



Title	Photocatalytic Organic Syntheses : Selective Cyclization of Amino Acids in Aqueous Suspensions
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Citation	Catalysis Surveys from Asia, 7(2/3), 165-176 https://doi.org/10.1023/A:1025389725637
Issue Date	2003-09
Doc URL	http://hdl.handle.net/2115/14646
Rights	The original publication is available at www.springerlink.com
Type	article (author version)
File Information	CSA2003-7-2-3.pdf



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(Short title for running heads: Photocatalytic organic synthesis)

Photocatalytic organic syntheses:
Selective cyclization of amino acids in aqueous suspensions

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Photocatalytic reactions occurring at semiconductor particles/solution interfaces can be applied to organic syntheses. In this review article, examples of photocatalytic syntheses of cyclic amino acids by suspended semiconductor particles, e.g., titanium(IV) oxide or cadmium(II) sulfide are introduced and interpreted. Different from the photocatalytic decomposition of pollutants under aerobic conditions, selective conversion of organic compounds can be driven by the photocatalytic reactions under deaerated conditions.

Keywords: photocatalysis, deaerated conditions, titanium(IV) oxide, cadmium(II) sulfide, platinum loading, pipercolinic acid, lysine, 2,6-diaminopimelic acid, piperidine-2,6-dicarboxylic acid

1. Introduction

Semiconductor photocatalytic reaction is the chemical reaction that proceeds by photoirradiation onto semiconductor particles in contact with solutions or gases containing reaction substrates. This reaction has attracted much attention

of scientists since early 1980's, while the phenomena caused by the reaction have been recognized much earlier, e.g., chalking of paint containing titanium(IV) oxide as a pigment has been well known, but its principle had not been clarified. Many articles concerning the semiconductor photocatalysis have been published so far from the standpoint of catalysis, photochemistry, electrochemistry, inorganic, organic, physical, polymer, and environmental chemistry, etc.. One of the most attractive and significant targets of research on semiconductor photocatalytic reaction is its practical application to organic syntheses [1-5], as well as solar-energy conversion and storage [6-10], reductive fixation of carbon dioxide [11], and mineralization and/or detoxification of organic compounds [12-19].

In this review, the application of semiconductor photocatalysis to organic synthesis, especially to selective formation of useful and valuable organic cyclic compounds is interpreted. The potential ability of photocatalysis is shown by reviewing several reaction systems, and design and technique leading to selective reactions is also discussed.

2. Semiconductor photocatalysis

Semiconductor photocatalytic reaction is initiated by photoabsorption of semiconductor to excite electron in the valence band (VB) into the conduction band (CB) leaving positive hole in VB. This is expressed, in electrochemical sense, as that both cathodic potential due to the photoexcited electron (e^-) and anodic potential due to the positive hole (h^+) are applied simultaneously. In other words, a semiconductor particle acts as a micro electrochemical cell consisting of an anode, a cathode, and a photochemically charged battery as schematically shown in Figure 1.

(Figure 1)

Since both oxidation and reduction occur, in principle, on the photoirradiated semiconductor particles, reactions like electrolytic organic synthesis are expected to proceed efficiently on each particle by using neither electrolyte nor electrical wiring, both of which are requisites in the conventional electrolyses. Furthermore, these redox reactions by e^- and h^+ leave no by-product originated in the reductant and oxidant; this is contrastive to conventional redox reagents such as permanganate or lithium aluminum hydride to leave, respectively, manganese ion or aluminum hydroxide after oxidation and reduction. In the early studies of photocatalytic reactions, several chemists claimed that redox (reduction-oxidation) combined chemical reactions might proceed on the photocatalyst particles of nano- or micrometer size. One of the examples is deaminocyclization of lysine into pipercolinic acid and will be described later.

The above-mentioned characteristics of photocatalysis make the photocatalytic reaction much simple and feasible for applying to organic synthesis; the photocatalytic products can be isolated simply by centrifugation or filtering to separate the photocatalysts followed by evaporation of solvent without tedious work-up procedures. In the recent studies, we have developed liquid-liquid phase boundary catalysts, which are located spontaneously at an interface between water and water-immiscible organic compound or at a water-air interface [20-22]. Such modification on photocatalysts enables us to operate the work-up procedure more easily, since the solution part of reaction mixture can be separated simultaneously [23]. Furthermore, if stable thin film of photocatalysts can be prepared (in fact, many papers have reported the film preparation), we can also omit the process of photocatalyst preparation. Another characteristic of photocatalytic reactions being superior to general synthetic processes is that they proceed smoothly even in their aqueous suspensions at ambient temperature. Therefore, hydrophilic and/or thermally unstable organic compounds, especially those originated biologically, can be a starting material without derivatization of functional group(s); e.g., (S)-lysine (Lys),

being dissolved only in water, undergoes deaminocyclization in the deaerated aqueous solution into pipercolinic acid (PCA) by the one-step photocatalytic reaction as described in the following section [24,25].

Unfortunately, especially for the chemists in this field of photocatalysis, it is rather sorry to know that no photocatalytic reactions have been industrialized so far. This is mainly because it is necessary to construct new type of photoreaction systems and optimize the operating conditions, but not due to fatal disadvantages, if any, of the photocatalytic reaction. For example, photoreaction (not photocatalytic reaction) is producing ϵ -caprolactam, an intermediate product of Nylon in 500,000 tons every year in Japan. In relation with the environmental problems, development of "Green Chemistry" processes, which enable us to make sustainable progress for life on the earth, is highly desired [26]. The advantageous features of photocatalysis well satisfy the requirement of "Green Chemistry" and the photocatalytic synthesis of pipercolinic acid is one of the significant examples.

3. Photocatalytic intramolecular cyclization of diamines

3.1. Historical background of the study on photocatalytic reactions under deaerated conditions

In the early stage of our studies, we screened various types of organic compounds, especially those include heteroatoms, such as nitrogen and/or oxygen, under deaerated conditions. We found that under such conditions reduction by e^- proceeds smoothly and is independent of the corresponding oxidation reaction by simultaneously generated h^+ : under the aerated conditions, e^- reacts with molecular oxygen (O_2) to produce hydroxyl ($\bullet OH$), superoxide anion ($O_2^{\bullet -}$) and/or hydroperoxide ($HO_2\bullet$) radicals as well as singlet oxygen (1O_2) and hydrogen peroxide (H_2O_2) to result in the oxidation in overall (while O_2 is solely reduced). Alcohols, such as methanol, ethanol, and 2-propanol [27], dissolved in water give dehydrogenated products, formaldehyde, acetaldehyde, and acetone, respectively, along with the equimolar liberation of molecular hydrogen

(H₂) through the photocatalytic reaction by platinumized titanium(IV) oxide (Pt/TiO₂) under an argon (Ar) atmosphere [28-31]. t-Butyl alcohol, which has no α-hydrogen, undergoes mainly intermolecular dimerization into 2,5-dimethyl-2,5-hexanediol with H₂ formation [32]. As for the nitrogen containing organic compounds are concerned, secondary and tertiary amines gave degraded compounds with by-products, aldehydes. Branched chain primary amines, such as isopropylamine, undergo deamination into ketones along with the equimolar formation of H₂. The modes of these photocatalytic reactions of organic compounds under deaerated conditions resemble those of the reported electrochemical anodic oxidation at metal electrodes immersed in the aqueous solutions [33]. Therefore, it seemed that the Pt/TiO₂ induced photocatalytic reactions occurring in deaerated aqueous solutions, including oxidation of organic substrates with h⁺ as well as reduction of water (or H⁺) by e⁻ into H₂.

