

Supplementary Information

Continuous photocatalytic preparation of hydrogen peroxide with anthraquinone photosensitizers

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1. Synthesis of 2,6-Di-tert-butylanthraquinone

Alkylation of Anthracene for the Synthesis of 2,6-Di-tert-butylanthracene.

The synthesis of 2,6-di-tert-butyl anthracene involved the reflux of anthracene with tert-butyl alcohol in trifluoroacetic acid as a solvent for 24 hours¹, as depicted in **Fig. S1**.

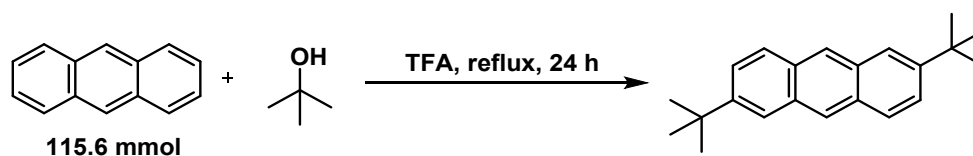


Fig. S1 Preparation of 2, 6-di-tert-butylanthracene by alkylation of anthracene.

In a 250 mL round-bottom flask, a mixture of 115.6 mmol (20.6 g) of anthracene, 334.6 mmol (24.8 g) of tert-butyl alcohol, and 150 mL of trifluoroacetic acid was prepared. The mixture was then heated to 120 °C and refluxed for 24 hours. After terminating the reaction, the reaction mixture was allowed to cool to room temperature. Subsequently, 20 mL of ice water and 20 mL of petroleum ether were introduced to quench the reaction. The entire system was then transferred to a 1000 mL beaker, and 260 mL of distilled water was added. Sodium bicarbonate was incrementally added to neutralize any excess acid. Subsequently, the system was transferred to a separatory funnel and washed repeatedly with organic phase using distilled water and saturated saline solution. After washing, the organic phase was filtered through a Büchner funnel under reduced pressure. The filter cake was washed with ice-cold petroleum ether, yielding a white solid powder. The filter cake was then transferred to a surface dish and dried in a vacuum oven at 50 °C for 12 hours. Finally, the white powdered product, 2,6-di-tert-butylanthracene, was obtained with a yield of 15.96 g, corresponding to a 47.5% yield.

Oxidative Synthesis of 2,6-Di-tert-butylanthraquinone (DBAQ) from 2,6-Di-tert-butylanthracene

In a 500 mL round-bottom flask, 55.0 mmol (15.96 g) of 2,6-di-tert-butylanthracene and 160 g of glacial acetic acid were combined. The reaction mixture was then heated to 124 °C and maintained at this temperature for 15 minutes before cooling it to room temperature² (Fig.S2).

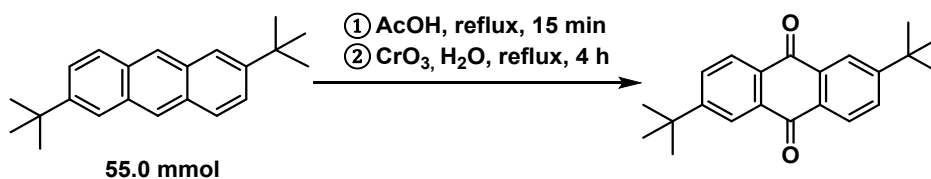


Fig. S2 Preparation of 2, 6-di-tert-butylanthraquinone by oxidation of 2, 6-di-tert-butylanthracene.

A solution composed of 24 mL of distilled water, 160 g of ice-cold acetic acid, and 153.6 mmol (15.36 g) of chromium trioxide (CrO₃) was added to the flask. The reaction was then refluxed at 110 °C for 4 hours. After heating was stopped and the reaction mixture was cooled to room temperature, 80 mL of ice water was added to quench the reaction.

The reaction mixture was filtered using a Büchner funnel to isolate green crystals. These crystals were subsequently washed, first with hot water and then with a 1 M NaOH solution in separate batches. During this process, the solid transitioned from green to pale yellow. Finally, the solid was transferred to a surface dish after a wash with ice-cold water. It was then subjected to drying in a vacuum oven at 50°C for 12 hours, resulting in the production of 14.78g of yellow crystalline product, 2,6-di-tert-butylanthraquinone, with a yield of 84.0%.

