W Very Important Publication

Bandgap Engineering of Conjugated Nanoporous Poly-benzobisthiadiazoles *via* Copolymerization for Enhanced Photocatalytic 1,2,3,4-Tetrahydroquinoline Synthesis under Visible Light

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Abstract: Conveniently combining properties such as high interfacial surface area, excellent visible light absorption and semiconductor-range bandgap, conjugated nanoporous polymer networks are promising candidates as pure organic, metal-free, visible light-responsive and heterogeneous photocatalysts. Here, a facile yet precise bandgap engineering strategy to achieve fine justification of the valence and conduction band positions of a series of nanoporous polymers to optimally bracket the redox potential of the targeted individual photoredox reaction via copolymerization of the electronwithdrawing benzobisthiadiazole moieties into the polymer network backbone is presented. The enhanced photocatalytic activity of the nanoporous polymer networks was demonstrated in the synthesis of 1,2,3,4-tetrahydroquinoline, an important motif in pharmaceutical compounds, via photooxidative cyclization of N,N-dimethylanilines with maleimides.

Keywords: bandgap engineering; conjugated nanoporous polymers; metal-free process; photocatalysis; tetrahydroquinolines

Sunlight, as a clean and inexhaustible source of renewable energy, has inspired tremendous efforts from material scientists to harvest, convert, store and utilize solar energy.^[1] Indeed, the field of photocatalysis has witnessed significant progress toward the development of visible light-responsive photocatalysts and the discovery of photocatalytic reactions yielding high value-added products in the past decade.^[2] In the past two decades, various research groups have successfully investigated a plethora of organic photochemical transformations using transition metal-based complexes (e.g., Ru²⁺ or Ir³⁺) or organic chromophores.^[3] However, the prohibitively high cost and potential toxicity of these rare metals often raise concerns about their long-term sustainability. As a result, there has been a surging interest in the field of heterogeneous visible light photocatalysis to pursue stable, recyclable, reusable and metal-free photocatalysts for organic synthesis, such as graphitic carbon nitride as one prominent example.^[4]

Conjugated nanoporous polymers (CNPs) conveniently combine a number of interesting properties,^[5] such as nanoporosity, high interfacial surface area and semiconductor-range bandgap, which make them promising candidates for heterogeneous visible light photocatalysts. Recent studies have successfully demonstrated CNPs with various functionalities and morphologies to serve as effective, robust heterogeneous visible light photocatalysts for a wide range of chemical transformations such as singlet oxygen activation,^[6] selective oxidation of organic sulfides,^[7] organic dye degradation,^[8] oxidative hydroxylation of arylboronic acids,^[9] photooxidative coupling of benzylamines,^[10] reductive dehalogenation reaction,^[11] photocatalytic reduction of Cr(VI) to Cr(III),^[12] visible light-initiated free radical and cationic polymerization^[13] and light-induced hydrogen evolution.^[14] However, systematic investigations into the in-depth understanding and further optimization of the catalyst design for higher photocatalytic efficiencies still need to be undertaken.

To match the specific activation energies of individual photochemical reactions, the redox potentials of transition metal-based homogeneous organometallic complexes can be easily adjusted by modifying the metal center and surrounding ligands.^[15] Likewise, the effective valence (VB) and conduction band (CB) positions of heterogeneous metal oxide-based photocatalysts (e.g., TiO₂ and Nb₂O₅) can be modified *via* surface functionalization with heteroatoms (e.g., O, N and S) or formation of hybrid- or hetero-structures with selected metals.^[16] A few examples using co-

