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HIPE Polymerization Materials Functionalized with Iodic-BODIPY on the Surface as Porous Heterogeneous Visible-light Photocatalysts

Wenliang Li+,[a,d,e] Leijiao Li+,[c] Guihua Cui*[a] Yu Bai,[a] Xiao Xiao,[a] Yuxin Li,[d] Lesan Yan*[b]

Abstract: High internal phase emulsion polymerization (PolyHIPE) material, with iodine-functionalized Boron-dipyrromethene (iodic-BODIPY) immobilized on its surface, composes a porous heterogeneous organic photocatalyst (iodic-BODIPY-PolyHIPE). It shows high catalytic efficiency on the selective oxidation reaction of aromatic sulphides under visible light. Over 99% substrates were converted to sulfoxide. No sulfones, the peroxidation products of sulphides, were founded. Most importantly, iodic-BODIPY-PolyHIPE shows > 1.6 fold reaction rate compared to the previous non-inorganic heterogeneous photocatalysts.

Heterogeneous catalysis refers to a kind of catalysis in which the phase of the catalyst differs from that of the reactants. Heterogeneous catalysts are easily separated from the product after the reaction. Many inorganic materials, such as silica gels,[1] sepiolites,[2] zeolites,[3] carbon nanotubes,[4] and mesoporous titanium dioxide[5] have been used extensively as photocatalyst supports. A big disadvantage of these materials, however, is that for many inorganic supports there are no available functional groups on the surface. Active catalysts are typically loaded by physical adsorption, thus it is difficult to control the contents of catalysts. Moreover, the catalyst may remain in the solution by desorption, making the separation a big concern. To create new high-porosity materials, a new method, HIPE polymerization, is in development.[6] These porous materials are attractive candidates as catalyst supports because of their unique tunable architecture.[7] In our previous work, HIPE polymerization of styrylated active BODIPY moieties, styrene, and divinylbenzene was used to develop another novel porous heterogeneous photocatalyst (Short for PHP5).[8] The active photocatalysts were chemically attached to the polystyrene backbone and were thus available to the substrate molecules. This heterogeneous photocatalyst showed high photocatalytic efficiency in the oxidation of sulfides as well as high photostability under visible light. However, the reaction rate (>60 hours to consume all the thioanisole) was disappointing due to the heterogeneous nature of the photocatalyst and the limited availability of the BODIPY species on the surface.

BODIPY compounds have been recognized as a group of outstanding dyes due to their excellent characteristics such as high fluorescence quantum yields, large molar absorption coefficients, and most importantly, excellent thermal and photochemical stability both in solution and in solid states.[9] Because of their impressive qualities, we have focused on BODIPY-based photocatalysts and proved that BODIPYs are a category of effective, alternative organic photocatalysts.[10] Recently, we reported for the first time that the use of iodine-functionalized BODIPY achieved higher photocatalytic efficiency and faster reaction rates (it is enough to complete the reaction in 3 hours) in the oxidation of sulfides under visible light (Supporting information, Figure S1), since fluorophores carrying heavy atoms generally have high intersystem crossing quantum yield (Φ_{isc}) and high singlet oxygen quantum yield (Φ_{Δ}) due to the heavy atom effect.[11] In the meantime, Zhao and co-works produced iodo-BODIPY immobilized on porous silica as an efficient photocatalyst for photoredox catalytic organic reaction.[5b] More recently, Patra's group developed a series of porous organic polymers incorporating BODIPY moiety and explored its application as photocatalyst on the oxidation reaction of thioanisole within 24 h under visible light.[12] Liras' group reported the synthesis of CMPBDP, a conjugated microporous polymer based on halogen-free BODIPY moiety. The material was used as heterogeneous photocatalyst for the oxidation of thioanisole and it took 24 hours to completely consume the substrate.[13] All of these results suggesting that BODIPY based photocatalyst are useful on the oxidation of sulphides, but the reaction rate is still far from our expectation.

