Chapter 18
Nanostructured Porous Polymers for Metal-Free Photocatalysis

Wei Huang, Run Li, Beatriz Chiyin Ma and Kai A.I. Zhang

Abstract The direct utilization of sunlight, especially the visible light part of solar spectrum as a clean and abundant energy source to activate organic reactions is a great challenge in organic chemistry and materials science. Beside the well-developed metal-based photocatalysts such as inorganic semiconductors or transition metal complexes, pure organic photocatalytic systems have gained much attention currently. Among metal-free photocatalysts, nanostructured and highly porous conjugated polymers are of particular interest due to their flexible tunability of optical and electronic properties. In this chapter, an overview on the development of this new class of functional materials is given. Various structural design methods such as donor–acceptor combination on the molecular level, band positions modification, and *p*/*n* character variation are shown, and porosity, morphology control and their impact on the photocatalytic efficiency are also described.

18.1 Introduction

Sunlight has been regarded as a clean and abundant energy source. The direct utilization of sunlight, especially the visible light part of solar spectrum as the activation energy for organic transformation reactions has attracted much attention in the field of organic chemistry and materials science [1]. Tremendous effort has been paid for the development of visible light photocatalytic systems. Beside the well-developed metal-based photocatalysts such as inorganic semiconductors or transition metal complexes, organic photocatalytic systems have gained much attention currently. Among those, binary carbon nitrides, a state-of-art example, have been recently wildly employed as metal-free photocatalysts due to their promising electronic and optical properties. Another emerging class of metal-free photocatalysts, conjugated polymer-based nanostructured and highly porous materials, is of particular interest due to the ease tunability of their semiconductor

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properties via donor–acceptor combination on the molecular level, and the ability of modifying the band gap, band positions, and p/n characters. In this chapter, a general overview on this new class of functional materials for applications in metal-free photocatalysis is given and the impact of important properties such as porosity, morphology, and band structures on the photocatalytic efficiency is also described.

18.2 Conjugated Microporous Polymers (CMPs) for Visible Light Photocatalysis

Conjugated microporous polymers (CMPs) are a subclass of porous organic materials with an amorphous three-dimensional conjugated network combined with permanent microporosity [2–5]. Recently, CMPs have been employed as promising photocatalysts for a vast number of organic reactions, taking advantage of their broad absorption in the visible range and highly tunable energy band positions.

18.2.1 Singlet Oxygen Generation

Singlet oxygen ($^1O_2$), a reactive oxygen species, has been applied in a wide spectrum of applications including wastewater purification, photodynamic therapy, and selective oxidation of organic compounds due to its high reactivity and oxidative ability [6–8]. In 2013, Vilela and coworkers reported the first example of photocatalytic application of CMPs as photosensitizer for $^1O_2$ generation under visible light irradiation [9]. A string electron-withdrawing unit, benzothiadiazole was introduced into the polymer backbone combined with 1,3,5-triethynylbenzene as a weak electron donor and cross-linker via Sonogashira–Hagihara cross-coupling reaction (Fig. 18.1). The authors introduced a template method using silica nanoparticles (SiO_2NPs) to modify the surface area of the polymer networks. They found out that the photocatalytic activity of the polymers depended strongly on their surface area, and the polymer with highest surface area of 660 m^2/g could oxidize α-terpinene with a conversion of 96% upon irradiation at 420 nm, with a singlet oxygen generation quantum yield of 0.06.

Han and coworkers presented a series of metallophthalocyanine-based CMPs (MPc-CMPs) as photosensitizer for the generation of $^1O_2$ [10]. The CMPs were synthesized by Schiff base chemistry between tetraaminometallophthalocyanime ($MPc(NH_2)_4$) and terephthalaldehyde under solvothermal conditions (Fig. 18.2). The CMPs exhibited high efficiency for $^1O_2$ generation upon irradiation in long wavelength range at 700 nm.

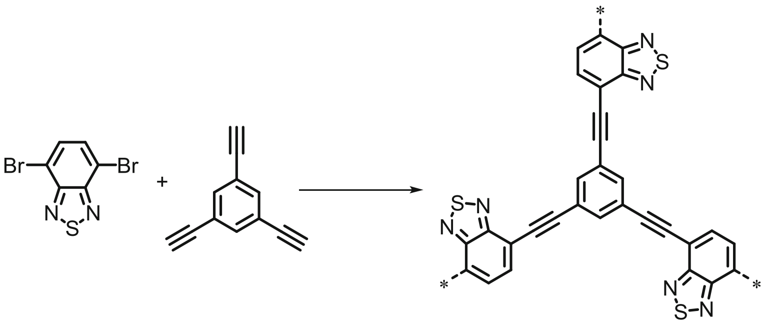


Fig. 18.1 Schematic representation of the synthesis of a benzothiadiazole-based CMP

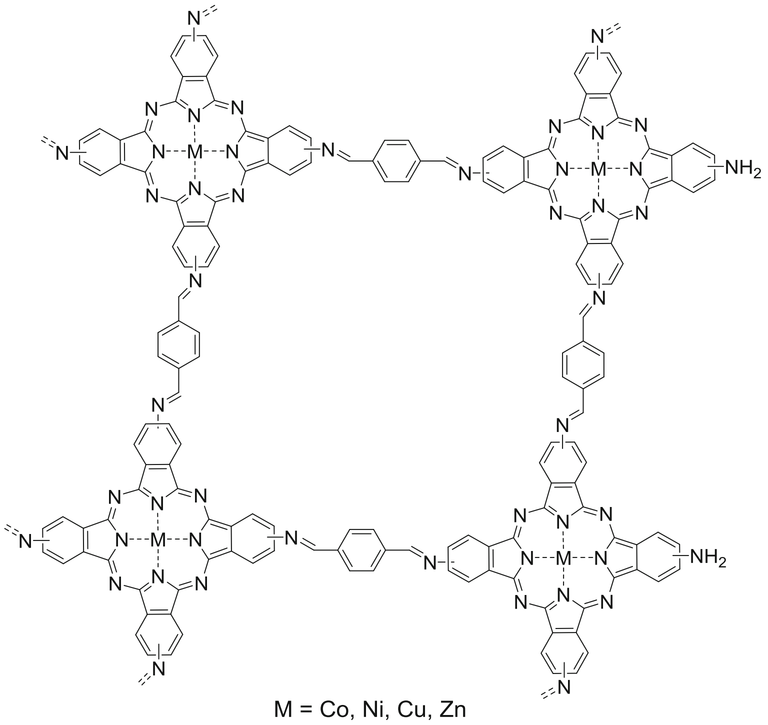


Fig. 18.2 Representative of the MPc-CMPs

18.2.2 Organic Transformation Reactions

Recently, CMPs have recently emerged as an efficient and stable platform for heterogeneous visible-light-promoted chemical transformations owing to their semiconductor-range band gaps and excellent absorption of visible light. The