However, we have found only one exception during the screening; primary straight chain amine, e.g., propylamine, underwent deaminodimerization into corresponding secondary amine, e.g., dipropylamine, with liberation of NH₃. The H₂ evolution could be observed, but its molar amount was much smaller than that expected from that had been observed in the other photocatalytic reaction systems. The stoichiometry of the predominant reaction has been clarified as;



It is noticeable that this is not a simple oxidation or reduction of the substrate, i.e., formally intermolecular deamination without redox reactions. It has been also shown that at least one methylene group neighboring to the amino group is necessary and corresponding aldehyde (RCHO) was detected in an appreciable amount that was almost same as that of H₂. This intermolecular deamination could be extended to intramolecular one; α, ω-diamines gave cyclic secondary amines such as piperidine [34].

3.2. Mechanism of intermolecular and intramolecular deaminocondensation

On the basis of the results of isotope (D) distribution in the product obtained in the photocatalytic reaction in deuterium oxide, heavy water (D₂O), we elucidated the following reaction mechanism including both oxidation and reduction, as shown in Figure 2 [34].

(Figure 2)

For example, when propylamine is used as a substrate, first, propylamine is oxidized by h^+ into propylimine ($\text{CH}_3\text{CH}_2\text{CH}=\text{NH}$) followed by hydrolysis to give propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$). In the second step of reaction, the aldehyde is condensed with another amine to yield a Schiff base intermediate ($\text{CH}_3\text{CH}_2\text{CH}=\text{NCH}_2\text{CH}_2\text{CH}_3$), which is then, in the final step, reduced by e^- along with H^+ (or D^+ in the case where D_2O is used as a solvent) addition to the final product dipropylamine. Thus, the primary amine/water system gives "symmetrical" secondary amine through photocatalytic reactions. One of the intermediates in the intermolecular deaminocyclization, aldehydes (or ketones), has been proved to be liberated by the above-mentioned photocatalytic reaction of primary and secondary alcohols. As easily expected from these facts, photoirradiation in the presence of Pt/TiO₂ onto alcoholic or aqueous alcoholic solutions containing amines or ammonia induced their N-alkylation. For example, N-ethyl and N,N-diethyl derivatives are produced photocatalytically from benzylamine in ethanol [35], and triethylamine from ammonia in ethanol [36]. Therefore, amine/alcohol system is appropriate to synthesize "asymmetrical" secondary amines, as shown in Figure 2. In acetonitrile, instead of water, however, no secondary amines can be obtained photocatalytically from primary amines, since the final step, reduction of the corresponding Schiff base is strongly retarded by the solvent molecules to leave the Schiff base as a main product [37].

As a further extension of the photocatalytic deaminocyclization, photocatalytic

conversion of Lys is clarified to proceed as shown in Figure 3.

(Figure 3)

Similar to the series of photocatalytic N-cyclization and N-alkylation of amines, the reaction of Lys proceeds also *via* combination of oxidation with h^+ and reduction with e^- [24]. One of the important points in the mechanism of PCA production is a position of the first attack by h^+ . Different from simple α,ω -diamines, two amino groups which are the candidate for oxidation are not the same, the oxidation of α and ω -amino groups yields, respectively, α -keto acid, losing its chirality, and ω -aldehyde without affecting the stereo structure at α -carbon. These modes of photocatalytic reaction may govern the product selectivity and will be discussed in detail later.

3.3. Redox combined process as a unique feature of photocatalysis [5]

Again, combination of oxidation and reduction to produce PCA from Lys is contrastive to the other reported photocatalytic reactions, e.g., splitting of water, or reduction of carbon dioxide, in which h^+ and e^- are used separately for oxidation and reduction, respectively. The combination of oxidation and reduction affords, in principle, no by-products and needs no electrolytes as used in electrolyses since both reactions occur in the neighborhood of the particle surface. Figure 4 shows the other examples of photocatalytic reaction in which both oxidation and reduction participate in product formation processes.

(Figure 4)

In most of cases, the oxidation involves dehydrogenation of alcohol, ethanol or methanol, to yield aldehyde and the reduction step induces conversion of nitro and azo moieties into amino, or hydroxyamino group, leading to nitrogen-containing heterocyclic

compounds [38-42]. In other words, these are coupling of the oxidized and reduced products, i.e., the combination of oxidation and reduction may be categorized as "parallel." On the other hand, the above-mentioned cyclization of amino acids can be "serial," since the oxidation is followed by the reduction. Number of e^- and h^+ used in these "parallel" reactions shown in Figure 4 were not always identical; intermediate species such as acetaldehyde sometimes might be left unreacted after the reaction. Practically, however, alcohols are much cheaper than the starting material, such as azobenzenes or nitrobenzenes, and this should not be a serious problem in the application. The fact that these kinds of reactions can be seen only by the photocatalytic reaction systems is more significant for the application. Although control of product selectivity for this photocatalytic cyclization has not yet been achieved, further detailed study is expected to clarify this.

Recently, photocatalytic selective epoxidation of aliphatic olefins under aerated conditions is reported [43]. While the epoxidation of olefin seems to be an oxidation process, without reduction, such photocatalytic epoxidation may be also a redox combined reaction requiring oxidation of the olefin with h^+ and reduction of molecular oxygen by e^- to yield active species such as superoxide anion or hydroxyl radical which attack the resulting cation radical of olefins.

4. Photocatalysts for cyclization of amino acids

4.1. Potential photocatalysts

Among semiconductors, cadmium(II) sulfide (CdS), as well as titanium(IV) oxide (TiO_2), has been used as a material for a potential and promising photocatalyst. These two semiconductors behave similarly and both of their suspensions induce the photocatalytic redox reactions due to e^- and h^+ . However, the differences between these two semiconductors have been reported in

some reactions and thereby in the reaction products. For instance, in the photocatalytic reaction of lactic acid, CdS gave mainly dehydrogenated product, pyruvic acid, while TiO₂ did oxidatively decarboxylated product, acetaldehyde [44]. Similarly, in the above-mentioned photocatalytic reaction of Lys, the product PCA from TiO₂ suspensions retains its (S)-configuration but that from CdS is almost racemic [24]. The reason for such differences has not completely clarified yet, because of negligible detailed investigation on the primary steps of electron transfer (or positive hole) between semiconducting materials and substrates adsorbed on their surface. However, this should be the most significant problem to be solved for the development of novel selective organic reactions. Control of selectivity in the Lys system is discussed later. Another photocatalyst possessing an ability to induce deaminocyclization (or deaminodimerization) is zinc(II) sulfide (ZnS). The first paper on the ZnS photocatalyzed reaction of amines has been reported by the Yanagida's group [45]. The photocatalytic deaminodimerization similar to the above-mentioned TiO₂-induced reaction was observed. Since band gap of ZnS is much larger than that of TiO₂ and CdS, only shorter wavelength light could be utilized. Moreover, under certain reaction conditions, zinc metal deposition as a result of photoinduced decomposition of ZnS itself occurred and the deposits might affect the photocatalytic activity and product selectivity in the PCA synthesis [46]. Similar behavior of photoinduced decomposition followed by metal deposition of metal sulfide particles has been observed for mercury(II) sulfide (HgS). HgS maybe a semiconducting material and we could determine the band position on the basis of results on photoinduced reaction when suspended in aqueous solutions. We have also detected the photoinduced production of PCA from Lys, but could not observed chiral discrimination due to the chiral crystal structure of HgS, like quartz, when we examined using natural specimen of HgS single crystal, *Cinnabar* [47]. As far as we know, only these four kinds of photocatalysts have been used for the deaminocyclization.

4.2. TiO₂

It has been clarified that the photocatalytic activity of TiO₂ strongly depends on its physical properties; a certain TiO₂ powder showed no appreciable activity but another powder was quite active. There have been many articles reporting the correlation of photocatalytic activity with the physical properties of TiO₂ powders, such as crystal structure [48,49], surface area [50], particle size [51], surface hydroxyls [52,53], etc.. It is believed by most of researchers in this field that the crystal structure, anatase, rutile, or brookite, is the most primitive and essential properties to predict the photocatalytic activity, e.g., anatase, but not rutile, crystallites have relatively high photocatalytic activity [54]. Moreover, the photocatalytic activities of amorphous or less crystallized TiO₂ particles was also reported [55].

