

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: A Cross-linked Conjugated Polymer Photosensitizer Enables Efficient Sunlight-induced Photooxidation

Authors: Wenbo Wu, Shidang Xu, Guobin Qi, Han Zhu, Fang Hu, Zitong Liu, Deqing Zhang, and Bin Liu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201811067 Angew. Chem. 10.1002/ange.201811067

Link to VoR: http://dx.doi.org/10.1002/anie.201811067 http://dx.doi.org/10.1002/ange.201811067

WILEY-VCH

COMMUNICATION

WILEY-VCH

A Cross-linked Conjugated Polymer Photosensitizer Enables Efficient Sunlight-induced Photooxidation

Wenbo Wu,* Shidang Xu,* Guobin Qi, Han Zhu, Fang Hu, Zitong Liu, Deqing Zhang, and Bin Liu*

Abstract: Photooxidation under sunlight has great potentials in organic synthesis, bacterial killing, organic waste treatment, etc. Photosensitizers (PSs) often play a very important role in this process. High ¹O₂ generation efficiency and excellent photostability under sunlight, as well as easy recyclability are ideal properties for PSs used for photooxidation, which are not easy to achieve simultaneously. Herein, a pure organic porous conjugated polymer PS of CPTF was designed and synthesized to show great photostability, large specific surface area and high ¹O₂ generation efficiency under sunlight for photooxidation in different applications. Taking the oxidation of aromatic aldehyde to aromatic acid as an example, the PS catalyst shows excellent recyclability, which enables solvent-free reactions in high yields both under direct sunlight and simulated AM1.5G irradiation. In addition, the successful application of CPTF in bacterial killing and organic waste decomposition under simulated AM1.5G irradiation indicates the potential of CPTF in sunlight-induced waste water treatment

Green chemistry, which focuses on the design of products and processes with minimized usage and generation of hazardous substances, has attracted much research interest from the synthetic chemistry community.^[1] Reactions that could proceed at room temperature or relatively low temperature, using water as the solvent or solvent-free in the presence of non-toxic or lowtoxic recyclable catalysts with easy purification are regarded as green reactions.^[1] Despite of much effort, all the key features of green reactions are often not very easy to meet simultaneously. Light-driven chemical reactions, especially sunlight-driven chemical reactions, have attracted much attention as potential green reactions due to their relatively energy conserving and environmentally benign synthetic processes.^[2] Among these reactions, light-driven oxidation of organic compounds in the presence of photosensitizers (PSs) and oxygen is of particular interest.^[3-5] Upon light irradiation, the excited PSs help convert molecular oxygen to singlet oxygen $({}^{1}O_{2})$ or other reactive oxygen species (ROS) with strong oxidizing property (Figure S1), which

[*]	Dr. W. Wu, ⁺ Mr. S. Xu, ⁺ Mr. G. Qi, Dr. F. Hu, Prof. B. Liu Department of Chemical and Biomolecular Engineering	V
	National University of Singapore	
	4 Engineering Drive 4, Singapore, 117585	
	E-mail: cheliub@nus.edu.sg	
	Prof. H. Zhu	
	Key Laboratory of Synthetic and Biological Colloids	
	Ministry of Education	
	School of Chemical and Material Engineering	
	Jiangnan University	
	Wuxi, 214122, China	
	Prof. Z. Liu, Prof. D. Zhang	
	Beijing National Laboratory for Molecular Sciences	
	Organic Solids Laboratory	
	Institute of Chemistry CAS	
	Beijing, 100190, China	
	⁺ These authors contributed equally to this work.	

