Zinc porphyrin-based electron donor–acceptor-conjugated microporous polymer for the efficient photocatalytic oxidative coupling of amines under visible light

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Graphical Abstract



Zinc porphyrin-based polymer (ZnTEPP-PBI) has wide optical absorption range. By using ZnTEPP-PBI as the photocatalyst, the oxidative coupling of amines to imines was efficiently realized under visible light.

Abstract:

The application of porous organic polymers is an emerging area of heterogeneous photocatalytic organic synthesis. In principle, the transfer of energy and electrons is significant to improve the photocatalytic efficiency. To obtain an efficient energy- and electron-transfer catalytic system, a porous organic polymer exhibiting both electron donor and electron acceptor properties (ZnTEPP-PBI) was synthesized using zinc porphyrin (ZnTEPP) and perylene bisimide (PBI) monomers as the structural units. Compared with that of ZnTEPP, the optical absorption range of the ZnTEPP-PBI polymer was expanded due to the introduction of the PBI monomer. By using ZnTEPP-PBI as the photocatalyst, the oxidative coupling of amines to imines was efficiently realized under visible light. In addition, a plausible pathway for the mechanism for the enhanced energy and electron transfer was proposed.

Keywords: Porphyrin; Perylene bisimide; Visible light; Amine; Oxidative coupling

1. Introduction

Photocatalysis can not only use solar energy as the light source but also prevent the use of strong oxidants, deleterious reducing agents, and toxic substances [1,2]. Photocatalysis considerably meets the societal requirements in terms of the energy and environment [3]. By optimizing a photocatalytic system, the selective synthesis of target products can be achieved, affording a green, energy-efficient method for organic synthesis [4–6]. Metalloporphyrin exhibits good light-trapping properties, which can

be used as a highly efficient homogeneous photocatalyst [7]. However, porphyrin is prone to oxidation, degradation, or dimerization, leading to deactivation, and its separation and recovery are difficult. Hence, from the practical viewpoint, the preparation of heterogeneous catalysts using porphyrin exhibits more advantages than homogeneous catalysts [8].

Currently, a majority of studies have prepared composite materials from metal porphyrins to achieve heterogeneous catalysis. Typical preparation methods include physical adsorption for the loading of a metalloporphyrins onto molecular sieves or resins or the combination of porphyrin molecules with carriers *via* electrostatic forces, coordination bonds, and covalent bonds [9–11]. However, these methods exhibit some limitations, including low immobilization ability, poor catalytic activity, and poor selectivity. Compared to the use of conventional methods, porous organic polymers prepared using metalloporphyrins as the bonding units can not only enhance their catalytic activity via the increased density of their active centers but also render a "limited effect" on substrates due to their porous structure [12–14]. Notably, the porous inner surface can considerably shorten the transmission distance of the photogenerated electrons and holes and improve the utilization of light [15].

The porphyrin ring is an N-containing conjugated system, which can be used as an electron donor [16], and porphyrin is also considered to be a good photosensitizer for the generation of ${}^{1}O_{2}$ [17]. Perylene bisimide exhibits high thermal stability, photochemical stability, and high electrophilicity. To obtain an efficient photocatalytic system under visible light, catalysts that exhibiting both electron donor and electron

acceptor properties could be favorable for the transfer of energy and electrons.

With this idea in mind, the donor–acceptor (D–A) conjugated polymer ZnTEPP-PBI was synthesized by the Sonogashira coupling using zinc porphyrin and perylene bisimide as the structural units in this study. By the introduction of electron donors and electron acceptors into conjugated polymer chains, the transfer of charge in conjugated polymer molecules can be effectively controlled. The optical properties of the ZnTEPP monomer, PBI, and ZnTEPP-PBI polymer were compared by UV–Vis–NIR absorption spectroscopy, steady-state fluorescence spectroscopy, and theoretical calculations. The results revealed that ZnTEPP-PBI can not only improve the utilization of light and recyclability but also exhibit high catalytic activity and wide substrate scope for the visible-light photocatalytic oxidative coupling of amines. The catalytic system comprises abundant active species ¹O₂ and O₂⁺⁻, forming the "trinity" photocatalytic process of energy transfer, electron transfer, and hole oxidation.