In a series of studies on TiO₂ photocatalytic reactions [52,56], we have shown that the overall kinetics depend on both amount of substrate(s) adsorbed on the surface to be reduced or oxidized by e⁻ or h⁺, respectively, and rate of geminate recombination of e⁻ and h⁺. To obtain highly active TiO₂ photocatalyst, therefore, it is necessary to give simultaneously a couple of properties, generally of contradiction, to the powders; large surface area to adsorb substrates and high crystallinity (or lesser surface and bulk defects) to diminish the e⁻-h⁺ recombination. This hypothesis has been supported by the ultra-highly active TiO₂ photocatalyst prepared by newly developed method, hydrothermal crystallization in organic media (HyCOM) [57,58], thermal decomposition of metal alkoxide (TD) [59], and transfer hydrolytic crystallization in alcohols (THyCA) [60]. The design and development of polycrystalline TiO₂ photocatalyst are in progress along this line. The performance of HyCOM TiO₂ which is so much higher than that of commercial TiO₂ samples toward the photocatalytic PCA production has been demonstrated clearly [58] and detailed study will be published soon [61].

The photocatalytic performance of TiO₂ depends also on the metal and/or metal oxide loading onto its surface. For the photocatalytic reaction under deaerated conditions, loading of noble metal, e.g., Pt, is indispensable to produce H₂

as a reduction product. The final reduction step including (formally) hydrogenation of a Schiff base intermediate also requires the presence of Pt or other noble metals, which acts as a reduction site. Since the corresponding oxidation occurs at the bare TiO₂ surface, it is reasonable to expect that the reaction intermediate, a Schiff base, must migrate on the TiO₂ surface where it forms to reach the reduction site, Pt deposits, and that the distribution of Pt deposits on the TiO₂ surface may be a decisive factor toward the selective formation of PCA. Actually, we have tried to control the Pt distribution and found that a Schiff base intermediate can be efficiently reduced to give PCA if one small (a few nm) Pt particle is deposited on TiO₂ particles of ca. 20 nm [62].

4.3. CdS

Different from the above-mentioned TiO₂ photocatalysts, for CdS photocatalysts, only several papers have reported the structural factor(s) affecting the photocatalytic activities. As one of the most distinguished difference with TiO₂, it has been pointed out that position of conduction and valence bands of CdS is energetically higher than that of TiO₂. This corresponds to the more and less ability for reduction and oxidation, respectively. However, it seems impossible to interpret all the difference between the photocatalytic activity and product selectivity of TiO₂ and CdS only by this difference in the band positions.

As for the activation of CdS photocatalyst, a few reports have shown that annealing, i.e., heat-treatment, generally under an inert atmosphere, of the powder at higher temperature enhances the photocatalytic activity of deaerated aqueous CdS suspensions and this effect was attributed to crystal transformation from sphalerite (cubic) to wurtzite (hexagonal) [63,64]. More recently, Lee and coworkers claimed that the heat-treatment under air improves the CdS photocatalytic activity, especially for reduction of intermediate organic compounds, due to oxidized surface moiety. The effect of such activation will be discussed in the last section.

For the photocatalytic N-cyclization of Lys, the Pt loading is indispensable; apparently no consumption of Lys and production of PCA could be seen by bare TiO₂ powders [24]. Similar to the H₂ evolution systems, Pt acts as a reduction site also in this case. Under deaerated conditions, generally, platinization of TiO₂ is required to observe the photocatalytic activity, as described above. On the other hand, surface of CdS can be a reduction site for e⁻ and CdS does not require Pt deposits, though the product selectivity is drastically influenced by the metal loading as also described later.

Another interesting feature of CdS photocatalyst is its ability to induce racemization of amino acids, including L-leucine, L-phenylalanine, and L-glutamic acid, as well as Lys, in deaerated aqueous suspensions; photoirradiation onto the CdS suspension racemizes these amino acid under mild conditions [65]. Generally, such racemization needs high temperature, e.g., boiling water, and highly concentrated mineral acids or alkali hydroxides, which must be removed from the reaction mixture after completion of racemization. The photocatalytic racemization supplies easier work-up procedure. The mechanism of the CdS-photocatalyzed racemization has been proved to be also a redox-combined process [65].

5. Selectivity control in photocatalytic deaminocyclization of amino acids

5.1. Lys (lysine) system

PCA is one of the most useful intermediates for the syntheses of biologically active heterocyclic compounds, e.g., a local anesthetic involves PCA skeleton and is synthesized from PCA [66]. Although PCA is naturally occurring, it is practically impossible to extract from, e.g., leaves of plants, since it is not proteinogenic and distributed in very low concentration. Therefore, optically active PCA is obtained by optical resolution or enzymatic resolution of its ester. Since its synthesis from inexpensive optically active starting material, e.g. Lys, has been

strongly expected [67], the photocatalytic synthesis is much promising.

It is clarified that the optical activity of photocatalytic product, PCA, is determined by which amino group in Lys is oxidized; oxidation of α and ϵ -amino group leads to keto acid and ω -aldehyde, respectively, and then to racemic and optically active cyclic Schiff base intermediate (CSB), as shown in Figure 3. Therefore, selective oxidation at an ϵ -amino group should give optically active PCA, retaining the original configuration of Lys, (S)-isomer. This mechanism is supported by the observation in experiments using ^2D and ^{15}N -labeled Lys [24,61]. In fact, substitution of ϵ -amino group with various reactive functional group induced PDC of almost 100% optical purity [25]. The fact that the product PCA from TiO_2 suspensions retained its (S)-configuration but that from CdS was almost racemic shows that α and ϵ -amino group of Lys might be oxidized in TiO_2 and CdS suspensions, respectively. Thus the product selectivity is controlled by the kind of photocatalyst. Because the photocatalytic reaction proceeds *via* electron (hole) transfer between the surface and adsorbed molecule, the adsorbed form of substrates, e.g., site(s) of binding, may give decisive influence on the product selectivity. It has been clarified by *in situ* spectroscopic observation of the photocatalytic reaction of Lys on thin-film photocatalysts that TiO_2 tends to adsorb Lys in the form of diammonium salt while CdS in the form of α -amino and ϵ -ammonium salt [68]. This is reasonable because the surface of TiO_2 is reported to be acidic to give proton to the adsorbed amines. In the case of lactic acid, being converted in different ways by TiO_2 and CdS, as described earlier, the different adsorption onto TiO_2 and CdS could be detected also in the IR spectra [69]. Judging from the relatively lower oxidation potential of amino group than that of ammonium salt, the free α -amino moiety undergoes feasible oxidation by h^+ in CdS, leading to selective formation of racemic PCA. Another factor is potential of e^- and h^+ in semiconductors. TiO_2 has rather lower valence band edge, i.e., strong oxidation ability, which is capable of oxidizing even ammonium ions on both side of adsorbed Lys. This is contrastive to the fact h^+ in CdS can oxidize only free amino group of Lys as discussed above. Thus, both adsorption properties and oxidation potential

are decisive factor of selectivity of products in the photocatalytic cyclization of Lys.