In light of the above results, a novel porous heterogeneous photocatalyst, iodic-BODIPY-PolyHIPE, as shown in Scheme 1, was prepared by attaching the iodic-BODIPY moieties onto the inner surface of the PolyHIPE porous matrix via the click reaction. Iodic-BODIPY-PolyHIPE can work under visible-light irradiation with high stability and excellent catalytic efficiency for the selective oxidation reaction of sulfides. More importantly, to the best of our knowledge, the reaction rate for sulfides selective oxidation is the fastest compared to those of previously reported non-inorganic heterogeneous materials.

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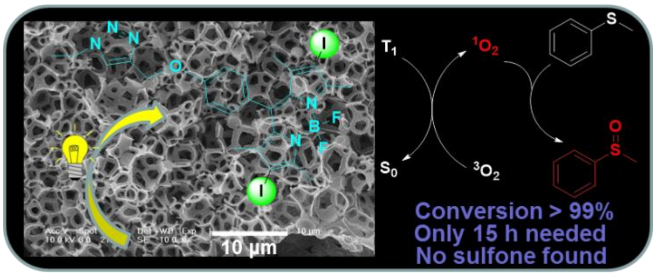
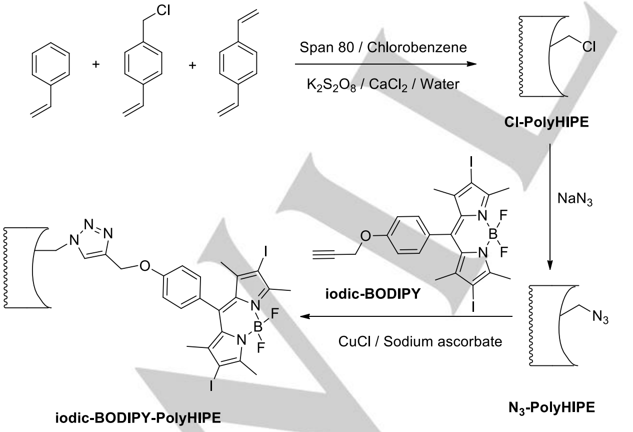


Scheme 1. Iodic-BODIPY-PolyHIPE and its application in photocatalyzed sulfide oxidation.

The HIPE polymerization procedure used to obtain highly porous materials was adopted from our previous report.[8] The organic phase consisted of vinylbenzyl chloride, styrene, and divinylbenzene. The Span 80 was added to the organic phase (0.3 mL/mL) as a surfactant for emulsion formation. The inner phase was an aqueous solution of $CaCl_2$ (~1 wt%) and $K_2S_2O_8$ (~0.2 wt%). Its volume percent was 90% in the emulsion system. After HIPE polymerization, Cl-PolyHIPE, a highly tough monolithic material was obtained. Azide functioned N_3-PolyHIPE was prepared from the reaction of Cl-PolyHIPE and sodium azide. To conjugate with N_3-PolyHIPE, iodic-BODIPY, an active moiety with an alkyne group and two iodine atoms was synthesised as previously described (Figure S2 in supporting information).[14] Finally, iodic-BODIPY-PolyHIPE, a porous heterogeneous organic photocatalyst with iodic-BODIPY moieties on the surface, was prepared by “click” reaction between N_3-PolyHIPE and iodic-BODIPY (Scheme 2). Since HIPE material has been proved to be an effective catalyst surpport, and iodine functionalized BODIPY has been recognized as a better photocatalyst with higher singlet oxygen generation quantum yields than halogen-free BODIPY, the iodic-BODIPY-PolyHIPE, should be no doubt an excellent heterogeneous photocatalyst by combining both of the advantages.



Scheme 2. Preparation of iodic-BODIPY-PolyHIPE.

As shown in Fig. 1A, iodic-BODIPY-PolyHIPE is in the form of dark red powder. It exhibits a bright red fluorescence emission excited with a 6 W UV lamp (λ_{ex} = 365 nm, Fig. 1B).

