Copper-Mediated Oxidative Deconstruction of Polyethylene Terephthalate via Photoinduced Ligand-to-Metal Charge Transfer

Guangyao Li,[a] Mingsen Han,[a] Zezheng Leng,[a] Yazhi Deng,[a] Jin Liu,[a] Yu Guo,[c] Bin Yang,*[a] Jiazhu Li,*[a] Feng Liu*[b] and Chang-Cheng Wang*[a]

*Corresponding authors. Email: ccwang@ytu.edu.cn, liufeng@fudan.edu.cn, jiazhu82@ytu.edu.cn, yangbin_hy@ytu.edu.cn

Contents

Number of page: 22
Number of figure: 7
Number of table: 7

1. General information

1.1. Materials and methods

Unless otherwise noted, all commercial reagents and solvents were used as received and reactions were run under air atmosphere. All plastics (polyethylene terephthalate: PET; Polybutylene terephthalate: PBT are commercially available unless otherwise noted. Chlorobenzene was purchased from Adamas-beta Reagent Co., Ltd. CH_3CN was purchased from Sinopharm Chemical Reagent Co., Ltd. $CDCl_3$ and DMSO-d_6 were purchased from J&K. Column chromatography was performed on silica gel 200-300 meshes.

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on Bruker 400 M spectrometers. ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded using Bruker Avance 400 spectrometer with $CDCl_3$, or DMSO-d_6 as solvent. NMR spectra were calibrated using the solvent residual signals ($CDCl_3$: δ ^1H 7.26, δ ^{13}C 77.00; DMSO-d_6: δ ^1H 2.50, δ ^{13}C 39.52). Data are presented as follows: chemical shift (ppm), multiplicity (s singlet, d doublet, t triplet, dd doublet of doublets, m multiplet, br broad), coupling constant *J* (Hz) and integration. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm.

1.2. Description of the LED light source and homemade setup

395 nm LEDs: The LED lights were purchased from Xinxingyuan Optoelectronics Co., Ltd. The reaction vial was irradiated with a 30 W 395 nm LED.

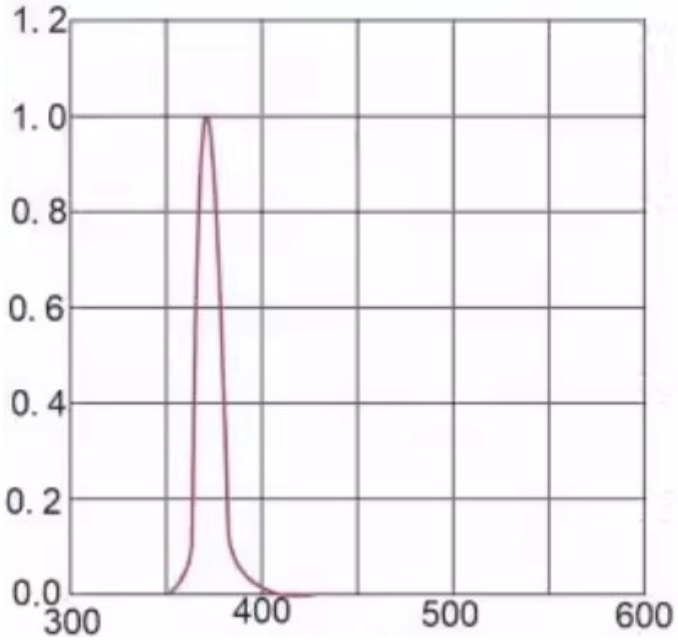


Figure S1. The spectrum of the 395 nm LEDs light.

The test tube holder placed at the center of a stirring plate. A 395 nm LEDs light was placed perpendicular above the stirring plate (approximately 4.0 cm between the stirring plate and the light source). An electric fan was placed at the other side of the reaction tube and kept working during the reaction. The fan was necessary to keep the reaction temperature at room temperature (Fig. S2).

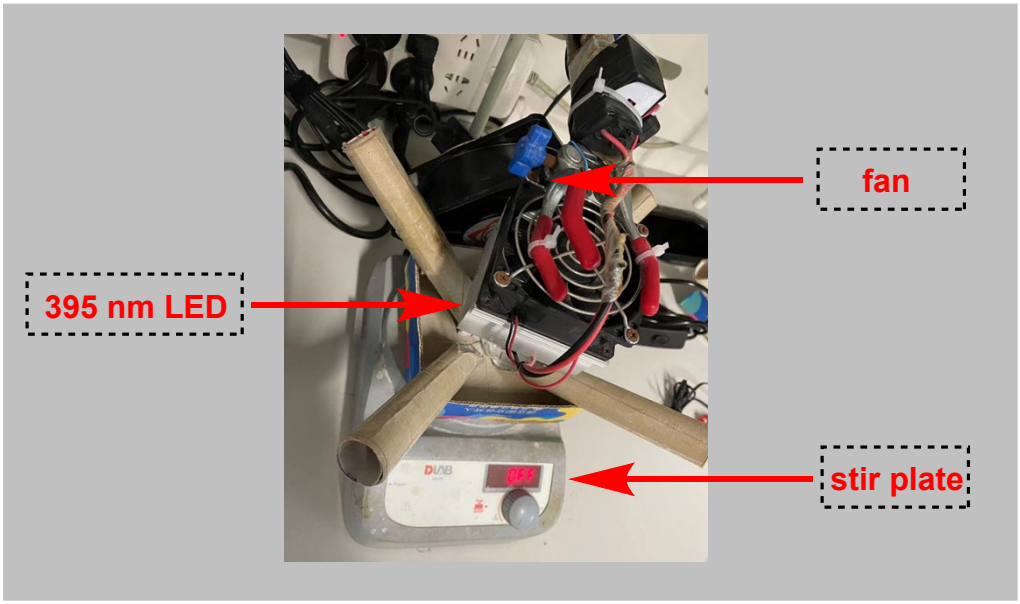


Figure S2. The detailed set-up of the 395 nm photoreaction.

