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Molecular Transmission: Visible and Rate-Controllable Photoreactivity and Synergy of Aggregation-Induced Emission and Host-Guest Assembly

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Supporting Information

ABSTRACT: The ability to modulate reaction rates like controlling speeds by the transmission of vehicles is highly desirable and challenging. Herein, a regioand stereoselective photodimerization with four tunable and visible rates were realized at the molecular level via the synergy of host-guest chemistry and AIE technology: (i) normal rate without adding macrocycles (ν_1) , (ii) greatly accelerated rate by the formation of 2:2 complex between γ -cyclodextrin (γ -CD) and an AIE luminogen (AIEgen) (ν_2) , (iii) deactivated reaction by 1:1 binding of β -cyclodextrin (β -CD) with the AIEgen (ν_3), and (iv) completely inhibited photoreaction in the β -CD-based hydrogel (ν_{4}). The restriction of intramolecular motions of AIEgen activates the fluorescence of the transmission with the rate of $\nu_2 > \nu_1 > \nu_3 > \nu_4 \approx 0$ and enhances the fluorescent contrast before and after photoirradiation, which not only provides in situ trackability to the microscopic process, but also endows intuitive mechanistic insights. The synergy of AIE and host-guest chemistry can also



amplify the signal of the reversible reaction and visualize "tiny" ring-opening product. Microscopic mechanism was further applied to the construction of a porous hydrogel-based microreactor which exhibited enhanced microscopic visualization and excellent recyclability. The present approach demonstrated a powerful platform for the understanding, monitoring and controlling reaction kinetics. Meanwhile, the porous hydrogel reactor based on precise molecular design serves as a new inspiration for heterogeneous catalysis.

INTRODUCTION

A harmonious moving world, ranging from plants and animals to vehicles and earth, relies on transmission to control them to work in an adequate rate. Our body exhibits many elegant examples of processes that respond to external stimuli by modulating the response speed to carry out various biological functions, which work like the transmission of vehicles. For example, immunity is the balanced state of organisms with adequate biological defenses to fight infection, disease, or other unwanted biological invasion. When harmful pathogen enters to our body, activated defensing system will speed up the defense process to protect us. However, for allergy, we need to slow down the over-reaction of the immune system to typically harmless substances. Controlling photoreaction rates attracts our interest due to its connection with energy efficiency and atom economy.¹⁻⁷ Although some external methods including optimization of light wavelength and intensity have been devoted to realize this purpose, they cannot realize precise control and seldom illustrate detailed mechanisms.^{8,9} Thus, constructing photoreactive transmission at the molecular level with on-demand controllability remains a big challenge.

A clear process monitoring will be helpful for the mechanistic understanding of photoreactions, which will further be instructive to the design of precise controllable systems. Although chemists have developed many methods including nuclear magnetic resonance (NMR), ultraviolet (UV) spectroscopy, infrared spectroscopy, and mass spectroscopy (MS) to monitor the processes, they are either insensitive

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or invisible to our naked eyes.^{10–14} Fluorescence-based technique is a perfect choice for process unveiling, in light of its superior sensitivity, fast response, low background noise, and simplicity.^{15,16} More importantly, it can provide high spatiotemporal resolution for precise visualization of complicated processes at the molecular level.^{17–22}

From the mechanistic viewpoint, single molecular emission will be the best choice, while for real application, most of the materials function in solid states and meet with unfavorable aggregation-caused quenching (ACQ) effect. Aggregationinduced emission luminogens (AIEgens) provide the chance to be emissive in the aggregate state.^{23–28} This satisfies the application needs in the solid state but sacrifices exploitation in the molecular state.²⁹ However, if a photoreactive AIEgen is restrained in a confined space, such as the cavity of macrocycles, $^{30-35}$ it is anticipated that its emission will light up both in the solution and solid states.^{36,37} Meanwhile, the encapsulated molecule in the tailored microenvironments will be constrained to adopt a specific binding model or packing style or intermolecular distance, 38-46 which can further influence the reactivity of the AIEgen. On the basis of this supramolecular regulation method, we can thus install visualization and precise controllability into one molecular transmission in both solution and solid states. Further experiments indeed confirm the feasibility of this strategy: a visible molecular transmission based on host-guest interaction between a photoreactive AIEgen and macrocycles was realized and the microscopic mechanism was further applied to the construction of macroscopic porous hydrogel-based transmission (Scheme 1).

