mm diameter and 1.3 mm height) on top of the gel, and an aqueous suspension of sulfate tracer particles (0.08% w/v; 2 μm in diameter) was injected by a syringe. We ensured that no air bubbles were trapped inside the chamber and sealed the chamber with tape. The setup was then examined under a microscope (Zeiss Axiovert 200 reflectance/transmission), and videos were captured at 20× magnification (EC Epiplan-NEOFLUAR 20×/0.5 HD DIC) using a CCD camera attached to the microscope. A UV lamp (HBO 100, 100 W) attached to the microscope was used as the light source with a wavelength of 365 nm and a maximum power of 2.5 W cm^{-2}. The gel was placed at the center of the light source, and videos were captured for further analysis.

Chemically Responsive Microdevices. The experimental setup was the same as discussed above. Here, tracer particles were suspended in different concentrations of ADA-NH_2·HCl solution and injected into the imaging chamber. Videos of particle motion were captured for further analysis.

Micropump Recharge Experiment. The β-CD-PEG/*trans*-azobenzene complex was sealed in a closed chamber, and tracer particles suspended in deionized water were injected. Then, the whole system was exposed to a high-power UV lamp to achieve a complete dissociation of the host and guest molecules until no pumping was observed under the microscope. After UV exposure, most of the *cis*-azobenzene molecules were released into the aqueous solution outside the gel. Then, the *cis*-azobenzene molecules were allowed to switch back to

trans-azobenzene. The β-CD-PEG gel and the free *trans*-azobenzene were left in visible light for 3 days, which allowed the β-CD-PEG gel to recapture the free *trans*-azobenzene molecules. The old solution was discarded, and a fresh aqueous suspension of tracer particles was injected into the chamber and observed under a microscope.

Tracking Analysis. For measuring fluid velocity, 30 particles were tracked using PhysVis, a motion analysis software. The videos were processed to be 5 times faster, and particles were tracked for 5 s.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Experimental procedures and supporting videos 1−11. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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