5.2. Stereoselective cyclization of 2,6-diaminopimelic acid

5.2.1. Extension to synthesis of piperidine-2,6-dicarboxylic acid

As a further extension of photocatalytic cyclization, we have shown that photoirradiation onto an aqueous CdS suspension containing 2,6-diaminopimelic acid (DAP), which is similar to Lys but possessing an extra carboxylic group on the end of side chain, leads to the deaminocyclization into piperidine-2,6-dicarboxylic acid (PDC) [70-72]. This is reasonable to assume a reaction pathway similar to the Lys system. In this case, however, it is interesting to know that the product PDC has three stereoisomers; (S,S), (R,R), and (R,S) (meso) forms. The former two isomers are *trans*, and the last one is *cis*. Because the starting material DAP was a 1:1:2 mixture of (S,S), (R,R), and (R,S) isomers, which is optically inactive totally, and no other optically active materials were not present in the reaction mixtures, we could not expect the formation of optically active products, i.e., a ratio of optically active (S,S) and (R,R) isomers should be always unity. The ratio of *trans/cis* isomers, which are diastereomers, would be changed by the reaction conditions. Although one of the stereo isomers of product, *trans*-(S,S)-PDC, is naturally occurring and can be used as a starting material for syntheses of various types of piperidine alkaloid (e.g., Solenopsin A [73]), its stereoselective chemical synthesis is known to be much difficult [74]. There seem to be no established pathways for the synthesis. Therefore, the one-step synthesis of *trans*-PDC through the semiconductor photocatalytic reaction is of great importance.

5.2.2. Photocatalytic Production of PDC's by Aqueous Suspension of CdS

Table 1 shows the representative results of photocatalytic reaction of aqueous DAP solutions by various types of CdS powders. Although the photocatalytic reaction by Pt/TiO₂ gave *cis*-PDC as well as racemic PCA, a decarboxylated product, negligible formation

of *trans*-PDC could be observed (data not shown). On the other hand, bare CdS photocatalyzed the conversion of DAP into PDC, a mixture of *cis* and *trans* isomers, without appreciable formation of PCA. It has been proved to be photocatalytic with the fact that this reaction proceeds only in the co-presence of photoirradiation and catalyst. As clearly seen in Table 1, the *trans/cis* ratios of PDC depended on the nature of CdS photocatalysts. Bare CdS particles tend to produce *trans*-PDC predominantly, except for the case of Katayama CdS of poor photocatalytic activity. Especially, pigment grade CdS (Diapigment from Mitsubishi Material) and heat-treated Furuuchi CdS showed relatively higher activity for *trans*-PDC production. On the contrary, in all the cases of platinum(IV) oxide (PtO₂)-loaded CdS, the *cis* isomer was produced selectively (*trans/cis* ratio < 0.3). In this study, one of the best photocatalyst for the *trans*-PDC production was found to be the heat-treated Furuuchi CdS.

Figure 5 shows the effect of pre-treatment of Furuuchi CdS on the rate of DAP consumption, total PDC yield, and *trans/cis* ratio.

(Figure 5)

The annealing at 1023 K under completely deaerated conditions decreased both the DAP conversion and the PDC yield, while it improved the *trans/cis* ratio a little. On the other hand, the treatment with a contaminated small amount of air is markedly effective for both the enhancement of photocatalytic activity and *trans/cis* ratio of PDC. Similar treatment under air caused the formation of a CdO layer (as proved by X-ray diffraction analysis) to result in a relatively lower rate of DAP consumption and a lower *trans/cis* ratio, as compared to the CdS treated under the partly aerated conditions. The change in physical properties of CdS particles by the heat-treatment under the aerated conditions will be discussed later.

The proposed reaction mechanism is depicted in Figure 6.

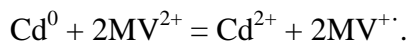
(Figure 6)

From analogy of the photocatalytic reaction of Lys, an amino group in DAP may be oxidized first by h^+ . In the present experiments, the addition of NaOH was necessary to convert DAP, indicating that the deprotonated amino group undergo feasible oxidation. It should be noted that the composition of (R,S) isomer in the remaining DAP was almost half, unchanged by the photocatalytic reaction, irrespective of the CdS catalyst used (Table 1). This means that the DAP isomers are consumed almost equally during the course of photocatalytic reaction. The stereo selection for *trans*-PDC production, therefore, is attributable to the step of reduction of a cyclic Schiff base (CSB) intermediate by the photoexcited electrons (e^-). Under the conditions of higher pH, formation of the CSB (or α -keto acid being in equilibrium with CSB, see Figure 6) intermediate was observed by enantiomer-separation HPLC analyses; two peaks with almost the same intensity and width appeared. It has been reported that CSB is stable under alkaline conditions. The split peaks in HPLC are attributable to enantiomers of CSB's, since they disappeared by the post treatment in the dark with platinum black under H_2 atmosphere, along with increase of *cis*-PDC. These facts suggest both that the present photocatalytic reaction proceeds *via* the CSB intermediate as shown in Figure 6 and that its hydrogenation on the Pt surface leads to *cis*-PDC, maybe *via syn*-addition of hydrogen atoms to the C=N bond in CSB. In the presence of loaded platinum, or its oxide, on CdS particles, the photoexcited electrons could move to the Pt surface and produce hydrogen atoms to result in the selective formation of *cis*-PDC. On the other hand, the bare CdS surface also reduces CSB not by hydrogen atom addition but, presumably, by electron transfer, because CdS particles themselves showed no catalytic activity for hydrogenation of CSB under H_2 atmosphere in the dark; the CdS surface could not produce hydrogen atoms. The surface modification of CdS enhances the electron transfer and, furthermore, induces higher selectivity for *trans* isomer, maybe due to interaction with the intermediate species, CSB and/or its one-electron reduced form. The modification to higher extent, annealing in air,

may cause the decrease in reduction ability for PDC production.

5.2.3. Cd^0 Formation during the Photocatalytic Reaction by Activated CdS

Careful inspection of the irradiated reaction mixtures revealed that the suspension of active CdS had turned a little brownish and darkened, and the original bright yellow color was recovered by introduction of air. Furthermore, addition of a deaerated aqueous solution of methylviologen (MV^{2+}) to the irradiated suspension caused the appearance of intense blue color owing to its cation radical ($MV^{+\cdot}$). Such behavior has been reported first by Gutierrez and Henglein [75] for the suspension of a commercial (Fulka) CdS powder, and later by Shiragami et al. [76] for a CdS colloid; photoinduced formation of Cd^0 and its oxidative dissolution with air or MV^{2+} were suggested in both papers. Consistent with the latter paper, the untreated CdS powders gave negligible $MV^{+\cdot}$ even after the 24 h irradiation. The molar amount of Cd^0 deposited on CdS was evaluated from that of $MV^{+\cdot}$ on the assumption of stoichiometry,



The yield of *trans*-PDC increased with increasing Cd^0 , while *cis*-PDC seemed to be independent of Cd^0 , leading to higher *trans/cis* ratio. Thus, the deposited Cd^0 improves the photocatalytic activity of CdS for N-cyclization of DAP into PDC and stereoselectivity for the *trans*-isomers, and the annealing under partly deaerated conditions makes the CdS powders feasible for *in situ* Cd^0 photodeposition.

During the photoirradiation, the Cd^0 amount was increased drastically within 2-h irradiation and became constant after 5 h. The photocatalytic PDC formation seems to start at the time when Cd^0 was accumulated on the CdS surface. On the other hand, efficient consumption was observed during the first stage and might correspond to the complimentary oxidation reaction to produce Cd^0 . Anyway, the amount of Cd^0 was small enough to recognize that the change in CdS photocatalyst is negligible.

5.2.4. Physical Properties of Active CdS Particles [72]

X-ray diffraction analyses of the CdS powders gave no evidence for the formation of surface layer on the active photocatalyst, while annealing under aerated conditions led to the formation of CdO layer. X-ray photoelectron spectroscopic analyses suggested that surface oxide species appeared with the annealing under partly aerated conditions, i.e., on the active CdS. The annealing gave a shoulder in the lower binding energy region (ca. 529.5 eV) of an intense O1s peak assigned to surface hydroxyls (531.2 eV). Comparison with the previous reports leads to the idea that O^{2-} (lattice), CO_3^{2-} , or O_2^{2-} species could not account for the shoulder. Since for a commercial cadmium(II) oxide (CdO, Nakarai) powder, the similar peak, as well as peaks of hydroxyls (531.2 eV) and lattice oxide (O^{2-} ; 528.2 eV), was observed, we concluded that the surface of the active CdS had been partially oxidized to have surface oxide species (e.g., chemisorbed oxygen), but not forming a thick CdO layer.

