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# Porphyrin-containing Polyimide with Enhanced Light Absorption and Photocatalysis Activity

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**Abstract:** A series of porphyrin-containing polyimide (PI) photocatalysts was synthesized by one-step solvothermal method. Characterization results revealed that porphyrin was uniformly coupled into PI framework through covalent bonding and the visible light absorption was greatly improved. The photodegradation activity of porphyrin-containing PIs for methyl orange (MO) under visible light was enhanced significantly, with highest pseudo-first-order rate constant 35 times more than that of neat porphyrin and 10 times more than that of porphyrin-free PI. The enhancement is mainly attributed to the increased light harvesting accompanied by varied HOMO level, which was clarified by controlled experiments, characterizations and theoretical calculations. This work provides an insight into multiple effects of dye molecules in dye-containing heterogeneous photocatalysts.

## Introduction

In recent decades, photocatalysis has attracted increasing attention because of its great potential in solving serious environmental pollution and energy shortage problems utilizing the cleanest and abundant solar energy. Apart from the traditional inorganic semiconductors like TiO2 and CdS, some polymer semiconductors, such as carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) can also function as photocatalysts for water splitting and degradation of organic pollutants under light irradiation.<sup>[1]</sup> Moreover, organic polymers have several advantages such as free of toxic metal elements, structural tunability, plentiful sources, and low production costs. Polyimides (PIs) are one kind of high performance polymers and have been widely applied in adhesives, resin matrices for composite materials, insulation in electronic industries, gas separation, airplanes and spacecraft.<sup>[2]</sup> However, no investigations of the photocatalytic properties of Pls had been reported until our group developed a Pl

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photocatalyst (PI-TC) based on solid-state thermal condensation of melamine (MA) and pyromellitic dianhydride (PMDA) under 325 °C.<sup>[3]</sup> Although PI-TC possessed moderate activity of photocatalytic hydrogen evolution and degradation of organic dyes, the band gap of PI-TC was relatively wide (2.7 eV) like g-C<sub>3</sub>N<sub>4</sub>, so it mainly absorbed ultraviolet light and the absorption in visible region was weak, which confined its photocatalytic efficiency. So it remains crucial to broaden the light absorption of PI photocatalysts. Apart from MA based PI, Zhao et.al recently reported some PI aerogel based composite photocatalysts: PI(MWCNT) and PI/AgBr@Ag, both exhibiting excellent photocatalytic activity and stability for oxytetracycline degradation, greatly expanding the application of PI in photocatalysis.<sup>[4]</sup>

Recently, our group reported a novel (001) dominated PI photocatalyst (PI-SM) synthesized under solvothermal condition in a mixture of N, N-dimethylformamide (DMF) and ethylene glycol (EG) at 180 °C, with higher photocatalytic hydrogen evolution rate than pristine g-C<sub>3</sub>N<sub>4</sub> and PI-TC.<sup>[5]</sup> Under solvothermal conditions, the chemical composition of PIs can be more easily varied than solid-state thermal condensations under high temperature (> 300 °C), and dye molecules can be employed to enhance the absorption of visible light. Porphyrins are a kind of heterocyclic macrocycle organic dyes with great absorption in visible region, and often used as photosensitizer in dye sensitized solar cells (DSSCs) and photocatalytic systems.<sup>[6]</sup> They can also be used as building blocks of metal organic frameworks and covalent organic frameworks for their unique symmetry, and some materials also have catalytic capability.<sup>[7]</sup> Although porphyrins have been applied in various fields, no studies of porphyrin-containing PI photocatalyst have been reported to the best of our knowledge.

Herein, we report porphyrin-containing PI photocatalysts synthesized via one step solvothermal method. The resulting samples showed significant enhancement in both absorption of visible light and photocatalytic activity comparing to porphyrin monomer or porphyrin-free PI. Various characterization techniques were used to study the optical, structural and morphology properties of prepared samples carefully, and the incorporation of porphyrin into PI framework was confirmed. The degradation activity of methyl orange (MO) on the porphyrin-containing PI under visible light irradiation was evaluated, and the mechanism of degradation was also explored. Moreover, the roles of the porphyrin, the band structure of the photocatalysts and the enhancement of photo activity were investigated, discussed and clarified by combining experimental results and theoretical studies.

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Scheme 1. Schematic representation of the synthesis of Porphyrin-containing Pls.

## **Results and Discussion**

#### **Characterizations of PI samples**

A series of porphyrin-containing PIs samples (PI-X) was synthesized via a one-step solvothermal method according to modified literature procedure (Scheme 1),<sup>[5]</sup> using mesotetrakis(4-aminophenyl)porphyrin (TAPP) as the source of porphyrin, and the X changed from 1 to 5 presenting an increasing amount of porphyrin in the samples (0, 0.1, 0.5, 1.0, and 2.0 mole % of amines in reactants, respectively, and details can be seen in experimental section and Table S1). Figure 1 displays the UV-vis diffuse reflection spectra (DRS) and the color photo (inset) of PI samples, combined with UV-vis absorption spectrum of TAPP in chloroform. TAPP in chloroform has one Soret band centered at 428 nm and four Q bands at 655, 596, 564 and 524 nm, respectively.<sup>[8]</sup> The porphyrin-free PI-1 has a strong absorption band in UV region with absorption onset below 400 nm, and a much weak broadened peak in 400 to 520 nm. The light yellow PI-1 cannot absorb light at wavelengths longer than 520 nm, while the porphyrin-containing PI samples have much stronger absorption in the whole visible region (400 to 750 nm). The absorption in visible region of PI-2 to PI-5 can be ascribed to porphyrin contained, because these bands correspond well to the characteristic absorption bands of TAPP in chloroform, and these bands also become significantly stronger with increasing amount of TAPP, while the color of samples turns from yellow-green to dark brown. In the meantime, the absorption spectra of porphyrin-containing PI samples are not simply overlap of porphyrin-free PI and TAPP. Comparing to TAPP in chloroform, the absorption bands of porphyrin in the PI samples redshift slightly and broaden evidently, and the  $I_{\rm Q}/I_{\rm Soret}$ increases distinctly, suggesting the reaction of TAPP and PMDA