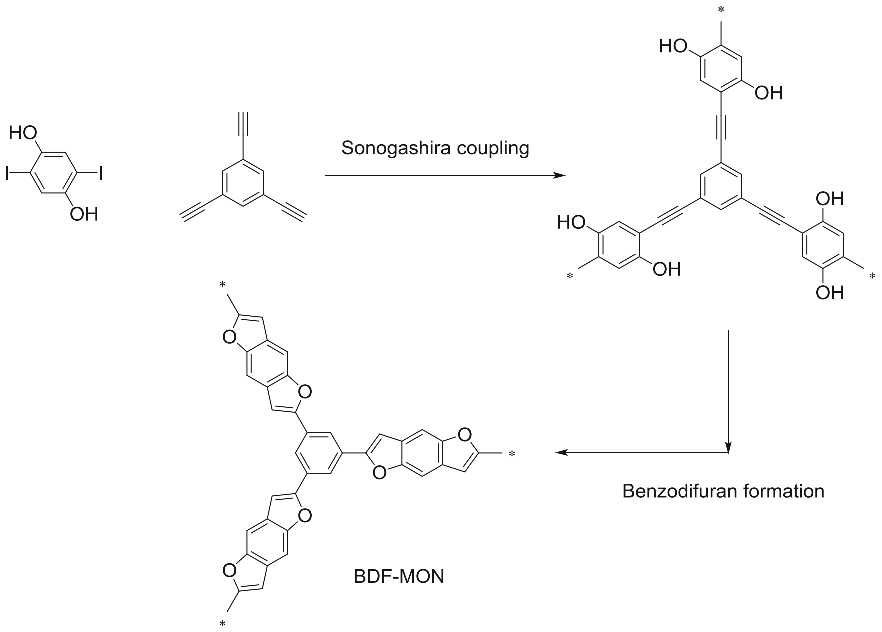


Fig. 18.3 Synthesis of microporous organic networks containing benzodifuran moieties

incorporation of designed photoactive units into the polymer network backbone is a promising strategy to obtain polymer-based organic materials with photocatalytic activity. As displayed in Fig. 18.3, Son et al. reported a tandem synthetic strategy for the preparation of microporous organic networks containing benzodifuran moieties (BDF-MON) [11]. The corresponding polymers networks showed promising photocatalytic activities in the oxidation conversion of primary amine into imines under visible light irradiation.

Rose Bengal is an effective molecular organic photocatalyst and has been used in the field of homogeneous photocatalysis due to its low cost and low toxicity [12]. Jiang et al. [13] have recently reported on CMP networks by incorporating the photoactive Rose Bengal unit into the polymer skeletons via Sonogashira–Hagihara cross-coupling reaction (Fig. 18.4). The polymers were used for aza-Henry reaction at room temperature under visible light irradiation.

For the light-induced photoredox reactions, one of the main factors of the catalyst is the photo-generated valance band (VB) and conduction band (CB) positions, which represent the crucial oxidative and reductive potentials of the catalyst. Zhang and coworkers showed recently a structural design principle of a series of conjugated microporous polymer networks to allow the fine alignment of the valence and conduction band levels for enhanced catalytic activity [14]. As shown in Fig. 18.5, via merely altering the substitution positions on the centered phenyl unit, which functions as the 3D center of a series of poly(benzooxadiazole) networks, the resulted VB and CB positions of the polymers can be optimally

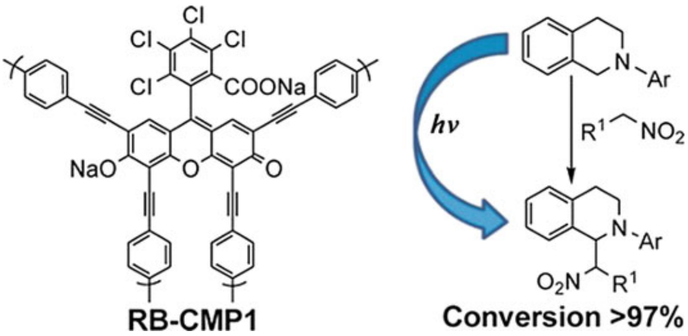


Fig. 18.4 Molecular structure of RB-CMP1 and its application for photocatalytic aza-Henry reactions (reproduced from Ref. [13] with kind permission of © 2013 American Chemical Society)

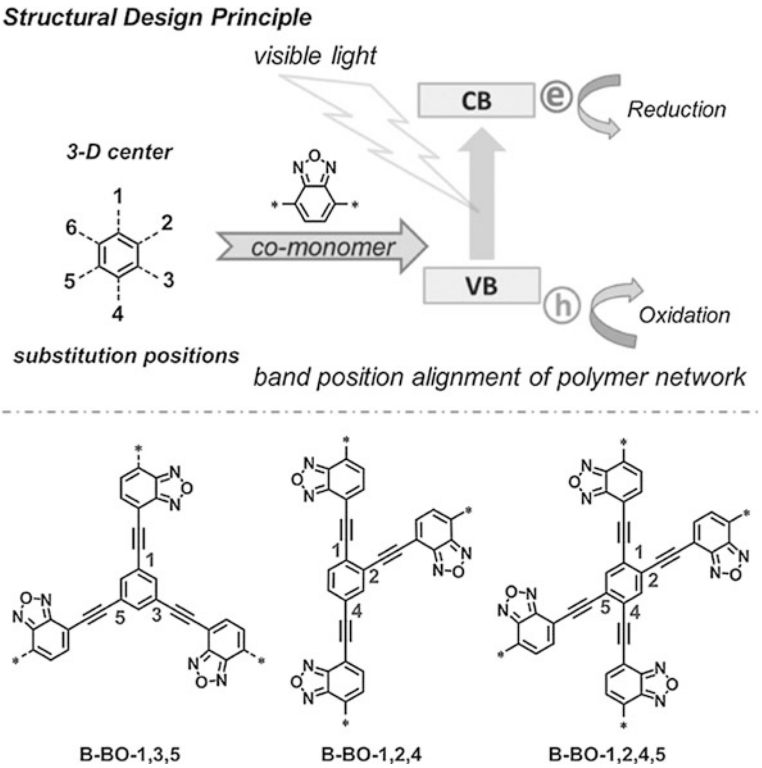


Fig. 18.5 Structural design principle of valence and conduction band position modification of conjugated microporous poly(benzooxadiazole) networks by altering the substitution position on the 3D center (reproduced from Ref. [14] with kind permission of © 2015 Wiley-VCH)