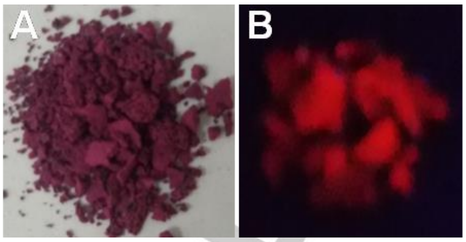


Figure 1. Photographs of iodic-BODIPY-PolyHIPE. (A) Photograph in dry solid state under typical ambient light. (B) Fluorescence emission photograph in solid state excited with a 6 W UV lamp (λex = 365 nm).

Fig. 2A shows typical SEM image of iodic-BODIPY-PolyHIPE, revealing its interconnected porous structure. It is full of fairly large cavities separated by thin walls. There are many small holes in the walls to promote interconnection between adjacent cavities. The big cavities correspond to the inner aqueous phase and the walls correspond to the continuous phase before HIPE polymerization. Formation of these small holes is due to volume contraction of the cavity walls during polymerization and subsequent solvent extraction.[15] The biggest cavities have a diameter of ca. 9 µm while the interconnecting pores are ca. 1.3 µm in diameter. The average cavity size of iodic-BODIPY-PolyHIPE is ca. 4.5 µm in diameter (Figure 2B) and the surface area is 230 m^2g^{-1}, as measured by mercury intrusion porosimetry. Thus, the porosity was calculated to be 77%, which is a little lower than what we estimated (~90%, as mentioned above). This is likely due to the damage of the emulsion during polymerization process or the collapse of HIPE architecture during the reaction process of attaching the iodic-BODIPY dyes.

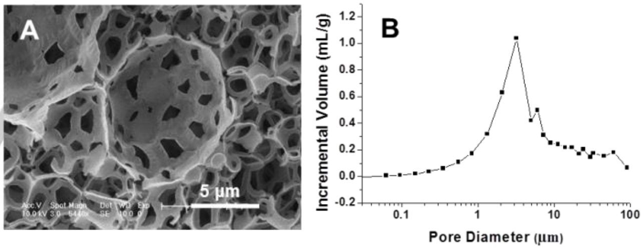


Figure 2. (A) Typical SEM image of iodic-BODIPY-PolyHIPE. (B) Pore size distribution of iodic-BODIPY-PolyHIPE measured by mercury intrusion porosimetry.

The UV-visible diffuse reflectance spectra (DRS) showed that iodic-BODIPY-PolyHIPE and iodic-BODIPY have similar absorption (Fig. 3A), confirming the presence of iodic-BODIPY moieties on the surface of PolyHIPE material. In the FTIR spectrum (Fig. 3B), the v_{N3} bands at 2100 cm^{-1} are greatly weakened after the “click” reaction, demonstrating that the azide groups were consumed. All the above results indicated that iodic-BODIPY moieties were successfully attached to the surface of PolyHIPE materials, and provided convincing evidences for the potential photoactivity of iodic-BODIPY-PolyHIPE in the solid state.

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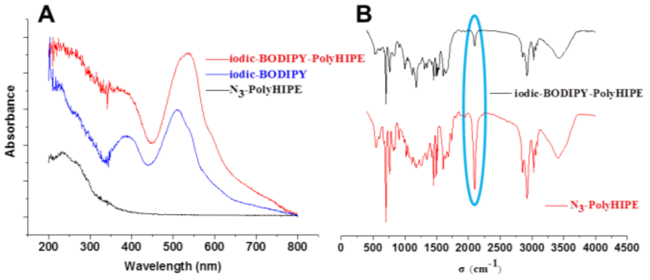


Figure 3 (A) UV-vis DRS spectra of iodic-BODIPY-PolyHIPE, iodic-BODIPY and N_3-PolyHIPE. (B) FTIR spectra of iodic-BODIPY-PolyHIPE and N_3-PolyHIPE.

