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A photoswitchable organocatalyst based on a catalyst-imprinted polymer containing azobenzene†

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An L-proline-catalyzed aldol reaction was photo-controlled using an L-proline-imprinted polymer containing azobenzene. Upon UV irradiation, azobenzene chromophores underwent *trans* → *cis* isomerization, thereby releasing L-proline to catalyze the aldol reaction.

Gated catalytic systems can translate an incoming stimulus into a chemical signal. As such, these systems have been extensively investigated. Different stimuli, such as anions,[1] light,[2,3] redox,[4] pH,[5] and acid–base compounds,[6] have been exploited to control these catalytic systems. Among these stimuli, light likely exhibits the most remarkable effect on the control of these systems because light irradiation is nondestructive; light irradiation can also be controlled remotely, spatially, and temporally to help inhibit side effects.[7] In these photoresponsive systems, photochromic moieties, including spiropyran,[8] dithienylethene,[9–11] azobenzene,[7,12–19] overcrowded alkenes and retinal-based switches[20] are commonly incorporated into catalyst systems; the reactivity of a photoswitchable catalyst can be gated *via* photo-irradiation at different wavelengths. Azobenzene and its derivatives have been widely studied because of their unique properties, such as good stability, good photomechanical properties,[21] and fast and reversible photoisomerization.[7,12–18] In these reported methods, functional units are tethered to azobenzene, and catalytic activities are modified by either changing the steric around the functional units[7,12–14] or modulating the relative disposition of two cooperative functional units.[15–18]

Molecular imprinting is a technology for the preparation of molecularly imprinted polymer (MIP) which possesses specific recognition sites with memory of the shape, size, and functionality of templates and its structural analogs.[22–25] The uptake and release of the template in response to a light stimulus can be induced by incorporating photoresponsive azobenzene into MIP matrices.[26–28] By utilizing substrate analogues,[29] transition state analogues,[30] and product analogues[31] as the templates, MIP has been applied in catalysis successfully. However, to the best of our knowledge, the report on MIP in catalysis utilizing catalyst or catalyst analogues as the template is scarce. In the present study, a photoswitchable organocatalyst based on MIP containing azobenzene is developed using a catalyst as the template (Fig. 1). In the “OFF state”, the catalyst is bound to azobenzene functional monomer (in a *trans* form); therefore, the catalyst cannot promote a reaction. Upon UV irradiation, *trans* → *cis* isomerization occurs and triggers the “ON state”; in the ON state, the catalyst is released and the reaction is promoted. For instance, aldol reaction is catalyzed by L-proline;[32,33] in this catalytic reaction, MIP is fabricated using L-proline as the template and catalyst, ethyleneglycol dimethacrylate as the cross-linker, azo-bis-isobutyronitrile as the initiator, and 4-[(4-methacryloyloxy)phenylazo]-benzenesulfonic acid[34] as the functional monomer (see ESI† for the detailed information of the fabrication and characterization of MIP). The uptake and release of L-proline are likely photoswitchable.

Photoresponsive structural changes in L-proline-MIP were evaluated through spectral studies (Fig. 2). MIP exhibits a typical photoisomerization behavior of an azobenzene; the MIP solution in DMSO (0.15 mg mL^{-1}) irradiated at 365 nm for 45 min undergoes *trans* → *cis* isomerization (Fig. 2a). By contrast, the same MIP solution subsequently irradiated at 440 nm for 8 min undergoes *cis* → *trans* isomerization (Fig. 2b). The rate constants of *trans* → *cis* and *cis* → *trans* isomerization of the azobenzene chromophores of the MIP material are $(2.23 \pm 0.12) \times 10^{-3}$ and $(10.7 \pm 1.18) \times 10^{-3}$ s^{-1}, respectively.[35] This result indicates that azobenzene chromophore of MIP undergoes reversible photoisomerization between *trans* and *cis* forms.