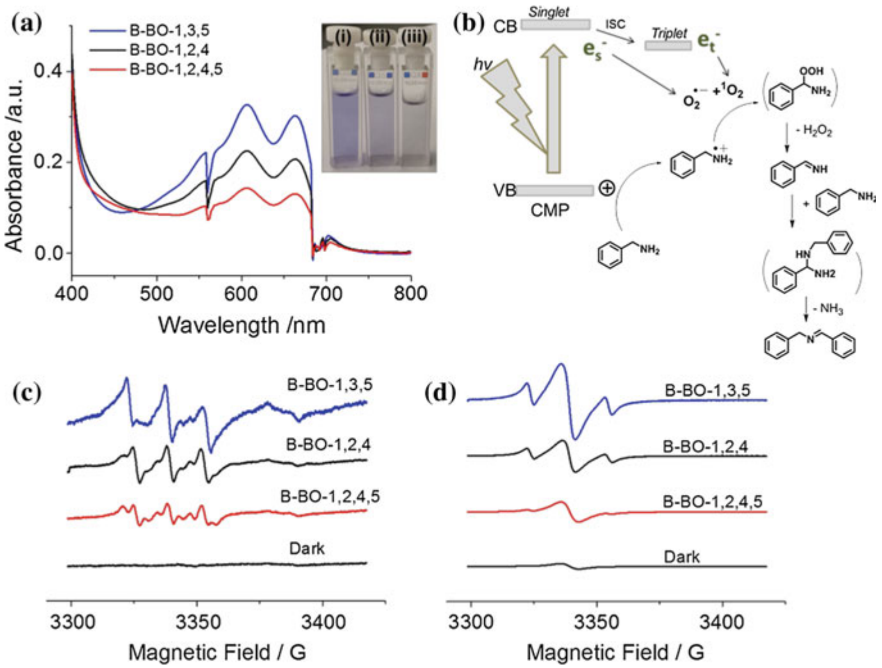


Fig. 18.6 **a** UV/Vis spectra and photograph of the cationic radical of TMPD (100 mM in 3 mL CH_3CN) after photo-inducted oxidation by CMPs (2 mg/mL) in after 1 h under *blue* LED in air. *Inset* (i) B–BO–1,3,5; (ii) B–BO–1,2,4; (iii) B–BO–1,2,4,5; **b** Proposed reaction mechanism of the photocatalytic oxidative coupling of benzylamine. *ISC* intersystem crossing. **c** ESR spectra of DMPO–O_2^-, and **d** TEMPO–$^1O_2$ adducts for different CMPs under light and in dark (reproduced from Ref. [14] with kind permission of © 2015 Wiley-VCH)

aligned without changing the electron donor and acceptor moieties in the polymer network backbone. It was shown that the photocatalyst designed with the 1,3,5-substitution positions of the centered phenyl ring demonstrated the superior photocatalytic activity in the oxidative coupling of benzyl amines (Fig. 18.6). The superior photo-oxidative activity of B-BO-1,3,5 compared to B-BO-1,2,4 and B-BO-1,2,4,5 results from the highest oxidation potential of 1.55 V and reduction potential of −1.19 V of B–BO–1,3,5. The authors also demonstrated that during the catalytic reaction, both reactive oxygen species (O_2^- and $^1O_2$) could be generated, indicating the existence of photo-generated electrons from both singlet and triplet states (Fig. 18.6).

By keeping the same geometric structure of the polymer network, Zhang and coworkers also demonstrated that the chemical composition inside the polymer backbone also had a considerable impact on the photocatalytic efficiency [15]. In their report, a series of poly(benzochalcogenadiazole)s were synthesized and applied for the photocatalytic oxidation of amines (Fig. 18.7). It was found that the benzothiadiazole-based polymer exhibited the highest catalytic activity.

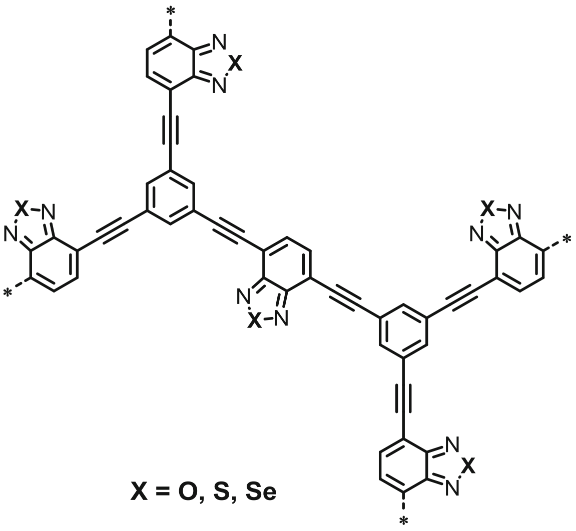


Fig. 18.7 Representative structures of the designed conjugated porous poly(benzochalcogenadiazole)s

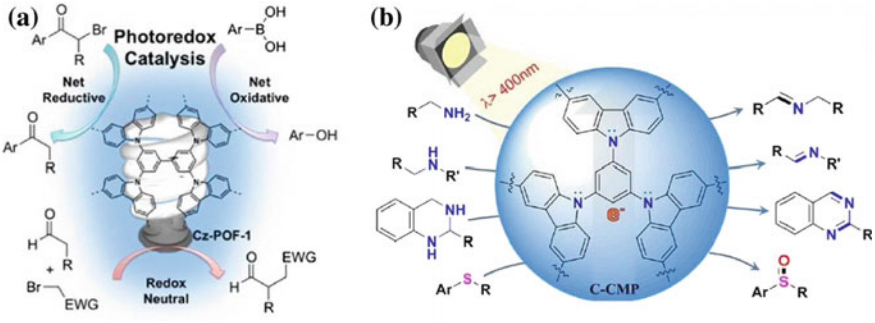


Fig. 18.8 Chemical composition of carbazolic-based CMPs and their application as visible light photocatalyst for **a** a series of photoredox reactions and **b** photocatalytic oxidation of organic compounds (reproduced from Ref. [16, 17] with kind permission of © 2015, 2016 American Chemical Society)

Very recently, Zhang and Loh prepared a series of carbazolic-based CMPs for photocatalytic applications [16, 17]. The chemical compositions are shown in Fig. 18.8. Unlike the convenient CMPs prepared via palladium (Pd)-catalyzed cross-coupling reaction, these carbazolic-based CMPs can be easily synthesized by $FeCl_3$-induced oxidative polymerization of the carbazolic monomers and usually exhibit extremely high-BET surface area (up to 2065 m^2/g). These carbazolic-based CMPs show highly efficient photocatalytic efficiency toward a broad range of organic reaction, including dehalogenation of phenacyl bromide derivatives, α-alkylation of aldehydes, hydroxylation of arylboronic acids, oxidative coupling of primary amines, aerobic dehydrogenation of non-active secondary amines, and selective oxidation of sulfides.