460 nm LEDs: The LED lights were purchased from Xinxingyuan Optoelectronics Co., Ltd. The reaction vial was irradiated with a 30 W 460 nm LED.

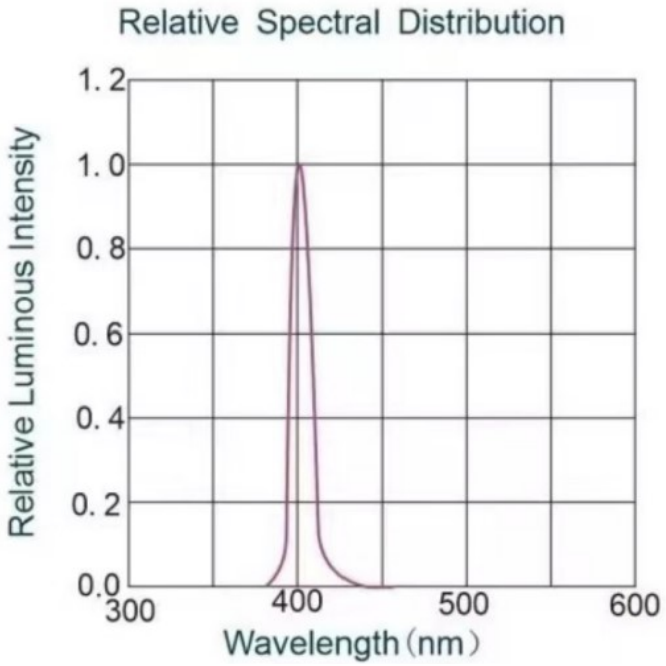


Figure S3. The spectrum of the 460 nm LEDs light.

The test tube holder placed at the center of a stirring plate. A 460 nm LED light was placed perpendicular above the stirring plate (approximately 4.0 cm between the stirring plate and the light source). An electric fan was placed at the other side of the reaction tube and kept working during the reaction. The fan was necessary to keep the reaction temperature at room temperature (Fig. S4).

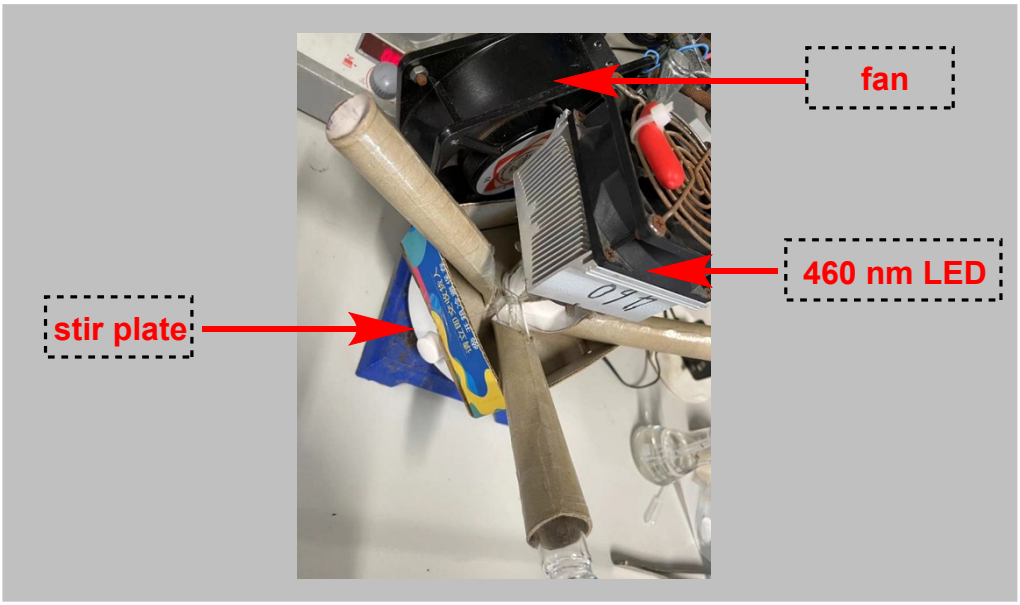


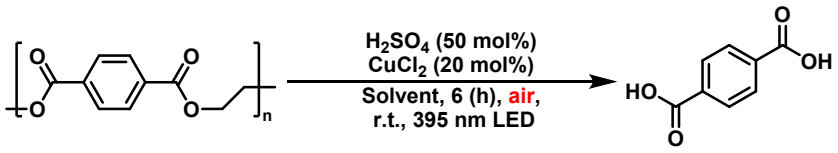
Figure S4. The detailed set-up of the 460 nm photoreaction.