Figure 1. UV-vis diffuse reflection spectra of PI samples and UV-vis absorption spectrum of TAPP in CHCl<sub>3</sub>. The inset is a photo of PI samples. Note that the unit of  $F(R \infty)$  (left) and absorption (right) is not comparable.

extended the conjugated system and greatly enhanced the light absorption capability of porphyrins. In addition, the adsorption of TAPP on the surface of PI can be excluded because samples were washed thoroughly. Neat TAPP is readily soluble in various organic solvents including chloroform, dichloromethane, DMF, ethanol and acetone with high molar absorbance (log  $\varepsilon$  = 5.55 at 421 nm in benzene, 5.31 at 428 nm in dichloromethane)<sup>[9]</sup> and appears distinct color (yellow when very dilute, wine red when concentrated), while in the synthetic procedure, the resultant samples were filtered and washed thoroughly with ethanol and acetone until the filtrate was colorless, indicating that the adsorbed TAPP was removed completely from the surface of PI. These results confirm that the TAPP moieties in PI sample are exactly linked to the imide frameworks through covalent coupling and can no longer be removed.

The formation of imide bonds was confirmed by FT-IR spectra (Figure 2). The spectra of all PI samples are almost the same,



Figure 2. FT-IR spectra of PI samples.

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indicating that the chemical bonds and molecular structure varied little with small amount of porphyrin (less than 2.0 mole %). The bands at 1733, 1780 (shoulder) and 730 cm<sup>-1</sup> are assigned to the symmetric stretching, asymmetric stretching, and bending vibrations of the imide carbonyl groups, respectively.<sup>[10]</sup> The band at 1374 cm<sup>-1</sup> is attributed to the C-N-C stretching vibration of the imide ring.<sup>[10]</sup> There are also strong bands at 1546 cm<sup>-1</sup> and 1448 cm<sup>-1</sup> corresponding to the quadrant and semicircle stretching of triazine ring, respectively,<sup>[11]</sup> demonstrating the successful condensation of MA and PMDA and the formation of imide structure. The bands around 3200 - 3500 cm<sup>-1</sup> are assigned to N-H and O-H vibrations. Furthermore, it's worth noting that the peak at 3444 cm<sup>-1</sup> of PI-5 is weaker than peaks of other samples, which is consistent with the highest amount of TAPP and lowest amount of MA in the reactants of PI-5.

The crystallinity of PI samples was determined by powder Xray diffraction (PXRD) analysis (Figure 3(a)). All samples are crystalline and have several distinct diffraction peaks of PI,<sup>[5]</sup> and no new peaks relative to the diffraction of crystal TAPP can be observed (Figure S2), indicating that TAPP coupled into the framework of PI. When the amount of TAPP was low (0.1 mole %), the peak intensity of PI-2 remained the same as PI-1, indicating that very small amount of TAPP could be tolerated in



Figure 3. (a) PXRD patterns of PI samples, and (b) optimized imide model calculated by B3LYP/6-311g(d) method. The carbon atoms are grey, nitrogen atoms are blue, hydrogen atoms are white and oxygen atoms are red.

the framework of PI, and did not significantly decrease the crystallinity of PI. However, with higher TAPP concentration of 0.5 and 1.0 mole %, the intensity of peak at around  $2\theta = 27.7^{\circ}$  (d = 0.32 nm) assigned to interplanar facets (001) became weak quickly in the spectra of the samples.<sup>[5]</sup> Interestingly, the XRD pattern of PI-5 with concentration of 2.0 mole % is different. The crystallinity of PI-5 is apparently the lowest, and the peak at 14.4° appears with several peaks vanish, indicating the variation of crystal structure. These changes are probably due to the significant differences in size and topology between TAPP and MA (Figure 3b). MA is a kind of trigonal building block with 0.46 nm distance between two amine nitrogen atoms  $(d_1)$ , while TAPP is square and the distance between diagonal amine nitrogen atoms  $(d_2)$  is 1.84 nm, according to density functional theory (DFT) simulations. In addition, the DFT calculated dihedral angle between triazine ring and pyromellitic ring ( $\varphi_1$ ) is as large as 50 degrees, while that between porphyrin ring and pyromellitic ring ( $\varphi_2$ ) is about 25 degrees and much smaller than the former. As a result, introducing large amount of TAPP would naturally break the structure order of MA-PI frameworks and form new structure order. Based on structural charaterization and DFT calculation results, chemical bonds or short range order of PIs are given in Scheme 1 and Fig. 3(b). But the complete structure (the position of all atoms) of PI was too complex to be solved, because the XRD patterns didn't provide sufficient information of the position of all atoms in the crystal cell, and we tried several different crystal models of PI, each having tens of atoms in unit cell, but none of the simulated XRD agreed well with the experimental results. After introducing porphyrin, the complexity of structure of PI was greatly increased because the geometry of porphyrin was much different from MA. Since the complete structures of the materials was too complex to be determined, only the unit structure of PI was given in Scheme 1 and Fig. 3(b).

