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Thiophene-embedded Conjugated Microporous Polymers for Photocatalysis

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Various photoactive building blocks can be incorporated into porous organic polymers (POPs). The congenital properties, such as various synthetic methods, outstanding inherent porosity, easy tunability, rigid conjugated skeletons and high stability, endow the polymeric organic networks with wonderful potential to act as heterogeneous photocatalytic platforms. Whereas, exploiting efficient synthetic strategies for metal-free and nontoxic heterogenous photocatalysts, and further insight into the photocatalytic process in organic transformation are still necessary. In this context, we report the concise synthesis of two polymeric frameworks (BTP-CMP and TBTP-CMP) incorporated bithiophene and thiophthene units via a "bottom-up" strategy. BTP-CMP and TBTP-CMP were employed as heterogeneous photocatalysts in the synthesis of benzimidazoles, and exhibited excellent catalytic activity (up to 98% yield, at least 15 iterative runs). Therefore, the thiophene-embedded networks can serve as stable efficient and recyclable heterogeneous photocatalysts. Additionally, based on the catalytic results of control experiments and energy band structures of materials and intermediates, the possible photocatalytic reaction mechanism has been proposed.

Introduction

More recently, exploiting greener and concise synthetic methods to high value-added fine chemicals has become the common pursuit in labs and chemical industries.¹ As a clean energy source, sunlight is essential for numerous of life process on the earth, e.g. natural photosynthesis.² In the meanwhile, many of the key intermediates (i.e. radicals, radical ions and ions) that will further fabricate complicated functional molecules can be generated in situ under illumination.³ Driven by photocatalysts under light radiation, photocatalysis, a powerful synthetic technique which offers a viable solution for traditional organic transformations and energy issues. The classical photocatalysts are mainly metal oxides/suifides (TiO₂, CdS, ZnS etc.),⁴ polyoxometalates,⁵ organic noble-metal complexes [Ru(bpy)₃Cl₂, Ir(ppy)₃ etc, bpy = bipyridine, ppy = 2-phenylpyridine]⁶ and organic dyes (Eosin Y, Rose Bengal, methylene blue etc).7 However, most catalysts above are costly or highly toxic, even suffer from the limited visible-light absorption, high catalyst loading, poor efficiency and unable to achieve applications in large scale.⁴⁻⁷ In addition, it is not easy to separate the homogeneous catalysts from reaction systems and then reuse them. In consequence, a practicable solution to the issues is to exploit efficient, stable, cost-effective, metal-free and nontoxic heterogenous photocatalysts which are recyclable and reusable.⁸

Porous organic polymers (POPs) have recently emerged as excellent platforms to assemble structural building blocks (SBBs) and functional building blocks (FBBs) via strong covalent linkages.9 Represented by conjugated microporous polymers (CMPs)¹⁰ and covalent organic frameworks (COFs)^{9h, 9j, 11} etc., POPs have been widely used in photoelectricity,¹² molecular recognition/sensors,¹³ gas adsorption/separation/storage,14 membrane separation,15 energy storage,¹⁶ pollutants elimination,¹⁷ drug delivery,¹⁸ and heterogeneous catalysis.^{8a, 19-21} Benefiting from the various synthesis methods and easy tunability for POPs, numbers of versatile porous organic catalysts that with photocatalytic^{22, 21e} or asymmetric catalytic activity^{8b, 23} showcase wonderful potential in the preparation of fine chemicals. The pure organic skeleton enable POPs could enrich organic guest molecules inside pores, and thus improve the relative concentration of reactants. Besides, the photoactive units and rigid π - π conjugated skeletons can assist POPs to harvest photon and transfer electron.^{22j, 24} The congenital advantages above render POPs can be served as photocatalysts carrier to induce the produce of intermediates and promote organic transformation under mild lighting conditions. Furthermore, these solid catalysts undoubtedly simplify the purification procedures and enhance the utilizability of homogeneous catalysts.