Supporting information for this article is given via a link at the end of the document.

can further oxidize the organic compounds to yield desirable targets. $\ensuremath{^{[3-5]}}$

During the past several years, alcohol oxidation,^[3] aldehyde oxidation,^[3c,4] bromination reaction,^[5] and oxidative Ugi-type reaction,^[6] etc. have been realized using PS-assisted photooxidation. However, most of these reactions require a high power light source (usually 300-1000 mW/cm²),^[5-8] much higher than that of sunlight (100 mW/cm² for AM1.5G) to proceed, due to the lack of highly efficient PSs designed for specific reactions. As PSs may react with the ROS they produce, the use of high power irradiation makes them more vulnerable to photobleaching with reduced photostability, which prevents them from being used under long-term light irradiation.^[9] Besides, the relatively narrow absorption of the existing PSs is another issue, which requires most reactions to be driven by blue LED^[5,7] or other high power lamps^[6,8] rather than sunlight. In fact, when the same organic reactions were driven by sunlight or natural light, the oxidation efficiency became very low.^[8] Due to the lack of suitable PSs, it remains challenging for these light-induced oxidation reactions to meet the requirements of green chemistry.

For metal-based inorganic and complex PSs, their potential toxicity and high cost together with the limited availability of precious metals in nature make them not ideal for green oxidation.^[5] Therefore, the recent years have witnessed the rapid development of pure organic PSs. Different strategies, such as introducing heavy atoms, modulating intersystem crossing, improving light absorption, reducing non-radiative decay, etc, have been successfully used to effectively improve the ROS generation of organic PSs.^[10] As most of these PS designs were driven by their applications in photodynamic therapy (PDT), photostability is less of the concern since the duration of PDT usually lasts only for several minutes. In fact, many of the most successful commercial PSs, such as Rose Begal (RB), show poor photostability, which makes them less suitable for photooxidation reactions. In one of the recent publications, RB was integrated with porous conjugated polymers for improving its photostability.^[8] However, due to the narrow absorption of RB, the corresponding reaction still requires light source rather than sunlight to activate.^[8] As such, how to develop highly stable and efficient PSs is the key to drive the success of sunlight-induced photooxidation reactions.



Figure 1. Design principle of cross-linked conjugated polymer PS.

Recently, we observed that the photostability of many small molecular dyes could be improved upon polymerization.^[4a,5,8,11] More importantly, the photosensitization capability of small

WILEY-VCH

COMMUNICATION

molecular PSs may also be improved upon polymerization.[11] Motivated by these observations, we started to desian photostable PSs with high ¹O₂ generation efficiency via a threestep process. In the first step, we selected DTF (Figure 1A) as a model compound, as it shows a broad absorption peak and good photostability.^[12] In DTF, triphenylamine (TPA) is used as the donor and fumaronitrile (FN) is used as the acceptor. The phenyl rings between donor and acceptor can separate the HOMO-LUMO distribution of DTF, which is helpful to promote the intersystem crossing (ISC) process and favor ¹O₂ generation.^[13] Subsequently, a conjugated polymer PTF (Figure 1A) with the same donor and acceptor as DTF was designed to improve ¹O₂ generation. Meanwhile, due to its elongated conjugation, a broader absorption peak is expected for PTF to better match the sunlight spectrum than DTF does. In the last step, to optimize the PS functions, such as to endow the PS with easy separation and recyclability after the photooxidation reaction, to increase its specific surface area for catalytic reactions and to further enhance its photostability in photooxidation,[5] a cross-linked porous conjugated polymer CPTF (Figure 1A) was further designed based on PTF. Detailed analysis and characterization revealed that CPTF showed good performance in sunlight-induced green photooxidation. Under natural sunlight or simulated AM1.5G irradiation, benzaldehyde can be converted to benzoic acid without any solvent using CPTF as the photooxidation catalyst. Inspired by this result, we further investigated the performance of CPTF in bacterial killing and organic waste decomposition under simulated AM1.5G irradiation, and the result showes that CPTF has great potential in sunlight-induced wastewater treatment.

According to the literature,^[12] **DTF** was prepared by Suzuki reaction between **TPA-2B** and **FN-2Br** in a yield of 82.4%. Through Suzuki coupling polymerization between triphenylaminebased monomer **TPA-2B** (or **TPA-3B**) and fumaronitrile-based monomer **FN-2Br**, both **PTF** and **CPTF** were synthesized easily (Scheme S1) with 58.8% and 85.4% yields, respectively, whose structures have been confirmed by NMR spectra (Figure S2-S5). In the solid ¹³C NMR spectrum of **CPTF**, the broad peak from 140 to 150 ppm can be assigned to the carbon next to the nitrogen atom in TPA moieties (marked with a in Figure S5), while the peak from 116 to 120 ppm can be assigned to the nitrile group (marked with b in Figure S5) from the FN moieties, indicating successful polymerization.