Covalent triazine frameworks (CTFs), a type of nitrogen-rich porous polymer, have been intensely studied in various application fields in the past decade such as energy storage, catalysis, and gas absorption/separation, due to their extraordinary chemical stability and high porosity [18–21]. However, the optical property of the CTFs has been largely ignored. To date, the utilization of CTFs as catalyst for photocatalytic organic transformation is rarely reported. Very recently, Zhang and coworkers reported nanoporous CTF-based materials as a metal-free photocatalyst for photocatalytic reduction of 4-nitropheno (4-NP) to 4-aminepheno (4-AP) [22]. The photoactive CTFs were synthesized based on trimerization reaction of aromatic nitrile units catalyzed by trifluoromethanesulfonic acid (TfOH) vapor in a solid state with silica nanoparticle as templates (Fig. 18.9).

In addition to the pure organic photocatalytic systems, a hybrid material of Pd nanoparticles deposited on CMP network was recently developed for visible-light-promoted Suzuki cross-coupling reactions [23], via the formation of a hybrid heterojunction, i.e., a metal–semiconductor contact between Pd nanoparticles and CMP, resulting in a positively charged region on the CMP and a negatively charged site on the Pd nanoparticles at the interface due to the Schottky effect [24–27]. As shown in Fig. 18.10, a conjugated microporous poly(benzoxadiazole) network (B–BO_3) was chosen as the semiconductive polymer support, on which Pd NPs with sizes between 5 and 10 nm were subsequently immobilized. The coupling reactions of aryl halides with arylboronic acid yielded excellent conversions up to 98% under visible light irradiation at room temperature (Fig. 18.11).

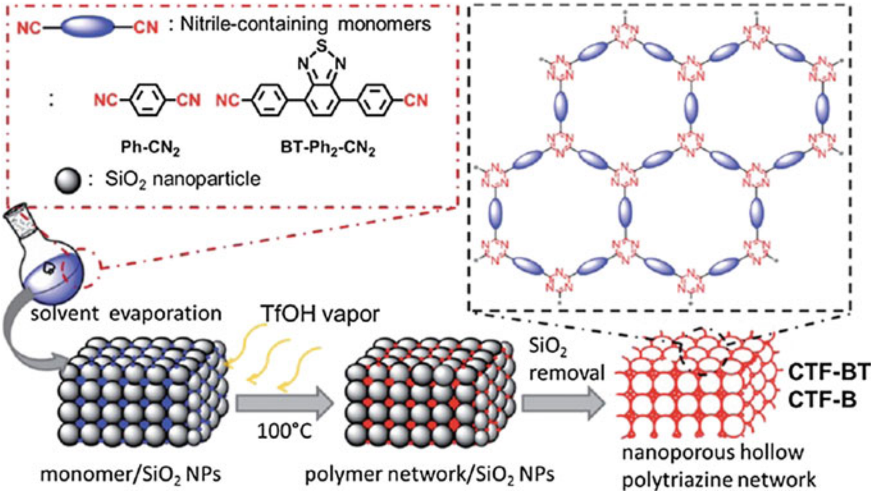


Fig. 18.9 Schematic of solid–vapor synthesis and idealized structures of the nanoporous hollow polytriazine networks (reproduced from Ref. [22] with kind permission of © 2016 Royal Society of Chemistry)

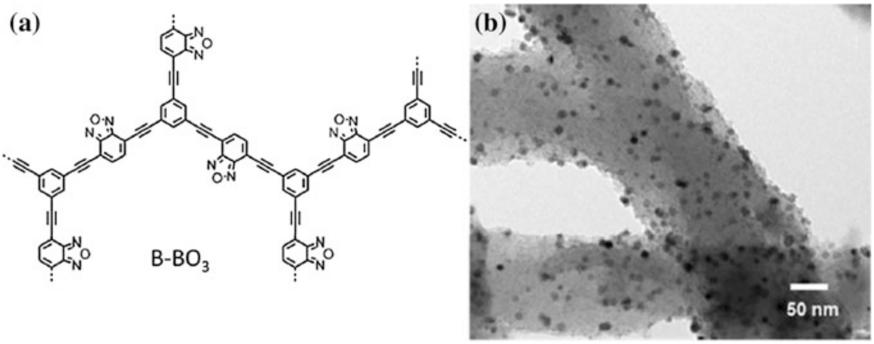


Fig. 18.10 **a** Polymer backbone structure of B–BO$_3$. **b** TEM image of B–BO$_3$ immobilized with Pd NPs with sizes between 5 and 10 nm (reproduced from Ref. [23] with kind permission of © 2015 American Chemical Society)

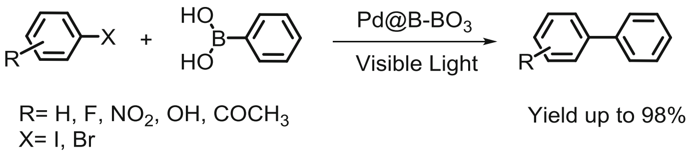


Fig. 18.11 Photocatalytic Suzuki cross-coupling reaction using a conjugated microporous polymer network with immobilized with Pd nanoparticles

18.2.3 Photocatalytic Water Splitting

Solar-driven hydrogen generation through a photocatalytic process has been attracting strong research attentions as one of the most promising strategies to obtain sustainable energy resources [28]. A vast number of studies have focused on inorganic semiconductors as photocatalysts for hydrogen production from water using ultraviolet (UV) or visible light. In the past decade, the use of organic semiconductor as metal-free photocatalysts for visible-light-induced hydrogen production from water has attracted increasing interest because of their vast synthetic diversities for modifying the electronic and structural properties of the photocatalysts [29, 30]. Cooper et al. currently prepared a series of amorphous, microporous organic polymers with exquisite synthetic control over the optical gap in the range 1.94–2.95 eV by varying monomer composition with the best hydrogen evolution rate of 18.4 μmol h^{-1} (Fig.18.12) [31]. Interestingly, the polymers do not require the deposition of an additional metal cocatalyst.