2. General procedure for the degradation of PET

2.1 The degradation of PET under various conditions

To a 25 mL glass tube was added PET (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%), H_2SO_4 (50 mol%, 18.4 M-98%), Chlorobenzene (2.0 mL) under air atmosphere. The mixture was placed perpendicular to a 395 nm LEDs light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate.

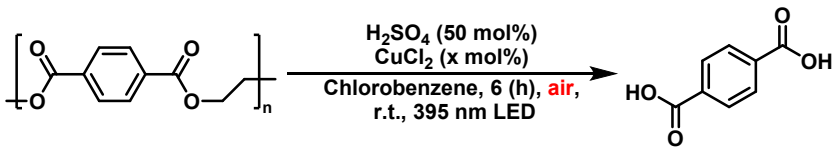
Table S1. Screening of different solvent[a]



Entry	Solvent	Yield (%)[b]
1	Chlorobenzene	26
2	CH_3CN	N.D.
3	$CHCl_3$	20
4	DCE	N.D.
5	CH_3CN:Chlorobenzene (1:1)	N.D.
6	MeOH	N.D.
7	MeOH:Chlorobenzene (1:1)	N.D.
8	EA	N.D.
9	EtOAC:Chlorobenzene (1:1)	N.D.
10	DCM	N.D.
11	DMF	trace
12	1,4-Dioxane	N.D.
13	Toluene	16

[a]Reaction conditions: PET (0.2 mmol based on $C_{10}H_8O_4$, 1.0 equiv.), $CuCl_2$ (20 mol%), H_2SO_4 (50 mol%), solvent (2.0 mL), room temperature, air atmosphere, and irradiation of 395 nm LED for 6 h. [b]The yields were calculated based on isolation.

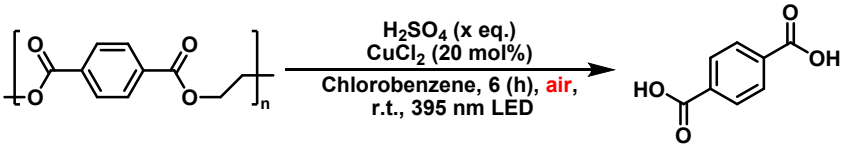
Table S2. Different catalyst loading affecting the conversion[a]



Entry	Catalyst (mol%)	Yield (%)[b]
1	--	Trace
2	5	10
3	20	26
4	50	26

[a]Reaction conditions: PET (0.2 mmol based on $C_{10}H_8O_4$, 1.0 equiv.), $CuCl_2$ (x mol%), H_2SO_4 (50 mol%), chlorobenzene (2.0 mL), room temperature, air atmosphere, and irradiation of 395 nm LED for 6 h. [b]The yields were calculated based on isolation.

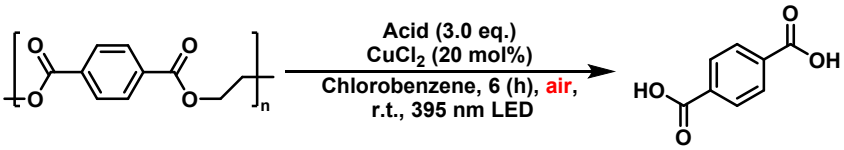
Table S3. Different additive loading affecting the conversion[a]



Entry	Additive (equiv.)	Yield (%)[b]
1	--	N.D.
2	0.5	26
3	1.0	35
4	3.0	85
5	5.0	85

[a]Reaction conditions: PET (0.2 mmol based on $C_{10}H_8O_4$, 1.0 equiv.), $CuCl_2$ (20 mol%), H_2SO_4 (x equiv.), chlorobenzene (2.0 mL), room temperature, air atmosphere, and irradiation of 395 nm LED for 6 h. [b]The yields were calculated based on isolation.

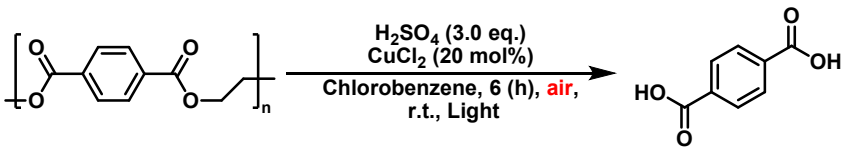
Table S4. Screening of different additives[a]



Entry	additive	Yield (%)[b]
1	H_2SO_4	85
2	HCl	Trace
3	Trifluoroacetic Acid	N.D.
4	HNO_3	N.D.
5	Methanesulfonic Acid	N.D.

[a]Reaction conditions: PET (0.2 mmol based on $C_{10}H_8O_4$, 1.0 equiv.), $CuCl_2$ (20 mol%), Acid (3.0 equiv.), chlorobenzene (2.0 mL), room temperature, air atmosphere, and irradiation of 395 nm LED for 6 h. [b]The yields were calculated based on isolation.

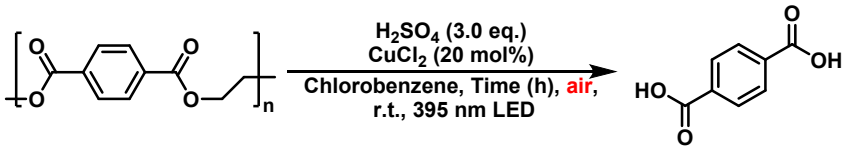
Table S5. Screening of different light[a]



Entry	Light (nm)	Yield (%)[b]
1	395	85
2	460	N.D.
3	--	N.D.