Scheme 1. Proposed Mechanism of Visible and Rate-Controllable Photodimerization a



^{*a*}Blue and red macrocycles indicate β -CD and γ -CD, respectively. PD = photodimerization.

RESULTS AND DISCUSSION

AlE Property and Host–Guest Study. In our previous work, a tailored cyanostilbene-based molecule with AIE characteristic was found to exhibit photodimerization in solution with a high water fraction with microcrystal formation.⁴⁷ Herein, we changed the counteranion from PF_6^- to I⁻, which endowed the AIEgen (G) with partial water solubility and further promoted the formation of host–guest complex by hydrophobic interaction (Scheme S1 and Figure S1). We then investigated the photophysics of G.

Molecule **G** showed weak emission in CH₃OH, but with a gradual addition of tetrahydrofuran (THF) into the solution, enhanced photoluminescence (PL) was recorded (Figure S2A,B). Since **G** was insoluble in THF, its aggregates should be readily formed in CH₃OH/THF mixtures with high THF fractions. It means that aggregate formation has enhanced the PL of **G**. Much stronger emission was also observed with the addition of viscous glycerol into the CH₃OH solution of **G** because the intramolecular rotations of **G** was slow down in high viscous solution (Figure S2C,D). The weak emission of **G** in the solid state with a quantum yield of 3.40% may be attributed to the heavy atom effect of I⁻ (Figure S3). All these experiments demonstrate that **G** is AIE-active.

Cyclodextrins (CDs) are a class of macrocyclic compounds with variable cavity sizes and the ability to form host–guest complexes with hydrophobic molecules. The inner cavity diameter increases as the number of glucopyranose units increases from 5.7 Å (6 units, α -CD) to 7.8 Å (7 units, β -CD) and to 9.5 Å (8 units, γ -CD) (Scheme S2). The single crystal structure of **G** was reported in our previous work. Herein, after further analyzing, we found that **G** was almost coplanar and the length of the short-axle was about 5.3 Å, which provided the prerequisites for encapsulation with β -CD and γ -CD (Figure 1A). Another significant structural feature was that the



Figure 1. (A) Crystal structure of **G** and (B) its crystal packing. (C) Simulated structures of 1:1 complex of β -CD \supset **G** and (D) 2:2 complex of γ -CD₂ \supset **G**₂ obtained by MD calculations. Absorption spectral changes of **G** (40.0 μ M) upon addition of (E) β -CD (2.00 mM) and (F) γ -CD (4.00 mM). Insets in panels E and F are the cartoon representations of β -CD \supset **G** and γ -CD₂ \supset **G**₂, respectively.

adjacent molecules experienced antiparallel head-to-tail molecular packing with multiple intermolecular interactions such as $\pi-\pi$ stacking and C–N··· π to form a "dimer" with a distance of 3.4 Å (Figure 1B). What is the major existing state of **G** in water: monomer or "dimer"? To answer this, we prepared a methanol mixture of poly(acrylic acid) (PAA) and 1 wt % **G** and then spun the solution on a quartz sheet. The prepared film emitted at $\lambda = 507$ nm, which is assigned to emission of monodispersed **G** with restricted rotation (Figure S4). The emission wavelength of **G** in water of 566 nm indicated that **G** might prefer to form "dimer" in water.