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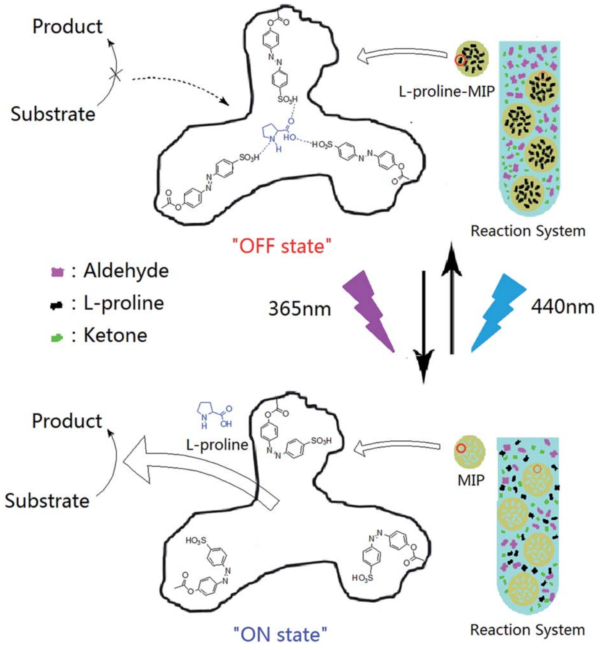


Fig. 1 Concept of photoswitchable catalyst based on photo-induced reversible azobenzene isomerization.

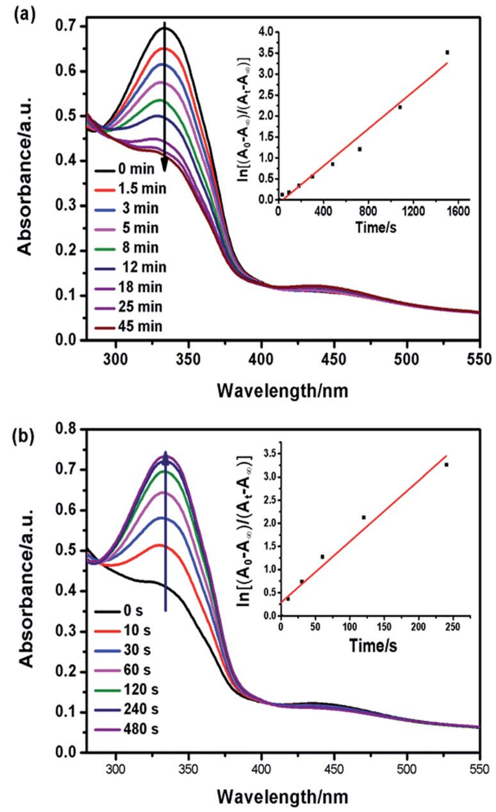


Fig. 2 UV-Vis spectra and spectral changes of MIP (0.15 mg mL^{-1}) in DMSO irradiated (a) at 365 nm for 1.5, 3, 5, 8, 12, 18, 25, and 45 min and (b) at 440 nm for 10, 30, 60, 120, 240, and 480 s. Insets: kinetics of MIP photoisomerization.

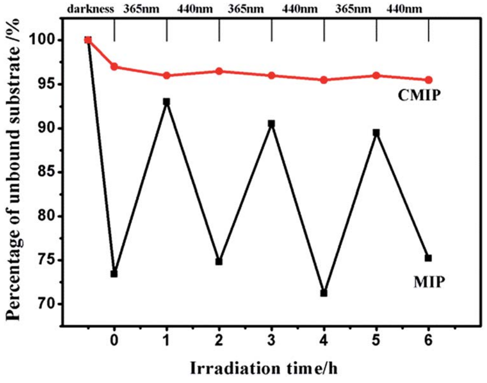
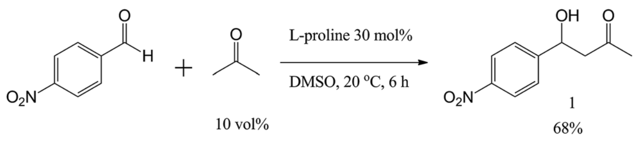


Fig. 3 Photo-regulated release and uptake of L-proline by MIP and CMIP in DMSO.