Wang et al. [32] recently reported on a series of conjugated polybenzothiadiazole polymers for hydrogen production using visible light. By alternating the substitution position of the electron-withdrawing benzothiadizole unit on the phenyl unit as a comonomer, various polymers with either one- or three-dimensional

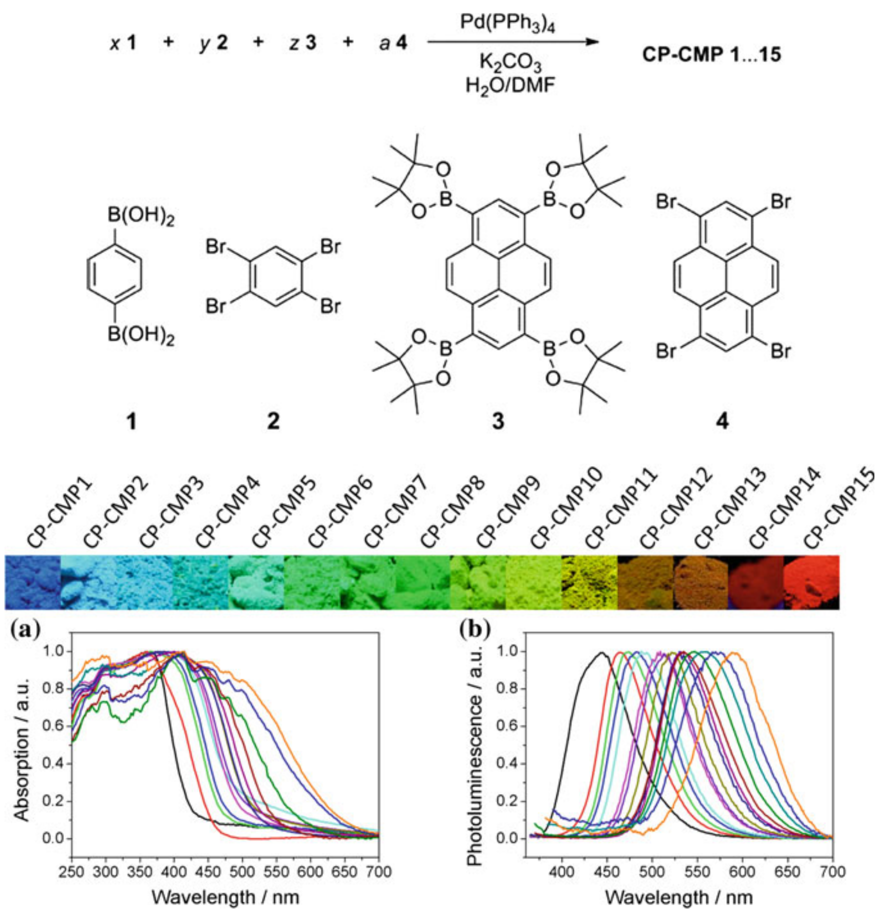


Fig. 18.12 (*Top*) Synthesis of conjugated copolymer photocatalysts (CP-CMP1-15) via Suzuki–Miyaura cross-coupling reaction. (*bottom*) Optical properties of the polymers with **a** UV/Vis absorption and **b** photoluminescence spectra of the polymers (reproduced from Ref. [31] with kind permission of © 2015 American Chemical Society)

structures were synthesized and the effect of the molecular structure on their catalytic activity was investigated (Fig. 18.13). Significantly, the linear conjugated polymers exhibited superior photocatalytic activity, compared to its three-dimensional polymer network counterparts in H_2 evolution from water with a hydrogen evolution rate (HER) of 116 μm mol h^{-1} (Fig. 18.14). The authors proposed that the main reason for the superior efficiency of the linear polymers was likely the high efficiency of its light-induced charge-transfer, charge-separation, and electron-transfer ability.

Yu et al. presented noble porous conjugated polymers, which were synthesized with different light-harvesting chromophores and transition metal-binding bipyridyl

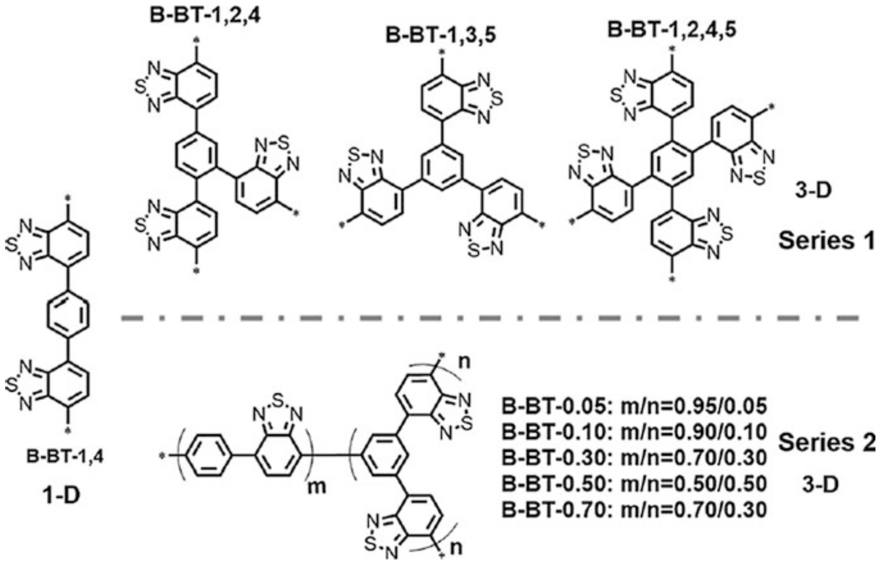


Fig. 18.13 Structures of two series of polybenzothiadiazoles with different molecular designs (reproduced from Ref. [32] with kind permission of © 2016 Wiley-VCH)