[a]Reaction conditions: PET (0.2 mmol based on $C_{10}H_8O_4$, 1.0 equiv.), $CuCl_2$ (20 mol%), H_2SO_4 (3.0 equiv.), chlorobenzene (2.0 mL), room temperature, air atmosphere, and irradiation of light for 6 h. [b]The yields were calculated based on isolation.

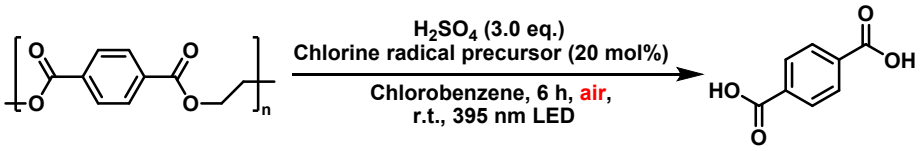
Table S6. Different reaction times affecting the conversion[a]



Entry	Time (h)	Yield (%)[b]
1	3	55
2	6	85
3	12	85
4	24	85

[a]Reaction conditions: PET (0.2 mmol based on $C_{10}H_8O_4$, 1.0 equiv.), $CuCl_2$ (20 mol%), H_2SO_4 (3.0 equiv.), chlorobenzene (2.0 mL), room temperature, air atmosphere, and irradiation of 395 nm LED for x h. [b]The yields were calculated based on isolation.

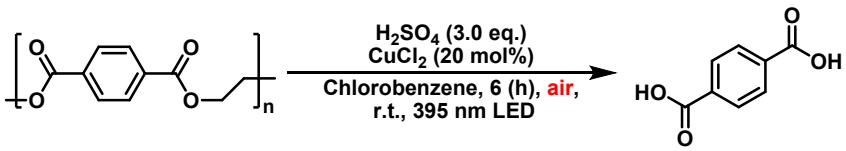
Table S7. Different chlorine radical precursor affecting the conversion[a]



Entry	Chlorine radical precursor	Yield (%)[b]
1	*t*-BuOCl	32
2	$FeCl_3$	64
3	$ZnCl_2$	73
4	$SnCl_2$	61

[a]Reaction conditions: PET (0.2 mmol based on $C_{10}H_8O_4$, 1.0 equiv.), chlorine radical precursor (20 mol%), H_2SO_4 (3.0 equiv.), chlorobenzene (2.0 mL), room temperature, air atmosphere, and irradiation of 395 nm LED for 6 h. [b]The yields were calculated based on isolation.

2.2 Standard procedure for the conversion

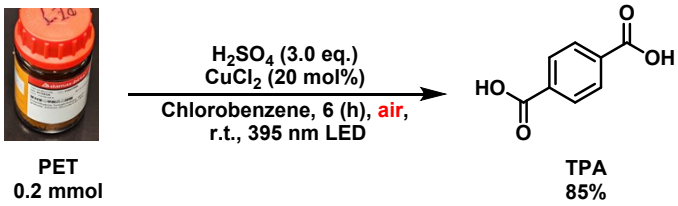


To a 25 mL glass tube containing a stirring bar was added polyethylene terephthalate (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%), H_2SO_4 (3.0 equiv.), chlorobenzene (2.0 mL) under air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying.

2.3 Standard procedure for aerobic degradation of commercial PET/PBT/PET waste

To a 25 mL glass tube containing a stirring bar was added polyethylene terephthalate (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%), H_2SO_4 (3.0 equiv.), chlorobenzene (2.0 mL) under air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate.

Commercial PET acidolysis conversion:

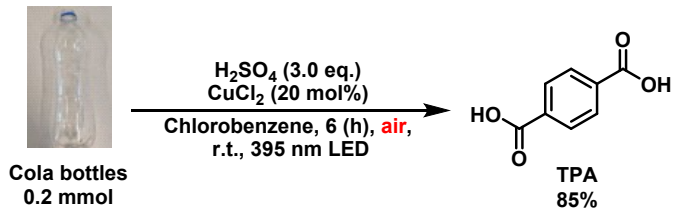


PET
0.2 mmol

TPA
85%

To a 25 mL sealed-tube, PET (0.2 mmol, 38.6 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (28.4 mg, 85%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Cola bottles acidolysis conversion:

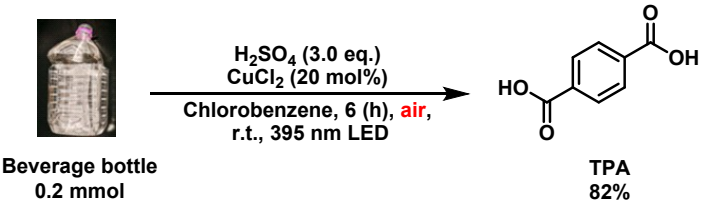


Cola bottles
0.2 mmol

TPA
85%

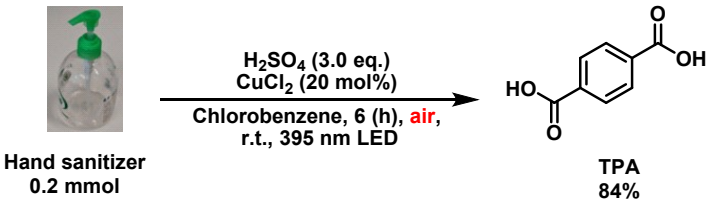
To a 25 mL sealed-tube, Cola bottle (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (28.2 mg, 85%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Beverage bottle acidolysis conversion:



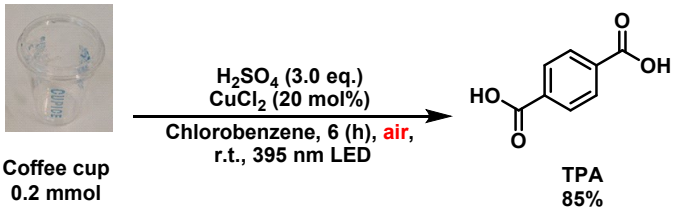
To a 25 mL sealed-tube, beverage bottle (0.2 mmol, 38.0 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (26.9 mg, 82%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Hand sanitizer bottle acidolysis conversion:



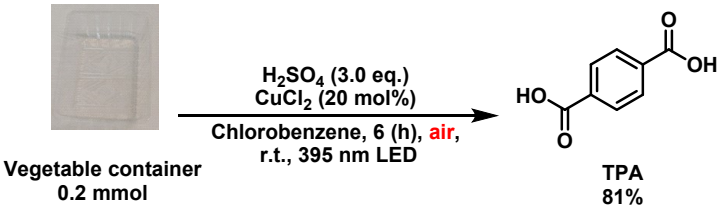
To a 25 mL sealed-tube, Hand sanitizerbottle (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (27.9 mg, 84%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Coffee cup acidolysis conversion:



To a 25 mL sealed-tube, Coffee cup (0.2 mmol, 38.0 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (27.9 mg, 85%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

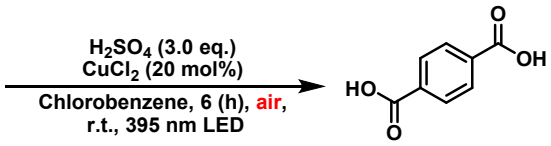
PET waste Vegetable trays acidolysis conversion:



To a 25 mL sealed-tube, Vegetable container (0.2 mmol, 37.9 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (26.5 mg, 81%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Detergent bottle acidolysis conversion:

Detergent bottle
0.2 mmol

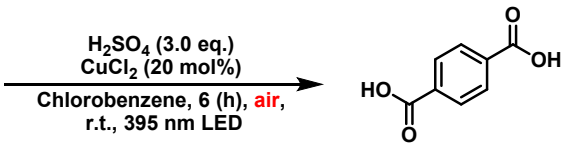


TPA
73%

To a 25 mL sealed-tube, Detergent bottle (0.2 mmol, 38.5 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (24.3 mg, 73%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Facewash bottle acidolysis conversion:

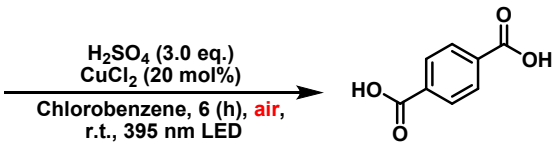
Facewash bottle
0.2 mmol



TPA
70%

To a 25 mL sealed-tube, Facewash bottle (0.2 mmol, 38.7 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (23.4 mg, 70%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Sprite bottles acidolysis conversion:

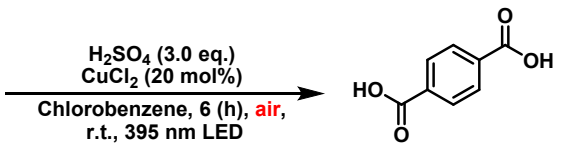


Sprite bottles
0.2 mmol

TPA
77%

To a 25 mL sealed-tube, Sprite bottle (0.2 mmol, 38.0 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (25.3 mg, 77%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Energy drink bottle acidolysis conversion:

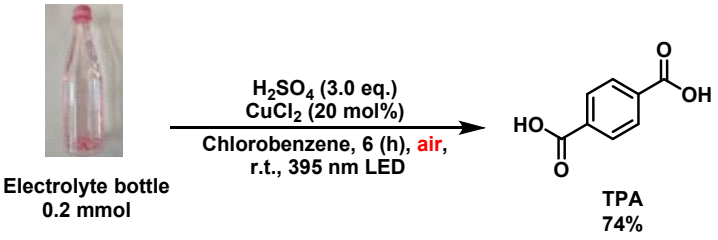


Energy drink bottle
0.2 mmol

TPA
70%

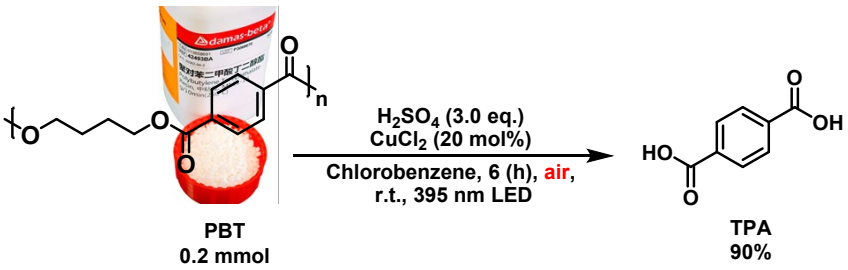
To a 25 mL sealed-tube, Energy drink bottle (0.2 mmol, 38.1 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (23.1 mg, 70%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PET waste Electrolyte bottle acidolysis conversion:



To a 25 mL sealed-tube, Electrolyte bottle (0.2 mmol, 38.2 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (24.4 mg, 74%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of polyethylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

PBT acidolysis conversion:



To a 25 mL sealed-tube, PBT (0.2 mmol, 51.0 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (29.8 mg, 90%) White solid. Note: The catalytic amount and yield of products are based on the single repeat unit of Polybutylene terephthalate. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

2.4 Gram-scale reaction and isolation of the by-product

To a 100 mL round-bottom flask, PET fragments (10.4 mmol, 2.0 g), $CuCl_2$ (20 mol%, 279.2 mg), H_2SO_4 (3.0 equiv., 3062.5 mg), chlorobenzene (30.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to two 395 nm LED lights and stirred under light irradiation for 6 hours. After the completion of the reaction, chlorobenzene was collected by 110 ℃ vacuum distillation of diaphragm pump. And NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (1.52 g, 88%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

Figure S5. Gram-scale depolymerization of PET bottles: a) Comparison before and after hydrolysis reaction. b) The overall perspective of reaction device. c) PET bottle fragments. d) Added PhCl. e) Distillation device. f) Crude product. g) Recycled solvent. h) Alkalization treatment. i) Acidification treatment. j) Suction filtration. k) Product TPA.

2.5 Mix plastic selective oxidation conversion

To a 25 mL sealed-tube containing a stirring bar was added PET fragments (1.0 mmol, 192.0 mg), 0.2 mmol each for LDPE fragments, PP fragments, $CuCl_2$ (20 mol%, 26.8 mg), H_2SO_4 (3.0 equiv., 294.0 mg), chlorobenzene (10.0 mL) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED lights and stirred under light irradiation for 12 hours. After the completion of the reaction, NaOH solution was added dropwise to adjust the pH to approximately 10, the reaction mixture was extracted with EtOAc, the organic phases were removed, and hydrochloric acid solution was added dropwise to adjust the pH to approximately 2. Subsequently, a large amount of white solid precipitated. The product TPA was obtained by filtration, washing with water, and drying. Yielded product terephthalic acid (116.2 mg, 70%) White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 2H), 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 135.0, 129.9.

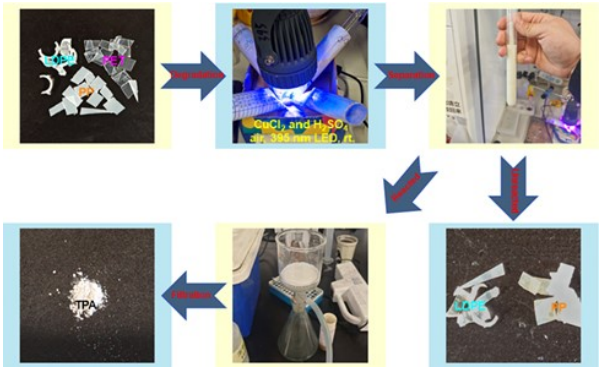
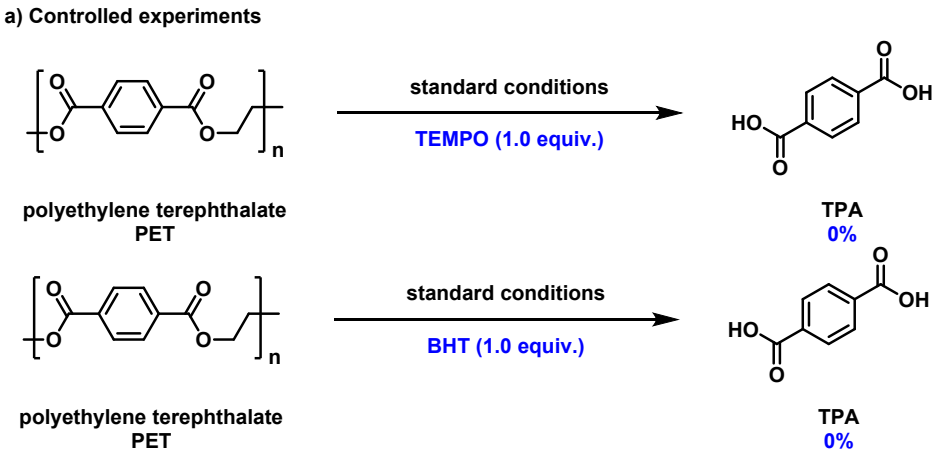


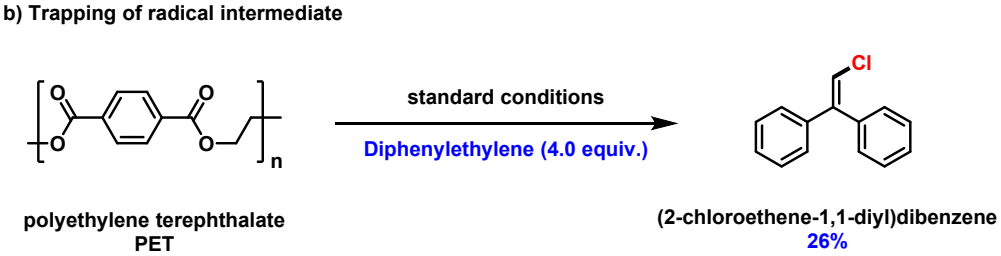
Figure S6. Mixed stream PET/LDPE/PP waste acidolysis and selective precipitation.

