Green Chemistry



View Article Online

PAPER

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Cite this: *Green Chem.*, 2021, **23**, 1292

Received 3rd November 2020, Accepted 14th January 2021 DOI: 10.1039/d0gc03719b

rsc.li/greenchem

Introduction

The vital task of green chemistry is to take reasonable measures, *e.g.*, using greener and safer solvents and reagents, searching for suitable synthesis approaches, and exploiting non-noxious, highly efficient and selective catalysts, to improve the atomic economy.¹ In this context, many environmentally friendly catalytic technologies, such as photocatalysis, a powerful synthetic technique for traditional synthesis, have been developed.² Upon exposure of substrates to light, free radicals or radical ions, *etc.*, will be generated *in situ* with the assistance of photocatalysts.³ The classical photocatalysts are mainly metal complexes,⁴ organic dyes,⁵ and metal oxides/sulfides.⁶ However, these catalysts are either expensive, highly toxic, have low visible-light utilization, or are unstable.^{3–6} Meanwhile, most homogeneous molecule catalysts suffer from other problems; for example, they are not easy to recover from reaction

s-Tetrazine-functionalized hyper-crosslinked polymers for efficient photocatalytic synthesis of benzimidazoles[†]

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Developing green-safe, efficient and recyclable catalysts is crucial for the chemical industry. So far, organic photocatalysis has been proved to be an environmentally friendly and energy-efficient synthetic technology compared with traditional metal catalysis. As a versatile catalytic platform, hyper-crosslinked polymers (HCPs) with large surface area and high stability are easily prepared. In this report, we successfully constructed two porous HCP photocatalysts (TZ-HCPs) featuring *s*-tetrazine units and surface areas larger than 700 m² g⁻¹ through Friedel–Crafts alkylation reactions. The rational energy-band structures and coexisting micro- and mesopores endow TZ-HCPs with excellent activities to realize the green synthesis of benzimidazoles (28 examples, up to 99% yield, 0.5–4.0 h) in ethanol. Furthermore, at least 21 iterative catalytic runs mediated by TZ-HCP1D were performed efficiently, with 96–99% yield. This study of TZ-HCPs sheds light on the wide-ranging prospects of application of HCPs as metal-free and green photocatalysts for the preparation of fine chemicals.

systems and then reuse. For this reason, much effort has been devoted to realizing heterogeneity in homogeneous catalysts.⁷ As a consequence, a series of solid catalysts based on porous frameworks, such as periodic mesoporous organosilicas (PMOs),⁸ metal–organic frameworks (MOFs),⁹ and porous organic polymers (POPs)¹⁰ have been successfully developed. Nevertheless, the precise construction of efficient and highly recyclable heterogeneous organic photocatalysts with favorable robustness still remains a challenge.

Compared with MOFs,9 PMOs,8 covalent organic frameworks (COFs),¹¹ conjugated microporous polymers (CMPs) and porous aromatic frameworks (PAFs),¹² hyper-crosslinked polymers (HCPs) are constructed directly from undecorated building blocks.¹³ With inexpensive Lewis acids (e.g., FeCl₃ or AlCl₃) as the catalyst, and chloromethyl methyl ether (MOMCl) or formaldehyde dimethyl acetal (FDA), or similar, as the crosslinker, precursors can be easily assembled into HCP networks via a Friedel-Crafts alkylation reaction. Moreover, HCPs generally have large specific surface areas, and are stable enough under harsh chemical conditions. In this respect, their concise and compatible synthetic strategy and their significant stability and porosity endow HCPs with great potential for selection as catalyst carriers. Studies using HCP catalysts are important for industrial chemistry. Molecular catalysts or ligands, such as triphenylphosphine (PPh₃), N-heterocyclic carbene, 2,2'-bis (diphenylphosphino)-1,1'-binaphthalene (BINAP), porphyrin,

