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Electronic Supporting Information

Efficient Photocatalytic Oxidation Sensitized by Conjugated Polymers in Batch and Microreactors under Visible Light

Anqi Li,[ab] Chunyan Tan,*[ab] Tianying Yuan,[ab] Jiamei Liang,[ab] Dan Gao,*[ab] Ying Tan[ab] and Yuyang Jiang*[bc]

[a]Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.

[b]The State Key Laboratory of Chemical Oncogenomics, the Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, P. R. China. *E-mail: tancy@sz.tsinghua.edu.cn ; gao.dan@sz.tsinghua.edu.cn

[c]School of Pharmaceutical Sciences, Tsinghua University, Beijing 100084, P. R. China. *E-mail: jiangyy@sz.tsinghua.edu.cn

1. Experimental

1.1 Materials

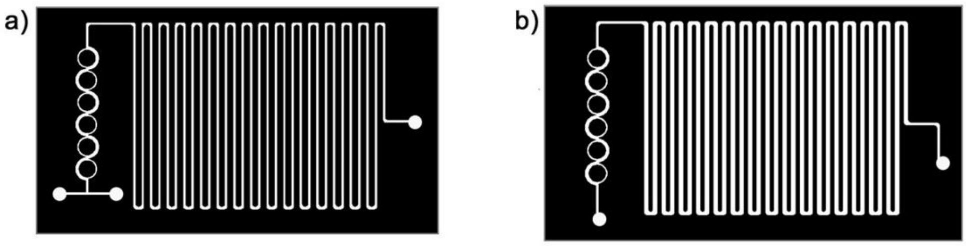
In this study, two conjugated polymers, PPET3-N$^+$ and PPET3-COOR, were synthesized according to our previously reported procedure.[1] Concentrations of the stock solutions of PPET3-N$^+$ and PPET3-COOR were 550 μM in water and 7.11 mM in THF, respectively. Methylene blue and α-terpinene were purchased from Energy Chemical Co. (Shanghai, China). Negative photoresist (SU-8 2050 and 2007) and developer were purchased from MicroChem (Newton, MA, USA). Polydimethylsiloxane (PDMS) and the curing agent were purchased from Dow Corning (Midland, MI, USA). Other chemicals and organic solvents were purchased from Adamas Reagent, Ltd, used without further purification.

1.2 Instrumentation

NMR spectra were recorded on a Bruker 400 MHz spectrometer and chemical shifts were reported in ppm using TMS as internal reference. UV-Vis absorption spectra were recorded on an Agilent Carry 100 UV-Vis spectrophotometer, and fluorescence emission spectra were measured on a SPEX Fluorolog 3-TCSPC spectrometer. AFM images were measured on a Bruker Dimension Icon.

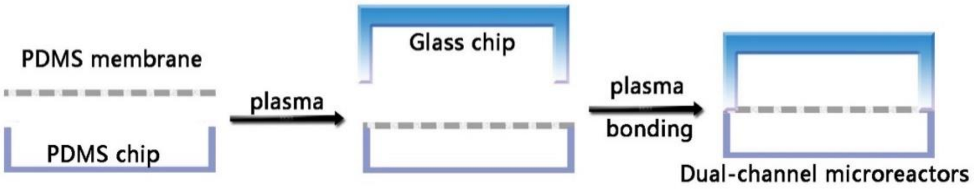
1.3 Microreactor fabrication

Mono-channel microreactor: The mono-channel microreactor was composed of glass chip and PDMS layer. The glass chips were obtained after the manufacture of Guangzhou Greenrays Glass Co. Ltd. according to our design. The glass chip contained two inlets allowing introduction of reagent solutions, one outlet for collecting the product as well as designed channel (Scheme S1a). The channel had an average width of 300 μm, an average depth of 100 μm, and total length of about 50 mm. PDMS prepolymer and cross-linker (10: 1 weight ratio) were poured onto the blank silicon master and cured at 70 °C for 4 hours to form a PDMS layer. Then the PDMS layer attached to glass chip having the built-in channel by a plasma treatment for 90 s and baked in an oven (60 °C, 2 h). Finally, the polytetrafluoroethylene (PTFE) tubes were adhered to the inlets and outlet by epoxy glue.