Adv. Synth. Catal. **0000**, *000*, 0–0

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building block control for enhancing photocatalytic efficiency were demonstrated for graphitic carbon nitride-based systems.^[17] Analogous to organic photovoltaics (OPV), an ideal conjugated polymeric photocatalyst should possess not only a broad absorption range (i.e., narrow bandgap, $E_g \approx 1.6-2.0 \text{ eV}$) to harvest light from the full solar spectrum, but also a high enough lowest unoccupied molecular orbital (LUMO) level for efficient charge separation.^[18] Motivated by this, our group recently showed that the valence and conduction band levels can be fine-tuned and the resulting photocatalytic efficiencies of the CNP photocatalysts can be boosted by a facile molecular structural design strategy^[10a] or the variation of the chemical composition in the electron-accepting moieties.^[10b] Nevertheless, a deeper understanding of control on the molecular level of this class of new photocatalysts is still of great importance for further development of the CNPs in order to achieve enhanced photocatalytic efficiency.

Metal-mediated dehydrogenative C-C bond formation via C-H bond cleavage has received significant interest from organic chemists because it eliminates the preactivation steps, such as halogenation of the starting compounds. Specifically, direct coupling at an sp^3 carbon center adjacent to heteroatoms (e.g., N and O) has been extensively investigated.^[19] Traditionally catalyzed by transition metal-based catalysts (e.g., Cu²⁺, Ru²⁺ or Ir³⁺),^[20] the oxidative direct cyclization of N-methylanilines with maleimides leads in one step to the corresponding tetrahydroquinoline products, which are common structural motifs found in numerous biologically active natural products and pharmacologically relevant therapeutic agents.^[21] To avoid metal residue in the products, non-metal-containing catalytic systems are therefore highly advantageous.

In this work, we present a bandgap engineering method to fine-tune the CB and VB levels and to achieve precise band position alignment by copolymerization. Certain amounts of benzo[1,2-c;4,5c']bis[1,2,5]thiadiazole (BBT) as electron acceptor moiety were incorporated into a 1,3,5-cross-linked benzene-based conjugated system to yield a series of polymer-based photocatalysts with distinctively different VB and CB band levels and bandgaps (Scheme 1). Furthermore, it was found that these conjugated nanoporous polymers could serve as effective metal-free heterogeneous photocatalysts for the visible light-induced direct coupling at sp^3 carbon centers adjacent to heteroatoms such as N and O.^[19,22] As a pure organic catalytic example, the oxidative cyclization of N,N-dimethylanilines with maleimides was chosen to demonstrate the photocatalytic activity of the well-designed conjugated nanoporous polymers. We also demonstrate that not only the optical absorption of the photocatalysts can be significantly extend-

Nanoporous Poly-benzobisthiadiazoles P-BBT-0: B/BBT = 100/0 P-BBT-10: B/BBT = 90/10 P-BBT-10: B/BBT = 50/50 P-BBT-10: B/BBT = 50/50 P-BBT-10: B/BBT = 0/100 BBT = 0/100

Scheme 1. Synthetic strategy and representative structures of the conjugated nanoporous polymer series, P-BBT-0, P-BBT-10, P-BBT-50 and P-BBT-100, where TB is 1,3,5-triethynylbenzene, B is 1,4-dibromobenzene and BBT is dibromobenzo[1,2-*c*;4,5-*c*']bis[1,2,5]thiadiazole. *Reaction conditions:* Pd(0), CuI, DIPA, DMF, 80–90 °C, 12 h.

ed into the visible region, but also that the band positions can be precisely aligned to bracket the targeted photoredox reaction to yield optimal photocatalytic efficiency by the copolymerization method with optimized composition of the electron-withdrawing comonomer (BBT).