Fig. 3 shows the changes in the binding capacities of the MIP and control MIP (CMIP) to L-proline under repeated photo-switching conditions. MIP irradiated at 365 nm releases the bound L-proline into the solution as a consequence of *trans* → *cis* photoisomerization; the percentage of unbound L-proline increases from approximately 73% to approximately 93%. By contrast, MIP subsequently irradiated at 440 nm undergoes *cis* → *trans* photoisomerization; as a result, MIP binds to L-proline. The percentage of unbound L-proline decreases from approximately 93% to approximately 74%. The release and uptake amounts of L-proline are similar to those of the previous cycles when photoswitching cycles are repeated. This result demonstrates the photocontrolled uptake and release of L-proline. However, under the same conditions, CMIP demonstrates unremarkable photocontrolled release and uptake of L-proline. The percentage of unbound L-proline only changes from approximately 97% to approximately 96% and from 96% to 96.5% upon irradiation at 365 nm and 440 nm, respectively, demonstrating that CMIP is not photocontrolled. The above results are similar to some previous reports using conventional MIP.[26,27,36] The bound L-proline could be increased if surface molecularly imprinted polymer is used.[28,37]

L-Proline-catalyzed aldol reaction between 4-nitrobenzaldehyde and acetone in DMSO is selected as a standard reaction to evaluate the photoswitchable catalyst activity of MIP.[38–40] L-Proline (30 mol%) in DMSO/acetone (9 : 1) catalyzes the reaction of *p*-nitrobenzaldehyde with acetone at 20 °C for 6 h, yielding 68% aldol product 1, which is comparable to that obtained in a previous report (Scheme 1).[33]

The amount of L-proline-MIP effect on the yield of aldol reaction was investigated (Table 2 in ESI†), and 40 mol% of L-proline with respect to 4-nitrobenzaldehyde performs best. L-Proline-MIP (40 mol% of L-proline with respect to 4-



Scheme 1 L-Proline catalyzed aldol reaction.

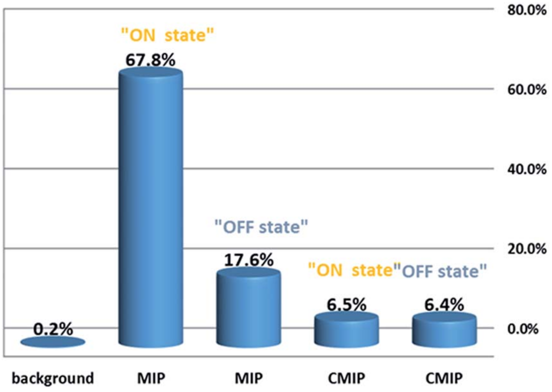


Fig. 4 Photoswitchable catalyst activity of L-proline-imprinted MIP in aldol reaction.

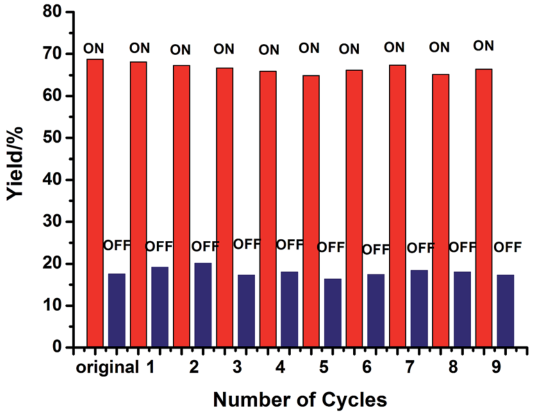


Fig. 5 Photocontrolled reusability of the catalyst.