The chemical states of PI samples were further measured by X-ray photoelectron spectroscopy (XPS) and shown in Figure 4. The binding energies of the elements were analysed by referring to PMDA-ODA PI (ODA-PI) and g-C<sub>3</sub>N<sub>4</sub>.<sup>[12]</sup> The C 1s peak at 285.6 eV which was assigned to phenyl ring (C=C) of pyromellitic diimide was used to calibrate the binding energies,<sup>[12a]</sup> because the commonly used adventitious carbon at 284.6 eV could not act as reference here since it was too small and not isolate in raw spectrum. Other two C 1s peaks of PI-1 at 288.4 eV and 289.6 eV were ascribed to the carbon atoms in the triazine rings (C=N), $^{[12b]}$  and the imide carbonyl groups (C=O), $^{[12a]}$ respectively. For PI-3, the C 1s peaks of phenyl rings (285.6 eV) and triazine rings (288.4 eV) were identical to those of PI-1, while the peak at 284.6 eV was slightly larger and the peak of carbonyl groups shifted toward lower binding energy at 289.3 eV. This is attributed to the introduce of TAPP, since most carbon atoms of porphyrin have low oxidation states and low binding energies at around 284.5 eV.[13] Meanwhile, the TAPP-PMDA system is similar to ODA-PI system because amino groups in both ODA and TAPP are linked to benzene ring, and the imide carbonyl groups have lower binding energy in the reference ODA-PI system (288.6 eV).[12a] However amino groups in melamine are linked to electron withdrawing triazine ring, so the

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binding energy of imide carbonyl carbon would be higher for the MA-PI system. The three N 1s peaks of PI-1 at 399.2, 400.4 and 401.6 eV were assigned to nitrogen atoms in the triazine rings (C=N),<sup>[12b]</sup> imide nitrogen (C-N-C),<sup>[12a]</sup> and unreacted amino groups (C-NH<sub>x</sub>),<sup>[12b]</sup> respectively. The N 1s peaks of PI-3 is almost identical to those of PI-1, while the peak of imide nitrogen shifted to slightly lower position at 400.3 eV, and the area proportion of imide nitrogen to triazine nitrogen was increased a little, which can also be interpreted as the incorporation of TAPP and its replacement of melamine. The N 1s peaks of porphyrin could not be separated due to low concentration and overlap.<sup>[13]</sup> A detailed comparison of XPS binding energies of our samples and the three reference systems (ODA-PI, <sup>[12a]</sup> g-C<sub>3</sub>N<sub>4</sub><sup>[12b]</sup> and TAPP<sup>[13]</sup>) are listed in Table S2 in the supporting information.



Figure 4. (a) C 1s and (b) N 1s XPS spectra of PI-1 and PI-3.

Moreover, the <sup>13</sup>C solid-state NMR spectroscopy (Figure S3) provided further information of the structure of PIs. The spectra of PI-1 and PI-3 are very similar, which is consistent with FT-IR, XRD and XPS results. The signal at 172 ppm can be ascribed to the imide carbonyl groups (C=O), and the peak at 165 ppm can be correlated to carbons in triazine rings, while the resonance at 138 and 119 ppm can be attributed to carbon atoms in the phenyl ring which are adjacent to the carbonyl groups, and C-H

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aromatic carbons of the phenyl ring, respectively, so the PI structure is further confirmed by these results.<sup>[3a]</sup> Some slight differences can be observed in the spectra of PI-3 (117, 153 and 159 ppm), which was inferred as aromatic carbons of porphyrin.<sup>[7b]</sup> In summary, the XPS and <sup>13</sup>C NMR results provide further evidence of the PI structure and the influence of introducing porphyrin.

The layered structure of PI samples was confirmed by morphology characterizations. Figure 5 shows the SEM and TEM images of PI-1 and PI-3 samples. Both samples have very similar sheet-like morphology and the sheets stacked into particles with size of several micrometers to tens of micrometers,<sup>[5]</sup> and the sizes of sheets and aggregations of both samples are not obviously different. This suggests that small amount of TAPP didn't have too much influence on the polymerization of PI, which is consistent with the retaining of XRD patterns.



Figure 5. SEM images of (a, c) PI-1 and (b, d) PI-3, and TEM images of (e) PI-1 and (f) PI-3.

Furthermore, the attempt of finding porphyrin of PI-3 under high resolution TEM (HRTEM) was not successful (Figure S4). No special spots with size near  $1 \times 1 \text{ nm}^2$ , which is the size of porphyrin ring, can be seen in the HRTEM image. This result is reasonable because both PI and porphyrins are organic compounds containing same elements (C, H and N) and they cannot be distinguished well under electron microscope, unlike metal particles on organic materials.

Based on the above characterization results, including the similarity and differences in light absorption between porphyrin in the PIs and TAPP, the differences in XPS spectra and solid-state NMR spectra, and the change in crystal structure, the porphyrin in the PIs could be deduced as uniformly coupled into

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PI framework through covalent bonding. Moreover, the nucleophilicity of MA is weaker than normal aromatic amine due to strong electron withdrawing nature of triazine group,<sup>[14]</sup> so TAPP has higher chemical reactivity and should react with PMDA ahead of MA. This hypothesis is not easy to verify, but we prepared a sample with only TAPP and PMDA under the solvothermal condition, and there are distinct imide bands (1722 cm<sup>-1</sup>, 1776 cm<sup>-1</sup>, 1369 cm<sup>-1</sup> and 730 cm<sup>-1</sup>) in its IR spectrum (Figure S5),<sup>[10]</sup> suggesting no difficulty in the reaction of TAPP and PMDA. In the meantime, the molar concentration of TAPP is much lower than MA as well as PMDA, so porphyrin imide (or amic-acid) molecules should formed and dispersed in the reaction solution, before the polymerization of MA-PI framework, and thus porphyrin blocks could finally incorporated and dispersed well in the PI framework. Based on the above evidence and reasoning, we can definitely confirm that TAPP was successfully transformed into porphyrin-containing PI.

#### **Photocatalytic activities**



**Figure 6.** (a) Time course of degradation of MO and (b) the corresponding kinetic fitting curves in the presence of different catalysts under visible light irradiation ( $\lambda > 420$  nm). MO means no catalyst added.