2. Results and discussion

2.1. Photocatalyst synthesis and characterization

In this study, ZnTEPP and PBI were synthesized according to previously reported studies [18,19]. The ZnTEPP and PBI structures were characterized by NMR and MALDI-TOF spectroscopy, respectively (Figure S1–S7). The D–A polymer ZnTEPP-PBI was successfully synthesized by the Sonogashira reaction using ZnTEPP and PBI monomers as the construction units (Scheme 1).

(Scheme 1)

ZnTEPP-PBI was obtained as a dark-purple powder, which was insoluble in a

majority of solvents. The FTIR spectra of PBI and ZnTEPP-PBI revealed a stretching vibration peak of -CH₃ at 2960 cm⁻¹ (Figure 1A). Two characteristic absorption peaks corresponding to R-C=CH were observed at 3293 cm⁻¹ and 2196 cm⁻¹ in the FTIR spectrum of ZnTEPP [18]; however, these two peaks disappeared in the FTIR spectrum of ZnTEPP-PBI, indicating that the ZnTEPP monomer is successfully polymerized by the PBI monomer in the Sonogashira reaction. Figure S8 shows the solid-state ¹³C NMR spectrum. Peaks observed at 20-165 ppm corresponded to the carbon atoms of the porphyrin ring, benzene ring, and PBI [19,20]. In addition, the XPS spectrum of ZnTEPP-PBI revealed peaks corresponding to C 1s, N 1s, O 1s, and Zn 2p (Figure S9-12). The binding energy of Zn $2p_{3/2}$ was reduced, indicating that the electrons in pyrrole N are transferred to the Zn empty orbitals, and the zinc metal center coordinates with porphyrin ligands [21] (Figure 1B). In the XPS spectrum of O 1s, the binding energies of 531.5 eV and 533.2 eV respectively belong to O atoms in the structure of C=O and C-O in PBI (Figure S10). In N 1s XPS spectra, the binding energy appears at 398.3 eV and 400.4 eV (Figure S11), which belong to acylamide N atom in PBI and pyrrole N atom in porphyrin unit.

(Figure 1)

Subsequently, the SEM image clearly revealed that ZnTEPP-PBI mainly comprises microspheres with various sizes ranging from 0.5 to 2 µm in diameter, and the TEM image provides direct evidence for the porosity of ZnTEPP-PBI (Figure S13). This porous structure is favorable for mass transfer [22]. Nitrogen gas adsorption measurements were conducted on pretreated ZnTEPP-PBI at 77 K to investigate the

permanent porosity. Typical type I isotherms were observed in the N₂ adsorption– desorption isotherm. At a low relative pressure ($P/P_0 < 0.01$), the adsorption isotherm revealed a sharp increase in the nitrogen uptake, corresponding to the presence of micropores. The Brunauer–Emmett–Teller surface area (S_{BET}) was 465 m²g⁻¹ with a total pore volume (V_{total}) of 0.20 cm³g⁻¹, indicative of a high surface area and large pore volume (Figure S14). Furthermore, ZnTEPP-PBI exhibited several micropores with diameters of 0.9–1.9 nm according to the nonlocal density functional theory method (Figure S15).

The light-harvesting capability of the samples was investigated by ultraviolet-visiblenear-infrared diffuse reflectance (UV-Vis-NIR DRS) spectroscopy and photoluminescence (PL) spectroscopy. The UV absorption peak of ZnTEPP-PBI was similar to that of ZnTEPP, but the absorption range of ZnTEPP-PBI was expanded due to the introduction of PBI (Figure 2A). Moreover, the UV-Vis-NIR DRS spectrum of ZnTEPP-PBI revealed a significant red-shift compared with that of the ZnTEPP monomer. This shift was related to the extension of the π -conjugated structure, resulting in exceptional light-harvesting capability in the long-wavelength visible region. The bandgap (Eg) of samples was determined from the UV-diffuse reflectance map. The positive slopes of Mott-Schottky plots for ZnTEPP-PBI are consistent with the behavior of a typical n-type semiconductor (Figure S16). According to the UV-Vis-NIR DRS spectrum, the bandgap of ZnTEPP-PBI was 1.83 eV (Figure S17).