The chemical structures of the synthesized polymers are displayed in Scheme 1. Increasing amounts of electron-accepting moiety BBT were incorporated into the conjugated network, which resulted in a series of conjugated nanoporous polymers, P-BBT-0, P-BBT-10, P-BBT-50, P-BBT-100 (the numbers 0, 10, 50, 100 denote the molar feed ratios of B (phenyl unit) to BBT, Scheme 1). The synthetic details and characterization data are described in the Experimental Section and the Supporting Information. The polymers obtained are insoluble in all common organic solvents tested. The Brunauer-Emmett-Teller (BET) surface areas of P-BBT-0, P-BBT-10, P-BBT-50 and P-BBT-100 were found to be $1017 \text{ m}^2\text{g}^{-1}$, $355 \text{ m}^2\text{g}^{-1}$, $110 \text{ m}^2\text{g}^{-1}$ and $57 \text{ m}^2\text{g}^{-1}$, with pore volumes of $0.82 \text{ cm}^3 \text{g}^{-1}$, $0.32 \text{ cm}^3 \text{g}^{-1}$, $0.12 \text{ cm}^3 \text{g}^{-1}$ and $0.07 \text{ cm}^3 \text{g}^{-1}$, respectively. Similar average pore diameters of around 1.5 nm were determined for all polymers (Table S1 and Figures S1-S5 in the Supporting Information). The SEM and TEM images of the four CNPs illustrated slightly different morphologies (Figure 1). In particular, P-BBT-0 and P-BBT-10 exhibited more loosely-packed, fibrous network structures whereas a flake-like morphology was observed for P-BBT-50 and P-BBT-100.

Solid state ¹³C/MAS NMR spectroscopy showed typical aromatic carbon signals between 120 and

Adv. Synth. Catal. 0000, 000, 0-0





Figure 1. Scanning electron microscopy (SEM) images of P-BBT-0 (a), P-BBT-10 (b), P-BBT-50 (c) and P-BBT-100 (d) with transmission electron microscopy (TEM) images as inserts.

145 ppm. The signals at about 90 ppm can be assigned to the C=C bonds. The signal at about 153 ppm was observed for the BBT-containing polymers P-BBT-10, P-BBT-50, and P-BBT-100, which can be assigned to the carbon of the C=N band in the BBT units (Figures S6–S9 in the Supporting Information). Thermal gravimetric analysis (TGA) measurements showed that the onset temperatures of thermal degradation with less than 5% weight loss are 491°C, 383°C, 236 °C and 237 °C, respectively, indicating a carbonized residue with rich nitrogen and sulfur content (Figure S10 in the Supporting Information). FT-IR spectra identified the typical stretching mode of the aromatic rings between 1370 and 1500 cm⁻¹; C=C and C≡C bond stretching modes could be observed at around 1600 cm^{-1} and 2250 cm^{-1} , respectively. Additionally, for polymers containing BBT units, the intensities of the peak around 1622 cm⁻¹ grew, which can be attributed to C=N bond stretching and corresponds to the increasing BBT content (Figure S11 in the Supporting Information).

In Figure 2a, the UV/Vis diffuse reflectance (DR) spectra of the CNPs are displayed. P-BBT-0 showed the narrowest absorption band, while the absorbance spectra of P-BBT-10, P-BBT-50 and P-BBT-100 are



Figure 2. (a) Diffuse reflectance (DR) UV/Vis spectra, (b) Kubelka–Munk-transformed reflectance spectra and (c) conduction band (CB) and valence band (VB) positions of the polymers. (d) Proposed reaction mechanism of the 1,2,3,4-tetrahydroquinoline synthesis.

Adv. Synth. Catal. 0000, 000, 0-0

bathochromically shifted towards longer wavelengths, up to near infrared region in the latter two cases. The Kubelka–Munk–transformed reflectance spectra of the four polymers are shown in Figure 2b. The estimated optical bandgaps are 3.12 eV, 2.20 eV, 1.92 eV and 1.86 eV for P-BBT-0, P-BBT-10, P-BBT-50 and P-BBT-100, respectively. The conduction band (CB) levels of the four polymers were measured by cyclic voltammetry (CV) (Figure 2c) and they are -1.14 V, -0.94 V, -0.76 V and -0.75 V (*versus* SCE) for P-BBT-0, P-BBT-10, P-BBT-50 and P-BBT-0, P-BBT-10, P-BBT-50 and P-BBT-100, respectively.