The photocatalytic activities of PI samples were evaluated by the degradation of MO in aqueous solution (4 mg  $L^{-1}$ ) under visible

light ( $\lambda$  > 420 nm) and shown in Figure 6(a). The decreases of concentration of MO before illumination were due to the adsorption of MO on the surface of catalysts, which is very common in all degradation experiments employing heterogeneous catalysts. From various tests, the apparent adsorption of MO on PIs were typically 0.01~0.04 C/C<sub>0</sub> in our experiment setup (100 mg catalysts in 100 ml 4 mg L<sup>-1</sup> MO solution), while the adsorption of MO on TAPP sample was obviously greater, and the reason we supposed was that the surface -NH<sub>2</sub> groups of TAPP would partly turn into -NH<sub>3</sub><sup>+</sup> due to alkalinity, and MO is anionic dye (benzenesulfonate) so there would be coulombic attraction between MO and TAPP. It can be seen that the photolysis of MO under visible light irradiation was negligible (< 1 %) in the absence of photocatalyst, and the porphyrin-free PI-1 showed moderate activity (21 % degradation in 8 h). TAPP was however the weakest photocatalyst with only 5 % of MO decomposed after 8 h light irradiation, suggesting that TAPP had the potential of photocatalysis, yet some modification was required to improve its performance. In this test TAPP was heterogeneous photocatalyst just like other photocatalysts used in this article because TAPP is insoluble in pure water and the MO solution used. For porphyrin-containing PI samples, as the amount of porphyrin increased from 0.1 to 2.0 mole %, the degradation activity rose first to 50 % (PI-2) and 84 % (PI-3), and fell later to 46 % (PI-4) and 47 % (PI-5), yet all porphyrin containing samples surpassed PI-1. The PI-3 sample with porphyrin amount of 0.5 mole % had highest activity with 84% degradation in 8 h, which was 4 times of that of PI-1, and PI-3 showed negligible activity in dark (Figure S6), indicating that the decomposition of MO on the sample was indeed driven by visible light. Moreover, the activity of PI-1 was higher than PI-TC synthesized via thermal condensation (Figure S6), and PI-TC was much surpassed by PI-3, indicating the advantage of solvothermal synthesized PIs against PI-TC. Solvothermal synthesized PIs not only have higher activity than PI-TC, but also allow the introduction of dyes which can further improve activity, while dyes cannot be applied in high-temprature thermal condensation due to carbonization. As plotted in Figure 6(b), there is a good linear correlation between  $-\ln(c/c_0)$  and reaction time (t), indicating that the degradation reaction follows pseudofirst-order kinetics. The calculated pseudo-first-order rate constant k of PI-3 is 0.283 h<sup>-1</sup>, more than 35 times of that of TAPP (0.008 h<sup>-1</sup>) and more than 11 times of that of PI-1 (0.024 h<sup>-1</sup>), suggesting that the transforming TAPP into porphyrincontaining PI can greatly promote the photodegradation of MO. In the following sections, some control experiments and theoretical studies will be introduced to shed light on the photodegradation mechanism and the roles of porphyrin.

Besides the photocatalytic activity test, the stability and recyclability of the PI-3 sample was evaluated by repeating the photodegradation test of MO for 4 cycles. After each cycle, the sample was filtered, washed and dried for next cycle. As illustrated in Figure 7, PI-3 remained most of its degradation activity, and the slight decrease in photocatalytic performance was mainly due to the loss of catalyst during sampling, repeated recovering and filtering processes because of the adhering of sample on wall of vessels, centrifuge tubes and filter

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membranes. Besides, no obvious change was observed in the FTIR and XRD spectra of recovered sample after use for 32 hours (Figure S7), indicating that the sample didn't undergo obvious hydrolysis and the crystal structure was not destroyed. In brief, the stability of the catalyst was relative good.



Figure 7. Cycle runs for the degradation of MO over PI-3 under visible light ( $\lambda$  > 420 nm).

The interaction between PI and porphyrin was measured by photoluminescence (PL) spectroscopy and electrochemical impedance spectroscopy (EIS). As shown in Figure 8(a), a strong PL peak at 513 nm can be observed for PI-1 when excited at 425 nm, and the PL intensity greatly decreased after introducing little amount of porphyrin (0.1 mole %, PI-2), and further decreased with increased amount of porphyrin (0.5 mole %, PI-3), indicating efficient energy transfer between PI and porphyrin. Furthermore, no obvious PL peak of porphyrin can be observed, and since porphyrin has stronger absorption of light than PI in UV-vis spectra, especially at around 425 nm (Figure 1), it can be deduced that the quantum yield of fluorescence of porphyrin in PI is much lower than even pristine PI, which is different from TAPP in solvents where it has strong fluorescence.<sup>[15]</sup> The EIS Nyquist plots (Figure 8b) of PI-1 and PI-3 are almost identical, indicating that the electronic resistance of PI in the non-photoexcited state was nearly unchanged after introducing porphyrin. Since porphyrin molecule is not conductive and it doesn't bear electric charge, it further suggests that porphyrin was dispersed well in the PI framework, rather than aggregated into a new phase and formed a heterojunction with PL

To further investigate the photocatalytic mechanism of PIs and the roles of porphyrin, several control experiments were conducted to determine the active species, including purging N<sub>2</sub> and adding various scavengers into the photodegradation system, and shown in Figure 9. It can be deduced that O<sub>2</sub><sup>-</sup> played the most important role in the photoreaction for both PI-1 and PI-3 since the activity dropped significantly after purging N<sub>2</sub> or adding p-benzoquinone (BQ) as O<sub>2</sub><sup>-</sup> scavenger. Generally,



Figure 8. (a) PL spectra of PI-1, PI-2 and PI-3, excited at 425 nm and (b) EIS Nyquist plots of PI-1 and PI-3.