The steady-state fluorescence emission spectra of the ZnTEPP monomer, PBI monomer, and ZnTEPP-PBI polymer were recorded. At an excitation wavelength of

470 nm, PBI exhibited a strong fluorescence emission peak at 691 nm (Figure 2B). ZnTEPP exhibited two weak fluorescence emission peaks at 692 nm and 745 nm, respectively. However, fluorescence emission peaks were not observed for ZnTEPP-PBI, which was related to the photoinduced electron-transfer process in ZnTEPPP-PBI. By the photoexcitation of ZnTEPP-PBI, the transfer of electrons occurred between the excited-state electron donor and electron acceptor, and charge-separation products ZnTEPP⁺-PBI⁻ were generated, leading to fluorescence quenching [23].

(Figure 2)

Cyclic voltammetry revealed that there was no oxidation peak in PBI, and the initial oxidation peak of ZnTEPP-PBI was similar to that of ZnTEPP monomer, indicative of the possibly high oxidizing nature of both ZnTEPP-PBI and ZnTEPP (Figures S18). Therefore, the D-A character of the ZnTEPP-PBI polymer is reflected in the ability to separate the electrons and holes produced more effectively by light excitation. The highest occupied molecular orbital (HOMO) of ZnTEPP-PBI is +0.72 V *vs* Ag/Ag⁺ (Figures S18 and S19). The bandgap is the energy difference between the HOMO and the lowest unoccupied molecular orbital (LUMO). Hence, the LUMO is -1.11 V (Figure S20).

2.2. Catalytic performance

By using benzylamine as the model substrate, the selective oxidation of amine to imine catalyzed by ZnTEPP-PBI under the illumination of a white-light-emitting diode (LED) lamp and molecular oxygen was examined. In the control experiment of the photocatalyst, the product was not obtained under the white-LED illumination for 4 h

(entry 1, Table 1). By only using ZnTEPP as the photocatalyst, imines were obtained in 70% yield (entry 2, Table 1). Surprisingly, when heterogeneous ZnTEPP-PBI was used as the photocatalyst, imine was obtained in a 99% yield (entry 3, Table 1). This enhancement was related to the intrinsic properties of the photocatalyst, which exhibits properties of both an electron donor and an electron acceptor after the introduction of PBI. Hence, the transfer of intramolecular electrons occurs easily, leading to the better photoelectric properties of the catalyst than the ZnTEPP monomers [24]. Moreover, a large number of micropores is favorable for the exposure of an increased number of active sites to active molecular oxygen [25]. Clearly, a reaction did not occur when the oxidative coupling of the amine reaction was conducted in the dark or under argon (entries 4 and 5, Table 1, respectively). The apparent quantum yields of N-benzylidene benzylamine at 420, 450, 485, 535, 595, 630 nm were tested. As shown in Figure S21, ZnTEPP-PBI has a wide range of light response. Compared with typical solid photocatalysts such as TiO₂, C₃N₄, BiMoO₆, the target product N-benzylidene benzylamine has a high apparent quantum yield with ZnTEPP-PBI at all wavelengths.

(Table 1)

To evaluate the scope of the photocatalytic system, the oxidative coupling of various primary amines under visible light was investigated by using the ZnTEPP-PBI catalyst (Table 2).

A majority of the amines were smoothly converted to the corresponding imines in high yields (Table 2). The efficiency for the oxidative coupling in this catalytic system was apparently not extremely dependent on the electronic property of the *para*

substituents of the substrate (entries 1–4, Table 2). However, the efficiency is quite different in terms of the electronic property of the *ortho* substituents of the substrate (entries 5–7, Table 2). Compared to the electron-withdrawing groups, electron-donating groups at the *ortho* position were apparently more conducive for the oxidative coupling of amines. The efficiency was improved by prolonging reaction time for the substrate bearing electron-withdrawing groups at the *ortho* position (entry 6, Table 2).

In addition, the catalytic system exhibited high activity for the oxidative coupling of heterocyclic amines (entry 8, Table 2). The steric hindrance of substrates was clearly observed in this photocatalytic system. For example, corresponding imines were obtained in only 53% yield when 1-phenylethanamine was used as the substrate. Prolonged the reaction time to 9 h, the yield of imines could be enhanced to 85% (entry 10, Table 2).