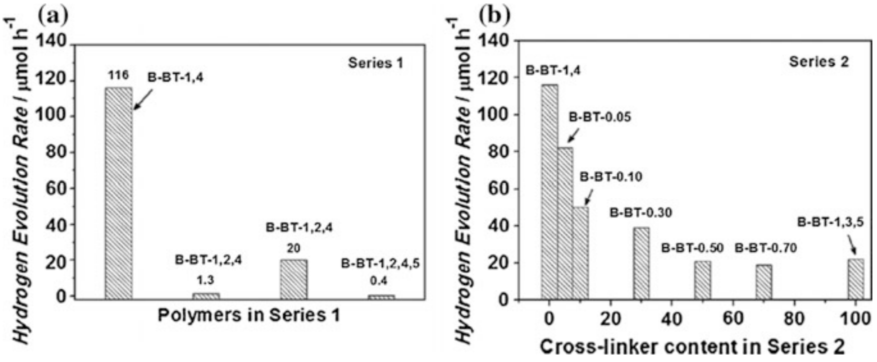
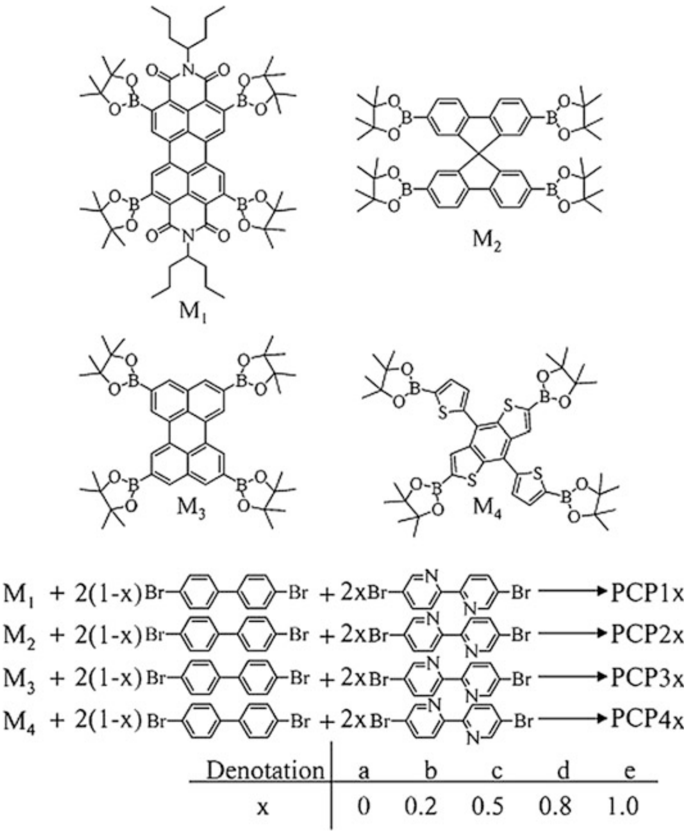


Fig. 18.14 H_2 evolution rates using polymers in Series 1 (**a**) and Series 2 (**b**) (reproduced from Ref. [32] with kind permission of © 2016 Wiley-VCH)

(bpy) sites (Fig. 18.15) [33]. Their results showed that the incorporation of bpy units can greatly increase the photocatalytic activity of hydrogen generation due to the improved light absorption, better wettability, local ordering structure, and the improved charge-separation process. The authors found that the hydrogen generation rate of photocatalyst increased rapidly as the residual metal content increases from 0.04 to 0.46% and becomes saturated at higher Pd content.



Denotation	a	b	c	d	e
x	0	0.2	0.5	0.8	1.0

Fig. 18.15 Structures of monomers and synthesis of PCP photocatalysts by Suzuki polycondensation (reproduced from Ref. [33] with kind permission of © 2016 American Chemical Society)

18.3 Water-Compatible Conjugated Microporous Polymers for Visible Light-Driven Photocatalysis in Aqueous Medium

Most of the CMPs are insoluble networks, which limit the range of processing options. Regarding the development of more sustainable reaction media for organic reactions, much effort has been devoted to the use of “green” solvents, in particular water, as a cheap and environment-friendly alternative for chemical transformations instead of hazardous halogenated solvents [34, 35]. So far, only few research reports have been described as steps toward the synthesis of water-soluble CMPs for photocatalytic reactions. Modifications of pristine CMPs [36, 37] and emulsion techniques for formation of nanoparticulate CMPs [38, 39] have been employed as strategies to enhance the water compatibility of the polymer networks. A post-modification method of alkyne-bearing conjugated microporous

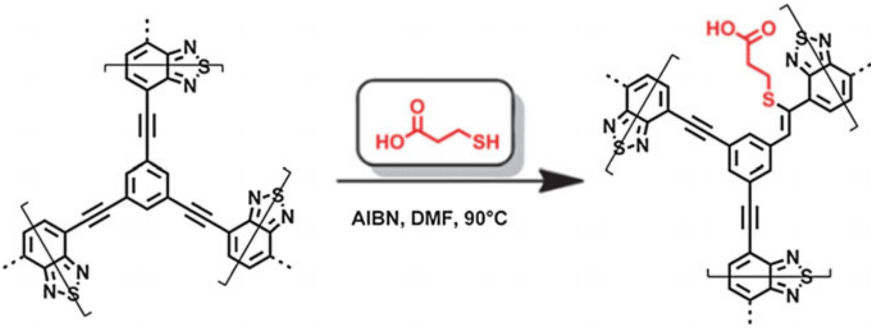


Fig. 18.16 Schematic representation of post-modification of CMP via thiol-yne chemistry (reproduced from Ref. [36] with kind permission of © 2013 Royal Society of Chemistry)

polybenzothiadiazoles via a thiol-yne chemistry (Fig. 18.16) was reported to generate *singlet* oxygen for the conversion of furoic acid to 5-hydroxy-2(5H)-furanone in water [36].

Another modification strategy based on a simple protonation method (Fig. 18.17) showed that stable water-compatible conjugated microporous polyazulenes were able to photoreduce Cr^{VI} to Cr^{III} in aqueous medium [37].

A recent report by Zhang and coworkers showed that CMP nanoparticles (CMP NPs) with a variety of shapes could be obtained via Suzuki–Miyaura and Sonogashira–Hagihara coupling in miniemulsion (Table 18.1, Fig. 18.18). The stable CMP NPs were employed in the reductive activation of molecular oxygen for the photodegradation of organic dyes and also showed the ability for the photooxidation of *N,N,N′,N′*-tetramethyl-p-phenylenediamine in water under visible light irradiation [39]. The authors also pointed out that by using the CMP NPs in water, different reactive species such as superoxide ($\bullet O_2^-$), *singlet* oxygen ($^1O_2$), •OH, and h^+ could be generated under visible light irradiation.

