Organized Aggregation Makes Insoluble Perylene Diimide Efficient for the Reduction of Aryl Halides via Consecutive Visible Light-Induced Electron-Transfer Processes

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S *Supporting Information*

ABSTRACT: The consecutive photo-induced electron-transfer (conPET) process found with perylene diimide (PDI) overcomes the limitation of visible-light photocatalysis and sheds light on effective solar energy conversion. By the incorporation of PDI into a metal-organic polymer Zn-PDI, a heterogeneous approach was achieved to tackle the poor solubility and strong tendency to aggregate of PDIs that restricted the exploitation of this outstanding homogeneous process. The interplay between metal-PDI coordination and $\pi \cdots \pi$ stacking of the organized PDI arrays in Zn-PDI facilitates the conPET process for the visible light-driven reduction of aryl halides by stabilizing the radical-anion intermediate and catalyst-substrate interacted moiety. These synergistic effects between the PDI arrays and Zn sites further render Zn-PDI photoactivity for fundamental oxidation of benzyl alcohols and amines. The tunable and modular nature of the two-dimensional metal-organic polymers makes the catalyst-embedding strategy promising for the development of ideal photocatalysts toward the better utilization of solar energy.

Visible light-driven photocatalysis is at the important edge of chemistry and has emerged into a clean, mild, and atom-efficient method for organic synthesis, as sunlight provides the most sustainable and redundant energy source.[1,2] Building on the seminal results obtained employing photo-induced electron transfer (PET), various kinds of dye molecules including organometallic compounds, conjugated organics, or inorganic semiconductors were demonstrated to be very efficient in photoredox reactions through the single-photon excitation.[3,4] As the energy conferred by visible light excitation for subsequent redox chemistry is limited to the one single absorbed photon, visible light-mediated chemical photocatalysis using the energies of more photons in one catalytic cycle, rather than the stepwise transformation mechanism, is highly desirable for several important transformations, i.e., reductive cleavage of the less active aryl bromides and chlorides.[5,6]

Recently Burkhard König et al. reported a significant finding that subsequent excitation of the perylene diimide (PDI) radical anion that formed after a typical PET process enabled the accumulation of sufficient energy for the reduction of inert aryl bromides and chlorides.[7] This consecutive PET (conPET)

process overcomes the current limitation of visible light photoredox catalysis and allows the photocatalytic conversion of less active chemical bonds in organic synthesis. The high planarity of the big conjugated system endows PDIs exceptional chemical, thermal, and optical stabilities in combination with strong visible-light absorption, which are favorable for the applications of this outstanding homogeneous process.[8,9] At the same time, the poor solubility and strong tendency to aggregate of PDIs, caused by their special structural fashion, severely hamper the development of this conPET process on other catalytic transformations. Similar to noble-metal complex-related photocatalytic reactions, heterogenizing organic dyes can be advantageous for the separation and recovery in potential practical applications.[10,11] As metal-organic polymers are fascinating hybrid solids with infinite ordered networks consisting of organic bridging ligands and inorganic nodes, the careful modification of PDI fragment within coordination polymers represents a promising approach to heterogenize these photoconversions especially concerning the conPET process and to overcome these restricts of the homogeneous process.[12,13]

Herein, we reported the successful incorporation and organization of photoactive PDI within metal-organic polymer (Zn-PDI) for the facile creation of aryl radical, a critical intermediate for the meaningful carbon-carbon bond formation, through conPET process (Figure 1). The organized arrangement
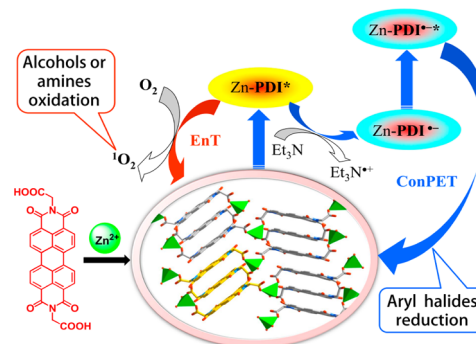

Figure 1. Diagram illustrating the strategy of assembling insoluble PDI into organized arrays in porous solid Zn-PDI to obtain an efficient photocatalyst for the visible-light-driven reduction of aryl halides and oxidation of alcohols and amines.

of PDI J-aggregates provides sufficient active sites, leaves enough space for substrate-catalyst interaction, and decreases self-quenching, making Zn-PDI a better catalyst than its homogeneous counterpart for the significant visible-light-driven reduction of aryl halides. In the meantime, the liver alcohol dehydrogenase (LADH)-mimicked Zn sites render Zn-PDI photoactivity for the efficient oxidation of benzylalcohols and benzylamines under mild reaction condition using dioxygen gas as the oxidizing agent.