The linear polymer PTF can be easily dissolved in common organic solvents, such as dichloromethane and tetrahydrofuran (THF), while the cross-linked CPTF is insoluble in any common solvent. Both PTF and CPTF show very board UV-vis diffuse reflectance spectra from 300 to 700 nm (Figure 2A) in powders. In comparison with the UV-vis spectra of DTF and RB, which show much narrow absorption peak centred at 480 and 550 nm, respectively (Figure 2A), the broad peak of CPTF is very beneficial to matching the sunlight radiation spectrum (Figure S6). Subsequently, the ¹O₂ generation efficiencies of DTF, PTF and CPTF in aqueous media were measured by using 9,10anthracenediyl-bis(methylene)dimalonic acid (ABDA) as the indicator (Figure 2B). From the reduced ABDA absorbance in the presence of DTF (0.01 mg/mL), it is calculated that 5.2 nmol of ABDA can be consumed by 0.01 mg of DTF under simulated AM 1.5G irradiation for 1 min. After polymerization, 18.9 nmol, and 20.8 nmol of ABDA can be consumed by 0.01 mg of PTF and

CPTF under the same condition, respectively, which are similar to that of RB (19.8 nmol of ABDA consumed by 0.01 mg RB under the same condition), confirming the highly efficient ¹O₂ generation by both polymers. In addition, after AM 1.5G irradiation for 4 h, the ${}^{1}O_{2}$ generation efficiencies of CPTF, PTF, DTF and RB (Figure 2C) are nearly 100%, 83%, 67% and <1% of their original values, respectively, indicating excellent photostability of CPTF in terms of ¹O₂ generation. As shown in Figure 2D, in powders, DTF shows very bright emission centred at 632 nm. For PTF, its emission peak is red-shifted to 668 nm due to extended conjugation as compared to that for DTF, but the emission intensity is dropped to one quarter of that for DTF. However, there is nearly no emission observed for CPTF. From DTF to PTF, then to CPTF, the improved ¹O₂ generation efficiency upon light illumination agrees with the gradually decreased fluorescence trend (Figure 2D), as a result of the competition between photosensitization and light emission (Figure S1). As shown in Figure S7, the Brunauer-Emmet-Teller (BET) surface area of CPTF is calculated to be 117.2 m³/g, much larger than that of PTF (14.2 m³/g), which represents another advantage of CPTF to be used for photooxidation. The morphology of CPTF was investigated by Scanning Electron Microscope (SEM), and the result is presented in Figure S8. It shows a fused particle-like structure, which should be driven by the strong π - π stacking between extended π -system during the cross-linking process.^[5]



Figure 2. (A) Normalized UV-vis diffuse reflectance spectra of PTF and CPTF in powders, and UV-vis absorption spectra of DTF and RB in THF/water = 1/99 (v/v). (B) Degradation rates of ABDA by DTF, PTF and CPTF in water; A_0 and A are the absorbance of ABDA in the presence of photosensitizers at 378 nm before and after AM1.5G irradiation, respectively. (C) The photostability was tested by comparing the relative ${}^{10}O_2$ generation efficiencies of DTF, PTF and CPTF (dispersed in water) under AM 1.5G irradiation for different time. Conditions: [ABDA] = 5×10⁵ M, [PS] = 0.01 mg/mL. (D) PL spectra (A_{ex} = 480 nm) of DTF, PTF and CPTF in solid state. (E) The Kohn-Sham frontier orbital analysis of different model compounds (S is short for singlet, T is short for triplet) by TD-DFT (Gaussian 09/B3LYP/6-31G(d)).