(Table 2)

2.3 Catalyst reuse and stability

The stability of the ZnTEPP-PBI catalyst was monitored by multiple sequential oxidative coupling reactions of benzylamine under visible light. The catalyst was recovered by centrifugation, filtration, washed with acetonitrile, and dried before using it in subsequent runs. Figure 3 shows the results obtained.

(Figure 3)

The results revealed that the photocatalytic activity can be maintained up to the fifth cycle when it was used for the selective oxidation of benzylamine (Figure 3). At the same time, according to the FTIR spectrum of fresh ZnTEPP-PBI and its use after five

recycles (Figure S22), the ZnTEPP-PBI structure did not change significantly, and the zinc active center was still fixed in a strong framework. The results clearly revealed that the photocatalyst is active for the oxidative coupling of benzylamine and can be reused without significant decrease in the catalytic activity and with almost similar selectivity.

2.4 Mechanism consideration

Further experiments were carried out to understand the mechanism for the ZnTEPP-PBI-photocatalyzed oxidative coupling of benzylamine. Figure 4 shows the profile for the oxidative coupling of benzylamine catalyzed by ZnTEPP-PBI under visible light. The conversion of benzylamine slowly increased within the first hour. Then, the reaction rate rapidly increased. Clearly, an induction period in the photocatalytic oxidation system was present. The oxidation of benzylamine revealed features of a radical reaction.

(Figure 4)

Various inhibitors to the oxidative coupling were used; thus, the active species for the reaction system can be indirectly investigated (Table 3). With the addition of KI as a hole inhibitor[4], the yield of the imine decreased to 6% (entry 1, Table 3), possibly due to the reduction of the photogenerated holes, and benzylamine cannot be further oxidized to produce benzylamine cation free radicals. Next, with the addition of β carotene [26] and benzoquinone [27] as inhibitors for ¹O₂ and O₂^{•-}, the yields of imine sharply decreased to only 11% and 22%, respectively (entries 2 and 3, Table 3), indicating that the main active species in the reaction system is ¹O₂ and O₂^{•-}. In addition, the LUMO of ZnTEPP-PBI was -1.11 V vs Ag/Ag⁺, which can also be considered as

theoretical evidence for the activation of molecular oxygen into $O_2^{\bullet-}$ by ZnTEPP-PBI $(O_2/O_2^{\bullet-} = -0.61 \text{ V } vs \text{ Ag/Ag}^+)$ [28]. With the addition of isopropanol as an inhibitor for OH· [4], the yield of the imine was only 16%, indicating that OH· is also an active oxygen species in the ZnTEPP-PBI-photocatalyzed oxidative coupling of benzylamine (entry 4, Table 3).

(Table 3)

Subsequently, electron spin resonance (ESR) was employed for the detection of the reactive oxygen species in the photocatalytic system of ZnTEPP-PBI. 2,2,6,6-Tetramethylpiperidine (TEMP) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were used as the ${}^{1}O_{2}$ and O_{2}^{-} capture agents, respectively [29]. An ${}^{1}O_{2}$ signal was not observed when the reaction was carried out in the dark (Figure 5A). By the exposure of the solution with the ZnTEPP-PBI catalyst to visible light for 3 min, a set of strong 1:1:1 triple peak signal (\bullet) was observed. These triple peaks corresponded to the signal of TEMPO, which was the product from the reaction of ${}^{1}O_{2}$ with TEMP [30,31]. Hence, the presence of ${}^{1}O_{2}$ in the system is verified. However, with the addition of benzylamine to the ZnTEPP-PBI photocatalytic system and exposure to visible light for 3 min, the intensity of the triple peak sharply decreased, indicative of the reaction of ${}^{1}O_{2}$ with benzylamine to obtain imine intermediates.