Scheme S1. Schematic illustration of glass chip (a) and PDMS chip (b).

Dual-channel microreactor: The dual-channel microreactor consists of PDMS chip, PDMS membrane and glass chip. The production process of PDMS chip is similar to PDMS layer, but PDMS chip has the built-in channel by using the silicon master within designed channel (Scheme S1b). PDMS chip were peeled from the silicon master, and the inlet and outlet were pierced before attachment. There were two differences between PDMS chip (S1b) and glass chip (S1a) that PDMS chip had only one inlet and wider channel. PDMS membrane was prepared by spin coating method. A 15:1 weight ratio mixture of PDMS prepolymer and cross-linker was spin-coated on the silicon plate (1200 rpm, 30 s) to get the 49 μm[2] thin membrane (Figure S1). The PDMS chip attached to PDMS membrane through a plasma treatment for 90 s, and baked at 60 °C for 4 h. Then the glass chip was bonded to the same PDMS membrane by a plasma treatment for 90 s. To reinforce bonding strength, the dual-channel microreactor was baked at 110 °C for 12 h. Scheme S2 illustrates the fabrication and combination of two chips with PDMS membrane.



Scheme S2. Schematic illustration of the fabrication and combination of PDMS chip, glass chip and PDMS membrane.

Polymer-coated microreactor: Polymer-coated microreactor were made after the preparation of dual-channel microreactor. Before glass chip was bonded to the PDMS membrane by a plasma treatment, the channel surface of glass chip was fabricated with polymer film through drop-casting method.[3] A glass chip was cleaned with deionized water and ethanol as well as dried by flowing nitrogen, and then we filled the channel in the glass chip with stock solution of PPET3-COOR. The polymer film was deposited on the surface after solvent evaporation at room temperature. Films with different thickness were obtained by repeating film formation process.

1.4 Photo-oxidation of α-terpinene

Batch reaction: Reactions of α-terpinene (0.1 M) with different concentrations of PPET3-N^+ (10, 20, 40, 60, 80 μM) under different light intensity (dark, 70 and 120 W) were condcuted. In a typical batch reaction, a mixture of α-terpinene (68.8 mg, 0.5 mmol), PPET3-N^+ (dilute from the stock solution) and ethanol (5 mL) or acetonitrile (5 mL) was added in a 25 mL round-bottom flask with stirring in an atmosphere of air (opened to air) under irradiation upon a LED light. The conversion of α-terpinene in solution was monitored every 20 minutes with UV–Vis spectrophotometer at the maximal absorption wavelength of α-terpinene 265 nm. In our experiment, the UV-Vis absorption spectra were acquired after dilution of 10 μL reaction solution to 2.5 mL ethanol in an 1 cm quartz cell and the quantification of α-terpinene was achieved according to its extinction coefficient ($\varepsilon = 7.03 \times 10^3\ M^{-1}cm^{-1}$). The product was obtained by evaporation of the solvent after passing of the reaction solution through a small silica column and washing with 5 mL of dichloromethane. NMR analysis confirmed that the product was ascaridole (yield 93%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 6.52 (d, J = 8.5 Hz, 1H), 6.43 (d, J = 8.5 Hz, 1H), 2.08-2.00 (m, 2H), 1.99-1.90 (m, 1H), 1.58-1.51 (m, 2H), 1.40 (s, 3H), 1.02 (d, J = 6.9 Hz, 6H). **^{13}C-NMR** (400 MHz, $CDCl_3$) δ 136.65, 133.31, 80.04, 74.61, 32.38, 29.77, 25.85, 21.65, 17.48, 17.40 ppm.

Mono-channel microreactor: Two solution, α-Terpinene (0.2 M, double of concentration in batch) in acetonitrile (2.5 mL) and PPET3-N$^+$ (160 μM) in acetonitrile (2.5mL), were loaded into two Hamilton syringe and introduced into the microreactor in a 1:1 ratio by the same syringe pump through the PTFE tubes linking to inlets. The irradiation light intensity for the microreactor reaction was 61.5 W/cm^2. The retention time (43 s, 85 s, 170 s, 212.5 s, 255 s, 306 s) of reagent and sensitizer varied by changing injection rates. The reaction solution was collected in a vial through the PTFE tubes linking to outlet. The conversion of α-Terpinene were acquired from UV-vis spectra. In the same manner, 10 μL of result solution was diluted to 2.5 mL ethanol before the UV-Vis test.