COMMUNICATION

functional (TD-DFT) Time-dependent density theory investigation^[14] was then performed to understand the different ¹O₂ generation efficiencies of **DTF**, **PTF** and **CPTF**. Three model compounds, which refer to the simplified DTF, PTF and CPTF, were used for calculation (Figure S9). Their HOMO-LUMO distributions at optimized structures are presented in Figures S10-S12. For the three model compounds, the HOMO is mainly distributed at the TPA moieties, while the LUMO is mainly distributed at the FN moieties, indicating good HOMO-LUMO separation, which favours for ¹O₂ generation.^[13] The energy levels of their singlet and triplet excited states were subsequently studied by TD-DFT method (Figure S13). It is easily seen that the differences between different energy levels of PTF and CPTN are much smaller than that of DTF. Detailed modelling results indicate that, in **DTF**, only S_1 to T_1 and T_3 transitions are possible (Figures 2E, S14, and Table S1). In PTF and CPTF, there are 8 possible ISC channels (S_1 to T_1 , T_2 , T_3 , T_4 , T_6 , T_9 , T_{10} , and T_{11} , Figures 2E, S15, and Table S2), and 10 possible ISC channels (S_1 to T_1 , T_2 , T₃, T₄, T₅, T₆, T₇, T₈, T₁₀, and T₁₁, Figures 2E, S16, and Table S3), respectively. The increased numbers of energy transition channels are beneficial to ISC process to favour ¹O₂ generation.



Figure 3. (A) The conversion of benzaldehyde photooxidation by using different PSs as the catalyst under AM1.5G irradiation. Benzaldehyde: 1 mmol, PS: 1 mg, CH₃CN: 1 mL. (B) The reaction results of different reactants by using CPTF as photosensitizer. Reactant: 1 mmol, PS: 1 mg, CH₃CN: 1 mL. Conversion in parentheses refers to solvent-free reaction under the following condition: Reactant: 10 mmol, PS: 2 mg. (C) The recycling process of sunlight-induced photooxidation of benzaldehyde.

Subsequently, the photooxidation catalysed by **CPTF** was studied using benzaldehyde as a model compound. As shown in Figure 3A, by using **CPTF** as the PS photocatalyst, 87.1% of benzaldehyde could be oxidized to benzoic acid under simulated AM 1.5G irradiation for 4h. Under the same conditions, a similar conversion of 82.4% can be acheived by using **PTF** as the catalyst, since the ¹O₂ generation efficiency between **CPTF** and **PTF** is smilar. As reference, by using **DTF** and **RB** as the PSs, the conversion efficiencies were only 34.2%, and 42.3%, respectively. Although the ¹O₂ generation efficiency of **RB** is similar to that of **CPTF**, the significantly lower conversion efficiency by **RB** is due to its poor photostability. By using sunlight as the light source, benzaldehyde could also be oxidized to benzoic acid within 4 h (from 10 am to 2 pm on a sunny day in Singapore) with a conversion yield of 81.2 %, which is similar to that under simulated AM 1.5G illumination.

To understand the oxidation mechanism, four control experiments were performed by adding different ROS scavengers to the reaction. As shown in Figure S17, by adding benzoquinone (superoxide scavenger), catalase (H_2O_2 scavenger), and TEMPO (hydroxyl radicals scavenger), respectively, the conversions were nearly the same as before. On the contrary, when adding NaN₃, an 1O_2 scavenger, the conversion efficiency was decreased sharply from 87.1% to 36.2%, indicating that 1O_2 is the key ROS during the oxidation process. Therefore, the mechanism of the photooxidaion reaction can be described as the following: under light irradiation of **CPTF**, molecular O_2 is first transferred to 1O_2 , which further oxides benzaldehyde to benzoic acid.