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[†]Electronic supplementary information (ESI) available: Synthesis of monomers and TZ-HCPs, TGA, PXRD, CV of TZ-HCPs, FT-IR and ¹³C CP/MAS NMR spectra of the fresh catalyst, recyclability test of TZ-HCP1D, and NMR spectra of products. See DOI: 10.1039/d0gc03719b

imidazolium/quaternary phosphonium salt, etc., have been successfully embedded into HCP platforms.^{10i-l,14} The resulting superligands/catalysts exhibit superior catalytic performance for cross-coupling reactions, click reactions, hetero-Diels-Alder reactions, hydroformylation and epoxidation of olefins. Recently, several available HCP photocatalysts for organic transformation have been reported.¹⁵ In 2014, two HCPs based on thioxanthone (TX-Ph and TX-TPM) were constructed by Thomas and co-workers.^{15a} These functional HCPs could be applied as effective photocatalysts for light-induced free radical/cationic polymerizations. Subsequently, Zhang et al. developed benzo[c][1,2,5]thiadiazole-embedded HCP catalysts (MOPs), and realized the photocatalytic selective bromination of electron-rich aromatic rings.^{15b} In order to promote selective photocatalytic aerobic oxidation reactions, the Liu group incorporated bis-(N-carbazolyl)-9-fluorenone into HCP networks yielding CF-HCP with highly catalytic efficiency.^{15c} In addition, these photocatalytic transformations could also be conducted efficiently by PS-HCPs, which were synthesized by Liu et al. in 2020.15d Furthermore, HCPs and metallic oxide can be assembled into composite photocatalysts and used for photodegradation of organic matter or CO₂ conversion.16 Despite this, available HCP photocatalysts are rare and yet to be further developed.

Herein, we report the concise construction of stable HCP networks (TZ-HCPs) embedded with s-tetrazine (TZ) units for highly efficient photocatalytic synthesis of benzimidazoles (BIs). As a representative electron-deficient structure, s-tetrazine has valuable applications in the synthesis of energetic compounds,¹⁷ synthetic and metal coordination chemistry,¹⁸ biorthogonal labeling¹⁹ and solar cells, etc.²⁰ Furthermore, 3,6disubstituted-s-tetrazines often display bright colors and exhibit excellent photoactivity and oxidation ability.20b Specifically, 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) has always served as a highly efficient catalyst because of its easy reduction by means of accepting an electron to form an anion radical.²¹ Replacing MOMCl with low toxic FDA as cross-linker, TZ-HCP catalysts could be facilely constructed by fabricating the modified pytz and structural building blocks. High surface area, and concomitant micro/mesopores within TZ-HCPs, greatly accelerate the molecular transport process. The abundant, opened-up nanopores efficiently facilitate contact of the catalytic sites with light and with substrates. Contributing to the remarkable visible-light absorption of pytz, TZ-HCPs displayed outstanding photocatalytic activity in the green preparation of BIs.

Results and discussion

As is well known, both pyridine and tetrazine are electrondeficient units that cannot meet the requirements of the classical Friedel–Crafts alkylation reaction. Thus, electron-rich aromatic rings should be incorporated into the modified pytz. However, the poor solubility of aromatic ring-substituted pytz is unfavorable to the generation of TZ-HCPs with the desired porosity. In this context, the rational design started by introducing p-methoxyphenyl (PMP) into pytz (Scheme 1). The methoxy group in PMP will, to some extent, enhance the activity of benzene and improve the solubility of pytz. TZ-functionalized 2 could be facilely synthesized from PMP-substituted picolinonitrile via cyclization and oxidation mediated by hydrazine hydrate and sodium nitrite, respectively.²² As shown in Scheme 1, we then constructed the photoactive porous framework TZ-HCPs from violet powder 2 and benzene or 9Hfluorene, through a two-stage synthesis strategy. With FeCl₃ as catalyst, and 1,2-dichloroethane (DCE) and FDA as solvent and/or cross-linking agent, the systems were first reacted at 45 °C for 5 h to obtain prepolymers, and then heated at 90 °C for 19 h to realize depth of polymerization. In general, greyish green, brownish red or brownish black powders, which are insoluble in common solvents (N,N-dimethylformamide, MeOH, etc.), could be easily obtained. Experimental results revealed that the content of benzene or compound 2 in the resulting polymers has obvious effects on the porosity of TZ-HCP1 and its thermostability. Investigation using nitrogen adsorptiondesorption tests indicated that the Brunauer-Emmett-Teller (BET) specific surface areas increased with benzene content, from 3 m² g⁻¹ for TZ-HCP1A to 73 m² g⁻¹ for TZ-HCP1B to 171 m² g⁻¹ for TZ-HCP1C (Table 1). Similar variation can also be observed in the Langmuir surface areas and pore volume. Additionally, the microporous area revealed by the t-plot method further demonstrated that fine-tuning of the molar ratio of benzene to compound 2 ($n_{\rm B}/n_2 = 0/1$ to 5.4/1) could indeed optimize the porosity of the TZ-HCPs. Considering the porosity and concentration of catalyst sites within the polymers, 20 equivalent knots were finally used and resulted in