The solvothermal reaction of the ligand bis(N-carboxymethyl) peryleneimide (H₂PDI) and Zn(ClO₄)₂·6H₂O in a mixed solvent of DMF and H₂O produced Zn-PDI in a yield of 44%. To the best of our knowledge, Zn-PDI is the first single crystalline perylene-based metal-organic polymer due to the difficulty of PDI assembly from run to run.[14−16] Single-crystal analysis revealed that Zn-PDI crystallized in the monoclinic space group $P2_1/n$. Each zinc ion was coordinated by three monodentate carboxylic groups from three deprotonated PDI ligands and one water molecule. The distorted tetrahedron geometry of Zn with one labile coordinated water molecule, which was forced by the strong $\pi\cdots\pi$ interactions between PDIs, suggested that zinc ions may coordinate to and activate the substrate molecules when the labile water molecules were removed.[17] Each PDI ligand bridged two zinc ions to form brick-wall-like, two-dimensional (2D) networks. Strong $\pi\cdots\pi$ interaction between PDIs was found to connect each three PDI molecules in a group and stabilize the 2D sheets (Figure 2). The parallel aligned PDIs within one group formed J-aggregate as the slip angel θ was calculated to be nearly 44° (the interplanar distances were 3.34−3.36 Å).[18] J-aggregates are of significant interest for organic materials thanks to their excellent ability to delocalize and migrate excitons, which benefits the formation and stabilization of the PDI radical anions in Zn-PDI. The J-aggregates were further organized in a ladder arrangement resulting from the interaction with Zn coordination geometry thus making space for the ingress and egress of fitted substrate and product.

The synergistic effect between metal-PDI coordination and $\pi\cdots\pi$ stacking endows Zn-PDI unique structure benefits and desirable photocatalysis potential. Our visible-light-driven reduction of aryl halides started with 4′-bromoacetophenone. A yield of ∼91% was obtained after 4 h of irradiation with blue LEDs while using 8 equiv of Et₃N. The efficiency of this reduction is highly related to the dose of electron donor. When 72 equiv Et₃N was added, the reduction reached 87% conversion after only 1 h, and Zn-PDI was nearly three times higher in efficiency than its homogeneous counterpart, demonstrating that the formation of coordinated polymer benefits this conPET process. Control experiments showed that light, an oxygen-free atmosphere, and Zn-PDI are all indispensable for the reduction. The nearly identical yields of the pristine and finely ground Zn-PDI catalysis further supported that the coordinated structure was more important than the surface area for the aryl halides reduction. The heterogeneous nature of Zn-PDI catalysis was obvious considering the results of recycle experiments and filtration reaction. The filtrate of the reaction mixture showed only 4% additional conversion rate after another hour of irradiation, indicating that the active species in this reduction is Zn-PDI. The filtrate was also substantially lighter in color compared with the dark-black color of the homogeneous reaction mixture because of the decomposition of H₂PDI. Thus, incorporation into Zn-PDI significantly improved the stability of PDI.

The heterogeneous system of visible-light-mediated conPET catalysis expands its scope with a series of substituted aryl halides under optimal conditions, and the reaction results are listed in
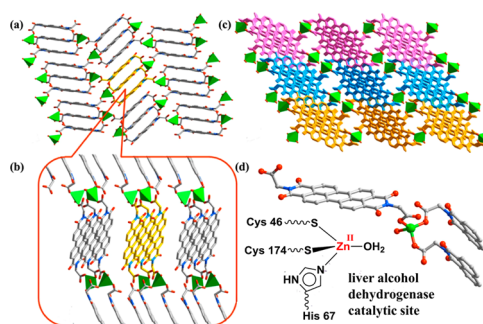

Figure 2. Structural features of Zn-PDI showing (a, b) the parallel stacking pattern of PDI fragments and the space between PDI stacks in a 2D layer and (c) stacking pattern of the 2D layers to create the 3D structure (each layer is shown in one color). (d) The unique distorted tetrahedron coordination environment of Zn ion resembles the active Zn site in LADH. Oxygen, nitrogen, carbon, and zinc atoms are drawn in red, blue, gray, and green, respectively. Hydrogen atoms are omitted for clarity.