Additionally, some other substrates, with different electronwithdrawing or electron-donating groups, and varying amount of aldehyde groups, were also tested to demonstrate the general applicability of CPTF for photooxidation (Figure 3B). The electronwithdrawing group linked to the aldehyde can enhance its electropositivity, making the aldehyde group more easily to be oxidized. Therefore, aldehyde with electron-withdrawing groups, such as -F and -NO₂, showed a higher conversion yield than those groups. electron donating with As for 4-(diethylamino)benzaldehyde, due to the very strong electrondonating ability of diethylamino group, the reaction did not occur under our reaction condition. To demonstrate the value of the photooxidation reaction, we further selected 5hydroxymethylfurfural as the reactant, as its oxidation products, such as 2,5-furandicarboxylic acid, are important substitutes for petro chemicals.^[15] As shown in Figure 3B, under simulated AM1.5G irradiation (100 mW/cm²) for 16 h, a conversion of 78.2% can be achieved by using CPTF as the photocatalyst. As compared to the literature,[3c] which required 0.5 W/cm2 light illumination for 14 h to yield the same product, our approach shows clear advantages.

For liquid aldehydes, we have also developed a solvent-free method to photooxidize them with high conversion yields. As the lifetime and effective diffusion distance of ${}^{1}O_{2}$ are very short, [${}^{16]}$ the absence of solvent reduces the distance between the generated ${}^{1}O_{2}$ and aldehyde molecules, which is beneficial to oxidation. Even when the amount of **CPTF** used was decreased to 20% of that used in the same reaction with solvent, all three examples showed high conversion efficiencies (Figure 3B). Based on this result, we further scaled up this photoreaction to a slightly larger scale. Under simulated AM1.5G irradiation for 6 h, 10 g of liquid benzaldehyde can be easily converted to solid benzoic acid with a conversion yield of 74.2% in the presence of **CPTF** (Figure S18).

Considering the excellent photostability of **CPTF** and its poor solubility in any organic solvent, we further designed a recycling process for the photooxidation of benzaldehyde (Figure 3C). One starts with benzaldehyde and **CPTF** in a flask, under simulated AM1.5G irradiation for 6h, ethanol was added to the reaction system to dissolve the benzoic acid and the unreacted benzaldehyde, but not **CPTF**. Therefore, the photocatalyst can be recovered by simple filtration. After ethanol removal, the pure

WILEY-VCH

COMMUNICATION

benzoic acid can be obtained by recrystallization from hexane. The filtrate contains the unreacted benzaldehyde and a little mount of benzoic acid, which can be reused for the next cycle of reaction. Through each cycle, 6~6.5 g of benzoic acid can be obtained, if we keep 10 g of benzaldehyde at the feed. Meanwhile, the catalytic activity of **CPTF** was also tested (Figure S19). After 10 cycles, the activity of **CPTF** was about 85% as that for the first run. As such, the reaction can be driven by sunlight without any solvent in a large scale, and the product can be easily purified. In addition, the catalyst of **CPTF** and unreacted reactant can be easily recycled, which meet all the requirements of green reactions.



Figure 4. (A) The degradation rates of Rhodamine 6G (1×10^{-4} M) by CPTF and Rose Begal (0.1 mg/mL); A_0 and A are the absorbance of Rhodamine 6G in the presence of the CPTF and Rose Begal at 530 nm before and after AM1.5G irradiation, respectively. (B) Photos of Rhodamine 6G solutions with CPTF before and after AM1.5G irradiation for 2h. From left to right: before irradiation; after irradiation and then filtration. (C) The killing efficiency of CPTF (0.1 mg/mL) to S. aureus (1×10^7 counts/mL) under AM1.5G irradiation for different times. (D) Plate photographs for S. aureus on LB agar plate supplemented with CPTF with AM1.5G irradiation for different times and then grew overnight. From left to right: 0 h, 1 h, and 2 h.