No discernible oxidative potentials of the conjugated polymers were observed by cyclic voltammetry, the valence band (VB) levels were estimated with the combined knowledge of the optical bandgaps and the CB levels of the polymers and they are 1.98 V, 1.26 V, 1.16 V and 1.10 V (*versus* SCE) for P-BBT-0, P-BBT-10, P-BBT-50 and P-BBT-100, respectively. It is worth-noting that the VB and CB levels are comparable to the redox potentials of established transition metal-based photocatalysts such as ruthenium complexes,^[3a] which indicates the promising potential of these conjugated nanoporous photocatalysts.

Previously, conjugated macromolecular systems were shown to be able to mediate the electron transfrom *N*,*N*,*N*,*N*'-tetramethylphenylenediamine fer (TMPD) ($E_{oxi} = 0.12 \text{ V vs. SCE}$) to molecular oxygen, which then produces a blue-colored cationic radical and the activated oxygen species superoxide (O_2^{-}) $(E_{red}=0.86 \text{ V vs. SCE})$ under light irradiation.^[23] Figure S12 (Supporting Information) shows the intensity variations in the UV/Vis absorption spectra of the blue-colored cationic radical, which implies that P-BBT-10 could generate the most superoxide O_2^{-1} under the same reaction conditions and is likely to have a superior photooxidative activity compared to the rest. This finding could probably be explained by the second highest oxidation potential of 1.26 V and reduction potential of -0.94 V of P-BBT-10 in combination with its optimal bandgap. Although P-BBT-0 exhibited even higher redox potentials than P-BBT-10, its inadequate light absorption in the visible region and the large bandgap are likely to be one of the major limiting factors.

We then tested oxidative cyclization reaction of *N*,*N*-dimethylaniline with *N*-phenylmaleimides using the nanoporous poylmers as photocatalysts in air at room temperature. It could be seen that not only were the nanoporous polymer-based photocatalysts successful in yielding the desired product, but they also exhibited different photocatalytic efficiencies under the same reaction conditions (Table 1). Specifically, the reaction catalyzed by P-BBT-10 led to the highest yield of 82% (Table 1, entry 2), which corroborates with the qualitative results showing that P-BBT-10 was the most efficient in generating superox-

Table 1. Oxidative direct cyclization of N,N-dimethylaniline with N-phenylmaleimide catalyzed by the polymer-based photocatalysts.^[a]



Entry	Catalysts	Oxidant	Light	Additive	Yield [%] ^[b]
1	P-BBT-0	air	+	_	< 5 ^[c]
2	P-BBT-10	air	+	-	82
3	P-BBT-50	air	+	-	43
4	P-BBT-100	air	+	_	29
5 ^[d]	P-BBT-10	O_2	+	_	86
6 ^[e]	P-BBT-10	_	+	_	7
7 ^[f]	P-BBT-10	air	_	-	trace
$8^{[g]}$	_	air	+	_	trace
9 ^[h]	P-BBT-10	air	+	KI	39
10 ^[i]	P-BBT-10	air	+	BQ	47
12 ^[j]	P-BBT-10	air	+	NaN ₃	73

^[a] Standard reaction conditions: **1a** (0.5 mmol), **2a** (0.25 mmol), photocatalyst (10 mg), DMF (3 mL), white LED, room temperature, 24 h.

^[b] Isolated yield by silica chromatography unless otherwise stated.