The structural uniqueness of thiophene (TP) has brought TPembedded molecules with various dimensions great potential for practical applications. In this aspect, diverse POPs that contain TP units (TP-POP) have been synthesized through C-C coupling, C-H activation, cyclotrimerization of cyano group, and imine linkage.²⁵ Several of the reported POP examples are mainly focused on the

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^{*}Electronic Supplementary Information (ESI) available: Synthesis of Monomers and TP-CMPs, SEM, TEM, TGA, PXRD, EDS and CV of TP-CMPs, FT-IR spectra of the fresh and recycled catalyst, recyclability test of BTP-CMP, and NMR spectra of products. See DOI: 10.1039/x0xx00000x.

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Scheme 1 Schematic representation for the synthesis of thiophenebased CMPs (TP-CMPs). Reagents and conditions: BTP-2Br or TBTP-2Br, TTDB, Pd(PPh₃)₄, 2 M K₂CO₃, N, N-dimethylformamide (DMF), Ar, 150 °C, 2 days.

applications in adsorption for iodine²⁶ or carbon dioxide,^{25j, 25k} lithium-ion batteries.²⁷ However, very few TP-POP catalysts have been reported so far, especially those cases of their catalytic activities derive from TP units.^{25a-g, 25m} Moreover, the excellent photoelectric properties demonstrate that TP-POPs might work as photocatalysts. For example, instructive works by Zhang *et al.* have confirmed the significant photocatalytic activities of TP-based POPs in organic transformation when incorporate with strong electron acceptor, *i.e.* triazine or benzothiadiazole.^{25e-g} Besides, Liu group and Thomas group realized the photocatalysis of hydrogen production and free radical polymerization, respectively.^{25c, 25d} To efficiently prepare advanced fine chemicals, however, further research on the synthetic method and catalytic performance of TP-POP photocatalysts is still necessary.

In this work, we targeted to develop TP-based CMPs (TP-CMPs) for efficient metal-free photocatalysis in organic reactions. Through our rational design, two representative thiophene derivatives, *i.e.* 2,2'bithiophene (BTP) and thieno[3,2-b]thiophene (TBTP), were selected as FBBs to investigate the structure-activity relationships within porous organic materials. Accordingly, we constructed two TP-CMPs (namely, BTP-CMP and TBTP-CMP) concisely *via* the Suzuki-Miyaura coupling reaction (Scheme 1) in one step. Experiments proved that the TP-CMPs could serve as stable, efficient and recyclable heterogeneous photocatalysts in the synthesis of benzimidazoles. Specifically, BTP-CMP exhibited more significant performance in electron transfer and redox processes than TBTP-CMP. Furthermore, energy band structures and control experiment results revealed the possible photocatalytic mechanism within the TP-CMP frameworks.

Experimental

General materials and methods

2,5-dibromothieno[3,2-b]thiophene (TBTP-2Br) and 1,3,5tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (TTDB) were prepared according to the literature procedures (see the ESI[†]).^{12c, 28} Other reagents, *e.g.* 5,5'-dibromo-2,2'-bithiophene (BTP-2Br), could be purchased from commercial suppliers (Energy Chemical Reagent Co. Ltd and Adamas Reagent Co. Ltd) used without further purification, unless otherwise noted. All Pd-mediated coupling reactions were first degassed and then carried out under Ar.

Liquid NMR spectra (¹H and ¹³C) were recorded on a Bruker Avance III 400 MHz NMR spectrometer (CDCl₃ or d_6 -DMSO as solvent). Solidstate NMR experiments were performed on a Bruker WB Avance II 400 MHz NMR spectrometer (4-mm double-resonance probe): contact time was 3 ms (ramp 100), recycle delay was 2 s and the spinning rate was 10,000 ± 1 Hz. FT-IR spectra were obtained with a Nicolet IS-20 instrument. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. Thermogravimetric analysis (TGA) were carried out on a SDT Q600 (V20.9 Build 20) instrument from 35 °C to 1000 °C (10 °C/min) under a nitrogen atmosphere. Scanning electron microscope (SEM) tests were used to examine the surface morphologies and microstructures of materials with Zeiss GeminiSEM 500 at a voltage of 15.0 kV. Elemental compositions within the porous networks were analysed by mapping experiments. High resolution transmission electron microscopy (HR-TEM) images were acquired by a Tecnai G2 F30 TEM operating at an acceleration voltage of 300 kV. UV-Vis diffuse reflectance analysis could be recorded on a JASCO model V-670 spectrometer. Cyclic voltammetry (CV) experiments were conducted on CHI660C Electrochemical Workstation by using a three-electrode electrochemical cell (a glassy-carbon working electrode, a saturated calomel electrode (SCE) as reference electrode, and a platinum wire counter electrode).