nitrobenzaldehyde), acetone (0.3 mL), DMSO (2.7 mL), and 4-nitrobenzaldehyde (0.076 mg) were placed in a 3.0 mL quartz cell (optical path length of 1.0 cm). Different measurements were performed for "OFF state" and "ON state". (1) In OFF state, the quartz cell was irradiated at 440 nm at 20 °C for 6 h with magnetic stirring. The mixture was treated with 3.0 mL of saturated ammonium chloride aqueous solution and then extracted with ethyl acetate (3 × 5.0 mL). The organic layer was dried with $MgSO_4$, and the organic solvent was removed through rotary evaporation.[33] The aldol reaction product was dissolved in 2.0 mL of isopropyl alcohol and subjected to yield analysis through HPLC. (2) In ON state, the quartz cell was irradiated at 365 nm for 6 h at 20 °C with magnetic stirring. After completion of the reaction, similar treatment to that in OFF state was adopted.[33] L-Proline-CMIP was prepared in the same manner as L-proline-MIP; however, CMIP was used instead of MIP. MIP without the rebound L-proline was used as background.

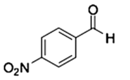
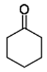
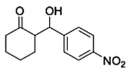
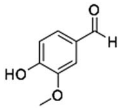
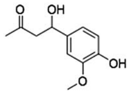
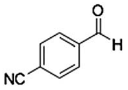
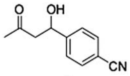
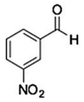
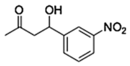
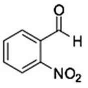
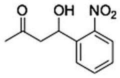
L-Proline-MIP can promote aldol reaction in response to a light stimulus (Fig. 4). A yield of 67.8% was obtained in the "ON state" (irradiation at 365 nm) compared with a yield of 17.6% in the "OFF state" (irradiation at 440 nm). A yield of only 0.2% was obtained for the background because of no presence of L-proline in MIP. However, photoswitching had nearly no effect for CMIP (the yield in the ON state was close to the yield in the OFF state). In comparison with a yield of 0.2% for background, a yield of about 6.5% for L-proline-CMIP was probably caused by unspecific adsorption of L-proline. These results show that the designed system can induce the photocontrolled release of L-proline to promote the corresponding reaction.

The catalyst can be easily recycled through irradiation at 440 nm after a catalyzed reaction is completed. Furthermore, *cis* → *trans* photoisomerization causes MIP-induced rebound of the catalyst. After centrifugation is performed, catalyst-MIP is obtained by discarding the supernatant; catalyst-MIP can also be used in another batch of the same reaction. This photocontrolled recycling procedure is simpler than previous methods by which the recycled catalyst is collected and washed.[41,42] In 20 batches of reactions, the yields of aldol reaction range from 64% to 69% in the ON state and approximately 17% in the OFF state (Fig. 5), demonstrating good fatigue resistance.[43]

The scope of L-proline-imprinted polymer-catalyzed aldol reaction with various substituted benzaldehydes and ketones was investigated (Table 1). Similar photoswitchable properties were observed. Lower yield was obtained with 4-cyanobenzaldehyde (entry 3) because the Hammett σ_p-value of –CN (0.70) was lower than that of $-NO_2$ (0.81).[39] The results with 2-substitued, 3-substituted (entries 4 and 5), and 4-substitued nitrobenzaldehyde were consistent with previous reports.[44,45] Compared with cyclohexanone (entry 1), better result was obtained with acetone, which was similar to two previous reports.[46,47]

In summary, a conceptually new approach based on catalyst-imprinted polymer containing azobenzene is described to

Table 1 Catalytic aldol reactions between ketones and aldehydes catalyzed by L-proline-MIP

Entry	Aldehyde	Ketones	Product	Yield (%) ON state	Yield (%) OFF state
1			 2	44.3	22.1
2			 3	79.1	29.2
3			 4	54.3	37.1
4			 5	47.4	24.8
5			 6	52.1	8.2

design photoswitchable organocatalysts. The photoinduced *trans* → *cis* isomerization of azobenzene switches the reaction from the OFF state to the ON state; thus, the reaction is promoted. The concept is successfully applied to perform photocontrolled L-proline-catalyzed aldol reaction; indeed, the proposed concept is feasible. This concept can be further extended to other reactions.

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