Further information on the annealing effect was obtained from photoluminescence (PL) measurements. As reported previously, excitation of bulk CdS powder at 300-400 nm leads to broad-band photoemissions at around 775 and 900 nm which are attributable to sulfur and cadmium vacancies, respectively. The annealing under partly aerated conditions markedly enhanced the 775 nm emission, rather than the 900 nm one, while the CdS annealed under Ar emitted predominantly in the longer wavelength region, suggesting that the active CdS particles possesses sulfur vacancies. The presence of MV^{2+} as a strong electron acceptor reduced the emission to an appreciable extent, and the loading of Pt from a colloid solution onto the CdS quenched almost completely, while the addition of electron donors such as alcohols or amino acids (DAP) gave negligible influence on the PL spectra. These facts are reasonably interpreted by that the emission arises from trapping of photoexcited electrons by sulfur vacancies followed by deactivation. Furthermore, the emission remaining even in the presence of large amount of electron acceptors suggest that the sulfur vacancies are located not only on the surface but

also in the bulk of CdS particles.

The PL intensity at 775 nm was measured in the aqueous suspensions under the conditions similar to the photocatalytic reaction, and plotted in Figure 6 as a common variable for *trans*-PDC and Cd⁰ yields. These almost parallel relations suggest that sulfur vacancies, produced by the oxidation of sulfur on the surface (as well as the formation of surface-oxide species as indicated by XPS analyses), promotes the *in situ* deposition of Cd⁰, leading to the selective and efficient formation of *trans*-PDC. Henglein [77] proposed the Cd⁰ photodeposition through a mechanism that a photoexcited electron (e⁻) is trapped at the sulfur vacancy and then reduces an adjacent Cd²⁺ to form Cd⁰.

The thus produced Cd⁰ may act as a reduction site for e⁻ and enhance the photocatalytic activity of CdS by prohibiting geminate recombination of e⁻ and h⁺. Different from deposited metals such as platinum, the surface of Cd⁰ might not produce hydrogen atoms which are added to C=N bond in a cyclic Schiff base intermediate to give *cis*-PDC, but reduce the bond, presumably, *via* consecutive electron transfer along with proton addition.

Although a similar product-selectivity switching by Cd⁰ has been reported for photocatalytic reduction of a nicotinamide over CdS colloids [76], this is the first example, to the best of our knowledge, of stereocontrol of photocatalytic reaction products by the surface modification.

5.2.5. Preparation of Optically Active *trans*-PDC from (S,S) or (R,R)-DAP [72]

On the basis of above-mentioned results, we can expect that active CdS photocatalyst, giving large *trans/cis* ratio, may induce the formation of optically active (S,S) or (R,R)-PDC from optically active substrate, (S,S) or (R,R)-DAP. Since the optical resolution of DAP is feasibly achieved through stereoselective enzymatic hydrolysis of amide derivative, the CdS-induced photocatalytic N-cyclization of DAP should be a potent synthetic procedure for enantiomers of *trans*-PDC. Table 2 shows the results. As expected, (S,S) and (R,R)-DAP's were converted mainly into (S,S) or (R,R)-PDC; >92 % optical purity was obtained for both enantiomers. This almost retained configuration of PDC

shows the consistency with the expected reaction mechanism, and furthermore, no (or negligible) racemization of enantiomeric cyclic Schiff base intermediates *via* imine-enamine tautomerism.

According to the reaction mechanism, no formation of racemic PDC could be expected; if the photocatalytic reaction only consists of reaction in Figure 7, *trans*-PDC should be of 100 % optical purity. However, in practice, the purity was at most 92 %, suggesting reaction pathway(s) other than expected. One of the most plausible process producing a racemic product is photocatalytic racemization of DAP. As shown in Table 2, the remaining DAP was partly racemized. Since photoirradiation in the absence of CdS or stirring the suspension in the dark led to no racemization of DAP, the formation of racemic DAP was attributable to the photocatalytic process, as observed in amino acid-CdS systems [65]. It has been proved that in the Lys system, Pt (or PtO₂) loading is effective to avoid unexpected racemization, but it can not be applied to the present system because of contradistinctive stereoselectivity of platinized catalysts.

6. Conclusive Remarks

One of the most significant features of semiconductor photocatalysis is that we can utilize both oxidation and reduction even in the one-pot and one-step process. As shown above, the combination of redox reactions affords several unique reactions, which are not achieved by conventional reaction techniques. Changing photocatalysts and/or reaction conditions could control the selectivity of products. In the photocatalytic N-cyclization of Lys, the optical activity of product PCA has been determined by the photocatalyst used. We can obtain racemic and optically active products by using CdS and TiO₂, respectively. It has been proved that one-step stereoselective (diastereoselective) preparation of 2,6-disubstituted piperidine is achieved at room temperature by activated CdS particles in their aqueous suspension. The stereoselectivity giving mainly *trans* isomers was complementary to tha

t by platinized catalyst producing the *cis* isomer. This arose from the *in situ* formation of Cd⁰ species on the surface *via* sulfur vacancies formed by the annealing under partly aerated conditions and traps photoexcited electrons to yield Cd⁰. The deposited Cd⁰ also enhances the efficiency of utilizing photogenerated electron-positive hole pairs and the previous report which showed the improvement of rate and selectivity of CdS-induced photocatalytic reaction by heat treatment may be caused by the similar mechanism. Thus, the Cd⁰ species play an important role in the photocatalytic reaction by CdS particles and the present method of preparing active CdS photocatalyst is applicable to wide range of stereoselective photocatalytic reactions including reduction step by photoexcited electrons.

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Table 1 Effect of physical properties of CdS particles on the yield, conversion, and selectivity in photocatalytic deaminocyclization of DAP in aqueous suspensions^a

catalyst ^b supplier	purity %	additive	cis-PDC / μmol	trans-PDC / μmol	yield ^c %	trans/cis	conv ^d %	meso ^e %
Diapigment	— ^f	none	5	15	25	3.1	78	50
Furuuchi	99.999	none	3	4	10	1.2	76	49
Kojundo	99.99	none	3	4	9	1.3	74	51
Katayama	96	none	2	2	5	0.7	74	51
Furuuchi*	99.999	none	6	26	39	4.1	84	48
Furuuchi	99.999	5wt% PtO ₂	25	7	37	0.3	86	51
Katayama	96	5wt% PtO ₂	3	< 1	5	0.2	77	51
Furuuchi*	99.999	5wt% PtO ₂	24	7	33	0.3	93	50

^aCatalyst 50 mg was suspended in an aqueous solution (5.0 cm³) of DAP (100 μmol with 50 μmol of NaOH) and irradiated under Ar at 298 K for 24 h.

^bAsterisk denotes heat-treated (1023 K under nitrogen with contaminated small amount of air) CdS. ^cHPLC yield based on DAP consumption. ^dConversion of DAP.

^eMeso isomer in remaining DAP. ^fNot determined.

Table 2 Photocatalytic deaminocyclization of optically active DAP's to yield *trans*-PDC's.

substrate	PDC yield/%			trans/cis	ee-(S) /%	ee-(R) /%	remaining DAP		
	(R,S)	(S,S)	(R,R)				(R,S)	(S,S)	(R,R)
(S,S)-DAP	5	22	2	4.8	93	—	9	44	< 1
(R,R)-DAP	5	2	21	4.6	—	92	9	< 1	54

^aCatalyst: CdS (Furuuchi) was annealed at 1023 K for 1 h under a stream of Ar (50 cm³ min⁻¹) with air (1.7 cm³ min⁻¹).

