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Modification of conjugated microporous poly-benzothiadiazole for photosensitized singlet oxygen generation in water†

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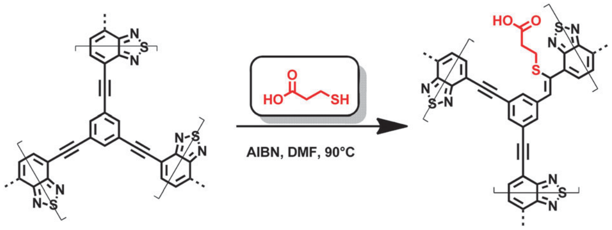
Water-dispersible alkyne-bearing conjugated microporous poly-benzothiadiazoles were synthesized using thiol–yne chemistry to enhance water compatibility. The water compatible polymer networks were used as heterogeneous photocatalysts to generate singlet oxygen for the conversion of furoic acid to 5-hydroxy-2(5*H*)-furanone.

Microporous organic polymers (MOPs) are a class of porous materials that have caught much attention due to their broad relevance in the field of adsorption, separation, storage, sensing, and heterogeneous catalysis owing to their high surface area and pore dimensions.[1,2] Conjugated microporous polymers (CMPs) are a sub-class of MOPs that combine the high surface area and porosity of a MOP and electronic and electroluminescent properties of a conjugated polymer.[1,3–14] The structural and electronic properties of CMPs can further be tuned by the selection of monomer units,[15] as well as applying approaches such as templating.[16] The potential control over electronic and morphological properties makes this class of polymers attractive especially for photo-induced energy applications.[17]

In order to achieve an economically and environmentally friendly chemical process, both homogeneous- and heterogeneous catalysis have been under heavy investigation. Although both systems have their advantages, heterogeneous systems are desired over the homogeneous counterpart due to their easy separation and efficient recovery. Considering the reaction media for these chemical processes, much effort has been made to utilize "greener solvents" instead of the more hazardous halogenated solvents. Water, in particular, has been considered as a hallmark as a green solvent for organic reactions.[18–20]

Previously, we have reported the synthesis of conjugated microporous poly-benzothiadiazole networks that generate singlet oxygen under irradiation with blue light at 420 nm in a heterogeneous environment.[16] The singlet-oxygen mediated conversion of α-terpinene to ascaridole was carried out in chloroform due to the favorable half-life of singlet oxygen as well as the dispersibility of CMPs in chloroform. However, these CMPs are highly hydrophobic, and since water soluble conjugated polymers have been used to produce singlet oxygen for photodynamic therapy[21] and in pursuit of performing singlet oxygen mediated reactions in aqueous heterogeneous environments, we have attempted the modification of pre-synthesized hydrophobic CMPs to allow for enhanced water-dispersibility. Modification of this alkyne bearing network was carried out by the utilization of thiol–yne chemistry as reported by Kiskan and Weber[22] The heterogeneous singlet oxygen generation in an aqueous environment was confirmed by the high conversion of furoic acid into 5-hydroxy-2(5*H*)-furanone as observed by others.[23–25]

The polymer networks were synthesized *via* palladium-catalyzed Sonogashira cross-coupling polycondensation of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole with 1,3,5-triethynylbenzene. The polymers were obtained as dark yellow powders, which were insoluble in all conventional organic solvents tested ($CHCl_3$, toluene, THF, EtOH, MeCN). As shown in Scheme 1, thiol–yne chemistry was performed on CMPs by treating the insoluble solid with 3-mercaptopropionic acid (MPA) and azobis(2-methylpropionitrile) (AIBN) at 90 °C in DMF. Detailed syntheses and



Scheme 1 Thiol–yne modification of WCMPs.