Table 1. Photoreduction of Various Aryl Halides by Zn-PDI and C-H Aromatic Substitution with N-Methyl Pyrrole[a]

[a]Reaction conditions: DMF (3 mL), N₂, blue LEDs. Conversion rates were determined by GC areas with internal standards. *Catalyst loading was 10 mol %. For aromatic substitution, the isolated yields were given.

Table 1. The ester group of the aryl bromides potentially blocks the ingress into Zn-PDI, thus resulting in a yield of nearly zero. In contrast, the reduction of the same substrate proceeds well when H₂PDI is used as catalyst, producing a yield of 26%. Notably, the aryl-iodine bond was selectively reduced in the presence of an aryl-bromine bond. More importantly, in addition to the nearly complete reduction of aryl iodides and aryl bromides, even the most inert aryl chlorides were transformed quite effectively, though higher loading of Zn-PDI was needed. Normally, highly air- and moisture-sensitive donor molecules were needed for the photoreduction of inert aryl chlorides, which require UV-A irradiation, strongly basic conditions, and strictly inert reaction conditions that are detrimental for wide application.[6,19] As a highly active, efficient, recyclable, and environmentally benign

photocatalyst with simple workup, Zn-PDI represents a meaningful step toward more efficient solar energy utilization with conPET process.

Since the reduction of aryl halides was confirmed in the heterogeneous system, we then applied the generated reactive aryl radical for carbon-carbon bond formation. N-Methyl pyrrole was used as the trapping agent because of its high affinity for radical species.[20] The amount of electron donor was reduced to 8 equiv to favor the coupling product. Unlike previous work in the literature,[7] this coupling reaction can proceed smoothly in DMF and may benefit from the stronger attraction of the rigid trapping agent N-methyl pyrrole to the large rigid π framework of Zn-PDI compared with Et_3N or DMF.[21] These studied halides exhibited good to excellent performance, even compared with the reported homogeneous catalysis (see Table S4 for detailed comparison), demonstrating the enormous potential of metal-organic polymers for active catalyst immobilization.

To get insight into the reasons for the improved performance of Zn-PDI compared to its homogeneous counterpart, experiments related to the reduction of aryl halides were designed and the results were displayed in Figure S45. With the successive addition of Et_3N, the fluorescence intensity of Zn-PDI decreased drastically, whereas no noticeable change in absorption occurred, suggesting a classical PET process.[22] When a blue LED was used to irradiate the suspension of Zn-PDI with Et_3N under N_2 atmosphere, new absorption bands at ~700, 800, and 950 nm increased steadily, while the original peaks decreased in intensity. Moreover, the three new peaks disappeared slowly when the mixture was exposed to air. This phenomenon is consistent with reports on the radical anion of PDI and clearly demonstrates the stability of this polymer-based anion in the absence of oxygen.[23] Solid-state differential pulse voltammetry of Zn-PDI illustrated the slight but observable movement of reductive peaks compared to H_2PDI that facilitates PDI receiving an electron from the donor.[24] The generated radical anion is more stable than that produced from H_2PDI, thereby increasing the probability of the next PET process. The changes in fluorescence intensity and lifetime upon the addition of the reaction substrate 4′-bromoacetophenone after the introduction of Et_3N were investigated to study the second PET process. The H_2PDI solution was prepared at the same perylene concentration with the Zn-PDI suspension. The self-quenching process was clearly observed in H_2PDI solution when compared the fluorescence intensity with Zn-PDI.[25] Although strong $\pi\cdots\pi$ interactions between perylene rings existed in Zn-PDI, the appropriate space between J-aggregates as well as the rigid framework helped to reduce self-quenching.[26] The broad Zn-PDI emission band at ~640 nm can be assigned to the formation of excimer, as confirmed by the relatively long excimer lifetime of 6.70 ns.[27] Such a long lifetime is favorable for the stabilization of excited states and the reduced PDI$^{\bullet-}$ species.[28] Excimer formation is also found in H_2PDI solution, while its lifetime is clearly shorter, which may be assigned to the fixation effect of rigid polymer. With the addition of Et_3N, both solutions exhibited drastic decreases in intensity and lifetime, revealing that the first PET process proceeded smoothly. The lifetime and intensity of the excimer band in Zn-PDI suspension continued to decrease with the addition of 4′-bromoacetophenone, while all other emission bands increased sharply because of the second PET process. The reasonable explanation for this behavior may be that the rigid compact stacking of perylene possesses a strong attraction to 4′-bromoacetophenone, and as a result, the formation of interacting pairs further shortens the lifetime.[21] The rigid Zn-PDI framework

isolated the active site-PDI but allowed them to be dense at the same time, which may be optimal for electron or energy transfer, thus making Zn-PDI a better catalyst than its homogeneous counterpart.[29]