Figure captions

- Figure 1 Schematic illustration of semiconductor photocatalytic reaction. Irradiation of light of energy greater than the band gap between valence and conduction bands produces photoexcited electron and positive hole pairs. In the case of Pt/TiO₂ photocatalyst, Pt works as a cathode for reduction and TiO₂ itself as an anode for oxidation.
- Figure 2 Photocatalytic N-alkylation to yield symmetrical and asymmetrical secondary amines from, respectively, primary amine (R¹CH₂NH₂)/water and primary amine/alcohol (R²CH₂OH) systems.
- Figure 3 Proposed reaction mechanism of photocatalytic one-step synthesis of pipercolinic acid (PCA) from (S)-lysine (Lys) in a deaerated aqueous solution at room temperature. One of amino group in Lys is first oxidized by h⁺ into corresponding imines, hydrolyzed to aldehyde or ketone, and then condensed with an amino group on another end of the molecule to form a cyclic Schiff base intermediate undergoing reduction by e⁻.
- Figure 4 Example of photocatalytic reaction utilizing both oxidation by h⁺ and reduction by e⁻. Syntheses of benzimidazoles: Wang et al., 1997 [39], tetrahydroquinolines: Park et al., 1995 [40], indazoles: Shibata et al., 1988 [38], and homofurylhydrazobenzenes; Reinheimer et al., 1999 and 2000 [41,42].
- Figure 5 Representative photocatalytic activities of CdS photocatalysts. Open and closed bars refer to DAP conversion and PDC yield, respectively. Open circle shows the molar ratio of *trans* and *cis*-PDC. A: Furuuchi CdS as received, B: A was heat treated at 1023 K under Ar, C: A was heat treated similarly with B, but with continual air pulses (20 cm³ every 10 min), D: A

was heat treated at 1023 K under Ar ($40 \text{ cm}^3 \text{ min}^{-1}$)-air ($1.7 \text{ cm}^3 \text{ min}^{-1}$), and E under air.

Figure 6 Reaction mechanism yielding *trans* and *cis*-piperidine-2,6-dicarboxylic acid (PDC) from 2,6-diaminopimelic acid (DAP). One of stereoisomers of DAP is shown for convenience. Adsorption of proposed intermediate, CSB, might occur at nitrogen leading to a carboxylic group to upside of the surface. Cadmium metal, having higher overvoltage for hydrogen liberation, reduces *via* electron transfer followed by proton addition from solution phase to produce *trans*-isomer, while platinum adds two hydrogen atoms to CSB into *cis*-PDC.

Figure 7 Yields of *trans*-PDC and Cd^0 as a function of arbitrary photoemission intensity at 775 nm measured under the same conditions as the photocatalytic reaction. Catalyst A: Furuuchi CdS (CdS(F)) as received, B: CdS(F) annealed at 1023 K for 1 h under Ar ($50 \text{ cm}^3 \text{ min}^{-1}$), and C: CdS(F) annealed at 1023 K under Ar ($50 \text{ cm}^3 \text{ min}^{-1}$) with continual air pulses (20 cm^3 every 10 min).