18.4 Macroporous Conjugated Polymers for Visible Light Photocatalysis

Polymerized high internal phase emulsion (polyHIPE) was a relatively novel method for the synthesis of conjugated macroporous polymers containing large-scale porosity in micrometer scale. In the past, the class of macroporous polymer-based materials has been used in a large range of applications such as tissue-engineering scaffolds [40], enzyme immobilization [41, 42], gas storage [43], and separation media [44]. The first examples of fully conjugated polyHIPEs were reported by Vilela and coworkers (Fig. 18.19) [45]. The authors showed that with the increase of benzothiadiazole moiety inside the polymer backbone, the

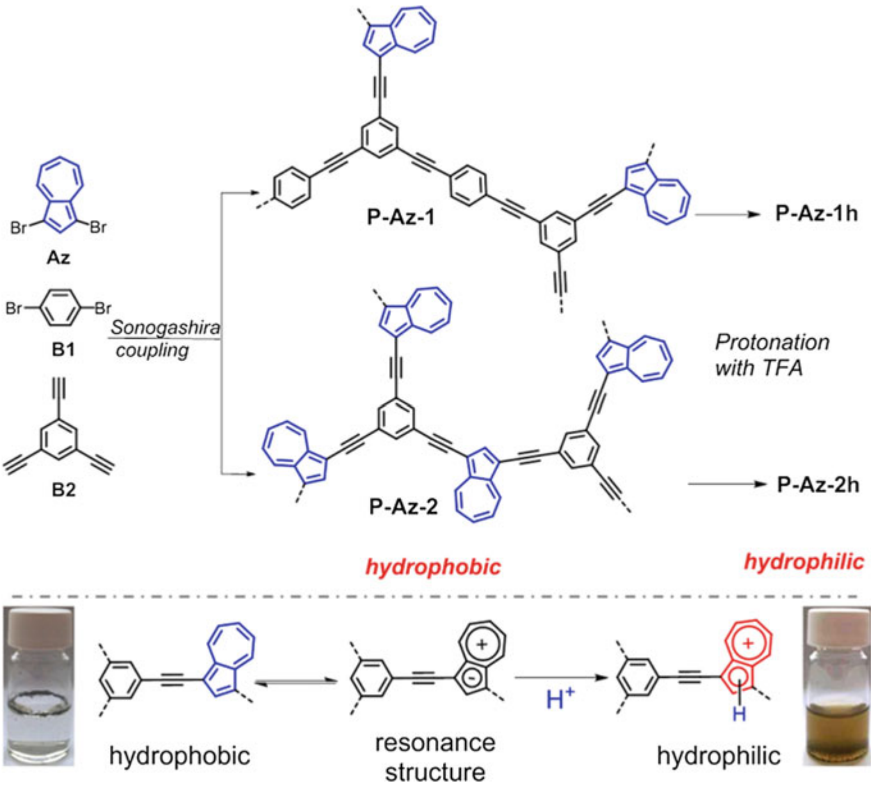


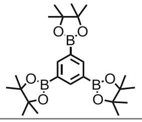
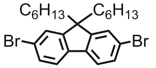
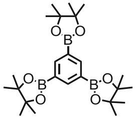
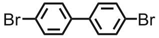
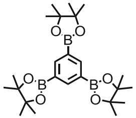
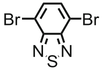
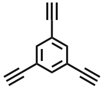
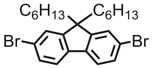
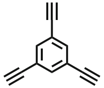
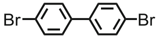
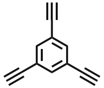
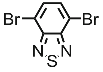
Fig. 18.17 Synthetic pathway and modification method for hydrophilic, conjugated microporous poly-azulene networks (reproduced from Ref. [37] with kind permission of © 2016 Wiley-VCH)

generation rate of singlet oxygen increased. In addition, a flow photoreactor was also designed for continuous and efficient singlet oxygen production.

Zhang and coworkers demonstrated a nanopore-engineering method of fully conjugated polyHIPEs in order to introduce micropores into the macorporous polymer networks [46]. By using cleavable *tert*-butyl carboxylate group as building unit for the polymer, extra nano-sized pores could be created by removing the *tert*-butyl carboxylate functional group, gaining a surface area increase by maximal eight times (Fig. 18.20). The photocatalytic oxidation of sulfides was carried out to demonstrate the photocatalytic efficiency in a continuous flow setup system. It was shown that mono-oxidized product of the thioethers could be obtained with yields of >99% and selectivity of >99% in best cases.

Two other examples of conjugated polyHIPEs were reported recently by Zhang et al. [47, 48]. The polyHIPE containing the strong electron-withdrawing benzobisthiadiazole (BBT) demonstrated a high photocatalytic efficiency in the dehalogenation reaction of a-bromoacetophenones under the irradiation of 23 W household bulb [47]. Another conjugated polyHIPE containing benzoxadiazole

Table 18.1 Various monomers used for the different CMP NPs and their physical properties (reproduced from Ref. [39] with kind permission of © 2015 Royal Society of Chemistry)

CMP NPs	Cross-linker (A_3-type)	Comonomer (B_2-type)	Shape	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)	Band gap/opt. (eV)
B–FL_3–a			Spherical	18	0.058	7.5	3.04
B–BPh_3–a			Irregular shape	281	0.264	1.5	2.52
B–BT_3–a			Rod-shape	93	0.220	1.5	1.96
B–FL_3–b			Spherical	48	0.067	3.8	2.64
B–BPh_3–b			Spherical	512	0.382	1.4	2.36
B–BT_3–b			Ring-shape	200	0.560	1.4	1.76

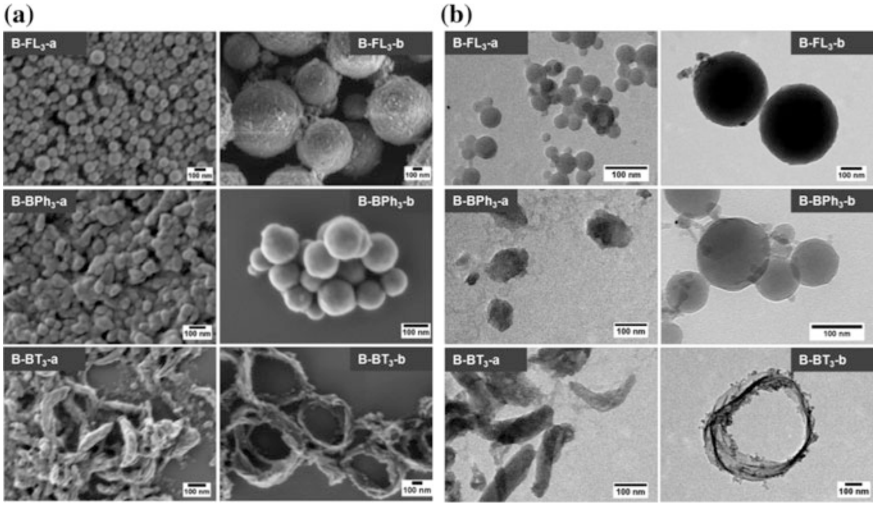


Fig. 18.18 **a** SEM and **b** TEM images of the CMP NPs with different shapes (reproduced from Ref. [39] with kind permission of © 2015 Royal Society of Chemistry)