The organized aggregation of PDI implements the conPET process in heterogeneous catalysis and expands the application range for this versatile functional dye. PDIs are normally thought as reducing agents because they are highly electron-deficient.[8] The incorporation of PDI rendered Zn-PDI the first PDI-based photosensitizer for catalysis oxidation. The $\pi\cdots\pi$ interactions between PDIs drive zinc center to adopt a coordination geometry analogous to that of the active zinc center in LADH,[30] which inspired us to explore the benzyl alcohol oxidation with Zn-PDI. The selective oxidation of benzyl alcohol and its derivatives is a fundamental transformation in the chemical industry, and efforts were made for catalyst functioning under ambient conditions with high efficiency.[31−33] The photooxidation of benzyl alcohol was optimized to perform at 60 °C in acetonitrile (MeCN) with 0.1 mol % dry Zn-PDI, and a turnover number (TON) of ~76 was obtained after 24 h of visible-light irradiation with a normal Xe lamp as light source and dioxygen gas as the oxidized agent (Table 2). Barely Zn salts and H_2PDI or their simple mixture could not

Table 2. Photooxidation of Benzyl Alcohols and Amines by Zn-PDI Due to the Synergistic Interaction Between PDI Stacks and Zn Nods[a]

(1)	(2)	(3)	(4)	(5)	(6) The Designed Bulk Alcohol
76	65	54	48	20	4.7

(7)	(8)	(9)	(10)	(11)	(12) The Designed Bulk Amine
74%	60%	99%	70%	25%	7%

[a]For alcohols or amines oxidation, TONs or conversion rates were determined by featured ^{1}H NMR peak areas or calculated by GC peaks, respectively.

initiate this conversion, demonstrating the significance of structure control. The incapability of fresh Zn-PDI for this oxidation consolidates the vital role of active Zn site.[34] Control experiments, filtrate reaction, and recycle experiments clarified the photocatalytic and heterogeneous nature of this Zn-PDI involved alcohol oxidation. While there are several examples on the photocatalytic oxidation of alcohols to aldehydes under air, most of the systems need additives to achieve efficient catalytic transformation. The Zn-PDI system is prominent because it performs under mild conditions with molecular oxygen as oxidant, avoiding the use of noble-metal and any additives.[31−34] Besides, the efficiency of Zn-PDI (TON of 76) is comparable to the newly reported porphyrin titanium MOF system[35] (TON > 100, and see Table S6 for detailed comparison).

The photooxidation of benzylamines by Zn-PDI was conducted to further test the oxidative capacity with benzylamine as the model substrate. The reaction was performed in mild conditions at room temperature with a normal Xe lamp as light source and air as the oxygen source. The yield was 74% after 4 h of visible light irradiation in MeCN. This is a satisfactory result that is comparable to the Ru(bpy)$_3$$^{2+}$-dopped MOF system (TON 83, see Table S8 for detailed comparison), considering the extremely simple workup compared to previously studied photocatalysts.[36,37] Control experiments and recycle tests clearly revealed the photocatalytic and heterogeneous nature. Using H$_2$PDI as catalyst, <5% conversion was obtained. These results suggest that the formation of Zn-PDI enhanced the catalytic efficiency of PDI and solved the problem arising from the poor solubility. IR spectra of the Zn-PDI impregnated with benzylamine showed a N–H stretching vibration doublet at 3307 and 3241 cm^{-1}. The red shift from 3363 and 3295 cm^{-1} (free benzylamine), respectively, suggested the adsorption and possible activation of benzylamine in the gaps of Zn-PDI.

Mechanism experiments exhibited that the oxidation was stopped in the case of 50 equiv (refer to Zn-PDI) DABCO addition, whereas the addition of the same amount benzoquinone decreased the conversion rate slightly. As DABCO is a well-known ^{1}O$_2$ scavenger and benzoquinone is a radical trap,[38] a singlet oxygen-mediated path is more plausible for the oxidation with Zn-PDI as photosensitizer. In contrast to the smooth reactions of other substituted benzylalcohols and the primary amines, the oxidations of the synthesized bulk alcohol and bulk primary amine obtained lower efficiencies under these reaction conditions. The size selectivity of the substrates suggested that the photocatalytic oxidation reactions occurred in the channel of Zn-PDI. While the primary amines produce imines at moderate to high conversion rates, the performance of secondary amine was quite poor, supporting the hypothesis that Zn plays a vital role in this oxidation reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12931.

Experimental details and data (PDF)
Crystal data (CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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