Figure 2. (A) Fluorescent images of the water solution of G (30.0 μ M), G (30.0 μ M) with β -CD (90.0 μ M) or γ -CD (90.0 μ M) before and after UV irradiation. (B) UV-vis and PL spectra of G (black), β -CD \supset G (red), and γ -CD₂ \supset G₂ (blue) in H₂O. (C) Diagram of conversion ratio of G (black square), β -CD \supset G (red circle), and γ -CD₂ \supset G₂ (blue triangle) based on absorbance intensity change at λ = 380 nm. (D) PL intensity change of G, β -CD \supset G and γ -CD₂ \supset G₂ at λ = 570 nm versus irradiation time. I_0 = initial intensity, I_t = intensity at different irradiation time. (E) Plot of 1/[G] versus irradiation time (0–180 s) at room temperature in the presence of β -CD or γ -CD or in the absence of CD. k_1 , k_2 , and k_3 indicate the reaction rate constants of G, β -CD \supset G, and γ -CD₂ \supset G₂. (F) (i) Crystal of P and (ii) cocrystal of P•G obtained from the irradiated solution of γ -CD₂ \supset G₂ and β -CD \supset G, respectively.

We first investigated the host-guest complexation between hosts (β -CD and γ -CD) and guest (G). Though G showed very low solubility in water, we could still obtain the ¹H NMR spectrum of complex formed by an equimolar water solution of hosts and guest. We attribute the observed large chemical shift of the proton signals of the naphthyl and pyridyl parts of G to engulfment of these groups within the CD cavity (Figure S5). 2D NOESY NMR spectrum of $(\gamma$ -CD + G) in D₂O further supported this conclusion. For example, NOE correlation signals were found between the inner protons of γ -CD (H_{av} H_{θ_1} and H_{η_2}) and the naphthyl protons of G, indicating that the formation of the threaded structure brings these two sets of protons close to each other in space (Figure S6). For the complex (β -CD + G) system, because of the low solubility of both β -CD and G in water, we failed to obtain satisfied 2D NOESY spectrum. The stoichiometry and association constants (K₁) of the complexes of **G** with β -CD and γ -CD were estimated by UV-vis titration experiments (Figure 1E,F). Both of the two systems were confirmed to be 1:1 stoichiometry by a mole ratio plot. It is in line with the expectation to form 1:1 complex between β -CD and **G** considering the matched size. The 1:1 binding ratio between γ -CD and G can also be regarded as 2:2, which will be further discussed later. The overall binding constant was calculated to be $(1.29 \pm 0.54) \times$ 10^{5} M^{-1} for β -CD \supset G and $(1.15 \pm 0.41) \times 10^{5} \text{ M}^{-1}$ for (γ -CD + G) (Figures S7 and S8).

The host–guest complexation of γ -CD and **G** was further quantitatively confirmed by isothermal titration calorimetry

(ITC).⁴⁸ The titration data could be well fitted by computer simulation using the "sequential binding sites" model, which confirmed that the stoichiometry of this complex should be 2:2 rather than 1:1 (Scheme S3). Electrospray ionization time-offlight mass spectrometry (ESI-TOF) gave further evidence: m/*z* 1511.5325 for $[\beta$ -CD \supset G – I]⁺, *m/z* 1674.0937 for $[\gamma$ -CD₂ \supset G₂ – 2I]²⁺ (Figures S9 and S10). To understand the conformation of G interacting with CD, we performed molecular dynamics (MD) simulations. Through simulating the dynamics of a mixture consisting of 8 molecules of G and 4 molecules of β -CD, a 1:1 complex was located in the trajectory in which β -CD located at the stilbene C=C bonds (Figure 1C). However, similar complex was not found in the trajectory simulated for γ -CD. It showed that G tended to form antiparallel "dimer" structures. On the basis of this fact, we constructed a 2:2 host-guest complex for G and γ -CD and carried out MD simulations in aqueous solution. The simulation showed that this 2:2 complex was very stable and did not decompose during the 80 ns simulation. The last frame of this 2:2 host-guest complex in the trajectory is shown in Figure 1D. By combining the aforementioned results, it was reasonable to give a conclusion that G could form 1:1 and 2:2 complexes with β -CD and γ -CD, respectively.