Dual-channel microreactor: The reaction procedure of upper glass channel in dual-channel microreactors is similar to mono-channel reactors. In addition, air was delivered into the down PDMS channel by another syringe pump at different injection rates (70, 150 and 210 μL·min^{-1}). The reaction solution was also collected in a vial, and analyzed by UV-Vis spectrophotometer after the same dilution treatment in mono-channel microreactor.

Polymer-coated microreactor: The reaction procedure followed the procedure in dual-channel microreactors, with the minor difference that the two injection solution were both α-terpinene (0.1 M).

1.5 Photostability evaluation of PPET3-N$^+$ and PPET3-COOR

PPET3-N$^+$: To examine the photostability of PPET3-N$^+$ and PPET3-COOR, we measured the absorption and fluorescence emission spectra of the polymers during the batch reaction of α-terpinene oxidation. The reaction of 0.1 M α-terpinene and 150 μM PPET3-N$^+$ in 5 mL acetonitrile under 120 W white LED light were conduted. We monitored the absorption and fluorescence emission every 20 minutes with UV–Vis and fluorescence spectrophotometer. The UV-Vis absorption spectra were acquired after dilution of 75 μL reaction solution to 2 mL acetonitrile in a quartz cell, while the fluorescence emission spectra were acquired after dilution of 10 μL reaction solution to 2.0 mL acetonitrile.

PPET3-COOR: The reaction of 0.1 M α-terpinene and 150 μM PPET3-COOR in 5 mL tetrahydrofuran under 120W white LED light were conduted. The UV-Vis absorption spectra were acquired after dilution of 75 μL reaction solution to 2 mL tetrahydrofuran in a quartz cell, while the fluorescence emission spectra were acquired after dilution of 10 μL reaction solution to 2.0 mL tetrahydrofuran.

2 Results and Discussion

2.1 Batch experiments in ethanol and acetonitrile

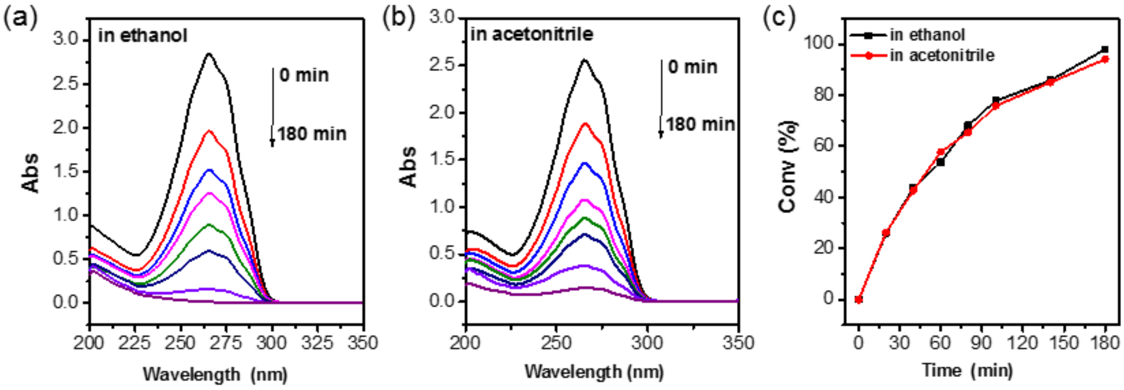


Figure S1. UV/Visible absorption spectra of α-terpinene at different reaction time periods in ethanol (a) and acetonitrile (b); (c) ascaridole conversion vs reaction time in different solvents. Reaction conditions: 0.1 M α-terpinene with 80 μM PPET3-N+ in 5 mL solvent under 120 W white LED light irradiation for different lengths of time periods.