DMPO was used as the capture agent for O_2^{-} (Figure 5B). When the reaction was conducted in the dark, a signal was not observed. By the irradiation of the solution with the ZnTEPP-PBI mixture under visible light for 3 min, a group of weak quadruple peaks was observed, corresponding to the adduct of O_2^{-} and DMPO [32]. This result

indicated the presence of O_2^{-} in the system. Subsequently, benzylamine was added to the photocatalytic system and irradiated under visible light for 3 min, and the signal of the quadruple peak signal (\bigstar) was significantly enhanced. From the observed phenomenon, photogenerated holes can easily oxidize benzylamine, and the free radical cation of benzylamine is obtained at the same time. This reduction was conducive to the inhibition of the recombination of photogenic hole and photogenic electrons. Accordingly, photogenic electrons can efficiently transfer an increased amount of O₂ to generate O₂⁻⁻.

(Figure 5)

According to the above results obtained from ESR and inhibition experiments, as well as previous studies [5,33,34], the mechanism for the photocatalytic oxidation of benzylamine by ZnTEPP-PBI was proposed (Scheme 2).

Under light irradiation, ZnTEPP-PBI is stimulated by the light absorption energy, and the single excited state containing electron-hole pairs is generated. Benzylamine is oxidized by photogenic holes, affording benzylamine free radical cations, and photogenic electrons are transferred to O₂ to generate O₂^{•-}. In addition, the triple excited states can be obtained by the intersystem crossing of the singlet excited states, and O₂ can be activated by the triplet excited states via energy transfer to obtain $^{1}O_{2}$. O₂^{•-} reacts with benzylamine free radical cations, and $^{1}O_{2}$ reacts with benzylamine. The two reactions produce H₂O₂ and imide intermediates. Then, H₂O₂ will form OH·, which reacts with benzylamine to form an imine intermediate. The imine intermediate further reacts with the benzylamine, affording the target product imine.

(Scheme 2)

3. Conclusion

In summary, a zinc-porphyrin-based porous organic polymer bearing an electron donor and an electron acceptor (ZnTEPP-PBI) was successfully synthesized. Compared with that of ZnTEPP, the optical absorption range of the ZnTEPP-PBI polymer was expanded due to the introduction of the PBI monomer. The heterogeneous photocatalyst was found to be efficient for the oxidative homocoupling of amines to imines under visible light. Various amines including primary and secondary amines were smoothly converted to the corresponding imines in good yield. The catalyst was easily recycled and reused for at least five runs without any clear decrease in the catalytic performance. From emission quenching experiments and ESR tests, molecular oxygen is activated into singlet oxygen ($^{1}O_{2}$) and superoxide radical anion (O_{2}^{-}) via energy transfer and electron transfer, respectively. Particularly, efficient electron transfer occurring between the electron donor and electron acceptor could enhance the photocatalytic activity.

Author Contribution Statement

Xiao-Xuan Guo: Conceptualization, Investigation, Writing-Original Draft Jun Jiang: Conceptualization, Methodology

Qi Han: Software, Data curation

Xiao-Hui Liu: Formal analysis, Visualization

Xian-Tai Zhou: Supervision, Writing-Review & Editing, Funding acquisition

Hong-Bing Ji: Project adminstration, Funding acquisition

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Captions

 Table 1. Photocatalytic oxidative coupling of benzylamine

Table 2. Photocatalytic oxidative coupling of amines into imines by ZnTEPP-PBI

Table 3. Control experiments for the photocatalytic oxidative coupling of benzylamine

Figure 1. (A) FTIR spectra of ZnTEPP, PBI, and ZnTEPP-PBI; (B) Zn 2*p* XPS spectra of ZnTEPP-PBI.

Figure 2. (A) UV-Vis-NIR DRS spectra of ZnTEPP, PBI, and ZnTEPP-PBI; (B) Photoluminescence spectra with an excitation wavelength of 470 nm at 298 K for ZnTEPP, PBI, and ZnTEPP-PBI.

Figure 3. Cycling performance of ZnTEPP-PBI for the oxidative coupling of benzylamine. Benzylamine (1 mmol), ZnTEPP-PBI (3.5 wt%), MeCN (24 mL), O₂ atmosphere (1 atm), white LED lamp (90 mW/cm²), room temperature, 4 h.

Figure 4. Reaction profile for the oxidative coupling of benzylamine. Benzylamine (0.5 mmol), ZnTEPP-PBI (3.5 wt %), MeCN (24 mL), O₂ atmosphere (1 atm), white LED lamp (90 mW/cm²), room temperature, 4 h.