Transmission in Solution. We then systematically explored the effect of UV light on the photoreaction of **G** under UV light irradiation at $\lambda = 365$ nm. The response of **G** to UV irradiation in CD₃CN was first investigated as that in our previous work.⁴⁷ The ¹H NMR spectra obtained at different

states of the photoreaction process were shown in Figure S11. As anticipated, the appearance of aromatic resonances at the upfield region indicated that Z/E isomerization was dominated at the initial state of the photoreaction. However, after 2 h, the photocyclization governed the photo process as a new singlet peak at δ 9.57 ppm and a doublet peak at δ 9.03 ppm gradually appeared, and their corresponding intensity was enhanced by lengthening the irradiation time (Figure S11, spectrum C to H). These results showed that G could undergo the same photoreaction in organic solvents as we previously reported. We further wondered the reaction-type in water solution. Although the color of water solution of **G** showed no obvious change to our naked eyes before and after 365 nm UV irradiation (Figure S12), UV-vis spectroscopy provided more detailed information. The absorption of G shifted progressively to the shorter wavelength with decreased intensity by prolonging the exposure time. This meant different species with lower conjugation were generated (Figure S13A). Meanwhile, one new absorption peak appeared at 290 nm, whose intensity increased with increasing the irradiation time. In addition, one isosbestic point of mixture was observed at λ = 314 nm, which indicated the presence of two absorbing species in water. To get more insight into the photoprocess in water solution upon UV irradiation, we carried the fluorescence analysis. G is AIE-active. However, its water solution shows orange emission possibly because of the formation of "dimer" as discussed before. Results showed that the orange emission gradually faded after irradiation (Figure 2A). We then further used PL spectroscopy to trace the process. The emission peak at $\lambda = 570$ nm decreased very quickly upon photoirradiation and a new peak with increased intensity appeared at $\lambda = 440$ nm (Figure S13D). Combining the above phenomena, we noticed that G showed quite similar absorption and fluorescence pattern upon photoirradiation as our previous reported photodimerization process. Thus, it is reasonable for us to give a speculation that G also undergoes photodimerization in water solution under 365 nm UV light irradiation.

Photodimerization is a process where two adjacent molecules are aligned in a well-ordered conformation for the topochemical [2 + 2] cycloaddition with center-to-center distance less than 4.2 Å. As we discussed above, G could form 1:1 and 2:2 complexes with β -CD and γ -CD in aqueous mixture. From the calculated structures, it is obvious that for the 1:1 complex, the host can act as an inhibitor for another molecule to approach so that the dimerization can be deactivated in some sense (Figure 1C). However, for 2:2 complex, the average distance between two double bonds is shortened to 3.9 Å, which is favorable for further dimerization (Figure 1D). UV-vis and PL were used to confirm our speculation. To avoid photoreactions from uncomplexed guest molecule, excess CD was used for both systems. Their absorbance intensity showed slightly decrease (Figure 2B), and the color had no obvious change (Figure S12). However, fluorescence gave intuitive information. The fluorescence stayed almost the same after adding glucopyranose, while the spontaneously formed γ -CD₂ \supset G₂ units efficiently restricted the intramolecular rotation and thereby resulted in strong emission in dilute solution, which confirmed the power of combining of AIE and host-guest chemistry (Figure S14). The nonobvious fluorescence change for β -CD \supset G is probably ascribed to two reasons. One is that the dynamic process cannot strictly compel all the "dimer" dissociate into monomer.

Another is that β -CD cannot fully accommodate **G** and the partially exposed parts contribute nonradiative decay at the excited state.