2.2 Batch experiments with various irradiation light intensities

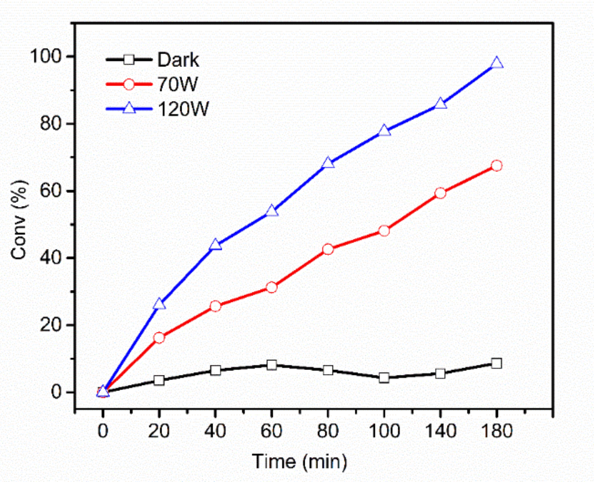


Figure S2. Photosensitized conversion of α-terpinene into ascaridole in batch reaction. Reaction conditions: 0.1 M α-terpinene with 80 μM PPET3-N^+ in 5 mL ethanol under 120 W white LED light irradiation for different lengths of time periods.

2.3 Photostability experiments

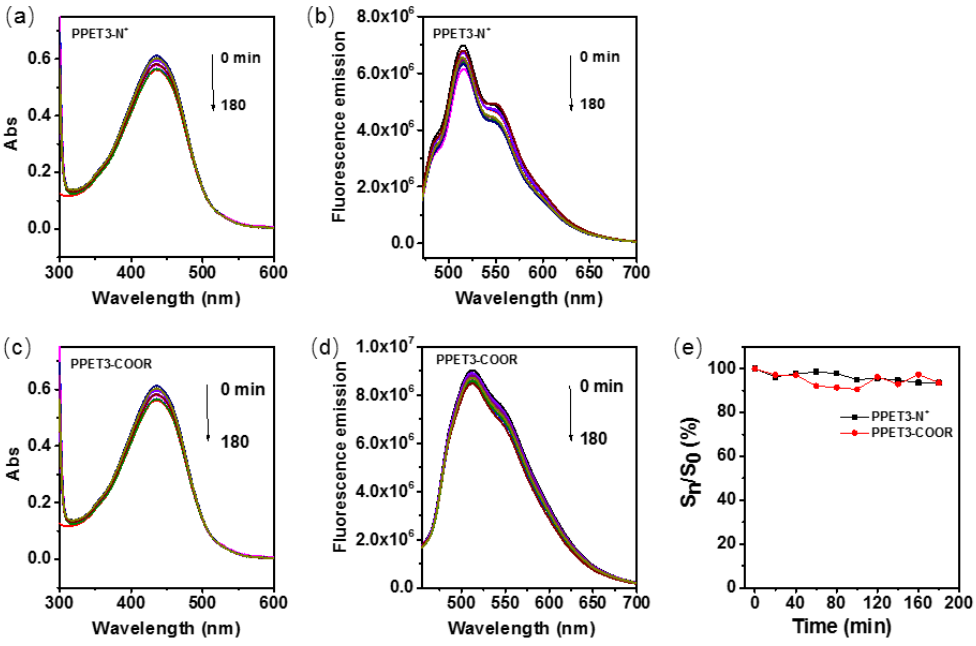


Figure S3: UV-visible absorption (a and c) and fluorescence emission spectra (b and d) of PPET3-N^+ and PPET3-COOR at different reaction time periods from 0 to 180 min during the batch reaction of α-terpinene oxidation; (e) fluorescence emission of PPET3-N^+ and PPET3-COOR vs reaction time. Reaction conditions: 0.1 M α-terpinene with 150 μM polymer in 5 mL ethanol under 120 W white LED light irradiation.

2.4 Optic microscope images

Figure S4. Cross section picture of PDMS channel with PDMS membrane.

2.5 Atomic force microscope images

To collect the different thickness of PPET3-COOR film, small part of film sample was removed by blade to expose the surface of glass substrate. The sectional height figures of three mark line (Figure S6 d-f) were acquired after data processing of Nanoscope Analysis software. Finally, the thichkess was the average values that were calculated from selected points.