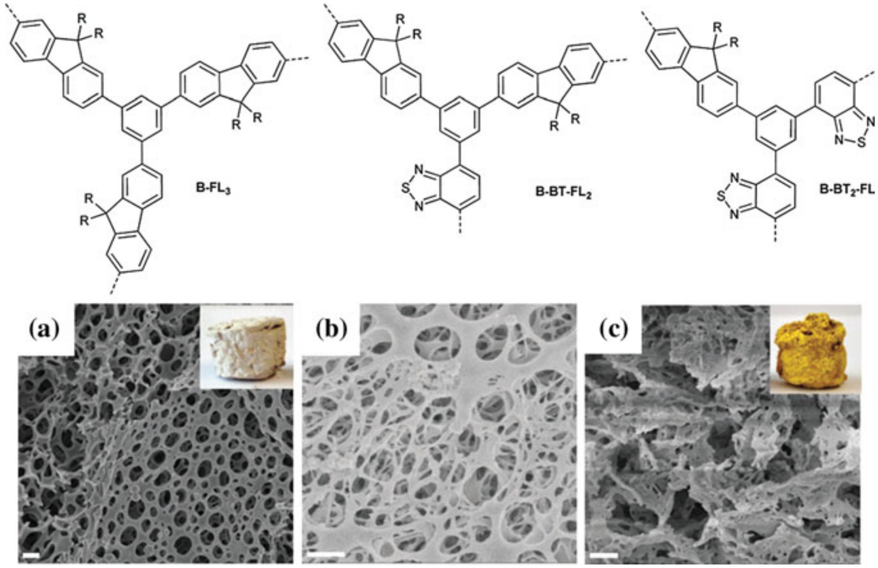
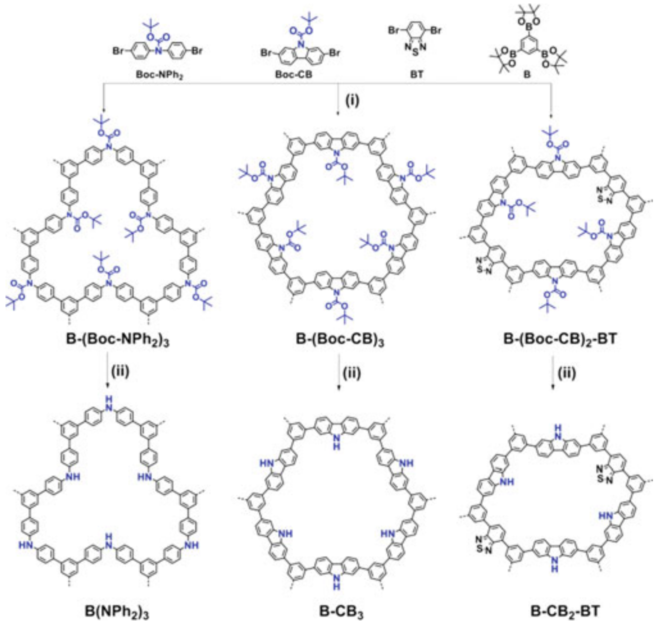


Fig. 18.19 Chemical structures and morphology of the conjugated polyHIPEs (reproduced from Ref. [45] with kind permission of © 2013 Royal Society of Chemistry)



only macropores
surface areas: 27~45m^2/g

micropores (d=1.5 nm)
in macropores
surface areas: 53~230m^2/g

Fig. 18.20 Idealized structures and surface area control via nanopore engineering of macroporous polymer networks (reproduced from Ref. [46] with kind permission of © 2014 Royal Society of Chemistry)

(BO) as photoactive moiety showed a high activity for visible-light-activated radical polymerization of methyl methacrylate (MMA) [48].

18.5 Non-conjugated Nanoporous Polymer Containing Organic Semiconductor Moieties

Besides the fully conjugated polymer networks, non-conjugated nanoporous polymers have also been developed as visible-light-active photocatalysts. To achieve a high catalytic efficiency, highly photoactive units such as benzothiadiazole [49], boron-dipyrromethene [50], and thioxanthone [51] were introduced into cross-linked polymer networks for the design of photocatalysts. The cross-linking of the photoactive units could be realized in various methods, for example, Friedel–Crafts alkylation reaction [49], "click" reaction [50] and anion polymerization [52].

Various organic reactions driven by active oxygen species such as oxygenation of sulfides [50] and olefinic compounds [53] and degradation of organic pollutions [54] were reported. Jing et al. prepared cross-linked porous polymers by introducing the Boron-dipyrromethene (BODIPY) unit into a polystyrene matrix, which demonstrated a high catalytic efficiency for the oxidation of organic sulfides [50].

Yagci et al. [51] reported the photo-generated radical initiator could be used for the polymerization of MMA with both conjugated polymer and non-conjugated polymer containing thioxanthone unit. A recent report of Vilela et al. [54] demonstrated that a benzothiadiazole-containing polyamide polymer could efficiently photo-generated singlet oxygen and therefore degrade organic contaminants such as bisphenol A and cimetidine. Zhang and coworkers reported a series of microporous polymers containing 4,7-diphenyl-2,1,3-benzothiadiazole as photoactive moiety via Friedel–Crafts alkylation reaction [49]. The polymers were employed for highly selective bromination reaction of electron-rich aromatic compounds with conversion up to 99% and selectivity up to 99% in best cases.

18.6 Conclusions

In summary, in this chapter, an overview on the preparation and application of nanostructured and highly porous polymers containing conjugated organic semiconductor units in visible-light-promoted and metal-free photocatalysis is given. Due to the ease on tunability of their semiconductor properties via donor–acceptor combination on the molecular level, and the ability for modifying the band gap, band positions, and *p*/*n* characters, this new class of materials demonstrated a promising perspective in light-promoted organic synthesis. Important properties such as porosity, morphology, and band structures should be considered for the design of the polymer-based materials in order to achieve high photocatalytic efficiency. There is a high potential for further optimization and molecular design possibilities. Nevertheless, we believe that the nanostructured, highly porous polymers could offer a high potential for chemical reactions under sustainable and environmentally friendly conditions.

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