Figure 5. ESR spectra of the samples after mixing (A) TEMP or a (B) DMPO solution with ZnTEPP-PBI and O_2 in the absence or presence of benzylamine in dark under visible-light irradiation or after the addition of benzylamine.

Scheme 1. Structure of ZnTEPP-PBI.

Scheme 2. Proposed mechanism for the oxidative coupling of benzylamine photocatalyzed by ZnTEPP-PBI

	White LED, O ₂		
Entry	Catalyst	Conversion/% ^b	Yield/% ^b
1	-	ND	ND
2	ZnTEPP	70	70
3	ZnTEPP-PBI	>99	>99
4^c	ZnTEPP-PBI	ND	ND
5^d	ZnTEPP-PBI	ND	ND

Table 1. Photocatalytic oxidative coupling of benzylamine^a

ZnTEPP-PBI

^{*a*}Benzylamine (0.5 mmol), catalyst (3.5 wt%), MeCN (24 mL), O₂ atmosphere (1 atm), white LED lamp (90 mW/cm²), room temperature, 4 h.

^bBased on GC–MS analysis.

NH₂

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^cIn the dark.

^d Under argon.

Entry	Substrate	Product	$\operatorname{Yield}^{b}(\%)$
1	CI NH2		93
2	Br NH ₂	Br	99
3	NH ₂		99
4	NH ₂		99
5	€ NH ₂ Br	Br Br	51
6 ^c	€ NH ₂ Br	© CN ^N C Br Br	96
7			99
8	NH ₂		99
9	NH ₂		53
10^{d}	NH ₂		85

Table 2. Photocatalytic oxidative coupling of amines into imines by ZnTEPP-PBI^a

^{*a*}Benzylamine (0.5 mmol), ZnTEPP-PBI (3.5 wt%), MeCN (24 mL), O₂ atmosphere (1 atm), white LED lamp (90 mW/cm²), room temperature, 4 h.

^bBased on GC–MS analysis.

^cReaction time was 7 h.

^dReaction time was 9 h.

NH ₂	ZnTEPP-PBI / Inhibitor		
Entry	Inhibitor	Conversion/% ^b	Yield/% ^b
1	KI	6	6
2	β-carotene	11	11
3	Benzoquinone	22	22
4 ^{<i>c</i>}	Isopropanol	16	16

Table 3 Control experiments for the photocatalytic oxidative coupling of benzylamine^a

^{*a*}Benzylamine (0.5 mmol), ZnTEPP-PBI (3.5 wt%), inhibitor (1 equivalent), MeCN (24 mL), O₂ atmosphere (1 atm), white LED lamp, room temperature, 4 h.

^bBased on GC–MS analysis.

^cIsopropanol as the solvent.



Figure 1. (A) FTIR spectra of ZnTEPP, PBI, and ZnTEPP-PBI; (B) Zn 2*p* XPS spectra of ZnTEPP-PBI.



Figure 2. (A) UV-Vis-NIR DRS spectra of ZnTEPP, PBI, and ZnTEPP-PBI; (B) Photoluminescence spectra with an excitation wavelength of 470 nm at 298 K for ZnTEPP, PBI, and ZnTEPP-PBI.



Figure 3. Cycling performance of ZnTEPP-PBI for the oxidative coupling of benzylamine. Benzylamine (1 mmol), ZnTEPP-PBI (3.5 wt%), MeCN (24 mL), O_2 atmosphere (1 atm), white LED lamp (90 mW/cm²), room temperature, 4 h.



Figure 4. Reaction profile for the oxidative coupling of benzylamine. Benzylamine (0.5 mmol), ZnTEPP-PBI (3.5 wt %), MeCN (24 mL), O_2 atmosphere (1 atm), white LED lamp (90 mW/cm²), room temperature, 4 h.



Figure 5. ESR spectra of the samples after mixing (A) TEMP or a (B) DMPO solution with ZnTEPP-PBI and O_2 in the absence or presence of benzylamine in dark under visible-light irradiation or after the addition of benzylamine.



Scheme 2. Proposed mechanism for the oxidative coupling of benzylamine photocatalyzed by ZnTEPP-PBI