We then used 365 nm to irradiate the two solutions. Surprisingly but expectedly, the emission of γ -CD₂ \supset G₂ solution disappeared much more quickly than did that of G solution. However, for that of β -CD \supset G solution, its emission only slightly decreased in the same irradiation time (Video S1). The UV and PL spectral changing profile of β -CD \supset G and γ - $CD_2 \supset G_2$ after 365 nm UV irradiation for different time resembled that of G, which indicted the same photoreaction type under irradiation (Figure S13). However, for β -CD \supset G solution, the UV intensity at λ = 380 nm and PL intensity at λ = 570 nm decreased much slower than that of G. On the contrary, for γ -CD₂ \supset G₂ solution, the sparse line on the UV and PL spectra indicated that the time required for the solution to attain equilibrium was obviously shortened. From Figure 2C, we can see very clear that γ -CD₂ \supset G₂ needs the shortest time to reach nearly 100% photoconversion, while β -CD \supset G takes the longest time to finish the reaction. On the basis of Beer–Lambert law, the intensity at λ = 380 nm was changed to the corresponding concentration. For all the three systems, at room temperature, reaction time at the range of 0-180 s was proportional to the reciprocal of the concentration of G, which indicated they were all second-order reactions (Figure 2E). The reaction rate constants were estimated as follows: for G solution, $k_1 = 3030 \text{ L mol}^{-1} \text{ s}^{-1}$; for γ -CD₂ \supset G₂ solution, $k_2 =$ 33825 L mol⁻¹ s⁻¹; for β -CD \supset G solution, $k_3 = 730$ L mol⁻¹ s⁻¹. It is obvious, $k_2 > k_1 > k_3$, which means the introduction of γ -CD accelerates the photodimerization, while the reaction rate is decelerated by β -CD. Fluorescence intensity change in Figure 2D reveals the same trend as that in Figure 2C. However, the fluorescence profile shows enhanced contrast comparing with that of absorbance profile. Representative photos taken at 0 s, 20 s, 1 min, and 5 min were shown in Figure 2A, which suggested that the PL intensity or brightness decreased with irradiation time increased. From the absorbance and PL spectra, we could see that the rate of photoconversion was fast at the beginning but became slow afterward. Finally, a platform was reached. This may be due to the gradual consumption of G. The grayscale values at different time were then obtained, and the value against time was plotted (Figure S15). Similar to the relative fluorescence intensity change, the grayscale value also declined steadily with time. The slope change from γ -CD₂ \supset **G**₂ was much bigger than that from **G** and β -CD \supset **G**, while slope change for β -CD \supset **G** was smaller than that of G. The whole changing trend matched the fluorescence records perfectly. This means that activated fluorescence based on AIEgen can be used to visualize the controllable reaction rate and the whole reaction process.

Pure photodimer **P** was obtained by high performance liquid chromatography (Figures S16–S18). Because of the low water solubility of **G** and **P** and the broad ¹H NMR spectrum in water, it is difficult to use NMR to trace this process directly. We prepared a 200 mL water solution of **G**, β -CD \supset **G**, and γ -CD₂ \supset **G**₂ ($c = 100 \mu$ M), and after UV irradiating for certain time, water was evaporated under reduced pressure and the solid was redissolved in DMSO- d_6 for ¹H NMR. As the irradiation time increased, two sets of peaks appeared: one was assigned to the unreacted species from **G**, another one originated from the photodimerization product **P** (Figure 3). For **G** and β -CD \supset **G** solution, 67% and 40% of **G** was converted into the dimer within 2 h (Figure 3B,F), while for



Figure 3. ¹H NMR spectra of (A) **G**, (B) *β*-CD⊃**G**@365 for 2 h, (C) *β*-CD⊃**G**@365 for 24 h, (D) *γ*-CD₂⊃**G**₂@365 for 0.5 h, (E) *γ*-CD₂⊃**G**₂@365 for 1 h, (F) **G**@365 for 2 h, (G) **G**@365 for 10 h, and (H) **P** in DMSO-*d*₆.