2. Determination of H₂O₂, oxidation products of HADs and calculation of H₂O₂ production rate:

2.1 Iodometry redox titration^{3,4}

2.1.1 Preparation of Solutions:

(1) 2M H₂SO₄: Take 98 mL distilled water in a narrow-mouth bottle using a measuring cylinder. Using a dry measuring cylinder, measure 25 mL of 98% concentrated sulfuric acid and slowly add it to the water.

(2) Ammonium molybdate solution: Weigh 3.18 g of analytical grade ammonium molybdate and dissolve it in 100 mL of water.

(3) Na₂S₂O₃ solution: Weigh 12.5g of analytical grade Na₂S₂O₃ and place it in a wide-mouth bottle. Boil 500 mL of distilled water and allow it to cool to room temperature. Pour the cooled water into the wide-mouth bottle and add a small amount of analytical grade Na₂CO₃ (approximately 0.1g) to adjust the pH to between 9-10. Store the prepared solution in a light-protected area for one week before use.

(4) KI solution: Weigh 10 g of analytical grade KI and dissolve it in 100 mL of distilled water. Set it aside.

(5) Starch solution: Weigh 2.92 g of analytical grade NaCl and dilute it with distilled water to make a 0.1 M standard NaCl solution. Dissolve 3 g of soluble starch in 50 mL of the standard NaCl solution to make a suspension. Then, while stirring, add this suspension to 300 mL of boiling standard NaCl solution.

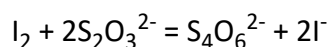
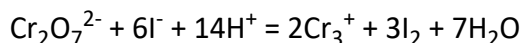
2.1.2 Solution Calibration:

(1) Na₂S₂O₃ Solution:

Weigh 0.15 g of potassium dichromate, dried to a constant weight at 120°C. Accurately measure 0.0001 grams of the potassium dichromate and transfer it to a 500 mL conical flask. Add 30 mL of distilled water. After complete dissolution of the potassium dichromate, add 12 mL of 2 M H₂SO₄ and 20 mL of KI solution. Immediately cover the flask with a watch glass to prevent iodine

evaporation and place it in a light-protected area for 7 minutes. After 5 minutes, dilute the solution with distilled water and calibrate it using Na₂S₂O₃ solution. Once the solution in the conical flask turns orange, add 1.5 mL of starch solution and continue titrating until the solution changes from blue to bright green.

Reaction equation:



The concentration of Na₂S₂O₃ solution is calculated using the following formula:

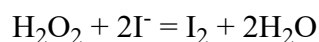
$$C_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{W \times 6 \times 1000}{294.2 \times V} \times 100\%$$

W— the mass of potassium dichromate (g)

V— the volume of Na₂S₂O₃ solution used (mL)

(2) H₂O₂ Calibration:

The quantification of H₂O₂ in the experiment was carried out through iodometry redox titration, and it was verified by KMnO₄ redox titration. The specific procedure is as follows: Take 0.2 g of the sample and transfer it to a beaker. Add three drops of 5% ammonium molybdate solution ((NH₄)₆Mo₇O₂₄·4H₂O) as the color developer, followed by the addition of H₂SO₄ (5.0 mL, 2.0 M) and KI solution (4.0 mL, 100.0 g L⁻¹). Cover the beaker with a watch glass and let it stand in a dark environment for 5 minutes. Subsequently, a Na₂S₂O₃ standard solution (0.10 M) was used for the redox titration of the generated I₂. When the color of the solution changes to light yellow, 1.0 mL of starch solution (10.0 g/L) is added, and the titration is continued until the dark blue color disappears and no longer reappears within 2 minutes. Reaction equation:



The concentration of H₂O₂ solution is calculated using the following formula:

$$wt.(H_2O_2) = \frac{M(H_2O_2) \times c(Na_2S_2O_3) \times V}{1000 \times 2 \times W} \quad (a)$$

$$c(H_2O_2) = \frac{wt.(H_2O_2) \times \rho(HADS) \times 10^6}{M(H_2O_2)} \quad (b)$$

V —the volume of the $Na_2S_2O_3$ titration solution (mL)

W —the mass of the H_2O_2 containing solution (g)

ρ (HADS)—the density of the hydrogen atom donor (g/mL)

2.2 $KMnO_4$ redox titration

2.2.1 Preparation of Solutions:

(1) 2 M H_2SO_4 : Take 98 mL distilled water in a narrow-mouth bottle using a measuring cylinder. Using a dry measuring cylinder, measure 25 mL of 98% concentrated sulfuric acid and slowly add it to the water. Allow it to cool and set it aside.