Synthesis of BTP-CMP and TBTP-CMP

BTP-CMP and TBTP-CMP were prepared via Suzuki-Miyaura coupling reaction. A two-necked flask was charged with TTDB (182.4 mg, 0.4 mmol), BTP-2Br (194.4 mg, 0.6 mmol) or TBTP-2Br (178.8 mg, 0.6 mmol), Pd(PPh₃)₄ (18.4 mg, 0.016 mmol). And then DMF (16 mL) and 2 M K₂CO₃ aqueous solution (3.2 mL) were added into the flask. The reaction mixtures were stirred and bubbled with a Ar ball for 30 minutes at room temperature. Then, the system was stirred under 150 °C and Ar atmosphere for 48 h. After cooling to ambient temperature, the precipitate was filtrated and washed in turn with deionized water, DMF, EtOH, dichloromethane and acetone. The resulted solid was further purified by the Soxhlet extraction for 24h with tetrahydrofuran (THF) and acetone as solvent, respectively. After drying in vacuum for 12 h at 80 °C, the reticular frameworks were obtained as deep-yellow powder.

Typical procedure for the preparation of 2-substituted benzimidazole catalyzed by BTP-CMP under visible light

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Benzene-1,2-diamine or its derivatives (0.2 mmol), aromatic aldehyde (0.2 mmol), BTP-CMP (12 mg, 4.2 mol%), and MeOH (4.0 mL) were added into a reaction tube. The reaction mixture was stirred at room temperature under 10 W blue LEDs (the distance between LEDs and reaction tube is about 10 cm) and air. After the reaction was completed (monitored by TLC), the heterogeneous catalyst was isolated through centrifugation and thoroughly washed by acetone (4 mL × 3). After removing the organic solvent under reduced pressure, the resulted crude products were further purified by flash column chromatography (with petroleum/acetone = 10/1 to 5/1 as eluent) to give 2-substituted benzimidazole.

Results and discussion

Designed synthesis and characterization of TP-CMPs

It has been demonstrated that TP and its derivatives are highly electron-rich aromatic nucleus. A series of thiophene-containing heterocycles, such as BTP and TBTP, are ubiquitous in electronics and spintronics,²⁹ organic light emitting diodes,³⁰ dye-sensitized solar cells,³¹ biosensing,³² organometallic chemistry,³³ pharmaceutical synthesis and protein receptor.³⁴ Beneficial from the enhanced light harvesting behaviour and electron-rich properties, thiophene-embedded molecules or materials can also be used as efficient photocatalysts.^{25c-g} In order to realize the heterogenization of TP, we selected trigeminal rigid monomer TTDB as the SBB, photoactive BTP-2Br and TBTP-2Br as the FBBs (Scheme 1). Deep-yellow powder BTP-CMP and TBTP-CMP were readily prepared via a concise one-step route with 95% yield and 93% yield through Suzuki-Miyaura co-



Fig. 1 The liquid ¹³C NMR spectra (100 MHz, CDCl₃) for the monomer BTP-2Br (a), TBTP-2Br (c), and the solid-state ¹³C CP/MAS NMR spectra (100 MHz) of BTP-CMP (b) and TBTP-CMP (d). The asterisks denote the spinning sidebands.