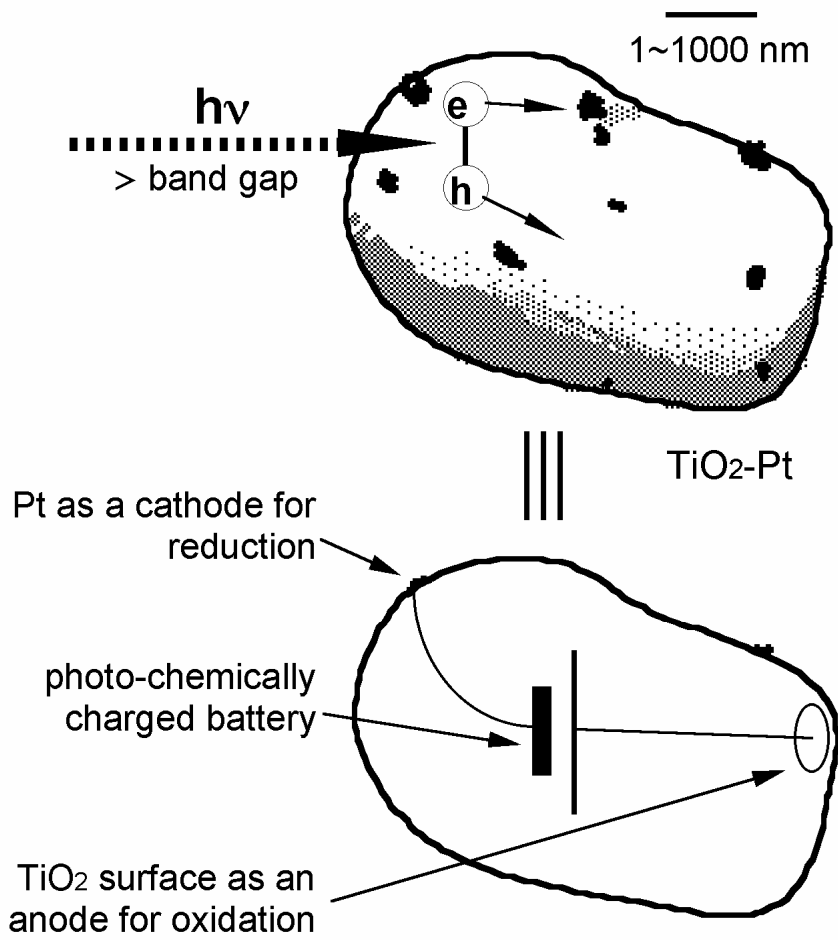


Figure 1

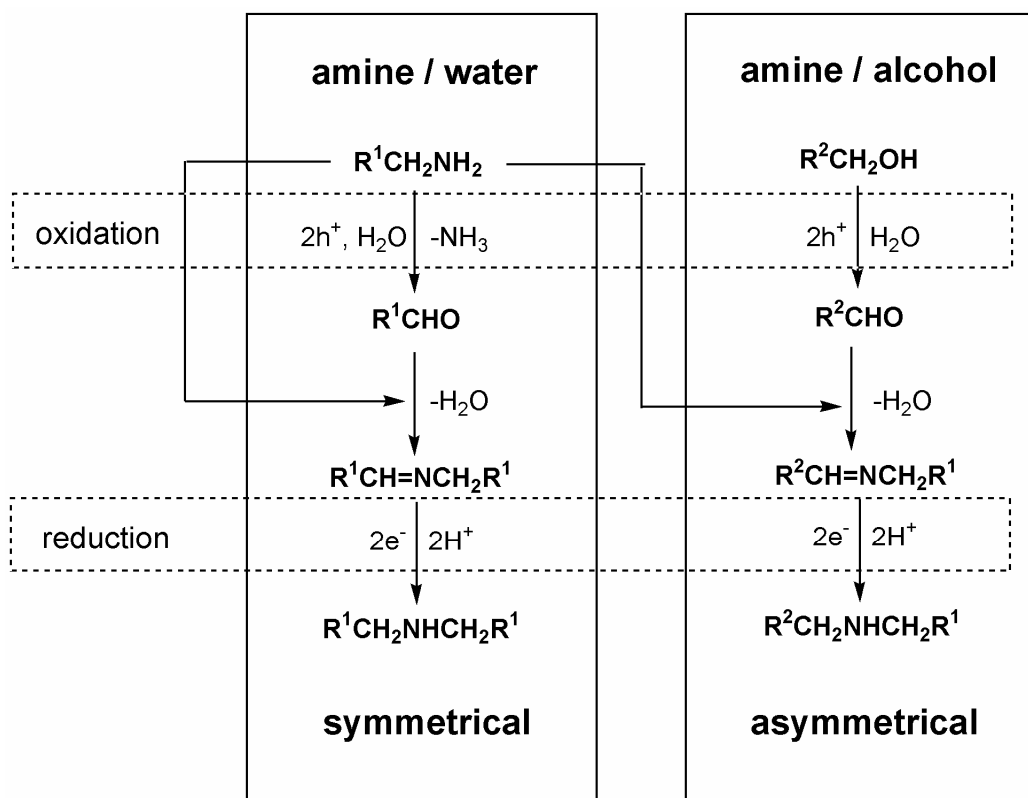


Figure 2

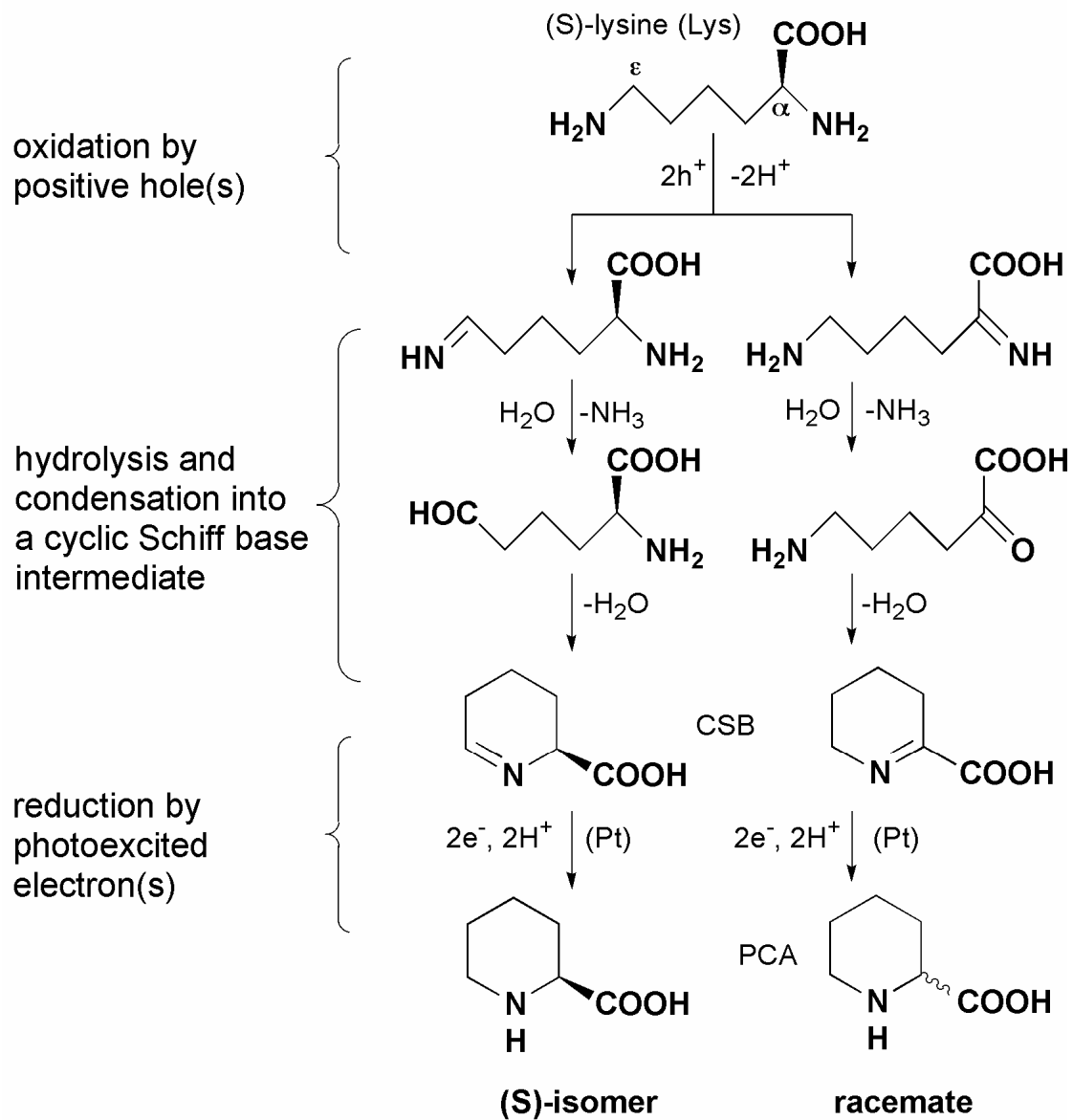
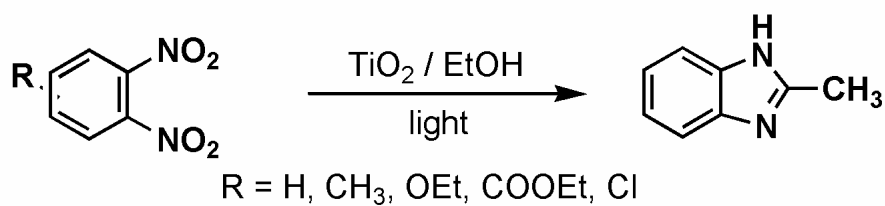
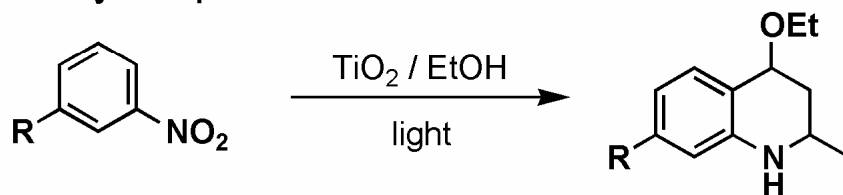