that of γ -CD₂ \supset G₂ solution, the conversion ratio reached 80% in only 30 min (Figure 3D). Longer irradiation time afforded the completely disappearance of unreacted signals accompanied by an increase of the peak intensity for the photoproduct. G without adding anything can finish the reaction within 10 h, and G in the presence of β -CD and γ -CD needs 24 and 1 h to complete the conversion, respectively (Figure 3C,E,G). The 2 h irradiated solution was further used for crystal growth. Single crystal of P was obtained from γ - $CD_2 \supset G_2$ solution (Figure 2F(i)). However, irradiated β -CD \supset G solution delivers cocrystal of P•G (Figure 2F(ii)). These results prove again that γ -CD significantly accelerated the reaction, while β -CD could decelerate the process. It should be noted that all three systems can deliver highly regioand stereoselectivity antihead-to-tail photodimer in an almost quantitative conversion yield.45

Abs@380 was used to monitor the kinetics of the photoreactions of **G** with varied γ -CD contents. As shown in Figure S19, with the addition of 0%, 10%, 30%, and 50% of γ -CD, their absorbance profile is similar and their slope change is smaller than that with 200% of γ -CD. Therefore, this indicates that a sufficient amount of γ -CD is needed to accelerate the photodimerization. This suggests that **P** or the hydrophobic naphthyl part of dimer may prefer to stay in the cavity of γ -CD and further prevent other molecules to be encapsulated. The cartoon representation of the rate-controllable photodimerization with different CDs was illustrated in Scheme S4.

Amplification of Microscopic Reversibility. Then we checked the reversibility of photodimerization by irradiating the solution of **G** with 365 nm UV light followed by exposure to 254 nm UV light. The absorption at $\lambda = 290$ nm gradually decreased, while the peak intensity at $\lambda = 370$ nm increased. After ~40 min, no further absorption change was observed, indicating that high-energy UV light could partially trigger the reverse conversion of the dimer (Figure S20A). Similar phenomenon was observed in γ -CD₂ \supset G₂ solution (Figure S20B). This reversible process could be repeated for several cycles (Figure S21). We calculated the photoconversion as a function of irradiation time based on the aforementioned UV spectra (Figure 4B). We observed that the reversible process for γ -CD₂ \supset G₂ solution proceeded in a much faster rate than that for **G** solution. This phenomenon was because of the



Figure 4. (A) Daylight (upper) and fluorescent (lower) images and (C) PL intensity at $\lambda = 570$ nm of water solution of **G** with and without γ -CD before and after 365 nm UV irradiation followed by exposure to 254 nm UV light. Inset in panel C shows contrast of PL intensity @570 nm of **G** with and without γ -CD before and after 254 nm UV irradiation. (B) Photoconversion of dimer to monomer with irradiation time evaluated from the absorbance intensity change at $\lambda =$ 380 nm.

newly generated **G** could form host–guest complex with γ -CD again, which further accelerated the reaction to reach an equilibrium state. Meanwhile, the ultimate conversion for both systems was estimated to be near 20%. This is reasonable considering that the yield of photoreaction depends on the balance of absorbance of reactant and product.

Such small absorbance change is not visible for our naked eyes (Figure 4A, upper), while fluorescence give us a big surprise (Figure 4A, lower and Video S2). For **G** solution, we could not see obvious emission throughout with prolonged irradiation time. However, the solution of γ -CD₂ \supset **G**₂ showed a very sharp increasing of emission intensity at $\lambda = 570$ nm compare with the nonemissive starting state (Figure 4C). Though the final conversion ratio is only 20%, small amount of **G** can still be captured by the cavity of γ -CD and the formation of γ -CD₂ \supset **G**₂ units can efficiently restricted the intramolecular rotation and thereby resulting in strong emission. The emission intensity shows 19.8- and 1.64-times enhancement in the presence and absence of γ -CD, respectively. The synergy of AIE and host–guest chemistry can amplify the signal of the reversible reaction and make "tiny" invisible reaction visible.