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upling reaction in DMF, respectively. The obtained polymeric frameworks are insoluble in the selected solvents doen and the sufficient of the selected solvents of the sele

The atomic-level linkages of the networks were verified by solidstate ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy (Fig. 1). To identify the affiliation of carbon signals in porous networks, we first studied the chemical shifts of carbon atoms in monomer BTP-2Br and TBTP-2Br through liquid ¹³C NMR spectra (Fig. 1a and 1c) and ¹³C DEPT135 NMR technology. It is now clear that 122 (124) and 131 ppm were the signals of *C*H, while 138 ppm could be ascribed to the quaternary carbon atoms in BTP-2Br or TBTP-2Br. Thus, for BTP-CMP, the peaks at 143, 123 and 136 ppm correspond to the sp²-carbon atoms on benzene rings and bithiophene units (Fig. 1b). The chemical shifts are in accordance with CP3^{25c} and MTP-1,²⁵¹ which were prepared via direct C–H and FeCl₃ mediated oxidation coupling reaction by Liu et al and L. Borchardt et al, respectively. Similar signals (125 and 145 ppm) of



Fig. 2 Nitrogen adsorption–desorption isotherms at 77 K and corresponding pore size distribution profiles (insert) calculated from desorption data using the NLDFT method for BTP-CMP (a) and TBTP-CMP (b). STP = standard temperature and pressure.

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benzene rings can be found in the 13 C NMR spectrum of TBTP-CMP (Fig. 1d), while the evident peaks at 118, 136 and 139 ppm are

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(Fig. 1d), while the evident peaks at 118, 136 and 139 ppm are ascribed to the carbon atoms from thieno[3,2-b] thiophene nodes. Additionally, the Fourier transform infrared (FT-IR) spectra (Fig. S1⁺ and S2⁺) of TP-CMPs showed strong peak of thiophen ring at 792–800 cm⁻¹. ^{25e, 25i} These results indicate that thiophene blocks BTP and TBTP were successfully embedded into the corresponding conjugated skeleton.

Nitrogen sorption measurements at 77 K were used to investigate the porosity of BTP-CMP and TBTP-CMP. As shown in Fig. 2, the two frameworks exhibit type II sorption isotherms.^{26c} Combine with the pore size distributions profiles (insert images in Fig. 2), we observed that both BTP-CMP and TBTP-CMP contain micropores, mesopores and macropores. For BTP-CMP, the Brunauer– Emmett–Teller (BET) surface area was 242 m² g⁻¹, while t-plot method revealed that the contribution from mesopores and macropores surface area upto 83%. Replacement of DMF use THF (80 °C), toluene (100 °C), 1,4dioxane (120 °C), N-methyl-pyrrolidone or N, N-dimethylacetamide (150 °C), or to perform the reaction in DMF under 130 °C didn't improve the BET surface areas of BTP-CMP (Table S1). The low surface areas might due to the geometry of repeat units in BTP-CMP network. A simple



Fig. 3 EDS mapping images of C and S for BTP-CMP (a-c) and TBTP-CMP (d-f).

structure optimization showed that the torsion angels of thiophenebenzene in BTP-CMP were smaller than TBTP-CMP (Fig. S3⁺). The resulted serious π - π stacking effects between the planers of material was unfavourable to improve the surface areas of BTP-CMP. While the slightly larger torsion angel enabled TBTP-CMP displayed higher BET surface areas (571 m² g⁻¹) than BTP-CMP, and the percentage of micropores surface area in TBTP-CMP was about 4 9 % . B e s i d e s , t h e



Fig 4. (a) UV/Vis absorption spectra and (b, c) Kubelka-Munk plots (to measure the band gap energy) for solid-state TP-CMPs. (d) Energy band positions of TP-CMPs and $O_2/O_2^{-\bullet}$ measured by CV. (e) UV-vis absorption spectra and images of the tertiary amine radical cationic generated by TP-CMPs under light and O_2 atmosphere.

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total pore volumes at 0.99 p/p_0 were 0.33 $m^3~g^{-1}$ for TBT-CMP and 0.77 $m^3~g^{-1}$ for TBTP-CMP.