Scheme 1 Rational design and "bottom-up" synthesis of photocatalytic hyper-crosslinked polymers (TZ-HCPs) embedded with *s*-tetrazine. Reaction conditions: (a) N_2H_4 · H_2O , EtOH, Ar, 90 °C, 18 h; (b) $NaNO_2$, AcOH, RT, 18 h; (c) DCE, FDA, FeCl₃, 45 °C for 5 h, then 90 °C for 19 h.

 Table 1
 Pore and surface properties of TZ-HCP1 prepared under selected conditions

		$S_{\rm BET}^{\ \ b}$	$S_{\rm L}^{\ c}$	MA^d		PV^{f}	MPV
Sample	$n_{\rm B}/n_2^{\ a}$	$(m^2 g)$	-1)		MA^{e} (%)	(cm ³	g^{-1})
TZ-HCP1A	0/1	3	_	_		_	_
TZ-HCP1B	3.1/1	73	110	11	15	0.23	_
TZ-HCP1C	5.4/1	171	262	94	55	0.25	0.05
TZ-HCP1D	20/1	754	1139	375	50	0.91	0.20

^{*a*} Molar ratio ($n_{\rm B}/n_2$) of benzene to 2. ^{*b*} BET surface area. ^{*c*} Langmuir surface area. ^{*d*} Micropore area analysed *via* the *t*-plot method. ^{*e*} Contribution of microporous area. ^{*f*} Total pore volume calculated with the N₂ adsorbed at $P/P_0 = 0.99$. ^{*g*} Micropore volume according to *t*-plot analysis.



Fig. 1 (a) Nitrogen sorption isotherms and (b) pore size distribution (PSD) of TZ-HCP1D and TZ-HCP2. PSD was calculated with non-local density functional theory (NLDFT). (c and d) SEM images of TZ-HCP1D (c) and TZ-HCP2(d).

TZ-HCP1D (Table 1, Fig. 1a and b) with a higher BET surface area (754 m² g⁻¹) and larger total pore volume (0.91 cm³ g⁻¹). It should be noted that the microporous and mesoporous surface areas display equal contributions. Notably, just 22% micropore volume was observed in TZ-HCP1D. This implied that the abundance of mesopores within the networks provides an ideal platform for organic transformations involving large-sized guest molecules. Besides, non-local density functional theory (NLDFT) showed that the pore size of TZ-HCP1D was approximately 1.7 nm and 5.3 nm, respectively (Fig. 1a and b). Furthermore, thermogravimetric analysis (TGA) under a nitrogen atmosphere showed that the degradation temperature was 220 °C, 371 °C, and 468 °C for TZ-HCP1B-D, respectively (Fig. S4[†]). The stability difference above confirmed that the degree of cross-linking might also be increased gradually from TZ-HCP1B to TZ-HCP1D and affected the formation of nanopores.²³ Thus, 20/1 was set as an appropriate ratio to prepare TZ-HCPs. Accordingly, TZ-HCP2, a polymer derived from compound 2 and 9H-fluorene, was then prepared using these optimized conditions. The porous network obtained was

stable up to 429 °C under N₂ (Fig. S5†). In comparison with TZ-HCP1D, TZ-HCP2 exhibited a lower BET surface area (718 m² g⁻¹) and smaller pore volume (0.72 cm³ g⁻¹, Fig. 1a and b). The pore size was mainly centered at 1.7 nm and 5.5 nm, suggesting that micro- and mesopores coexist in TZ-HCP2. Nevertheless, the microporous contribution was up to 538 m² g⁻¹ (75%).