- ^[c] Yield determined by GC-MS.
- ^[d] O_2 used as oxidant instead of air.
- ^[e] Under an N_2 atmosphere.
- ^[f] In the dark.
- ^[g] No photocatalyst.
- ^[h] KI used as hole scavenger.
- ^[i] Benzoquinone (BQ) used as radical scavenger.
- ^[j] NaN₃ used as singlet oxygen scavenger.

ide anion radical, an active species in this catalytic cycle (Figure S12 in the Supporting Information). It is worthwhile to point out that the catalytic efficiency of P-BBT-10 in this reaction is absolutely comparable with the metal-based catalysts such as thermally active copper chloride^[20b] or the state-of-art photocatalyst transition metal complex $Ru(byy)_3Cl_2$.^[20a] Hence, the CB and CB band positions appeared to be of vital importance to the photocatalytic efficiencies, we envision that other parameters such as light absorption, porosity, charge separation, lifetime of excited electrons and charge mobility can also play a role and the observed effective catalytic efficiency depends in fact on a combinatorial effect of all parameters.

To further investigate the reaction mechanism and the individual role of the photogenerated electronhole pairs during the oxidative cyclization of N,N-dimethylaniline with N-phenylmaleimide, control experiments were conducted using P-BBT-10 as photocatalyst (Table 1). Replacing air with oxygen only led

Adv. Synth. Catal. 0000, 000, 0-0

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to negligible improvement in yield (entry 5). Entries 6-8 show that all three components, photocatalyst, light and oxygen, are indispensable for achieving significant product yield. By adding KI as hole scavenger, a reduced yield of 39% was obtained (entry 9) and similarly, a lower yield of 47% was observed when benzoquinone (BQ) was added as superoxide scavenger, indicating that both the photogenerated electron and hole play a critical role in the photocatalytic cycle. To further investigate another possible active oxygen species, singlet oxygen $({}^{1}O_{2})$, which can also be generated by conjugated macromolecular systems,^[10,17b] we then conducted electron paramagnetic resonance (EPR) trapping experiments performed using 2,2,6,6-tetramethylpiperidine (TEMP) as a singlet oxygen trapping agent. The 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO-¹O₂) adduct could be clearly determined (Figure S13 in the Supporting Information). By using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as superoxide trapping agent, DMPO- O_2^{-1} was also determined, indicating that P-BBT-10 was able to generate both active oxygen species (Figure S14 in the Supporting Information). The addition of NaN₃ as singlet oxygen scavenger led to a slightly reduced yield of the 1,2,3,4-tetrahydroquinoline product compared to standard reaction conditions, indicating a minimal role played by the photogenerated ${}^{1}O_{2}$ species in the catalytic process (entry 12). It could be calculated that the ratio of both oxygen species was about 2:1 for superoxide/singlet oxygen. Additionally, changing the solvent system from DMF into toluene, DMSO and acetonitrile was found to be detrimental for all (not shown).

Based on our observations from the control experiments, we propose a plausible mechanism similar to the literature shown in Figure 2d.^[20] Upon light irradiation, a photogenerated electron-hole pair occurs. The photogenerated hole oxidizes N-methylaniline to form its cationic radical 1, which then loses a proton and rearranges to give the α -aminoalkyl radical 2. Subsequently, 2 reacts with maleimide to generate radical 3, which then undergoes cyclization to form the first intermediate 4, which then is oxidized by the active oxygen species, leading to the final product 1,2,3,4-tetrahydroquinoline and the side product hydrogen peroxide (H_2O_2) . The formation of H_2O_2 was determined by the catalytic oxidation of N,N-diethyl-1,4-phenylenediammonium sulfate (DPD) with horseradish peroxidase (POD) mixture and colorimetry by UV-Vis spectroscopy, confirming the suggested reaction mechanism (Figure S15 in the Supporting Information).

Furthermore, we examined the scope of this photocatalytic reaction by investigating substrates with both electron-donating and electron-withdrawing functional groups under the same reaction conditions using P-BBT-10 as catalyst (Table 2). All reactions afforded **Table 2.** The direct coupling of various N-methylanilines with N-substituted maleimides using P-BBT-10 as photoca-talyst.^[a,b]



[a] Reaction conditions: aniline (0.5 mmol), maleimide (0.25 mmol), P-BBT-10 (10 mg), DMF (3 mL), white LED, room temperature, air, 24 h.