(2) 0.02 M Standard $KMnO_4$ solution: Weigh 1.6 g of $KMnO_4$ and dissolve it in an appropriate amount of water. Heat the solution to boiling for 20-30 minutes, then allow it to cool. Place the solution in a dark location for 7-10 days. Afterward, remove impurities such as MnO_4 by filtration using a glass sand core funnel or glass fiber filter. Store the filtrate in a clean, glass-stoppered brown bottle and keep it in a dark place.

2.2.2 Solution Calibration:

(1) $KMnO_4$ solution: Accurately weigh 0.2 g of $Na_2C_2O_4$ reference substance in a 250mL conical flask. Add approximately 20 mL of water to dissolve it. Then add 10mL of 2 M H_2SO_4 solution and heat it to $80^\circ C$. Immediately titrate with the calibrated $KMnO_4$ solution until the solution turns pale pink and remains stable for 60 seconds, indicating the endpoint. Perform 2 or 3 parallel determinations. Based on the volume of $KMnO_4$ solution consumed and the mass of the reference substance, calculate the concentration of the $KMnO_4$ solution.

Reaction equation:



The concentration of H_2O_2 solution is calculated using the following formula:

$$C_{\text{KMnO}_4} = \frac{W \times 5 \times 1000}{134.0 \times 2 \times V} \times 100\%$$

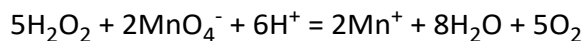
W— the mass of the $\text{Na}_2\text{C}_2\text{O}_4$ containing solution (g)

V— the volume of the KMnO_4 titration solution (mL)

(2) H_2O_2 Calibration:

Using a pipette, extract 10 mL of the hydrogen peroxide sample (approximately 30% concentration) and transfer it to a 250 mL volumetric flask. Dilute with water to the mark, ensuring thorough mixing. Then, pipette 20 mL of the diluted solution into a 250 mL conical flask. Add 20 mL of water and 20 mL of H_2SO_4 solution. Titrate the solution with the standard KMnO_4 solution until it turns pink and remains stable for 30 seconds, indicating the endpoint. Based on the volume of KMnO_4 standard solution used, calculate the mass fraction of H_2O_2 in the undiluted hydrogen peroxide sample.

Reaction equation:



The concentration of H_2O_2 solution is calculated using the following formula:

$$\text{wt.}(\text{H}_2\text{O}_2) = \frac{2 \times M(\text{H}_2\text{O}_2) \times c(\text{KMnO}_4) \times V}{5 \times W \times 1000} \times 100\% \quad (\text{c})$$

W— the mass of the H_2O_2 containing solution (g)

V— the volume of the KMnO_4 titration solution (mL)

2.3 Determination of the oxidation products of HADs

The composition of the reaction endpoint solution, whether under batch or continuous flow strategies, can be analyzed using gas chromatography (GC) or gas chromatography-mass spectrometry (GC-MS). Since hydrogen atom donors (HADs) also serve as solvents in this photocatalytic strategy, and in excess, even under optimal conditions (isopropanol-DBAQ system), the content of the oxidation product acetone in the endpoint H₂O₂ solution is only 4.7% (detected by GC). The oxidation products of other types of HADs can also be quantitatively detected using gas chromatography. (GC conditions: FID detector, FFAP gas chromatography column, GC-2014 Shimadzu Co., Ltd.)

2.4 Calculation of H₂O₂ production rate

2.4.1 Calculation of H₂O₂ production rate under intermittent conditions

First, the concentration of H₂O₂ (mmol/L) in the solution at the reaction endpoint is measured using the titration methods described in sections 2.1 and 2.2. The H₂O₂ production rate (mmol/L/h or mM/h) under intermittent photocatalytic conditions is then obtained by dividing the concentration of H₂O₂ at the endpoint by the actual reaction time.

$$r_{H_2O_2} (mM/h) = \frac{c(H_2O_2)}{Reaction\ time(h)} \quad (d)$$

2.4.2 Calculation of H₂O₂ production rate under continuous flow strategy

First, the concentration of the H₂O₂ solution (mmol/L) at the reaction endpoint is measured using the titration method described in sections 2.1 and 2.2. The production rate of H₂O₂ under continuous flow strategy (mM/h or mM/min) is then obtained by dividing the concentration of the H₂O₂ solution at the reactor outlet by the retention time for single-pass photocatalysis (eq. d), the retention time can be measured using a stopwatch and corrected by calculation (Section 5).