Solid-state ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy was used to verify the structural formation of the synthesized materials. As shown in Fig. S6,† the resonance peaks at δ = 110–147 ppm can be attributed to aromatic carbon in (non-)substituted benzene, pyridine and fluorene. In addition, NMR signals at ca. 36 ppm and 55 ppm indicated the existence of methylene carbon and methoxy groups, while the signal at 159 ppm can be ascribed to the carbon atoms of C=N in pytz.^{23,24} FT-IR spectra (Fig. S7†) of TZ-HCP showed obvious vibration peaks at 1605 cm⁻¹, which were in agreement with the signals of compound 2 and suggested the existence of tetrazine rings.^{20c} The signal peaks at 1495 and 1457 cm⁻¹ could be ascribed to vibrations from the aromatic ring skeleton, 15b,24b while that at 1249 cm⁻¹ was the signal for the C-O stretching vibrations.^{24c} Moreover, alkane signals at about 2923 and 2850 cm⁻¹ from C–H stretching vibrations can also be found in the FT-IR spectra of TZ-HCPs.^{23,24} Scanning electron microscope (SEM) analysis was performed to investigate the microtopography of the TZ-HCPs. Fig. 1c and d shows that TZ-HCP1D appears as aggregate porous particles with diameters of ca. 20-50 nm, whereas a loose flake-like shape was found for TZ-HCP2. This significant difference in morphology might be due to the larger ring-fused structure of 9H-fluorene compared with the benzene ring. Transmission electron microscope (TEM, Fig. S8[†]) results showed that TZ-HCPs consisted of nanometer-scale pores. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Fig. S9[†]) collected from the TEM analysis demonstrated that C, N and O elements were well distributed over the networks of TZ-HCPs. In addition, elemental analysis for nitrogen content (2.70% for TZ-HCP1D and 1.53% for TZ-HCP2) confirm that the loading of pytz catalyst in TZ-HCP1D and TZ-HCP2 is approximately 0.32 mmol g^{-1} and 0.18 mmol g^{-1} , respectively. The results clearly identify that the pytz unit has been well embedded into the TZ-HCP networks. As suggested by powder X-ray diffraction analysis, TZ-HCPs are amorphous polymers (Fig. S10[†]).

The light capture capacity of TZ-HCPs was precisely examined by UV-visible diffuse reflection (DR) spectra (Fig. 2a). Compared with pytz, precursor 2 generates a bathochromic shift and exhibits maximum absorption peaks at approximately 354 nm and 563 nm for the increase in degree of conjugation (Fig. S11†). The resulting TZ-HCPs display a broader photoresponse performance that ranges from 200 to 800 nm. In detail, the minimum reflections (*i.e.*, maximum absorptions) are centered at 300–550 nm and 300–400 nm for TZ-HCP1D and TZ-HCP2, respectively. However, TZ-HCP1D still exhibits strong absorption for visible light beyond 500 nm. This can be ascribed to the higher content of monomer 2 in TZ-HCP1D. In addition, a photocurrent could be detected



Fig. 2 (a) UV-visible DR spectra and (b) Kubelka–Munk plots of TZ-HCPs. (c) Energy-band positions for TZ-HCP1D and TZ-HCP2. (d and e) ESR spectra (in dark or under white light for 5 min) of TZ-HCPs (1.0 mg L^{-1}) in air-saturated EtOH that contained (d) 0.1 M DMPO or (e) TEMPO.

within the two polymers, but TZ-HCP1D displayed a slightly larger current density than TZ-HCP2 due to its lower electrochemical impedance (Fig. S13 and S14†). Optical band gaps (E_g) calculated *via* the Kubelka–Munk function were 1.92 eV and 2.43 eV for TZ-HCP1D and TZ-HCP2, respectively. The cyclic voltammetric curves in Fig. S12† reveal that the conduction band positions (E_c) *vs.* standard calomel electrode (SCE) are -0.48 V for TZ-HCP1D and -0.54 V for TZ-HCP2. These E_c values are unable to induce the formation of O₂⁻⁻ from O₂ (-0.86 V *vs.* SCE).²⁵ However, the estimated valence band positions (E_v) *vs.* SCE are 1.44 V (TZ-HCP1D) and 1.89 V (TZ-HCP2) and might show strong oxidizing ability.