Figure 3

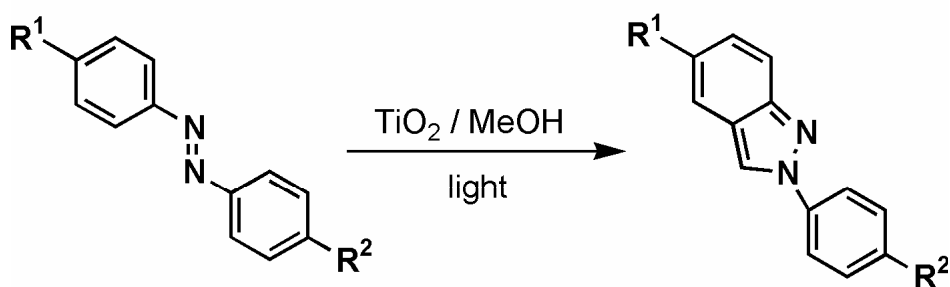
benzimidazoles



tetrahydroquinolines



indazoles



homofurylhydrazobenzenes

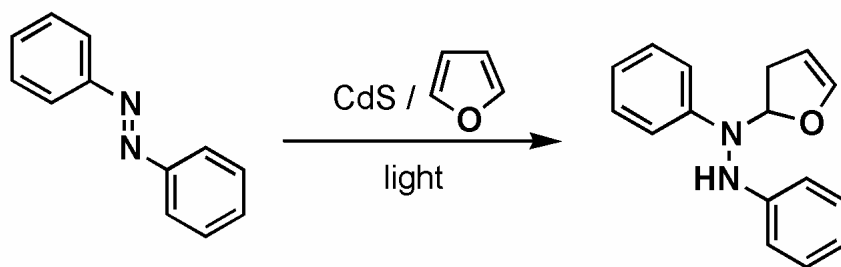


Figure 4

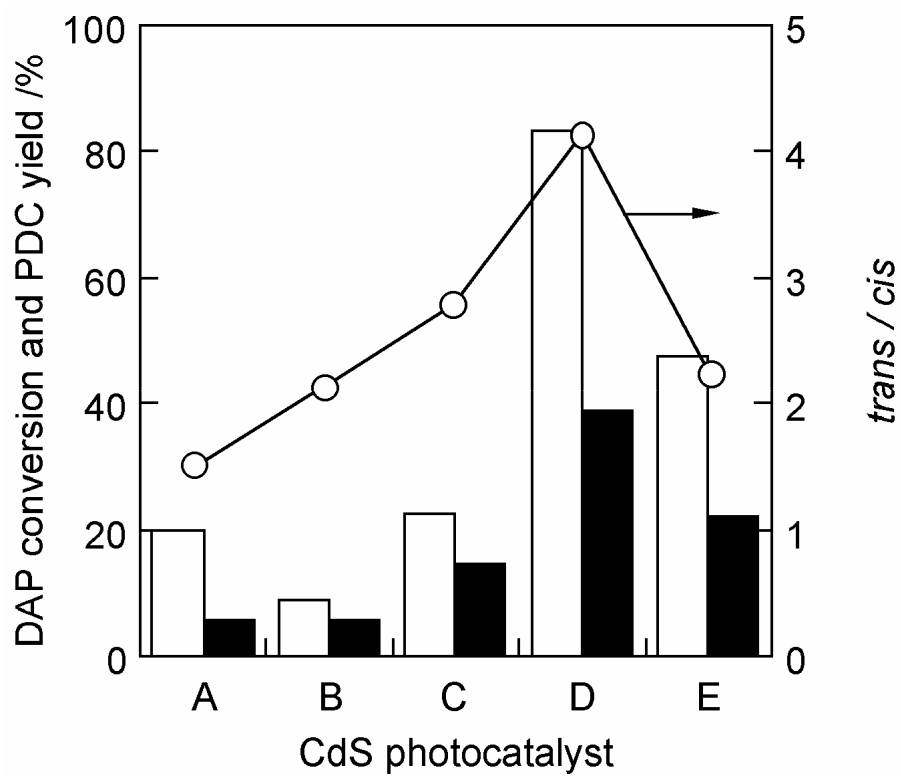


Figure 5

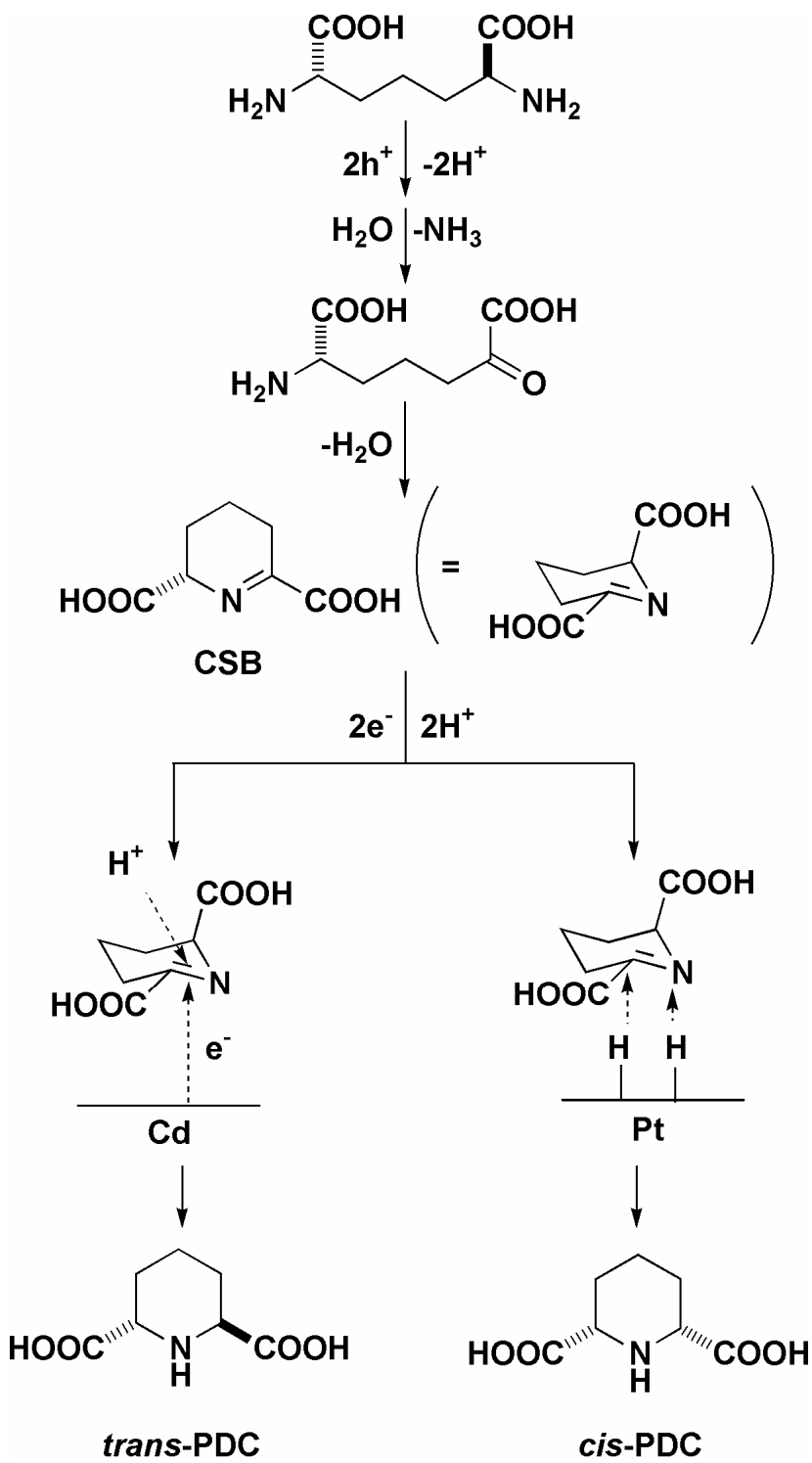


Figure 6

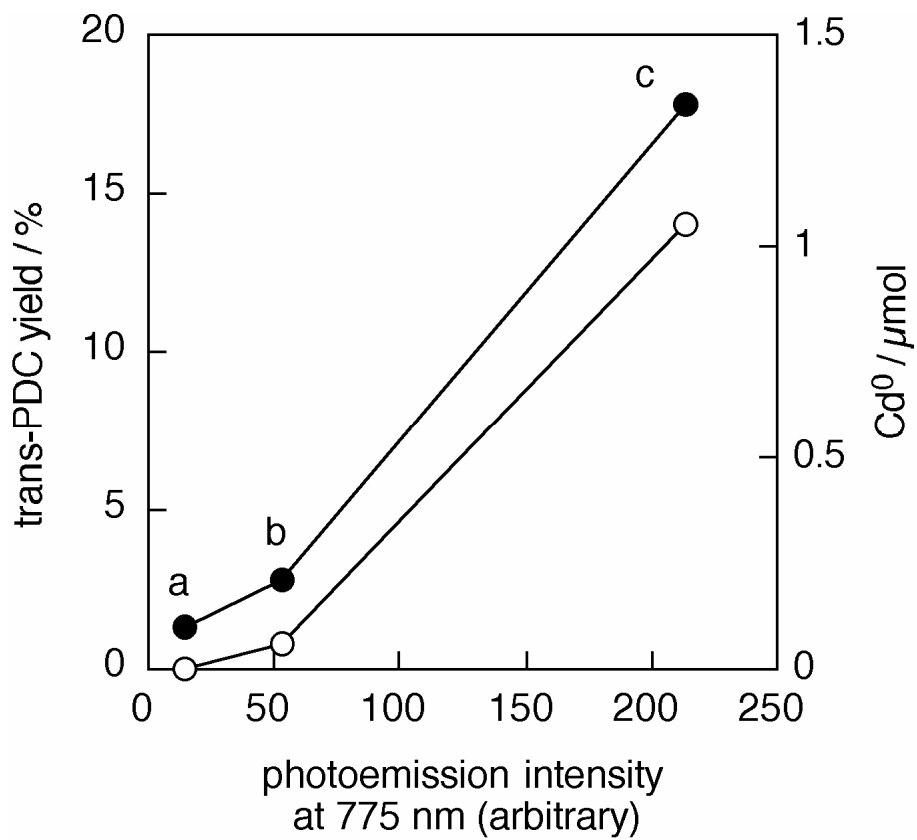


Figure 7