TGA under a nitrogen atmosphere showed that the as-synthesized TP-CMPs possess exceptional thermostability (up to about 550 °C, Fig. S4⁺). The similar ultrastability can be found in porous aromatic frameworks (PAFs) and thiophene-embedded SNPs that constructed with acetylene linkage.^{14a, 25h, 25l} Both BTP-CMP and TBTP-CMP are amorphous as proved by powder X-ray diffraction (Fig. S5⁺). The SEM images indicated that BTP-CMP and TBTP-CMP consisted of spherical and irregular nanoparticles with porous surfaces, respectively (Fig. S6⁺). HR-TEM measurements demonstrated that the two networks consisted of nanometer-scale pores (Fig. S7⁺). Energy-dispersive Xray spectroscopy (EDS) elemental mapping images in Fig. 3 suggested that the elements C and S were homogeneously spread on the networks of the TP-CMPs. The elemental composition (Fig. S8⁺) detected by quantitative EDS agrees well with the theoretical values and the element analysis results.

Photocatalytic performance and recyclability of TP-CMPs

Optoelectronic properties were first studied to examine the photocatalytic activity of TP-CMPs. As revealed by solid-state UV/vis spectra, BTP-CMP and TBTP-CMP displayed broad absorption region and similar edges at *ca*. 620 nm (Fig. 4a). The optical band gaps (E^g) of BTP-CMP and TBTP-CMP, calculated via Kubelka-Munk function, were 2.42 eV and 2.36 eV, respectively (Fig. 4b and 4c). Energy band structures of TP-CMPs were assessed through cyclic voltammetry (CV) measurements (Fig. S9⁺). The conduction band positions (E^c) vs. SCE at -0.92 V (BTP-CMP) and -0.88 V (TBTP-CMP) were negative enough to reduce O₂ to O₂⁻⁻ (-0.86 V vs. SCE).^{22e} Combined E^g with E^c , the valence band positions (E^v) vs. SCE of BTP-CMP and TBTP-CMP were estimated as 1.50 V and 1.48 V, respectively (Fig. 4d).

Upon exposing to light, the excited materials BTP-CMP^{*} and TBTP-CMP^{*} would effectively promote the generation of blue-coloured 1,4-bis(dimethylamino)benzene-cationic radical (0.12 V vs. SCE) and $O_2^{\bullet-}$, which were mediated via the electron transfer from tertiary amine to O_2 (Fig. 4e).^{22e, 22g} The higher absorbance of the obtained deeper blue cationic radical solvents (Fig 6e and insert) implied that BTP-CMP possess superior photocatalytic activity than TBTP-CMP. This is due to the existing superior π - π stacking effects in BTP-CMP facilitate the electronic transmission along the π -skeletons.³⁵ Besides, the catalytic results are consistent with the energy band positions in Fig. 4d, and suggest that TP-embedded CMPs can used as metal-free catalysts in photoredox organic reactions.

As one of the most common heterocyclic structure, benzimidazoles endow drugs with amazing bioactivity for insects, sphaerotheca fuliginea, penicilliosis, cancer cells, heart disease and HIV etc. ³⁶ Additionally, the significant moieties can be widely found in polybenzimidazole fibres, porous organic networks and photoelectric materials.³⁷ Thus, we initially examined the catalytic

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Table 1 Optimization of the reaction conditions^a

		visible ligh catalyst, solv air, rt, 2 h	nt rent -	-ci		
1a	2a			3a		
Entry	catalyst (mol%)	solvent	blue LEDs	yield (%) ^b		
1	BTP-CMP (2.1)	MeOH	5	65		
2	TBTP-CMP (2.3)	MeOH	5	50		
3	BTP-CMP (2.1)	MeOH	10	78		
4	BTP-CMP (2.1)	acetone	10	trace		
5	BTP-CMP (2.1)	THF	10	trace		
6	BTP-CMP (2.1)	CH ₃ CN	10	trace		
7	BTP-CMP (2.1)	CH_2CI_2	10	trace		
8	none	MeOH	10	24		
9 ^c	BTP-CMP (2.1)	MeOH	10	18		
10	BTP-CMP (2.1)	MeOH	none	27		
11	BTP-CMP (4.2)	MeOH	10	89 (98) ^d		
12	BTP-CMP (6.2)	MeOH	10	92		
13	BTP-2Br (2.1)	MeOH	10	29		

^aGeneral conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), solvent (4.0 mL). ^b Isolated yields. ^c no air. ^d 2.5 h.