Benzimidazole skeletons are widespread in pharmaceutical molecules and exhibit fascinating biological activity for cancer, viruses, funguses, psychoses and arrhythmias.²⁶ Besides, BIderived organic polymers, e.g., polybenzimidazoles (PBI), are often used in membrane fuel cells or adsorption materials.²⁷ Meanwhile, BIs can be employed as precursors of carbene or as privileged ligands for palladium, rhenium, etc.^{10j,28} So far, instructive synthesis strategies for BIs have been developed. However, high temperature, acid conditions, and long reaction times are needed for traditional methods of preparation from carboxylic acids and aromatic diamines. Some new approaches, developed later, addressed these problems, but ionic liquids, oxidants, Lewis acids, molecular iodine, acid/ base additives, or metal catalysts are often necessary for the conversion of aromatic diamines and aldehydes/alcohols.²⁹ These catalytic systems are either difficult to purify/prepare, or unstable in air/moisture, or are homogeneous and have less reusability and recyclability. A sustainable G-SO₃H catalyst was exploited to synthesize BIs efficiently by Suresh et al., yet the preparation is still tedious and less environmentally friendly, with large-scale use of H₂SO₄ and KMnO₄.³⁰ Green synthetic methods and non-noxious, metal-free, easily prepared, recyclable, reusable catalysts for preparation of BIs remain to be explored. Accordingly, increasing attention has been drawn toward green technologies, such as electrocatalysis, biomimetic catalysis, and, especially, photocatalysis.^{26b,31,38} In 2019, Chu and co-workers reported fluorescein-assisted photocatalytic synthesis of BIs in acetonitrile.^{26b} Recently, we employed thiophene-embedded porous organic photocatalysts (TP-CMPs) to prepare BIs in methanol.³² However, the toxic solvents in these two cases remain to be further optimized. Moreover, the homogeneous fluorescein is non-recyclable, and the porosities of TP-CMPs are also unsatisfactory. Considering these problems and the great significance of BIs, we envisage utilizing TZ-HCPs to realize green synthesis of BIs under light.

To evaluate the activities of TZ-HCPs as robust porous organic photocatalysts, we selected the condensation-cyclization reaction between *o*-phenylenediamine (**3a**) and *p*-chlorobenzaldehyde (**4a**) as a model reaction (Table 2). The noticeable influence of solvents on the conversion can be seen from Table 2. For example, TZ-HCP1D (0.8 mol%) was hardly able to promote the photoreaction in dichloromethane, acetone, tetrahydrofuran and acetonitrile (Table 2, entries 1–5). Fortunately, the reaction proceeded smoothly in EtOH, a safer solvent, and 90% yield was obtained after 1.5 h. Similar results could also be found for reported cases of photocatalytic synthesis of BIs. The possible reason is that the viscosity, polarity and polariz-

Table 2 Optimization of the photocatalytic conditions^a

	NH2 + OHC	-CI catalyst, so 6 W LEI air, rt	Ds C		—сі
	3a 4a	un, re		5a	
Entry	Catalyst ^{b} (mol%)	Light	Solvent	<i>t</i> (h)	Yield % ^c
1	TZ-HCP1D (0.8)	White	CH_2Cl_2	1.5	Trace
2	TZ-HCP1D (0.8)	White	acetone	1.5	Trace
3	TZ-HCP1D (0.8)	White	THF	1.5	Trace
4	TZ-HCP1D (0.8)	White	MeCN	1.5	Trace
5	TZ-HCP1D (0.8)	White	EtOH	1.5	90
6	TZ-HCP1D (1.6)	White	EtOH	1.0	98 $(90)^d$
7	TZ-HCP1D (2.4)	White	EtOH	1.0	88
8	TZ-HCP1D (1.6)	Red	EtOH	0.8	31
9	TZ-HCP1D (1.6)	Yellow	EtOH	0.8	58
10	TZ-HCP1D (1.6)	Green	EtOH	0.8	70
11	TZ-HCP1D (1.6)	Blue	EtOH	0.8	92
12^e	None	White	EtOH	1.0	Trace
13^{f}	TZ-HCP1D (1.6)	White	EtOH	1.0	Trace
14^g	TZ-HCP1D (1.6)	White	EtOH	1.0	Trace
15^h	TZ-HCP1D (1.6)	White	EtOH	1.0	38
16^{i}	TZ-HCP1D (1.6)	White	EtOH	1.0	26
17 ^j	TZ-HCP1D (1.6)	White	EtOH	1.0	Trace
18^k	TZ-HCP1D (1.6)	White	EtOH	1.0	92
19	TZ-HCP2 (1.6)	White	EtOH	1.0	97
20	2 (1.6)	White	EtOH	1.0	86
21	pytz (1.6)	White	EtOH	1.0	80