 $O_2^{*}$  is formed via the reduction of  $O_2$  by photogenerated electrons,<sup>[1b,10b]</sup> so we infer that the photodegradation of MO was mainly driven by photogenerated electrons for both PI-1 and PI-3. However, adding hole scavenger KI instead promoted the photoreaction for both samples. This can be explained by the fact that hole scavenger can reduce the recombination of photogenerated holes and electrons by consuming holes, thus helping generate more electrons.<sup>[16]</sup> It can also be inferred that the consumption of holes was slower and less efficient than that of electrons. In addition, adding OH' scavenger isopropanol (IPA) showed almost no change in activity of PI-3, indicating that OH' did not contribute much to the photodegradation. However the activity of PI-1 increased when adding OH' scavenger IPA or tert-butanol (t-BuOH) (Figure 9 (a)), and the activities were just very close to adding hole scavenger KI. In our opinion, IPA and t-BuOH here were oxidized by photogenerated holes of PI-1, playing the roles of hole scavenger instead of normally OH' scavenger. This result can prove the stronger oxidation ability of holes of PI-1 than that of PI-3. In addition, O2 - could be further reduced to form H<sub>2</sub>O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> was confirmed with PI-3 in pure water under visible light ( $\lambda > 420 \text{ nm}$ ) by DPD-POD colorimetric method (Figure S8).<sup>[17]</sup> Since sacrificial agents already suggested that the reduction pathway dominated, while the

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**Figure 9.** Controlled experiments of photocatalytic degradation of MO over (a) PI-1 and (b) PI-3 under visible light ( $\lambda > 420$  nm). For the BQ line, the concentrations and its errors of MO were estimated values due to the interference of BQ and its derivatives.

oxidation ability of PI was not very strong, and O<sub>2</sub> was critical in degradation process, the oxidation pathway for the generation of H<sub>2</sub>O<sub>2</sub> was not taken into consideration due to high potential of water oxidation. Thus the detected H<sub>2</sub>O<sub>2</sub> further suggests that O2<sup>-</sup> contributed in the photodegradation process. These control experiments demonstrated that the incorporation of porphyrin not only enhance the light absorption, but also changed the energy levels of PI. The thermodynamic driving force of holes for oxidation was sacrificed after introducing TAPP, as it was the side effect of the narrowed band gap and extended absorption range, yet holes could still fulfil MO degradation, and the overall degradation rate was improved significantly at low porphyrin concentration. In summary, O2 mainly contributed to the degradation of MO, while photogenerated holes were less effective, and introducing porphyrin further weakened the oxidation capability of holes.

To further clarify the difference between porphyrin-containing PI and porphyrin-free PI, DFT calculations were performed. Figure 10 shows HOMO and LUMO energy levels vs vacuum of some optimized imide models calculated by DFT methods under B3LYP/6-311g(d) level. Some other model molecules were calculated as well and shown in Figure S9, and all HOMO and LUMO data are listed in Table 1. For all imide models, the

LUMOs are always located at pyromellitic part, while HOMOs at amine moieties.<sup>[3]</sup> The LUMO energy level of porphyrin imide (-3.85 eV vs vacuum for TAPP-4PMDA) is similar to melamine imide (-3.71 eV for 3MA-3PMDA-L, -3.79 eV for 3MA-3PMDA-T), while the HOMO energy level of porphyrin imide (-5.65 eV for TAPP-4PMDA) is more than 1.0 eV higher than melamine imide (-6.99 eV for 3MA-3PMDA-L, -7.03 eV for 3MA-3PMDA-T), mainly due to the highest HOMO energy level of TAPP (-4.70 eV). It is worth noting that the HOMO energy level of porphyrin



Figure 10. HOMO and LUMO energy levels and corresponding molecular orbitals of some optimized models calculated under B3LYP/6-311g(d) level.

 $\label{eq:constraint} \begin{array}{l} \textbf{Table 1.} \ \mbox{Calculated HOMO and LUMO Energies (B3LYP/6-311G(d)) for All Studied Model Compounds.} \end{array}$ 

molecule	HOMO (eV)	LUMO (eV)
1MA-2PMDA	-7.83	-3.82
2MA-1PMDA	-6.89	-3.07
2MA-2PMDA	-7.01	-3.69
2MA-3PMDA	-7.10	-3.91
3MA-3PMDA-L	-6.99	-3.71
3MA-3PMDA-T	-7.03	-3.79
ТАРР	-4.70	-2.10
TAPP-1PMDA	-4.92	-3.67
TAPP-2PMDA-C	-5.19	-3.72
TAPP-2PMDA-T	-5.15	-3.73
TAPP-3PMDA	-5.19	-3.80
TAPP-4PMDA	-5.65	-3.85
MA-P-TAPP	-4.84	-3.19

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imide is always lower than TAPP, and decrease as the number of coupled PMDA increase, due to the electron withdrawing nature of PMDA.<sup>[18]</sup> In addition, when the imide model molecule MA-P-TAPP contains both TAPP and MA, the HOMO is located at porphyrin ring rather than triazine, and the HOMO energy level (-4.84 eV) is close to that of TAPP-1PMDA model (-4.92 eV), thus the porphyrin block can act as traps of holes, and the hole generated in MA-PI could firstly transfer to porphyrin blocks and then participate in photo oxidation reaction. This transferring was supported by control experiments using IPA, because it can be speculated that if the transferring was not happening, the holes in MA-PI of PI-3 would still oxidize IPA and the overall degradation rate should increase like PI-1, which is contrary to the experiment results.