2.4.3 Calculation of space-time yield (STY) under continuous flow strategy

Space-time yield (STY) refers to the amount of the target product obtained per unit volume of the apparatus per unit time. For this continuous flow strategy, the formula for calculating STY is as follows:

$$STY_{(H_2O_2)} (mol/L \cdot h) = \frac{r(H_2O_2) \times t \times V(H_2O_2)}{t \times V(retention) \times 1000} \quad (e)$$

$r(H_2O_2)$ — H_2O_2 production rate (mM/h)

t —retention time(h)

$V(H_2O_2)$ —volume of H_2O_2 solution produced in the retention time (L)

$V(retention)$ —retention volume of the reactor (L)

3. The catalyst recycling process

All the catalysts used in this manuscript are homogeneous catalysts. After the reaction, they are dissolved in the solvent and recovered for reuse.

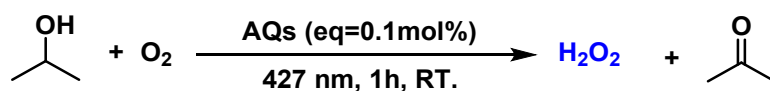
(1) Collect 300 mL of the reaction solution from the reactor outlet (main components are isopropanol, 2,6-di-tert-butylanthraquinone, H_2O_2 , and acetone) and transfer it to a 500 mL rotary evaporation flask. Concentrate the reaction solution to 30 mL using a rotary evaporator, resulting in the precipitation of a large amount of light yellow crystals.

(2) Add 50 mL of ice-cold pure water and transfer the concentrate to a 150 mL flask. Stir the mixture overnight at 0°C to allow complete crystallization.

(3) Filter the concentrate using a Büchner funnel while cold. Wash the obtained filter cake three times with 20 mL of ice-cold pure water each time, then transfer it to a watch glass. Dry it in a vacuum oven at 50°C for 12 hours. The resulting catalyst is 2,6-di-tert-butylanthraquinone, with an actual mass of 1.18 g (3.68 mmol) and a theoretical mass of 1.26 g (3.92 mmol), yielding a recovery rate of 93.6%.

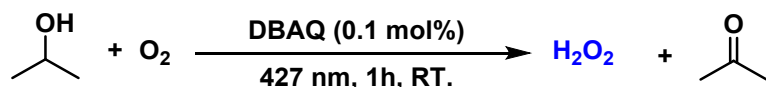
4. Screen of intermittent reaction condition screening.

Table S1. Catalyst investigation and control experiments.



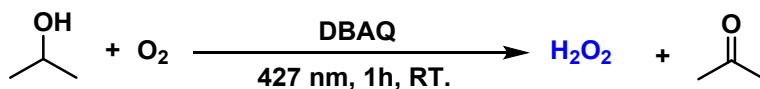
Entry ^a	Conditions	H ₂ O ₂ (wt%)	Generation rate of H ₂ O ₂ (mM/h)
1	DAAQ	0.03	7.9
2	Emodin	0.07	15.6
3	HAQ	0.07	16.0
4	Alizarin	0.09	20.3
5	1,8-DCAQ	0.07	15.3
6	TX	0.09	20.3
7	DBrAQ	0.19	42.8
8	CAQ	0.63	144.1
9	DCAQ	0.71	163.3
10	BrAQ	0.92	210.2
11	AQ	1.01	230.6
12	TAAQ	1.92	440.8
13	EAQ	2.02	463.8
14	BAQ	2.10	481.1
15	MAQ	2.29	525.7
16	DBAQ	2.71	621.2
17	DBAQ + Air	0.08	18.2
18	DBAQ + N ₂	N.D.	N.D.
19	Dark	N.D.	N.D.
20	Without DBAQ	0.05	10.9

^a Unless otherwise specified, isopropanol **1a** (2.33 g, 38.7 mmol), photocatalyst (0.0387 mmol, 0.1 mol %) were added to 10 mL vial equipped with a stirring bar. The mixture was sonicated to dissolve completely. Then, the mixture was stirred under O₂ atmosphere with exposure to 40 W Blue LED light (427 nm) at room temperature for 1 h.

Table S2. Selection of light source.