Transmission in Hydrogel. After systematically studying the photoreaction in solution, we wonder whether the mechanism of molecular transmission can be applied in the construction of macroscopic material with rate-controllable characteristic. Meanwhile, considering that the separation of product from the solution is difficult and time-consuming, it is charming to develop a system with both controllable catalytic performance and no need of purification. Thus, we synthesized porous CD-based hydrogel from nucleophilic aromatic substitution of hydroxyl groups of CD by epichlorohydrin (Scheme S5).⁵⁰ It is anticipated to be used as adsorbent, which can form well-defined host–guest complexes with G, are readily regenerated, and can exhibit cavity size controlled photoreaction rate. Specifically, we prepared two kinds of

hydrogel based on the aforementioned β -CD and γ -CD, named β -CD-gel and γ -CD-gel, respectively.

We immersed both of the hydrogels into the water solution of **G** for 2 h. The yellow solution faded over time accompanied by decreased emission (Figure 6A). UV spectra manifested that the absorption peak at $\lambda = 380$ nm was almost vanished, indicating the high adsorption efficiency of hydrogels (Figure 5A). This was also confirmed by an apparent color change in



Figure 5. (A) UV-vis (100 μ M) spectra of **G** in water before and after adding γ -CD-gel for 2 h (slit, 0.15 nm). (B) PL spectra of γ -CD-gel, γ -CD-gel \supset **G**, γ -CD-gel \supset **G**(@365. (C) Normalized PL spectra of β -CD-gel \supset **G**, β -CD-gel \supset **G**(@365. (D) **P** and (**P** + clay) in H₂O. Inserted are the corresponding fluorescent images.

the hydrogel from colorless to yellow (Figure 6A). Interestingly, emission of hydrogels changed from faint blue to strong green and yellow for β -CD-gel and γ -CD-gel,

respectively. The yellow emission at $\lambda = 554$ nm of γ -CD-gel after absorbing **G** (Figure 5B), namely γ -CD-gel \supset **G**, was similar as that at $\lambda = 560$ nm for γ -CD₂ \supset **G**₂ solution (Figure 2B), indicating the same binding model between γ -CD and **G**. However, β -CD-gel after absorbing **G**, namely β -CD-gel \supset **G**, emits at $\lambda = 515$ nm (Figure 5C), which is different from the $\lambda = 552$ nm emission of β -CD \supset **G** solution (Figure 2B). It is obvious that hydrogel can provide much more rigid and compact microenvironment compared with merely water solution (see Table 1). Thus, the conformation of 1:1 host–

Table 1. Opti	cal, Electronic	Properties,	and Rate
Constants ^a			

	$\lambda_{abs} (nm)$	$\lambda_{\rm em}~({\rm nm})$	Φ (%)	τ (ns)	$k (L \text{ mol}^{-1} \text{ s}^{-1})$
G	383	568	4.3	2.75	3030
β -CD \supset G	380	552	4.0	1.30	730
γ -CD ₂ \supset G ₂	392	560	12.0	3.36	33825
β-CD-gel⊃G		515	8.0	1.46	0
γ-CD-gel⊃G		554	10.1	3.55	
γ-CD-gel⊃ P		526	14.4	6.85	

^{*a*}Abbreviation: λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ = fluorescence quantum yield, τ = fluorescence lifetime, k = reaction rate constants.

guest complex is comparatively fixed, and the rotation of G is strictly restricted in the hydrogel, which can thus offer the similar aforementioned monomer emission of G in PAA (Figure S4).

We then used 365 nm UV light to irradiate the hydrogel. For γ -CD-gel \supset G, its 2:2 host-guest complexation characteristic enabled it to undergo facile photodimerization in 4 min to transform from yellow to green emissive at very high rate (Figure 6B and Video S3). The green emission is different from the weak blue emission of the irradiated γ -CD₂ \supset G₂ solution (Figure 2A). Though P can only emit weakly at λ = 430 nm (Figure S22), its dried mixture with γ -CD also shows similar green emission (Figure S23) as that in the irradiated γ -



Figure 6. (A) Daylight and fluorescent images of water solution of G (100 μ M) before and after adding γ -CD-gel for 2 h. (B) Fluorescent images of β -CD-gel \supset G and γ -CD-gel \supset G before and after photoirradiation. (C) Cartoon illustration of the recyclable and visible hydrogel-catalytic photodimerization process based on γ -CD-gel.