It can be inferred from DFT calculations that TAPP has highest HOMO energy level and lowest photo oxidation ability which would limit its photocatalytic activity. Also, holes of melamine imide have higher photo oxidation capability than that of porphyrin imide, while the difference of reduction ability of electrons is not obvious, in agreement with photodegradation experiments. To further verify these inferences, we prepared TAPP coated PI samples through physical mixing and tested their degradation abilities (Figure 11). The mass fractions of TAPP were chosen after careful calculation described in supporting information. Intriguingly, all samples showed negative apparent kinetic order: the initial degradation rate was very low, and the activity gradually increased as the reaction proceeded. PI-1 coated with 0.5 wt% TAPP (denoted as 0.5-PI-C) showed even less overall degradation rate than PI-1 while the degradation rate in the 8th hour was somewhat higher than PI-1. Increasing loading amount of TAPP to 1.0 wt% (denoted as 1.0-PI-C) further decreased the degradation activity, while decreasing the coating amount to 0.1 wt% (denoted as 0.1-PI-C) resulted in shorter induction period, and the final activity obviously surpassed PI-1. It can be inferred that the TAPP adsorbed on MA-PI surface couldn't photosensitize PI to accelerate the degradation of MO but obstruct the photo reaction. In the meantime, TAPP which is prone to oxidation due to its aniline moieties and high HOMO level as DFT calculated, could



**Figure 11.** Time course of degradation of MO in the presence of TAPP coated PI catalysts under visible light irradiation ( $\lambda > 420$  nm).

be oxidized by holes of PI. In other words, TAPP could be "slightly photodegraded" ahead of MO, and its oxidized form would have lower HOMO level, thus could photosensitize PI and finally accelerate the photo degradation of MO. In the aforementioned porphyrin-containing PI system, reacting with PMDA can similarly lowered the HOMO level of TAPP according to DFT studies, so the porphyrin-containing PI samples exhibited high activity, no induction period and normal apparent reaction kinetics, and the formation of covalent bond between TAPP and MA-PI can also reduce the dissolution and loss of porphyrin, killing two birds with one stone. Therefore although the TAPPcoated PIs and porphyrin-containing PIs showed different profiles in the photodegradation tests, same rule was followed that the energy level of dye molecules can strongly affect energy transportation and finally the photocatalytic activity.

Since the aforementioned DFT calculations cannot completely reflect the band structure of the photocatalyst, the actual band structure of PI-1 and PI-3 were further measured by cyclic voltammetry (CV) and valence band X-ray photoelectron spectroscopy (VBXPS). According to CV experiments in anhydrous acetonitrile (Figure S10(a and b)), the conduction band minimum (CBM) and valence band maximum (VBM) of PI-1 is -1.63 and +1.41 V vs. Fc/Fc<sup>+</sup>, which equals -1.00 and +2.04 V vs NHE as the potential of ferrocene is 0.63V vs NHE.<sup>[19]</sup> with the bandgap of 3.04 eV roughly in agreement with the absorption onset (about 400 nm) of the main peak in UV-vis spectrum. PI-3 has similar band structure and its CBM and VBM is -1.65 and +1.39 V vs. Fc/Fc<sup>+</sup> or -1.02 and +2.02 V vs NHE, respectively, and slightly more negative than PI-1. This slight shift in the CBM and VBM would not have much influence in the thermodynamic driving force, and this shift could be inferred as the influence of incorporated porphyrin. It can also be seen that there are some slight fluctuations from 0.2 V to 1.2 V vs Fc/Fc<sup>+</sup> for PI-3 (Figure S10(c)), which are absent for PI-1 and blank control. These small fluctuations could be speculated as the contribution of several occupied molecular orbitals of incorporated porphyrin. The first fluctuation at around 0.3 V vs Fc/Fc<sup>+</sup> was reckoned as near the HOMO of incorporated porphyrin, since its gap to CBM is near 2.0 V, roughly in agreement with Q1 band at 670 nm in UV-vis spectra (Figure 1). Although the precise HOMO level of incorporated porphyrin was not easy to be determined, the CV results suggest that HOMO level of incorporated porphyrin locate more than 1 eV higher than the VBM of MA-PI, which is in agreement with DFT calculations, and further provide evidence that the porphyrin imide can trap the holes generated in main band of MA-PI. No similar fluctuation was observed in cathode region, suggesting that incorporated porphyrin did not introduce impurity levels obviously below CBM, which is also consistent with DFT results. The binding energies of both PI-1 and PI-3 are both 2.8 eV from the VBXPS spectra (Figure S10(d)), so the fermi level of both samples are approximately -0.8 V vs NHE. The binding energy (2.8 eV) is close to the band gap (3.04 eV) and more than half of the band gap, so the samples are considered as n-type semiconductors. Combining these findings with VBXPS and CV, the experimental band structures of PI-1 and PI-3 were determined and shown in Figure 12.

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Figure 12. Band structures of PI-1 and PI-3 from CV and VBXPS experiments. The olive line which indicates HOMO of incorporated porphyrins in PI-3 is not accurate in energy level.

From both experiments and theoretical calculations, we can speculate that MO degradation was mainly contributed by O2, while h<sup>+</sup> is a less effective active species and a limiting factor. The visible light absorption of porphyrin-containing PI was enhanced compared to TAPP monomer and porphyrin-free PI, which benefits photocatalytic activity. Coupling TAPP with PI not only enhanced light absorption, but also lowered the HOMO level of porphyrin, thus significantly improved the photo oxidation ability and overall photocatalytic activity. Yet the HOMO level of porphyrin imide is still much higher than porphyrin-free PI, so the porphyrin blocks could act as traps of holes, and the photo oxidation ability of holes were reduced compared to porphyrinfree PI. If holes could not be consumed quickly due to low thermodynamic driving force, the generation rate of electrons would be limited and the overall photoreaction rate would be affected, which partially explained the weak photocatalytic activity of TAPP, PI-4 and PI-5. PI samples with high porphyrin amount may suffer from this weakness as well as the decreasing of crystallinity and polymerization degree which come from the geometrical differences of TAPP and MA, and high crystallinity and polymerization degree has been shown beneficial to photocatalytic activity for PIs, g-C<sub>3</sub>N<sub>4</sub> and covalent triazine frameworks in previous works.[10a,12b,20] This could provide another reason why PI-4 and PI-5 showed less activity than PI-3, even though the formers have much stronger absorption of visible light.