^{*a*} General conditions: **3a** (0.2 mmol), **4a** (0.2 mmol), solvent (4 mL), RT, air, 6 W white LEDs. ^{*b*} Catalyst dosage were based on pytz. ^{*c*} Isolated yields after chromatography. For entries 1–4, 12–13 and 17, almost no products are detected by thin layer chromatography (TLC). ^{*d*} 0.8 h. ^{*e*} No catalyst. ^{*f*} Under N₂ atmosphere. ^{*g*} In the dark. ^{*h*} C₂O₄(NH₄)₂ as hole scavenger. ^{*i*} KIO₃ as electron scavenger. ^{*j*} NaN₃ as ¹O₂ scavenger. ^{*k*} Benzoquinone as superoxide radical scavenger.

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ability of EtOH may influence the surface interaction between the porous photocatalysts and the substrates. In comparison with other solvents used here, EtOH might also have significant influence on the generation of light-generated electrons and holes, contributing to the electron transfer process and stabilizing the reactive intermediates.³³ TZ-HCP1D displayed significant advantages (98% yield, 1.0 h) over fluorescein and TP-CMPs after increasing the catalyst loading to 1.6 mol% (Table 2, entry 6).^{26b,32} However, the higher dosage of TZ-HCP1D did not have a positive impact on the catalytic efficiency (Table 2, entry 7), which could be attributed to the ineffective use of light because of blocking from the higher concentration of solid catalyst. Thus, the photocatalyst dosage here was set as 1.6 mol%. The influence of the nature of the light was examined precisely (Table 2, entries 6 and 8-11). With irradiation with 6 W white or blue LEDs for 0.8 h, TZ-HCP1D could provide 5a in 90-92% yield. However, unsatisfactory yields (31-70%) were obtained under red, yellow or green light within the same reaction time. In consequence, the photocatalytic effects really depend on the degree of matching of the irradiation with the light reflection/absorption of TZ-HCP1D (Fig. 2a). Considering that white light is easily available and similar to natural light, it was finally selected as the universal light source to promote the photocatalytic reaction. Control experiments showed that visible light and air (O_2) were essential for the photocatalytic synthesis of BIs (Table 2, entries 12-14). To our delight, TZ-HCP2 also displayed excellent catalytic effects (97% yield, Table 2, entry 19) under whitelight irradiation. Moreover, TZ-HCPs showed preferable activity compared with the homogeneous counterparts $pytz^{21a}$ and 2 (entries 6, 19-21). This information implies that it is practicable to prepare high efficiency, non-noxious and green heterogeneous photocatalysts from homogeneous pytz.

Once the standard reaction conditions were established, we then studied the substrate scope of the photocatalytic reaction (Table 3). With TZ-HCP1D as photocatalyst, most BIs could be synthesized efficiently within 0.5-4.0 hours. Various aromatic aldehydes with electron-donating/withdrawing substituents could react very well with unsubstituted or methyl/halogen (F, Cl, Br)-substituted aromatic diamines, and produced BIs (28 examples) in 82-99% yield. Noticeably, pyrene-1-carbaldehyde was well suited, giving 5p in a decent yield (99%), except that a longer reaction time was needed. The reason for this may be the slower mass transport process of 5p in the pores caused by poor solubility and larger steric hindrance. Experiments showed that TZ-HCP1D was tolerant of aliphatic aldehydes and produced four 2-alkyl-substituted BIs (5u-5x, 82-98% yield). In addition, heterocyclic aromatic aldehydes, e.g., furfuraldehyde, picolinaldehyde, thiophene-2-carbaldehyde and 1H-imidazole-4-carbaldehyde, could be assembled efficiently with aromatic diamines (up to 99% yield) and led to BIs (5q-5t) with double heterocycles. Specifically, 5s and 5t might be used as alternative metal ligands to promote Heck or Suzuki-Miyaura coupling reactions. TZ-HCP2 also showed impressive applicability in the green synthesis of BIs; for instance, 5a-5d, 5j-5m, 5u and 5aa could be prepared in high