activity of TP-CMPs in the conversion from ortho-diamine to 2arylbenzimidazoles (Table 1). After irradiation for 2 hours with 5 W blue LEDs in methanol, the desired product 3a was obtained in 65% and 50% yield for BTP-CMP and TBTP-CMP, respectively (Table 1, entries 1 and 2). Contribute to the π - π stacking effects, energy band structures and porosity in TP-CMPs, the more remarkable catalytic effects displayed in BTP-CMP than TBTP-CMP was reasonable. Obviously, the faster transfer of electrons, higher E^{v} and more negative E^{c} (Fig. 4d) guarantee the light-induced redox process easier in BTP-CMP. Meanwhile, the more affluent macro/meso pores provide convenience for the mass transfer of substrates and products. An enhanced catalytic efficiency could be obtained with 78% yield when the light source was replaced by 10 W blue LEDs (Table 1, entry 3). As confirmed by experiments (Table 1, entries 3-7), aprotic solvents such as acetone, acetonitrile, THF and dichloromethane could not give encouraging results. Investigation on the influence of catalyst loading revealed that an appropriate increase of BTP-CMP could improve the yield (Table 1, entry 11). Nevertheless, further increase of the BTP-CMP (6.2 mol%) loading didn't give marked improvement to the yield (Table 1, entry 12), which was ascribed to the higher concentration solid catalyst might



Table 2 Preparation of 2-arylbenzimidazoles with aldehydes and

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^{*o*} Reaction conditions: aromatic diamine (0.2 mmol), aldehyde (0.2 mmol), BTP-CMP (12 mg, 4.2 mol%), MeOH (4.0 mL). Isolated yields. ^{*b*} Scale-up experiment: **1a** (5 mmol), **2a** (5 mmol), BTP-CMP (180 mg, 2.5 mol%), MeOH (100 mL). ^{*c*} TBTP-CMP (10.8 mg, 4.2 mol%) as catalyst.

block the transmission of visible light and resulted in ineffective light absorption. Further experiment demonstrated 4.2 mol% BTP-CMP was adequate for the 0.2 mmol scale substrates and produced **3a** in 98% yield within 2.5 h. Meanwhile, control experiments indicated that air (O₂), light and photocatalysts were necessary to get the same result shown as entry 3 in Table 1. It should be noted that BTP-2Br as catalyst didn't give a favourable yield (29%, entry 13), implying shortrange π - π conjugated system was disadvantageous for photocatalytic activities. Therefore, the reaction conditions for the catalytic synthesis of 2-arylbenzimidazoles (**3**) were then set as 12 mg of BTP-CMP, methol as the solvent, with air (O₂) and 10 W blue LEDs at room temperature.

With the optimal reaction condition in hand, we next explored the substrate scope for the reaction system. As shown in Table 2, the asprepared BTP-CMP works very well for symmetrical/unsymmetrical aromatic diamines and various aldehydes. All substrates with different substituent groups, including 1-naphthaldehyde (3g), 2naphthaldehyde (3h), 4,5-dimethylbenzene-1,2-diamine (3k), and 4,5-dichlorobenzene-1,2-diamine (**3I**), could furnish the corresponding benzimidazole derivatives smoothly in 2.5-5.0 h with excellent yields (Table 2, 91-98%) and without by-products. Meanwhile, TBTP-CMP also displayed comparable catalytic effects as its counterpart BTP-CMP with 92-95% yield for 3b, 3d and 3k. Furthermore, gram-scale photocatalytic synthesis of 3a was successful with 93% yield (1.06 g) through concise procedures (i.e.

filtration, evaporation and washing, see the ESI $^{+}_{iew}$ This result indicated that TP-CMPs might have potential 1 applications of industrial catalysis.