Based on the above discussion, a simple diagram (Scheme 2) was presented to concisely describe the photodegradation mechanism in the porphyrin-containing PI system. The porphyrin-containing PI absorbs photons under visible light irradiation, generating electrons and holes. The excited electrons located at pyromellitic moieties will react with  $O_2$  to form active  $O_2$  radicals, and  $O_2^-$  then oxidize MO into oxidation products, which contribute mainly to the degradation of MO. Holes can be simultaneously generated on both triazine and porphyrin blocks, and due to the difference in the HOMO energy levels, the holes located at triazine ring transfer to porphyrin moieties, and then take part in the degradation process. The holes played less effective role in the degradation process

because the higher HOMO level of porphyrin cost the thermodynamic driving force of holes and limit the photo oxidation ability.



Scheme 2. Schematic representation of MO degradation mechanism in the Porphyrin-containing PI system.

#### Conclusions

In summary, we successfully synthesized porphyrin-containing PI photocatalysts by one step solvothermal method. The porphyrin-containing PIs showed significant enhancement in the absorption of visible light and the photocatalytic degradation of MO comparing to both TAPP and porphyrin-free PI. The sample with optimum mole ratio of TAPP at around 0.5 mole % showed highest activity. The porphyrin-containing PIs have lowered HOMO energy level than TAPP monomer, enhanced its photo oxidation ability. In turn, high concentration of porphyrin will cost thermodynamic driving force of holes for oxidation, crystallinity and polymerization degree, which are unfavorable in photocatalytic reactions. The degradation of MO was mainly driven by O2<sup>-</sup> via photo reduction pathway for porphyrincontaining Pls, and photogenerated holes were less effective and limited the activity as a side effect of narrower band gap and extended light absorption.

## **Experimental Section**

#### Materials

All chemicals unless otherwise stated, were used as received without further purification. Melamine (MA) was purchased from TCI Shanghai Chemical Reagent Co., Ltd. Pyromellitic dianhydride (PMDA), 4nitrobenzaldehyde and propionic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Pyrrole was obtained from Sinopharm Chemical Reagent Co., Ltd. Pyrrole was obtained from Sinopharm Chemical Reagent Co., Ltd. and distilled under reduced pressure before use. Propionic anhydride was purchased from Shanghai Aladdin Biochem Technology Co., Ltd. All other starting materials and solvents were obtained from Nanjing Chemical Reagent Co., Ltd. Meso-tetrakis(4aminophenyl)porphyrin (TAPP) was prepared according to modified literature procedures,<sup>[9a,21]</sup> and synthetic details are described in supporting information.

#### Synthesis of the photocatalysts

Porphyrin-containing PIs or porphyrin-free PIs were synthesized via a one-step solvothermal method according to modified literature procedure

(Scheme 1).  $^{\left[ 5\right] }$  The amount of the reactants used to prepare samples are listed in Table S1. Typically, for the synthesis of PI-2 (0.1 mole % TAPP of amine in reactants), a 50 ml PTFE liner with a magnetic stir bar was charged with 3.27 g PMDA, 0.009 g TAPP·6HCl, 15 ml of DMF and 5 ml of EG, and after PMDA was dissolved, then 1.26 g MA was slowly added under vigorous stirring, and 9.8 µl triethylamine (TEA) was added at last. The liner was purged with N2, and a clear solution was obtained after stirring for 10 mins, the stir bar was taken away and the liner was sealed and put into a stainless steel autoclave. The autoclave was then heated at 180 °C for 48 h in an oven. The resultant solid was filtered, washed with small amount of DMF, and then washed thoroughly with ethanol. water and acetone until the filtrate is colorless. The filter cake was then dried at 100 °C for 12 h. The resultant sample was ground into fine powder and denoted as PI-2. In the same way, a series of PI-X samples was prepared for which X changed from 1 to 5 presenting an increasing amount of porphyrin in the samples (0, 0.1, 0.5, 1.0, and 2.0 mole % of amines in reactants, respectively, see Table S1). To compare chemical reaction and physical mixing, porphyrin-coated PI samples were synthesized via impregnation method. Typically, 0.200 g of PI-1 samples were added into a solution of acetone containing different amounts of TAPP (0.2 mg, 1.0 mg or 2.0 mg), stirred overnight and dried at 80 °C. The products were grinded into fine powder and denoted as 0.1-PI-C, 0.5-PI-C and 1.0-PI-C, in which the mass fraction of TAPP was 0.1 wt%, 0.5 wt% and 1.0 wt%, respectively. PI-TC sample was synthesized by thermal condensation of PMDA and MA according to literature for comparison.<sup>[3]</sup> 1.26 g MA and 2.18 g PMDA (both 10 mmol) were mixed uniformly in an agate mortar, then transferred into a porcelain crucible with a cover, and heated in a tube furnace with a heating rate of 7 °C min<sup>-1</sup> up to 325 °C and kept for 4 h. The resultant light yellow solid were grinded into fine powder and denoted as PI-TC.

#### Characterization

UV-vis absorption spectra of solution samples were measured on a Shimadzu UV-1750 spectrometer with 1 cm cuvettes and pure solvents as reference. UV-vis diffuse reflection spectra (DRS) of solid samples was recorded on a Shimadzu UV-2600 spectrometer using  $BaSO_4$  as reference, with 10 mg sample for each test. The original reflection was transformed using Kubelka-Munk function. Fourier transformed infrared (FT-IR) spectra were recorded on a Nicolet NEXUS870 spectrometer using KBr pellets. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance employing Cu K  $\alpha$  radiation, from 20 = 3.0° to 60° with 0.02° increment and 0.1 sec per step. The scanning electron microscope (SEM) images were recorded on a Hitachi S-3400N II system. The transmission electron microscope (TEM) images were obtained on a JEM-2100 electron microscope. <sup>1</sup>H NMR data was collected on a Bruker ARX-400 (400 MHz) spectrometer in CDCl<sub>3</sub>. X-ray photoelectron spectroscopy (XPS) and valence band XPS (VBXPS) measurements were performed on a PHI 5000 Versa Probe X-ray photoelectron spectrometer. Photoluminescence spectroscopy was performed on a Hitachi F-7000 fluorescence spectrophotometer at room temperature with an excitation wavelength of 425 nm. Solid state <sup>13</sup>C magic-angle spinning (MAS) NMR experiments were performed on a 9.4 T Bruker Avance III spectrometer with a 4.0 mm MAS probe operating at 100.6 MHz at room temperature.