The iodic-BODIPY content on the surface of iodic-BODIPY-PolyHIPE was determined by elemental analysis (CHN). The nitrogen contents of N_3-PolyHIPE and iodic-BODIPY-PolyHIPE are 5.69 wt% and 4.64 wt%, respectively. According to its molecular formula, the nitrogen content in iodic-BODIPY is 4.45 wt%. Thus, the iodic-BODIPY content in PolyHIPE material was calculated to be 15.32% (w/w).

This active iodic-BODIPY content is much higher than that of our previously prepared PHP5 (6.5 wt% in halogen-free BODIPY).[8] In addition, the iodic-BODIPY was immobilized on the surface of PolyHIPE materials, not distributed in the skeleton of HIPE materials as PHP5 did. Therefore, we are convinced that iodic-BODIPY-HIPE will give better performance in photocatalyzed oxidation reaction.

To assess the photo-catalysis capability of iodic-BODIPY-PolyHIPE, the photocatalyzed sulfide oxidation reaction was performed in freshly distilled methanol at room temperature with no additives. The sulfide concentration was about 3.2% (v/v). Iodic-BODIPY-PolyHIPE was pulverized to a size of *ca*. 1 mm and was suspended in methanol at a concentration of *ca*. 5.6 mg/mL under stirring. A 24 W household fluorescent lamp with a highpass filter (λ = 395 nm) was used as the visible light source (400 ~ 700 nm).

Figure 4 shows the kinetic processes for iodic-BODIPY-PolyHIPE catalyzed sulfide oxidation reaction. It took only 15 h for all the thioanisoles to be converted into methyl phenyl sulfoxides. No sulfone was detected, suggesting the high selectivity of this reaction. We have also expanded the scope of substrates for the reaction under the catalysis of iodic-BODIPY-PolyHIPE in 15 h (Table 1, entries 2-5). Compared to PHP5 in 60 h, iodic-BODIPY-PolyHIPE showed a faster reaction rate and higher conversion in general.

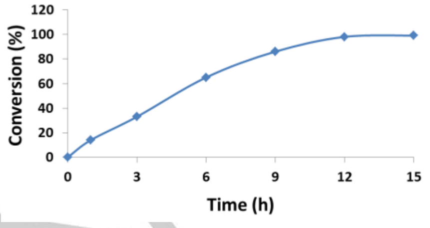
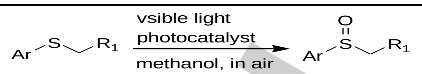


Figure 4. The conversion of thioanisole as a function of reaction time photocatalyzed by the iodic-BODIPY-PolyHIPE under visible light from a 24 W fluorescent lamp.

Table 1. Photocatalytic oxidation of sulfides.[a]

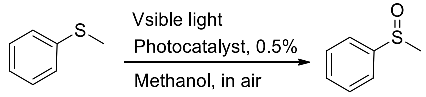


Entry	Ar	R_1	Conversion (%)[b]	
			iodic-BODIPY-PolyHIPE/15 h	PHP5/60 h
1	Ph	H	>99	>99
2	4-MeC_6H_4	H	91	92
3	4-ClC_6H_4	H	>99	92
4	2-ClC_6H_4	H	81	55
5	Ph	Me	60	77

[a] All the reactions were run at room temperature. [b] Conversions were determined by ^{1}H NMR.