^[b] Isolated yield by silica chromatography.

modest to good yields. It was also found that photocatalyst P-BBT-10 could be reused for up to five extra cycles in the model reaction (entry 2, Table 1) without significant loss in activity (Figure S16 in the Supporting Information). No morphological change was observed as shown by the SEM image (Figure S21 in the Supporting Information). Additionally, by increasing the catalyst loading – using the double amount of P-BBT-10 in the reaction mixture – the reaction time decreased to *ca.* 15 h to reach the same product yield. The non-proportional reaction time to the catalyst amount could be caused by the insufficient light penetration into the reaction medium.

In summary, we present a precise bandgap engineering strategy of conjugated nanoporous poly-benzobisthiadiazole networks as metal-free, heterogeneous photocatalysts to allow for fine justification of the photoredox potential and to achieve optimized catalytic efficiency. *Via* copolymerization with an optimal composition of electron-withdrawing benzobisthiadia-

Adv. Synth. Catal. **0000**, 000, 0-0



zole moiety, the resulting valence and conduction band positions of the polymers can be strategically aligned to bracket the redox potential of targeted individual reactions. The enhanced visible light-active photocatalytic activity of the polymers was demonstrated in the oxidative cyclization of *N*,*N*-dimethylanilines with maleimides to yield tetrahydroquinoline products, which are common structural motifs found in numerous pharmacologically relevant compounds.

Experimental Section

Polymer Synthesis

To a solution of 0.02 mmol (23 mg) of tetrakis(triphenylphosphine)palladium(0), 0.02 mmol (4 mg) of CuI in 20 mL of DMF and diisopropylamine (DIPA) (vol/vol 50/50), 0.67 mmol (100 mg) of 1,3,5-triethynylbenzene (TB), were added 1 mmol (236 mg) of dibromobenzene (B) for P-BBT-0; 0.9 mmol (212 mg) of B and 0.1 mmol (35.2 mg) of dibromobenzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (BBT) for P-BBT-10; 0.5 mmol (118 mg) of B and 0.5 mmol (176 mg) of BBT for P-BBT-50; 1 mmol (352 mg) of BBT for P-BB100. The solution was degassed for 20 min with N_2 and then was heated to 80-90°C depending on the feed ratios for 12 h. The resulted polymers were then rinsed with Milli-Q water several times and extracted with 50/50 dichloromethane and methanol solution in a Soxhlet for 24 h. The insoluble solid was then dried under vacuum overnight. Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that all three conjugated polymers have little or trace amount of residual Pd (50 ppm) and Cu (30 ppm).

Photocatalytic Synthesis of 1,2,3,4-Tetrahydroquinolines

In a typical procedure, *N*,*N*-dimethylaniline (0.5 mmol), maleimide (0.25 mmol) and the polymer-based photocatalyst (10 mg) were mixed in DMF (3 mL). The reaction mixture was degassed and irradiated using a white LED lamp (1.2 W/cm², Osa Optics) at room temperature for 24 h in air unless otherwise noted. The product 1,2,3,4-tetrahydroquinoline was isolated and purified *via* silica chromatography. For repeating experiments, P-BBT-10 was used as photocatalyst for the model reaction (entry 2, Table 1). After each cycle, P-BBT-10 was isolated, washed with DMF and reused for another cycle.

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Adv. Synth. Catal. 0000, 000, 0-0 These are not the final page numbers!

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COMMUNICATIONS

8 Bandgap Engineering of Conjugated Nanoporous Polybenzobisthiadiazoles *via* Copolymerization for Enhanced Photocatalytic 1,2,3,4-Tetrahydroquinoline Synthesis under Visible Light

Mov. Synth. Catal. **2016**, *358*, 1–8

Zi Jun Wang, Saman Ghasimi, Katharina Landfester, Kai A. I. Zhang*



Adv. Synth. Catal. 0000, 000, 0-0