CD-gel \supset G (Figure 6B). This means the green emission of the irradiated hydrogel does not come from impurities. To explain this phenomenon, we did the following two experiments. To the nonemissive water solution of **P**, we added AgNO₃ to precipitate I⁻, the light up emission indicated that I⁻ played an important role in the fluorescence quenching of the solution (Figure S24). The appearance of green emission after adding negative charged clay (Laponite XLG) to gather cationic part of **P** manifested that the green emission of γ -CD-gel \supset P might derived from through space conjugation of the **P** in the hydrogel (Figures 5D).⁵¹

The emission of β -CD-gel \supset G keeps no change under photoirradiation for 10 min. Even further extending the irradiation time to 10 h, we could not observe any emission change (Figures 5C and 6B, Video S3). The irradiated hydrogels were then immersed into DMF solution to release the formed products from the hydrogels. By comparing the ¹H NMR signal, we know that almost no reaction happens in the β -CD-gel, while all the G in the γ -CD-gel is converted to P (Figure S25). This indicates that instead of performing as a "decelerator" in solution state, the β -CD-gel is more like a "braker", which can stop the reaction completely. This phenomenon is in accordance with our proposed fixed conformation of G in β -CD-gel, which can totally inhibit the sliding out of threaded G and thus prevent the further dimerization. Thanks to the strong fluorescence contrast of hydrogel before and after photoirradiation, the whole process can be visualized. Fluorescent can provide a more intuitive insight into the photodimerization process, and it is much easier for us to tell when the reaction can be finished. Moreover, γ -CD-gel can also be developed as a promising solid-phase microreactor (Figure 6C). On the basis of this recyclable system, we can easily prepare large amount of photodimer without any purification. Overall, the porous γ -CD-gel encodes multiple functionalities in a single system: a microreactor, a self-accelerating catalysis, and a reaction signal monitor. The results manifested that macroscopic material based on explicit mechanism and precise molecular design could also exhibit excellent performance and sometimes might be even better than that in the solution state.

CONCLUSIONS

In this work, we realized a visible photoreaction with four tunable and visible rates at the molecular level based on hostguest interaction between an AIEgen and CDs with different cavity sizes. The 2:2 complex of γ -CD₂ \supset G₂ could greatly accelerate the photodimerization rate, while the 1:1 binding model of β -CD \supset G deactivated the reaction. Fluorescence not only endows clear mechanistic insights and trackable photodimerization process, but also enables the visualization of "tiny" ring-opening reaction. The microscopic mechanism was also applied to construct macroscopic porous hydrogel-based transmissions. The β -CD-based hydrogel could completely inhibit the photodimerization and functioned as a "braker", whereas the γ -CD-based hydrogel was developed into a solidphase recyclable microreactor encoded with visible, accelerated, and recyclable performance. Given that we not only constructed artificial transmission at the molecular level with on-demand controllability, but also provided intuitive insight into the elusive photoreaction mechanism based on the marriage of AIE and host-guest chemistry, we believe the present approach demonstrated a powerful platform for the understanding, monitoring, and controlling reaction kinetics.

Meanwhile, the porous hydrogel reactor based on precise molecular design serves as a new inspiration for heterogeneous catalysis.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.8b04909.

Experimental procedures, methods, product characterization (PDF) $% \left(PDF\right) =\left(PDF\right) \left(PD$

Three videos on photoreaction processes (ZIP)

Photophysical data and imaging data; optimized CIF structures (ZIP) (ZIP)

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Notes

The authors declare no competing financial interest.

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