Entry	Wavelength (nm)	H ₂ O ₂ (wt%)	Generation rate of H ₂ O ₂ (mM/h)
1	370nm (40 W LED)	1.54	356.3
2	390nm (40 W LED)	1.75	403.8
3	427nm (40 W LED)	2.58	591.6
4	456nm (40 W LED)	0.36	82.2
5	467nm (40 W LED)	0.14	32.4
6	>320nm(300W Xe Lamp)	1.55	356.8

^a Unless otherwise specified, isopropanol **1a** (2.33 g, 38.7 mmol), DBAQ (0.0387 mmol, 0.1 mol %) were added to 10 mL vial equipped with a stirring bar. The mixture was sonicated to dissolve completely. Then, the mixture was stirred under O₂ atmosphere with exposure to different kinds of light sources at room temperature for 1 h.

Table S3. Screen of the loading of catalyst.

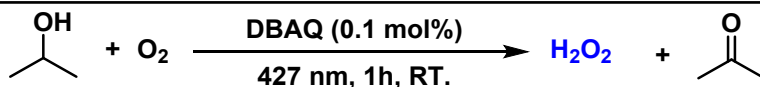
Entry	DBAQ	H ₂ O ₂ (wt%)	Generation rate of 2a (mM/h)
1	0.03%	1.42	327.6
2	0.07%	2.29	528.3
3	0.1%	2.71	621.2
4	0.2%	2.57	592.8
5	0.3%	2.33	538.1
6	0.5%	1.89	436.4
7	0.75%	2.25	519.6
8	1%	1.08	249.4
9	2%	1.10	254.0

^a Unless otherwise specified, isopropanol **1a** (2.33 g, 38.7 mmol), different equivalents of DBAQ (0.03 mol %—2.0 mol%) were added to 10 mL vial equipped with a stirring bar. The mixture was

sonicated to dissolve completely. Then, the mixture was stirred under O₂ atmosphere with exposure to 40W Blue LED light (427 nm) at room temperature for 1 h.

Table S4. Investigation of HADs.

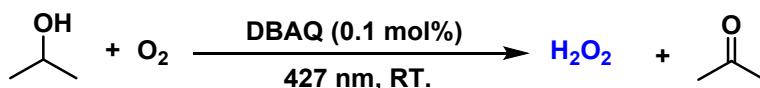
Entry ^a	HADs	2a(wt%)	Generation rate of 2a (mM/h)
1	1-Phenylethanol	0.10	30.1
2	Benzyl alcohol	0.13	39.7
3	1-Phenylpropanol	0.20	60.1
4	2-Phenylethanol	ND.	ND.
5	Cyclohexanol	0.03	8.54
6	Ethanol	2.10	487.1
7	Isopropanol	2.69	621.2
8	n-Butanol	1.52	361.9
9	Isobutanol	1.29	307.2
10	3-Chloro-1-propanol	ND.	ND.
11	2-Chloroethanol	0.10	35.3
12	1,3-Propanediol	0.10	30.0
13	1,3-Butanediol	0.03	7.96
14	Ethylbenzene	0.09	23.9
15	P-Xylene	0.29	73.2
16	Toluene	0.42	107.7
17	Cyclohexane	0.21	49.1
18	Cyclohexylamine	0.12	30.4
19	Water	ND.	ND.
20	Formic acid	0.07	24.5



^a Unless otherwise specified, different kinds of HADs (40.0 mmol), DBAQ (0.04 mmol, 0.1 mol %) were added to 10 mL vial equipped with a stirring bar. The mixture was sonicated to dissolve

completely. Then, the mixture was stirred under O₂ atmosphere with exposure to 40W Blue LED light (427 nm) at room temperature for 1 h.

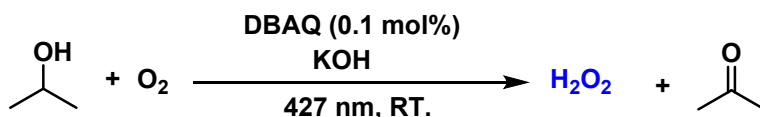
Table S5. The effect of reaction time on H₂O₂ concentration in DBAQ system under intermittent conditions



Time(h) ^a	wt%(H ₂ O ₂)	c(H ₂ O ₂)/(mM)
1	2.52	577.8
2	3.48	803.6
3	4.04	932.9
4	4.76	1099.2
5	5.00	1154.6
6	5.64	1302.4
7	5.63	1300.1
8	5.64	1302.4

^a Unless otherwise specified, isopropanol **1a** (4.66 g, 77.4 mmol), DBAQ (0.0774 mmol, 0.1 mol %) were added to 20 mL vial equipped with a stirring bar. The mixture was sonicated to dissolve completely. Then, the mixture was stirred under O₂ atmosphere with exposure to 40W Blue LED light (427 nm) at room temperature for 8 h.