Besides organic synthesis, another photooxidation application is photo-induced wastewater treatment. Under light irradiation, the generated ¹O₂ by PSs can ablate commonly seen microorganisms (such as bacteria, molds and fungi) and decompose organic waste in water to realize wastewater treatment.^[9] Herein, Rhodamine 6G, and staphylococcus aureus (S. aureus, ATCC 6538, one of Gram-positive bacteria) were used as the examples of organic waste, and microorganism, respectively, to demonstrate the sunlight-induced wastewater treatment ability and the results are presented in Figure 4. In the presence of CPTF (0.1 mg/mL), nearly all the Rhodamine 6G (1×10⁻⁴ M) can be decomposed under simulated AM1.5G irradiation for 2h (Figure 4A). As a reference, only 25% of Rhodamine 6G was decomposed by RB under the same condition. In addition, CPTF can be recovered by filtration easily (Figure 4B). The bacterial killing efficiency of CPTF was then performed to determine the percentage of live cells by a traditional colony counting method. After AM1.5G irradiation for 1h, the percentage of living cells decreased sharply and the relative viability of S. aureus was lower than 5% (Figures 4C and 4D, initial concentration: 1×10⁷ counts/mL), and after 2 h irradiation, nearly all the S. aureus can be killed by the generated ¹O₂ from CPTF. To obtain further evidence for the antimicrobial activity of CPTF, field emission SEM was employed to monitor the morphological changes of the bacteria before and after treatment with CPTF

under AM1.5G irradiation. As shown in Figure S20, once the bacteria were treated with **CPTF** under AM1.5G irradiation for 1 h, serious collapse and merge in membranes were observed. After the same irradiation for 2 h, some holes were observed in the bacteria. In contrast, the morphologies of bacteria exhibited clear edges and smooth bodies for the control group (bacteria without **CPTF** treatment). The positive results on organic waste decomposition and bacterial killing indicated good performance of **CPTF** in sunlight-induced wastewater treatment.

In conclusion, a cross-linked porous conjugated polymer PS of **CPTF** was designed and synthesized *via* A_3+B_2 Suzuki polymerization. **CPTF** shows good ${}^{1}O_2$ generation efficiency under sunlight irradiation, excellent photostability, and large specific surface area for photooxidation. Meanwhile, its excellent photostability and poor solubility endow it with good recyclability. Under simulated AM1.5G irradiation, the light-induced organic synthesis by using oxidation of aldehyde to acid as the example, and light-induced wastewater treatment by using organic waste decomposition and bacterial killing as the example indicate that **CPTF** is an excellent photocatalyst for sunlight-induced photooxidation. These results will open up new opportunities for green chemistry.

Acknowledgements

We thank the Singapore NRF Competitive Research Program (R279-000-483-281), NRF Investigatorship (R279-000-444-281), and National University of Singapore (R279-000-482-133) for financial support.

Keywords: photosensitizers • singlet oxygen • photooxidation • sunlight-induced organic synthesis • sunlight-induced wastewater treatment

- [1] I. T. Horváth, P. T. Anastas, Chem. Rev. 2007, 107, 2167-2168.
- a) D. Ravelli, M. Fagnoni, T. Fukuyama, T. Nishikawa, I. Ryu, ACS Catal.
 2018, 8, 701-713; b) F. E. Osterloh, ACS Energy Lett. 2017, 2, 445-453;
 c) D. Ravelli, D. Dondi, M. Fagnoni, Angelo Albini, Chem. Soc. Rev.
 2009, 38, 1999-2011.
- a) Y.-Z. Chen, Z. U. Wang, H. Wang, J. Lu, S.-H. Yu, H.-L. Jiang, *J. Am. Chem. Soc.* 2017, *139*, 2035-2044; b) Y. Chen, J. Zhang, M. Zhang, X. Wang, *Chem. Sci.* 2013, *4*, 3244-3248; c) S. Xu, P. Zhou, Z. Zhang, C. Yang, B. Zhang, K. Deng, S. Bottle, H. Zhu, *J. Am. Chem. Soc.* 2017, *139*, 14775-14782.
- [4] a) W. Wu, Chem 2018, 4, 1762-1764; b) M. Hajimohammadi, C. Schwarzinger, G. Knör, RSC Adv. 2012, 2, 3257-3260.
- [5] R. Li, Z. J. Wang, L. Wang, B. C. Ma, S. Ghasimi, H. Lu, K. Landfester, and K. A. I. Zhang, ACS Catal. 2016, 6, 1113-1121.
- [6] G. Jiang, J. Chen, J.-S. Huang, C.-M. Che, Org. Lett. 2009, 11, 4568-4571.
- [7] a) K. Zhang, D. Kopetzki, P. H. Seeberger, M. Antonietti, F. Vilela, *Angew. Chem. Int. Ed.* 2013, *52*, 1432-1436; b) Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang; *Chem. Commun.* 2014, *50*, 8177-8180; c) Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *Adv. Mater.* 2015, *27*, 6265-6270; d) N. Kang, J. H. Park, K. C. Ko, J. Chun, E. Kim, H.-W. Shin, S. M. Lee, H. J. Kim, T. K. Ahn, J. Y. Lee, S. U. Son, *Angew. Chem. Int. Ed.* 2013, *52*, 6228-6232.

