Electronic Supplementary Information

Designing conjugated microporous polymers for visible light-promoted photocatalytic carbon-carbon double bond cleavage in aqueous medium

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Fig. S1. X-ray diffraction pattern of the prepared CMPs



Fig. S2. (A) Nitrogen sorption and desorption isotherms and (B) Pore size distributions of the as synthesized materials.



Fig. S3. Cyclic voltammogram of (a) BTh, (b) BThBT and (c) BBT



Fig. S4. Solvent Polarity dependent conversion, Evaluation of the solvent effect on the photoxodation of styrene, using 10 mg of BBT as photocatalyst, under the irradiation of a blue LED lamp (460 nm, 0.065W cm⁻²), 1 atm. O₂, room temperature, 18h.



Fig. S5. Photooxidation of styrene over different CMPs. Reaction conditions: 0.1 mmol of styrene (without inhibitor), 1.5 mL MeCN: H_2O : (V : V) = 1 : 24, O₂, 10 mg catalyst, Blue Led 0.065 W.Cm⁻², 18h.



Fig. S6. Control experiments using 10 mg of BBT as photocatalyst, under the irradiation of a blue LED lamp (460 nm, 0.065W cm⁻²), 1 atm. O₂, room temperature, 18h.



Fig. S7: 1H NMR spectra of the starting compound and product for the photocatalytic selective oxidation of styrene. Reaction conditions: 0.1 mmol of styrene, 10 mg of BBT in 1,5 mL of D₂O: CD₃CN (24:1) under the irradiation of a blue LED lamp (460 nm, 0.16 W cm⁻²), 1 atm. O₂, room temperature. The samples were taken at point 0 and 12h.

Note for determination of possible formation of formaldehyde during the reaction cycle: Formaldehyde is a small molecule containing one carbon and one heterogeneous oxygen atom. This molecule could not be detected by gas chromatographic (GC) with flame ionization detection (FID). Additionally, formaldehyde is not easily ionizable and cannot be easily analyzed by mass spectrometry (MS). Therefore, the high-performance liquid chromatography (HPLC) method could be the better option to detect formaldehyde. However, Formaldehyde is reactive and might be challenging to separate and detect without prior derivtization with 2,4-dinitrophenylhydrazine, which might be complex when we have a complex reaction media. Moreover, we might be dealing with a very low ppm levels of formaldehyde, which would make the detection difficult.

HPLC analysis were carried out using our reaction media after a certain time of irradiation, different kind of columns, different solvent gradient and different wavelengths for the UV detection. No significant results were obtained.

As alternative, ¹H NMR was used to monitor the model reaction. 0.1 mmol of styrene and 10 mg of BBT were dispersed in 1.5 ml of deuterated solvents in a molar ratio of D₂O: CD₃CN (24:1), and kept under blue light irradiation for 12 hours. The sampling was done before irradiation (t=0h) and after 12 hours of irradiation. The pure formaldehyde ¹H NMR spectra was also recorded for comparison purpose. As shown in the figure 4, after 12h of irradiation, there is appearance of a singlet around 10 ppm, which corresponds to the aldehyde group in the benzaldehyde molecule (HC=O), with almost a complete disappearance of the signals characteristics of styrene (range from 5 to 6 ppm).

Furthermore, a small signal appears around 9.6 ppm, that may correspond to the formaldehyde (HC=O).



Fig. S8. Repeating experiments of the photooxidative cleavage of styrene using BBT as photocatalyst.



Fig. S9. (a) FTIR and UV/vis DR spectra of BBT before and after the repeating experiments.

I. Chromatograms











Fig. S10. Photooxidation of styrene, in various solvents, under Blue light irradiation and using BBT.



Fig. S11. Photooxidation of styrene, in water-based biphasic system, under Blue light irradiation and using different CMPs







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Fig. S12. Control experiments using 10 mg of BBT as photocatalyst, under the irradiation of a blue LED lamp (460 nm, 0.065W cm⁻²), 1 atm. O₂, room temperature, 18h.



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Fig. S13. Scope of the aerobic oxidative photocleavage reactions





Fig. S14. Repeating experiments of the photooxidative cleavage of styrene using BBT as photocatalyst.