 Table 3
 Green synthesis of BIs catalyzed by TZ-HCPs under visible light^a



^{*a*} Reaction conditions: **3** (0.2 mmol), **4** (0.2 mmol), TZ-HCP1D (1.6 mol%, 10 mg), EtOH (4.0 mL). Isolated yields after chromatography. ^{*b*} TZ-HCP2 (1.6 mol%, 17.8 mg) as photocatalyst. ^{*c*} Scale-up experiment: **3a** (10 mmol), **4s** (10 mmol), TZ-HCP1D (1.1 mol%, 350 mg), EtOH (200 mL).

yields (up to 98%). A scale-up experiment to synthesize **5s** was conducted, to investigate the potential of TZ-HCPs in industrial catalysis. Interestingly, the photocatalytic reaction of 10 mmol of substrate in 200 mL EtOH worked well (1.87 g, 96% yield, 0.8 h) when mediated by 1.1 mol% TZ-HCP1D. Therefore, TZ-HCPs are indeed efficient photocatalysts for the synthesis of BIs at large scale.

Catalytic recyclability and stability are the critical factors for heterogeneous catalysts in industrial applications. Therefore, the photocatalytic performances and intrinsic structures of TZ-HCPs were examined closely. The catalytic recycling experiments to synthesize **5a** were performed according to the standard conditions. TZ-HCP1D could be easily recovered *via* centrifugation or filtration from the reaction system, and then used in the next catalytic cycle. As revealed by Fig. 3, TZ-HCP1D could afford equivalent yields and maintained high catalytic activity even after 21 iterative runs. However, nitrogen sorption measurements (Fig. S17†) after the 21st run demonstrated that the BET surface area and pore volume of TZ-HCP1D decreased from 754 m² g⁻¹ to 302 m² g⁻¹ and 0.91 cm³ g⁻¹ to 0.37 cm³ g⁻¹, respectively. The decreased poro-



Fig. 3 Catalytic recycling test of TZ-HCP1D for the reaction of 3a and 4a.

sity within the network further led to the mass transport slowing down, which was confirmed by the variation in the reaction time from 60 to 110 min. Thus, perfect porosity is crucial for superior POP catalysts. In fact, the polymeric nanopores might be partially blocked by the residual products. Thus, small changes could also be found in the FT-IR spectra of the photocatalyst used after 21 runs (Fig. S18†). In addition, the structure of the porous catalyst might also be gradually affected by the reactive oxygen species generated in the photocatalysis. However, the remaining highly efficient catalytic results after 21 runs implied that the as-synthesized framework was robust enough to recycle and reuse.

Several control experiments (Table 2, entries 15-18) were conducted to study the reaction mechanism. The reactions were severely suppressed when photogenerated hole (h⁺) scavenger C2O4(NH4)234 or photoexcited electron (e-) scavenger KIO₃ was added into the reaction system, respectively (Table 2, entries 15 and 16). These results implied that h^+ and e^- are both crucial for the photocatalytic reaction. Meanwhile, trace product was observed in the presence of NaN_3 (¹O₂ scavenger), but the existence of benzoquinone (O2 - scavenger) did not have an adverse effect on the yield (Table 2, entries 17 and 18).³⁵ Thus, the major working oxygen species here might be $^{1}O_{2}$ rather than O_{2} ., which is in accordance with the energyband structures of TZ-HCPs. Furthermore, DMPO and TEMPO were selected as spin-trapping agents in electron-spin resonance (ESR) experiments to detect 1O2 and O2 - within TZ-HCPs, respectively.^{25a,34-36} Weak signals (Fig. 2d) for DMPO-O2^{•-} showed that O2^{•-} was not easy to generate in TZ-HCP1D and TZ-HCP2. Upon illumination, however, obvious peaks of TEMPO- $^{1}O_{2}$ were formed, which proved that $^{1}O_{2}$ was produced easily within the pytz-based organic polymers (Fig. 2e). It should be noted that traces of 2-methyl benzimidazole could be found in the reaction system (Fig. S19[†]). The results indicated that a small amount of EtOH could be oxidized into acetaldehyde by h^+ or 1O_2 , and then reacted with o-phenylenediamine to yield 2-methyl benzimidazole.