To give a perspective view on the reaction efficiency and the reaction rate of the iodic-BODIPY-PolyHIPE catalyst, a comparative study with the catalysts developed in Zhang's group (B-(Boc-CB)$_2$-BT) and our group (PHP5) has been summarized in Table 2. PhBDP-2I, a small molecular BODIPY dye, shows the highest reaction rate. It took only 3 h to complete the reaction with all of thioanisole converted to methyl phenyl sulfoxide (Entry 1, Table 2). In contrast, PhBDP, another small molecular BODIPY dye without iodine atoms, took 24 h to achieve the same effect (Entry 2, Table 2). Within the same time (3 h), only 33% of thioanisole was converted to methyl phenyl sulfoxide with iodic-BODIPY-PolyHIPE as the catalyst (Figure 1). It is reasonable that the reaction rate with iodic-BODIPY-PolyHIPE is slower than that with PhBDP-2I due to the heterogeneity in the case of iodic-BODIPY-PolyHIPE. However, iodic-BODIPY-PolyHIPE showed the fastest reaction rate in all of the heterogeneous catalysts. Reaction with 0.5 mol % of iodic-BODIPY-PolyHIPE photocatalyst in methanol yields more than 99% of product after 15 h (entry 3, Table 2), which is 4-fold faster than PHP5 in the same reaction conditions (entry4, Table 2) and 1.6-fold faster than B-(Boc-CB)$_2$-BT (entry 5, Table 2), respectively.

Table 2. Photocatalytic oxidation of thioanisole at room temperature.



Entry	Catalyst	Conversion (%) [a]	Time (h)
1	PhBDP-2I [b][11]	>99	3
2	PhBDP [b][11]	>99	24
3	iodic-BODIPY-PolyHIPE	>99	15
4	PHP5 [b][8]	>99	60
5	B-(Boc-CB)$_2$-BT [b][16]	99	24

[a] Conversions were determined by ^{1}H NMR. [b] The compounds have been named as published papers.

The recyclability of iodic-BODIPY-PolyHIPE was measured by thioanisole oxidation reaction driven by visible light. The photocatalytic activity can be maintained within 30 hours. After that, the conversion went down dramatically (Supporting information, Figure S8) as a result of the collapse of PolyHIPE architecture and/or the photobleaching of BODIPY dyes. To get a better understanding of the photocatalytic nature in the photocatalytic oxidation reaction of thioanisole, a series of control experiments were carried out. The reaction showed no conversion of the thioanisole, either in the absence of iodic-BODIPY-PolyHIPE or in the dark (Supporting information, table S2, entries 1 and 2). Moreover, only 2% thioanisole was converted to methyl phenyl sulfoxide when the reaction was carried out under N_2 protection (Table S2, entry 3 in supporting information). In addition, the evolution of a middle reaction was also monitored (Supporting information, Figure S9). The catalyst was removed at 7.5 h and the reaction was performed without catalyst for 5 hours. During this period, there was no increase in conversion of thioanisole. After that, iodic-BODIPY-PolyHIPE was re-added and irritated with visible light for another 7.5 h. At the end of the reaction, all the substrates were consumed. These results revealed that illumination, photocatalyst, and oxygen are essential for this reaction to take place.

In summary, iodic-BODIPY photocatalysts were immobilized on the surface of PolyHIPE materials by click chemistry. The porous heterogeneous photocatalyst, iodic-BODIPY-HIPE, demonstrated high photocatalytic activity, excellent selectivity and a reaction rate at least > 1.6 times faster than other organic heterogeneous photocatalysts in sulfide oxidation reaction. This simple strategy could open the door for designing new HIPE-based porous heterogeneous catalysts to increase reaction rates and will bring benefits to the future catalytic industry.