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† Electronic supplementary information (ESI) available: General synthetic procedure of post-modification, conditions of the photocatalytic reaction, solid state NMR spectra of the unmodified CMP and modified WCMP, elemental analysis data, UV/Vis absorption spectra, BET gas sorption isotherms and pore size distribution, and ^{1}H and ^{13}C NMR spectra of furoic acid and the resulting 5-hydroxy-2(5*H*)-furanone. See DOI: 10.1039/c3cc38956a

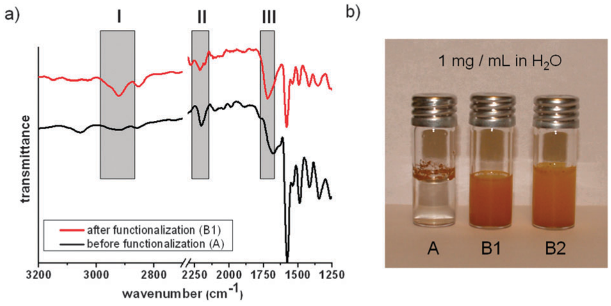


Fig. 1 (a) FTIR of WCMPs before and after the addition of 3-mercaptopropionic acid. Region I: alkane band; region II: alkyne band; region III: –COOH band. (b) Aqueous dispersion (1.0 mg mL^{-1}) of unmodified (A) and modified WCMPs (B1: WCMP_0.1 → 0.1 eq. MPA/AIBN, B2: WCMP_0.4 → 0.4 eq. MPA/AIBN).

characterization of the water compatible CMPs (WCMPs) and the subsequent modification are described in the ESI.† The FT-IR spectra of the unmodified CMP and modified WCMP are displayed in Fig. 1a. In region I, the band between 2850 and 2950 cm^{-1} can be ascribed to the added –COOH group as well as to a stronger signal at about 1700 cm^{-1} in region III, which indicates the addition of carbonyl groups. In region II at *ca.* 2200 cm^{-1}, the intensity of the alkyne band was observed to diminish. The modification was also confirmed from the solid state ^{13}C-NMR (ssNMR), with the emergence of the aliphatic peaks from MPA (∼28 ppm) as well as the small peaks attributed to carboxylic acid (∼170 ppm) (Fig. S1, ESI†). Furthermore, elemental analysis (Table S1, ESI†) showed a slight increase in sulfur and hydrogen contents, agreeing with the results observed from FT-IR and ssNMR. Furthermore, aqueous dispersions of the polymer networks were only observed for the modified samples (Fig. 1b). The conjugated polymer networks were dispersed in DMF, and the UV/Vis spectra were recorded. The polymer networks show two absorption maxima at about 320 and 440 nm. Modification of the CMPs had no influence on the absorption maxima (Fig. S2, ESI†).

In the following text, the modified water-dispersible WCMPs will be labeled as WCMP_*X*, where *X* stands for equivalence of MPA and AIBN used during the thiol–yne reaction with respect to the theoretical amount of alkyne on the pre-synthesized CMPs. To maintain the conjugation of the conjugated backbone, we avoided the excessive use of MPA/AIBN. WCMP_0.1 and WCMP_0.4 were utilized in the following studies.

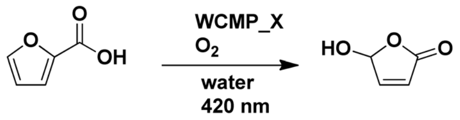
The Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the unmodified CMP were similar to the one reported.[16] After the addition of MPA *via* thiol–yne chemistry, the resulting BET surface area of WCMP_0.1 decreased slightly, whilst the BET surface area of WCMP_0.4 was 40 m^2 g^{-1} lower than that of the unmodified CMP. The tendency of the decreasing micro- and total pore volumes implies the revelation of micropores on the WCMP surface caused by the modification (Table 1). Furthermore, the pore diameter was found to diminish with the addition of MPA. This observation can be caused by rearrangement of the pore structure and/or the gas diffusion effect,[26] which is attributed to the thiol–yne chemistry and the associated alkyne-to-alkene/alkane transformation.[22] In WCMP_0.4, by addition of a larger amount of MPA (0.4 eq.) than WCMP_0.1 (0.1 eq.), more micropores could be filled, which could discourage the pore volume and micropore size determination. The gas sorption isotherms and pore size distribution are displayed in Fig. S3 in the ESI.†

Table 1 Structural properties of the polymer networks

Polymers	S_{BET}/ m^2 g^{-1}	$V_{micropore}{}^{a}$/ cm^3 g^{-1}	$V_{totalpore}{}^{b}$/ cm^3 g^{-1}	Pore size/nm
Unmodified CMP	285	0.184	0.263	1.4
WCMP_0.1	280	0.113	0.235	1.3
WCMP_0.4	244	0.096	0.195	1.2

[a] Micropore volume was calculated from the N_2 adsorption isotherms at $P/P_0 = 0.15$. [b] Total pore volume at $P/P_0 = 0.90$, using the BET method.