#### **Photocatalytic Test**

The activities of the samples for photocatalytic degradation of MO were measured in a Pyrex top-irradiation reactor. The temperature of the system was kept at 25 °C by constant-temperature circulating water. Typically, 100 mg of catalyst sample was added to a 100 mL aqueous solution of MO (4 mg L<sup>-1</sup>, 0.012 mM). The suspension was magnetically stirred in the dark for 1 h prior to irradiation in order to reach adsorption

equilibrium. A 300 W Xenon lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300, with a PerkinElmer PE300BF type light bulb) equipped with a cutoff filter ( $\lambda$  > 420 nm) was used as light source. The light intensity at 450±10 nm was ca. 10.0 mW cm<sup>-2</sup>, at 550±10 nm was ca. 11.4 mW cm<sup>-2</sup>, measured with Newport Model 1918-R power meter with 918D-UV-OD3R detector and monochromatic filter, and the exposure area was about 50 cm<sup>2</sup>. At the given time intervals, a reaction mixture (3-4 mL) was collected, then centrifuged and filtered through a 0.45  $\,\mu m$  filter membrane, and the filtrate was analyzed by measuring its absorbance at 464 nm (maximal of MO) with a Shimadzu UV-1750 spectrometer. For the recyclability test, the photodegradation test of the sample was repeated for 4 times, and after each test, the sample was collected, filtered, washed with water and then dried for use in the next cycle. The control experiments for mechanism studies were measured under similar conditions, while using a smaller reactor with 40 mg of catalyst sample and 40 ml solution of MO (4 mg L<sup>-1</sup>) under same light source described above, and in the presence of scavengers: 10 mM KI; 0.5 mM benzoguinone (BQ); 10mM isopropanol (IPA); 10mM t-butanol (t-BuOH); or N2-purged condition. In the BQ experiments, the absorbance of MO and its errors were estimated due to the interference of BQ and its derivatives. In the N2-purging experiments, the gas flow was started 30 min ahead of dark period, and kept at a rate of 200 mL min<sup>-1</sup> until the test finished. To determine the existence of H<sub>2</sub>O<sub>2</sub>, catalyst sample was added into pure water and illuminated ( $\lambda$  > 420 nm), and the collected filtrate analyzed through UV-vis after DPD (N,N-diethyl-pwas phenylenediamine) and POD (horseradish peroxidase) was added.<sup>[17b]</sup>

#### Electrochemical analysis

The cyclic voltammetry experiments were performed on a CHI-660E electrochemical workstation (Shanghai Chenhua, China) with three electrodes: a Pt plate working electrode (CHI102, 2 mm in diameter), a Aq/Aq<sup>+</sup> reference electrode and a Pt wire counter electrode. The supporting electrolyte solution was 0.1 mol L<sup>-1</sup> tetrabutylammonium hexafluorophosphate (TBAPF $_6$ ) in acetonitrile. To prepare working electrode, 10 mg sample was dispersed in 2 mL of isopropanol containing 0.5 mg of Nafion by sonication to get a suspension, and then 7 µL of suspension was drop-cast onto a pre-cleaned Pt electrode and dried at RT. The ferrocenium/ferrocene (Fc/Fc<sup>+</sup>) couple was used as internal standard in each experiment. The background was recorded using a pre-cleaned Pt working electrode. All solutions were degassed by bubbling high-purity argon for 15 min before measurements. The electrochemical impedance spectroscopy (EIS) was performed on the same electrochemical workstation with a different three-electrode system. SCE and Pt wire were used as reference electrode and counter electrode, respectively. The working electrode was a modified indium tin oxide (ITO) glass and prepared by drop-coating 200 µL of above-mentioned kind of suspension onto the precleaned ITO surface (ca. 1×1 cm<sup>2</sup>), and dried at 110 °C for 2 h. Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 mol L<sup>-1</sup>) was used as supporting electrolyte. EIS plots were obtained at premeasured open circuit potential, with the frequency ranging from 100 kHz to 0.01 Hz and the perturbation potential of 5 mV.

#### **Density Functional Theory (DFT) Calculations**

All calculations were performed with GAUSSIAN 09 program.<sup>[22]</sup> The geometries of all the model molecules were optimized under B3LYP/6-311g(d) level. The visualization of all model molecules and molecular orbitals (HOMO and LUMO) were accomplished by the Gaussview program based on the optimized results. The energy values of the molecular orbitals were taken from the Gaussian output file (in "Population analysis using the SCF density" section, HOMO is the last "Alpha occ. eigenvalues", and LUMO is the first "Alpha virt. Eigenvalues") and the unit was converted from Hartree to eV.

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**Keywords:** photocatalysis • polyimide • porphyrinoids • degradation • density functional calculations

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## Entry for the Table of Contents (Please choose one layout)

Layout 1:

# FULL PAPER

A series of porphyrin-containing polyimide (PI) photocatalysts was synthesized by one-step solvothermal method. The photodegradation activity for methyl orange (MO) under visible light was enhanced significantly, which is mainly attributed to the increased light harvesting accompanied by varied HOMO level, and clarified by experimental results and theoretical studies.



Zhiwei Cui, Jun Zhou, Teng liu, Yicong Wang, Yue Hu, Ying Wang\*, Zhigang Zou

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Porphyrin-containing Polyimide with Enhanced Light Absorption and Photocatalysis Activity