Experimental Section

Preparation of Cl-PolyHIPE

To prepare Cl-PolyHIPE by HIPE polymerization, the following steps were performed: (1) Preparation of the organic phase: In a three-necked round bottomed flask equipped with a mechanical stirrer and a dropping funnel, followed by addition of vinylbenzyl chloride (4.75 mL), styrene (4.75 mL), divinylbenzene (0.5 mL) and span 80 (3.0 mL). The solution was stirred at 400 rpm and purged with argon for 20 min at room temperature; (2) Preparation of the high internal phase emulsion: potassium persulfate (0.2 g) and calcium chloride (1.0 g) were dissolved in 90 mL water, which was purged with argon for 20 min. The volume ratio of the aqueous phase to organic phase was 9 : 1. The aqueous phase was placed in the dropping funnel and added dropwise to the organic phase. After complete addition of the $K_2S_2O_8$/$CaCl_2$/water solution, the emulsion was kept stirring for additional 5 min; (3) Polymerization of the emulsion: After stirring, the emulsion was immediately transferred into a polyethylene bottle, the neck of the bottle was covered with a polyethylene film to reduce evaporative losses. The bottle was placed in an oven at 60 ^{o}C for 24 h. (4) Washing the reaction product: After this period the polyethylene bottle was cut away from the reaction product. The product was then exhaustively extracted with hot ethanol to remove the water and residual organic compounds.[17] Finally, the product was dried under vacuum at room temperature to give Cl-PolyHIPE as a white monolithic material.

Preparation of N_3-PolyHIPE

Cl-PolyHIPE (2.0 g) was suspended in DMF (40 mL) in a 100 mL round bottomed flask. Sodium azide (1.0 g, 15.1 mmol) was added to the solution. Then, the mixtures were stirred at 80 ^{o}C overnight. After that, the white product was purified by a thorough washing with hot water and ethanol successively to give N_3-PolyHIPE.

Preparation of iodic-BODIPY-PolyHIPE

In a 100 mL round bottomed flask were added N_3-PolyHIPE (100 mg), iodic-BODIPY (82 mg, 0.13 mmol), sodium ascorbate (52 mg, 0.26 mmol) and dissolved in dry DMF (40 mL). The solution was purged with argon for 15 min. To the mixture was then added CuCl (9.9 mg, 0.1 mmol) and the reaction mixture was stirred under argon atmosphere at 70 ^{o}C for 12 h. After completion of the reaction, the solid product was filtered and washed with hot water and ethanol to remove the unreacted iodic-BODIPY. Iodic-BODIPY-PolyHIPE was obtained as a dark red porous material.

Sulfide oxidation catalyzed by iodic-BODIPY-PolyHIPE

Take oxidation of thioanisole as an example: To a flame-dried 10 mL vial equipped with a magnetic stir bar were added iodic-BODIPY-PolyHIPE (10.28 mg, containing iodic-BODIPY 2.5 μmol, 0.005 equiv) catalyst, thioanisole (62 μL, 0.5 mmol, 1.0 equiv), and dried methanol (0.5 mL). A 24 W household fluorescent light bulb with a highpass filter (λ = 395 nm) was used as the visible light source. The reaction mixture was stirred at room temperature in air at a distance of *ca.* 5 cm from the lamp (the irradiance is about 17.5 W/m^2 for the distance). After the reaction was completed, the iodic-BODIPY-PolyHIPE was then removed by centrifugation and the supernatant was collected. The reaction mixture was subjected to ^{1}H NMR test, and the integrated area ratio between the ^{1}H NMR peaks of the substrate and product was used to calculate the conversion yields.

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Keywords: HIPE polymerization • iodic-BODIPY • heterogeneous materials • photocatalysts • the oxidation of sulfides

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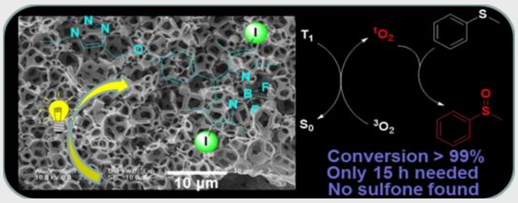

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Only 15 h needed
No sulfone found

A novel porous heterogeneous photocatalyst, prepared from the surface functionalization of high internal phase emulsion polymerization (PolyHIPE) materials, demonstrated high photocatalytic activity, excellent selectivity and fast reaction rate.

Wenliang Li, Leijiao Li, Guihua Cui, Yu Bai, Xiao Xiao, Yuxin Li, Lesan Yan**

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HIPE Polymerization Materials Functionalized with Iodic-BODIPY on the Surface as Porous Heterogeneous Visible-light Photocatalysts