To investigate the feasibility of the polymer network concerning singlet oxygen generation in water, oxygen was bubbled into aqueous WCMP dispersion (0.1 mg mL^{-1}) containing 0.1 M furoic acid at the rate of 15 mL min^{-1}, while irradiating with blue light at 420 nm. The conversion of the reaction was evaluated by recording ^{1}H-NMR spectra of aliquots removed from the reaction mixture at different time points. Unlike homogenous catalysis systems, our reaction was worked up simply by filtering off the WCMPs through a syringe filter. While modified WCMPs exhibited high conversion (∼90%) after 22 h, the use of unmodified CMP only led to moderate conversion (∼50%) of the furoic acid. As with UV/Vis and N_2 adsorption–desorption experiments, there seems to be no difference in the capability of producing singlet oxygen in an aqueous environment between WCMP_0.1 and WCMP_0.4. Likely, the addition of 0.1 or 0.4 equivalence of MPA/AIBN results in no difference in the photocatalytic activity between the two modified WCMPs (Scheme 2). For both modified and unmodified CMPs, we were not able to recover the catalyst after



Scheme 2 Photocatalytic conversion of furoic acid into 5-hydroxy-2(5*H*)-furanone.

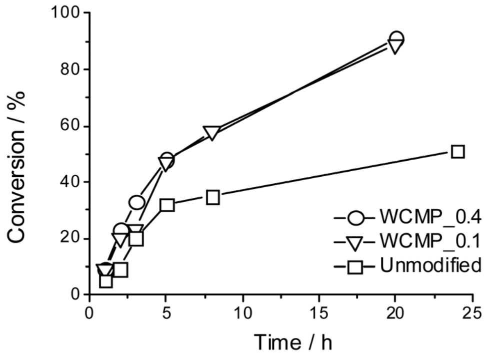


Fig. 2 Conversion of furoic acid into 5-hydroxy-2(5*H*)-furanone. Reaction conducted using 0.1 mg mL^{-1} catalyst loading, 100 mM of furoic acid, O_2 bubbling rate was controlled to be 15 mL min^{-1}. Squares: unmodified CMP, triangles: WCMP_0.1, circles: WCMP_0.4.

the overnight reaction. The exact mechanism is yet to be confirmed, however, it seems that the small amount of WCMPs (0.1 mg mL^{-1}) tend to decompose after 20 h. The difference in the conversion between the unmodified and the modified WCMP may be attributed to the competition between the substrate turnover *versus* the singlet oxygen induced WCMP degradation, where the higher conversion owed to the enhanced wettability of the modified WCMPs (Fig. 2).

In conclusion, the alkyne bearing conjugated microporous poly-benzothiadiazole was successfully modified *via* thiol–yne chemistry using MPA, transferring a highly hydrophobic polymer network to a highly hydrophilic material that is completely dispersible in water. Surface modification resulted in WCMP with lower surface area and smaller pore volume. The model reaction chosen for singlet oxygen generation, the conversion of furoic acid to 5-hydroxy-2(5*H*)-furanone in water, revealed that the modified WCMP with higher aqueous compatibility resulted in higher conversion of the substrate. Although we have not been able to demonstrate reusability of these materials, we were able to achieve high conversions (~90%) after 22 h employing concentrations of only 0.1 mg mL^{-1} of the modified CMP. Currently, we are optimizing the reaction conditions for the conversion of hydroxymethyl furfural (HMF), as well as for the synthesis of new WCMPs with higher (photo)stability.

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