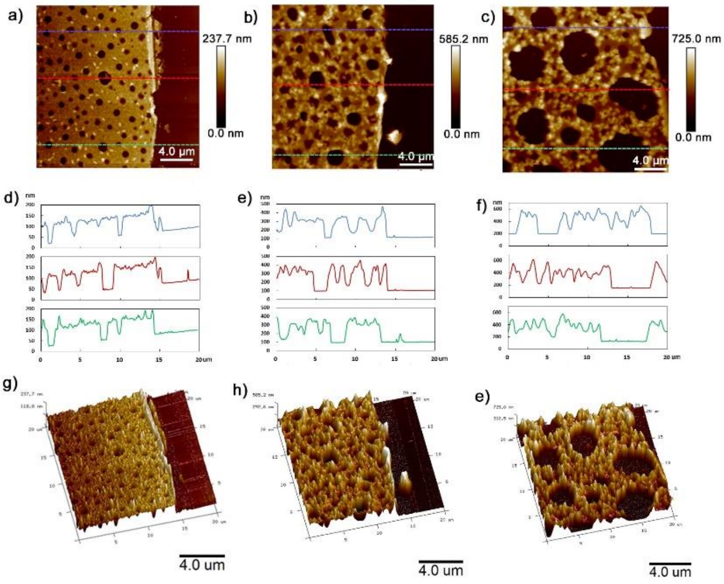


Figure S5 AFM images of PPET-COOR films. (a) 1 layer; (b) 3 layers; (c) 5 layers; (d-f) sectional height of three line in a-c, respectively; (g-i) three-dimensional images of a-c, respectively.

2.6 ^{1}H-NMR and ^{13}C-NMR spectra

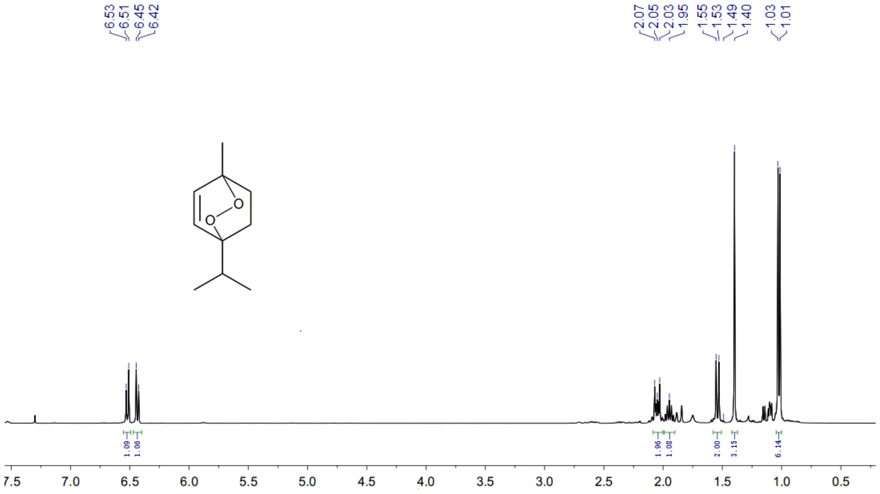


Figure S6. ^{1}H-NMR spectrum of ascaridole.

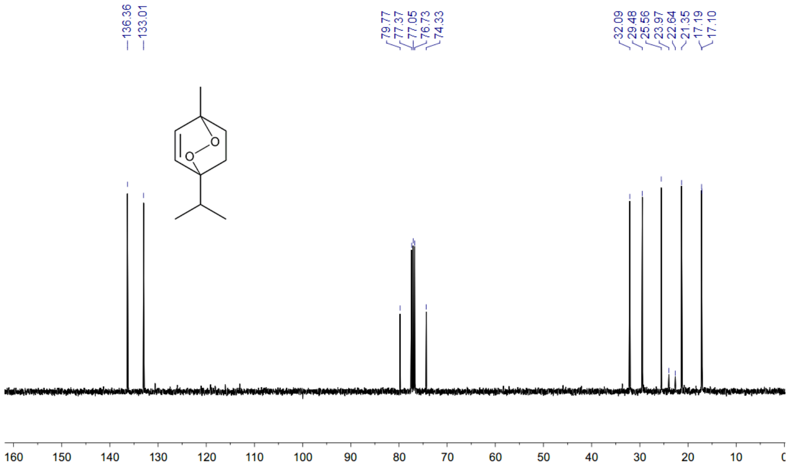


Figure S7. ^{13}C-NMR spectrum of ascaridole.

3. References

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