Based on the information obtained above, a possible photocatalytic reaction mechanism to prepare **5a** was proposed.^{21*a*,37}



Fig. 4 Possible mechanism for the condensation–cyclization reaction between 3 and 4 catalyzed by TZ-HCPs under light.

As shown in Fig. 4, upon irradiation with light, the h⁺ and e⁻ could initiate the following reaction: h⁺ ($E_v = 1.44$ V) could capture an electron from imine I ($E(I/I^{++}) = 0.45$ V),^{26b,32} and generate I'+, which then released a proton to provide II. Cyclization of the free radical intermediate took place and was reduced by photoexcited e⁻ to give III. Meanwhile, partial singlet electrons translated into excited triplet electrons *via* intersystem crossing, and this led to the generation of ¹O₂. Aminal IV, derived from intermediate III by acquiring a proton, further reacted with ¹O₂ to produce intermediate V. After losing hydrogen peroxide (Fig. S20⁺),³⁶ the final product **5a** could be obtained.

Conclusions

In summary, we incorporated a versatile photocatalyst with high nitrogen content, namely, pyzt, into porous polymers (TZ-HCPs) through a bottom-up fabrication strategy. The TZ-HCPs were easily formed via Friedel-Crafts alkylation promoted by inexpensive and safe FeCl₃. The high BET surface areas (>710 $\text{m}^2 \text{g}^{-1}$) and coexisting micro- and mesopores of TZ-HCPs increased the accessibility of photocatalytic sites and facilitated molecular transport. On account of the oxidation ability of electron-deficient s-tetrazine, TZ-HCPs exhibited rational energy-band structures and excellent activities to induce the formation of singlet oxygen under visible light. It was shown that TZ-HCPs displayed powerful photocatalytic efficiency for the green synthesis of benzimidazoles (up to 99% yield, 0.5-4.0 h) in EtOH. Benzimidazole products that contain pyridine or imidazole (91-99% yield) could also be easily prepared at gram-scale and acted as potential ligands. TZ-HCPs showed preferable recyclability (at least 21 iterative runs, 96-98% yield) and stability in the reaction system. The catalytic performance of TZ-HCPs was comparable with fluorescein and TP-CMPs reported in the literature. Additionally, the heterogeneous photocatalytic system is consistent with the principles of green chemistry because of its high efficiency and reusability, especially avoiding the use of high temperature, metals, strong oxidants and acid. We believe that TZ-HCPs will facilitate the extensive application of HCPs as

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environmentally friendly photocatalysts in the green-safe preparation of fine chemicals.

Author contributions

Z. Pan and W.-K. An conceived the scientific research project. W.-K. An, S.-J. Zheng, H.-X. Zhang, T.-T. Shang, H.-R. Wang, X.-J. Xu and M.-S. Hou prepared the TZ-HCPs and performed the experiments on synthesis, characterization and photocatalysis tests. Q. Jin and S. Jiang analysed the porosities of TZ-HCPs. W.-K. An and Y. Qin carried out the UV-vis DR spectra, energy-band structures and EDS elemental mapping analyses. S.-J. Zheng, W.-K. An and Z. Pan analyzed the catalytic mechanism and NMR spectra. Y.-L. Ren conducted the key experiments to capture 2-methyl benzimidazole, analysed the results and revised the catalytic mechanism. H.-X. Zhang, S.-J. Zheng and W.-K. An wrote the original manuscript. Z. Pan and C.-L. Xu revised the manuscript. All authors discussed the comments and contributed to generation of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China (No. 21702049 and 21702047), the Key Scientific Research Projects in Henan Colleges and Universities (No. 18A150006).

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