3. Mechanistic studies

3.1 Free radical trapping experiment

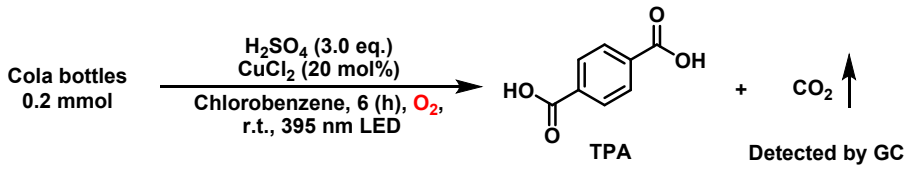


To a 25 mL sealed-tube containing a stirring bar was added PET fragments (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL), TEMPO/BHT (1.0 equiv.) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED lights and stirred under light irradiation for 6 hours. The addition of radical scavengers TEMPO and BHT inhibited the reaction, indicating the involvement of free radicals.



To a 25 mL sealed-tube containing a stirring bar was added PET fragments (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) and Diphenylethylene (4.0 equiv.) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED lights and stirred under light irradiation for 6 hours. After the completion of the reaction, the reaction mixture was extracted with EtOAc, the combined organic phases were dried and concentrated. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) yielded product (2-chloroethene-1,1-diyl)dibenzene (5.6 mg, 26%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.27 (m, 10H), 6.67 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 143.96, 140.21, 137.66, 129.94, 128.51, 128.35, 128.29, 128.24, 128.15, 128.05, 127.79, 115.97, 114.36, 31.60, 30.24.

3.2 CO_2 determination by GC



To a 25 mL Schlenk tube, Cola bottle (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) were added under an O_2 atmosphere. The mixture was placed perpendicular to a 395 nm LED light and stirred under light irradiation for 6 hours. After reaction completing, the gas phase was examined by the gas chromatography (GC) to analyze the potential gas products.

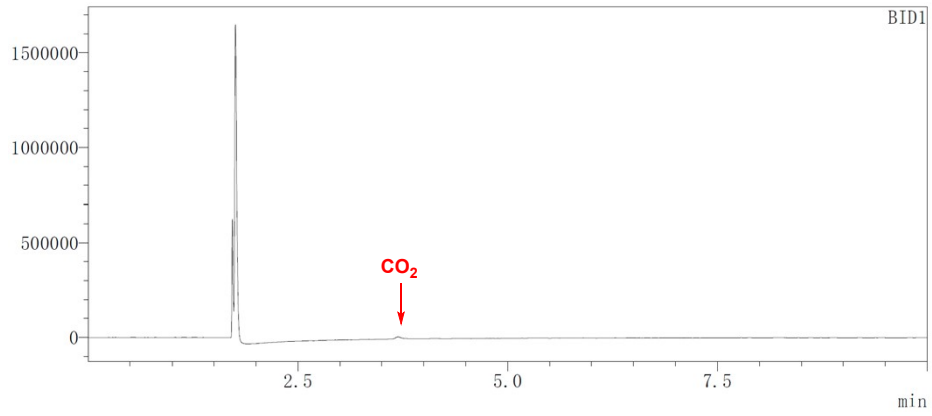
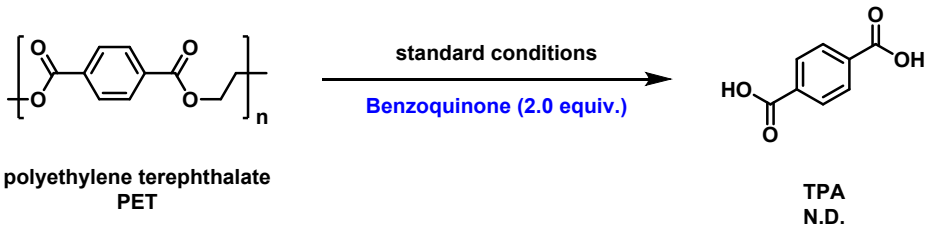


Figure S7. CO_2 determination by GC.