[8] J.-X. Jiang, Y. Li, X. Wu, J. Xiao, D. J. Adams, and A. I. Cooper, *Macromolecules* **2013**, *46*, 8779-8783.

COMMUNICATION

- [9] W. Wu, D. Mao, F. Hu, S. Xu, C. Chen, C.-J. Zhang, X. Cheng, Y. Yuan, D. Ding, D. Kong, B. Liu, *Adv. Mater.* 2017, *29*, 1700548.
- [10] a) F. Hu, S. Xu, B. Liu, Adv. Mater. 2018, 30, 1801350; b) W. Fan, P. Huang, X. Chen, Chem. Soc. Rev. 2016, 45, 6488-6519; c) S. S. Lucky, K. C. Soo, Y. Zhang, Chem. Rev. 2015, 115, 1990-2042; d) S. Ye, J. Rao, S. Qiu, J. Zhao, H. He, Z. Y, T. Yang, Y. Deng, H. Ke, H. Yang, Y. Zhao, Z. Guo, H. Chen, Adv. Mater. 2018, 30, 18011216.
- [11] W.Wu, D. Mao, S. Xu, Kenry, F. Hu, X. Li, D. Kong, B. Liu, *Chem* 2018, 4, 1937-1951.
- [12] a) X. Han, Q. Bai, L. Yao, H. C. Liu, Y. Gao, J. Y. Li, L. Q. Liu, Y. L. Liu, X. X. Li, P. Lu, B. Yang, *Adv. Funct. Mater.* **2015**, *25*, 7521-7529; b) Y.

Wang, X. Han, W. Xi, J. Li, A. W. Roe, P. Lu, J. Qian, *Adv. Healthcare Mater.* **2017**, *6*, 1700685.

- a) S. Xu, Y. Yuan, X. Cai, C.-J. Zhang, F. Hu, J. Liang, G. Zhang, D. Zhang, B. Liu, *Chem. Sci.* 2015, *6*, 5824-5830; b) W. Wu, D. Mao, S. Xu, S. Ji, F. Hu, D. Ding, D. Kong, B. Liu, *Mater. Horiz.* 2017, *4*, 1110-1114.
- [14] a) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012**, 492, 234-238; b) S. Y. Lee, T. Yasuda, Y. S. Yang, Q. Zhang, C. Adachi, *Angew. Chem. Int. Ed.* **2014**, 53, 6402-6406.
- [15] T. Werpy, G. Petersen, *Top Value Added Chemicals from Biomass, NREL/TP-510-35523*, National Renewable Energy Laboratory, Golden, CO, **2004**.
- [16] C. Schweitzer, R. Schmid, Chem. Rev. 2003, 103, 1685-1757.

Accepted Manuscrii

WILEY-VCH

COMMUNICATION

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

A cross-linked porous conjugated polymer photosensitizer **CPTF** was designed and synthesized for sunlightinduced photooxidation. Under simulated AM1.5G irradiation, benzaldehyde can be oxidized to benzoic acid easily in the scale of 10 g in the presence of **CPTF**. In addition, **CPTF** can also be used as photocatalyst for sunlight-induced organic waste decomposition and bacterial killing in water.



Wenbo Wu, Shidang Xu, Guobin Qi, Han Zhu, Fang Hu, Zitong Liu, Deqing Zhang, and Bin Liu*

Page No. – Page No.

A cross-linked conjugated polymer photosensitizer enables efficient sunlight-induced photooxidation