The catalytic stability and recyclability of TP-CMPs were examined with recovered BTP-CMP to perform the catalytic reaction as displayed in Table 1 under the standard conditions. We found BTP-CMP could be reused for at least 15 times with remarkable catalytic activity (96-98% yield, Fig. S12⁺). Nevertheless, the decrease of BET surface area (242 m² g⁻¹ to 30 m² g⁻¹) caused the reaction time to be prolonged (Fig. S12⁺ and S13⁺). These results indicate that the porosity have further effects on the catalytic abilities of POPs. Meanwhile, the recorded FT-IR spectra (Fig. S14⁺) demonstrated that the BTP-CMP almost maintained its skeleton structure after 15 iterative runs. These results confirmed the notable reusability and high stability of the designed TP-CMPs as photocatalyst.

Catalytic mechanism

In order to insight into the reaction process, we tested the yield of the possible intermedium I and II (Scheme 2A). In fact, the yield of I was up to 92% after 0.25 h, and remained about 90% to >99% yield within 12 h, while II and **3a** were not be observed in liquid NMR spectra (Fig. S15[†]). Furthermore, intermedium I could translate into the product **3a** quickly with 85% yield under visible light and BTP-CMP, however, the reaction proceeded slowly in the absence of BTP-CMP within the same time (Scheme 2B, i and ii). The results above implied that: 1) compound I may be the key intermedium that take part in the subsequent photocatalytic process; 2) both catalyst BTP-CMP and visible-light were essential to the reaction here.

Based on the results of control experiments above and those homogeneous photocatalysis systems^{36b, 38} for the synthesis of benzimidazoles, we proposed a possible reaction mechanism as



Scheme 2 Control experiments.



Scheme 3 Proposed mechanism for the transformation of benzene-1,2-diamine to benzimidazole in the presence of TP-CMP under light.

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described in Scheme 3. Initially, the excited materials (TP-CMP*) would generate upon ground-state TP-CMP was irradiated with appropriate light. Oxygen molecule in air captured an electron from TP-CMP*, and then produced $O_2^{-\bullet}$ and TP-CMP⁺. Meanwhile, the imine I that derived from aromatic diamine and aldehyde would provide an electron ($E_{I/II} = 0.45$ V, Fig. S16⁺) for TP-CMP⁺ to recover TP-CMP. The resulted cation radical intermediate III could release a proton easily to react with $O_2^{-\bullet}$, and generated the radical intermedium IV via a further intramolecular cyclization reaction.³⁹ Finally, IV was converted into the target product **3** through a dehydrogenation process.

Conclusions

In summary, by incorporating well-selected S-heterocycle monomers into polymeric framework through a "bottom-up" strategy, we have successfully developed thiophene-functionalized porous networks, TP-CMPs, via one step Suzuki-Miyaura coupling reaction. Owing to the property of electron-rich of thiophene derivatives, π - π conjugated TP-CMPs displayed appropriate energy band structures and good photochemical activities. We found the as-synthesized frameworks showed good photocatalytic activities to the reaction between aldehyde and diamine. Specially, bithiophene-embedded BTP-CMP displayed preferable catalytic effects (91-98% yield), excellent reusability (at least 15 times, 96-98% yield) and high stability in the synthesis of 2-arylbenzimidazoles under visible light. Meanwhile, we outline the possible reaction mechanism within heterogeneous system. Considering the tunability of functional monomers and structural features of POP materials, we expect that CMPs represented by TP-CMPs would become a class of efficient photocatalysts and toward the industrial catalysis for fine chemicals.

Author contributions

Wan-Kai An and Zhenliang Pan conceived the project. Wan-Kai An, Shi-Jia Zheng, and Ya-Nan Du prepared the CMPs and performed the experiments on characterization and photocatalysis. Xiaobiao Liu and San-Yuan Ding conducted the calculations. Wan-Kai An and Yuchen Qin carried out the energy band structures analyses. Wan-Kai An, Song Jiang, Pi-Feng Wei, Zhan-Qi Cao and Meirong Song analyzed the catalytic mechanism. Shi-Jia Zheng and Wan-Kai An wrote the original manuscript. San-Yuan Ding, Zhenliang Pan, and Zhi-Jun Li revised the manuscript. All authors discussed the comments and contributed to generation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Thiophene-embedded Conjugated Microporous Polymers for Photocatalysis

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"Bottom-up" embedding of thiophene derivatives into CMPs for highly efficient heterogeneous photocatalysis.