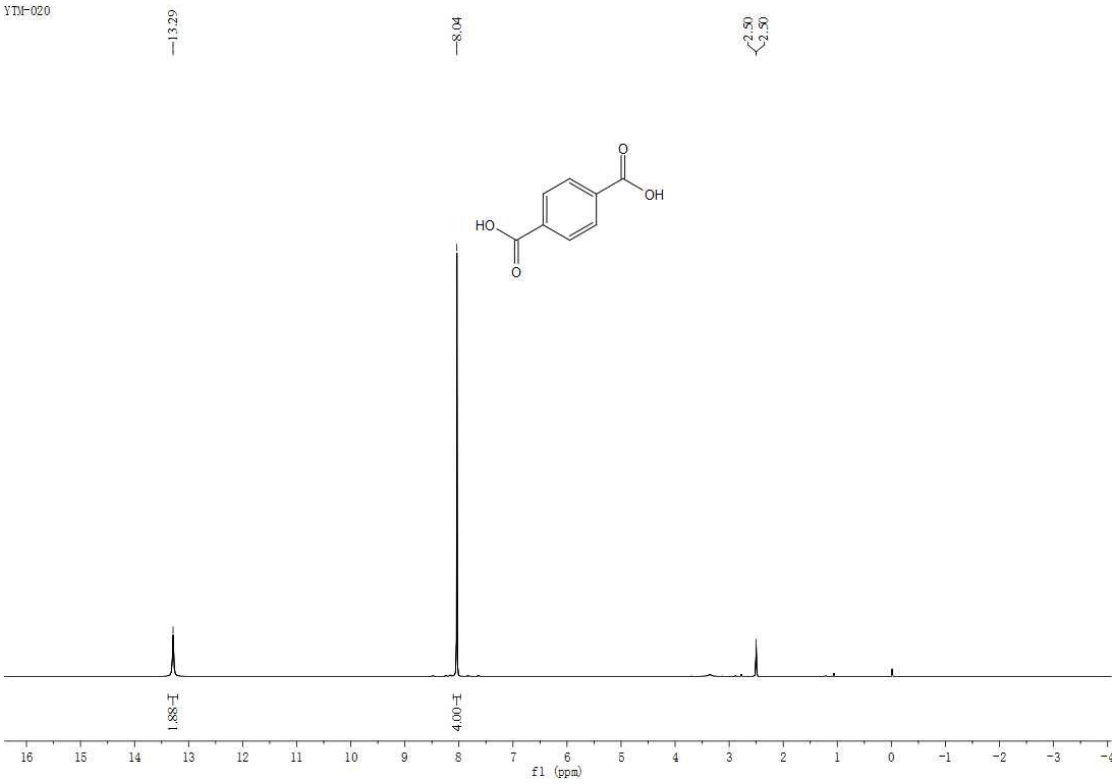
3.3 Superoxide radical quenching experiment

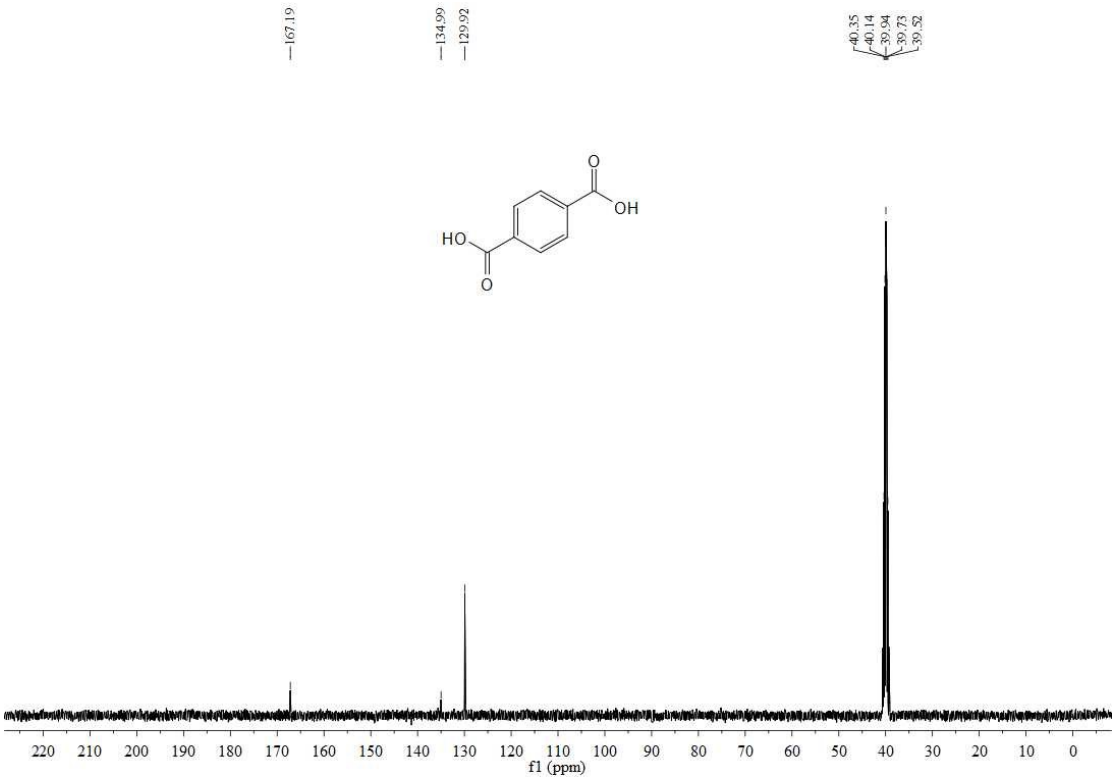


To a 25 mL sealed-tube containing a stirring bar was added PET fragments (0.2 mmol, 38.4 mg), $CuCl_2$ (20 mol%, 5.4 mg), H_2SO_4 (3.0 equiv., 58.8 mg), chlorobenzene (2.0 mL) and Benzoquinone (2.0 equiv.) were added under an air atmosphere. The mixture was placed perpendicular to a 395 nm LED lights and stirred under light irradiation for 6 hours. The reaction was completely suppressed.

4. Spectral data for compounds

TPA





2-chloroethene-1,1-diyl)dibenzene