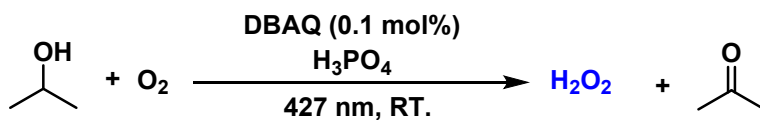
Table S6. Investigation of the effect of KOH addition on H₂O₂ production.



Entry ^a	equiv.	wt%(H ₂ O ₂)	Generation rate of 2a (mM/h)
1	1%	1.94	446.8
2	2%	1.27	293.3
3	3%	1.09	251.7
4	4%	0.46	106.2

^a Unless otherwise specified, isopropanol **1a** (2.33 g, 38.7 mmol), DBAQ (0.0387 mmol, 0.1 mol %) and different equivalents of KOH were added to 10 mL vial equipped with a stirring bar. The mixture was sonicated to dissolve completely. Then, the mixture was stirred under O₂ atmosphere with exposure to 40W Blue LED light (427 nm) at room temperature for 1 h.

Table S7. Investigation of the effect of phosphoric acid addition on H₂O₂ production.



Entry ^a	equiv.	wt%(H ₂ O ₂)	Generation rate of 2a (mM/h)
1	0	2.58	594.6
2	0.05%	2.54	586.6
3	0.1%	3.03	699.7
4	0.25%	2.90	669.6
5	0.5%	2.61	602.7
6	0.75%	2.67	616.5
7	1.0%	2.15	496.5
8	12.8%	2.27	524.2
9	22.3%	1.57	362.5
10	30.4%	1.02	235.6
11	36.8%	0.61	141.8

^a Unless otherwise specified, isopropanol **1a** (2.33 g, 38.7 mmol), DBAQ (0.0387 mmol, 0.1 mol %) and different equivalents of H₃PO₄ were added to 10 mL vial equipped with a stirring bar. The mixture was sonicated to dissolve completely. Then, the mixture was stirred under O₂ atmosphere with exposure to 40W Blue LED light (427 nm) at room temperature for 1 h.

5. Calculations about residence time⁵

Calculation of residence time in continuous flow reactor

$$\text{Total residence time} = N \times \frac{V_1}{v_{liq,R} + v_{gas,R}} \quad (\text{a})$$

$$\text{Total time} = N \times \frac{V_2}{v_{liq,R}} \quad (\text{b})$$

$$\text{Total residence time} = \text{Total time} \times \frac{V_1}{V_2} \times \frac{v_{liq,R}}{v_{liq,R} + v_{gas,R}} \quad (\text{c})$$

$$\text{Total residence time} = \text{Total time} \times \frac{V_1}{V_2} \times \frac{V_L}{V_L + \frac{T^* \times P}{T \times P^*} \times V_g} \quad (\text{d})$$

N—Total circulation times of liquid phase in reactor.

V₁—Total liquid holding volume of micro reactor (2.5 mL).

V₂—Total volume of organic reaction solution.

v_{liq}—Flow rate of liquid phase(mL/min)

v_{gas}—Flow rate of gas phase(mL/min)

T—273 K

T*—Reaction temperature.

P—0.1 Mpa

P*—Reaction pressure.

6. Reaction process detection and mechanism exploration

Monitoring of H₂O₂ concentration over time

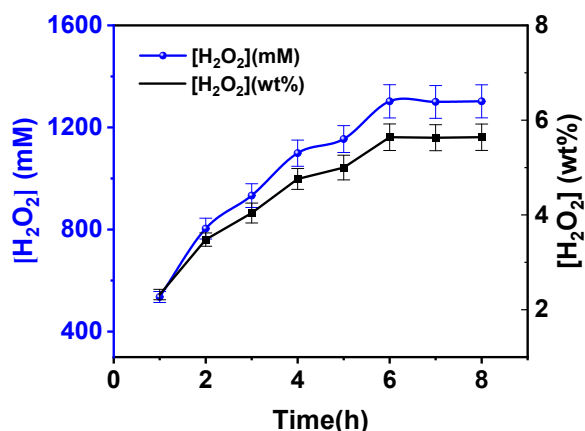


Fig. S3 The effect of reaction time on H₂O₂ concentration in DBAQ system under intermittent conditions.

HRMS spectra of key intermediates

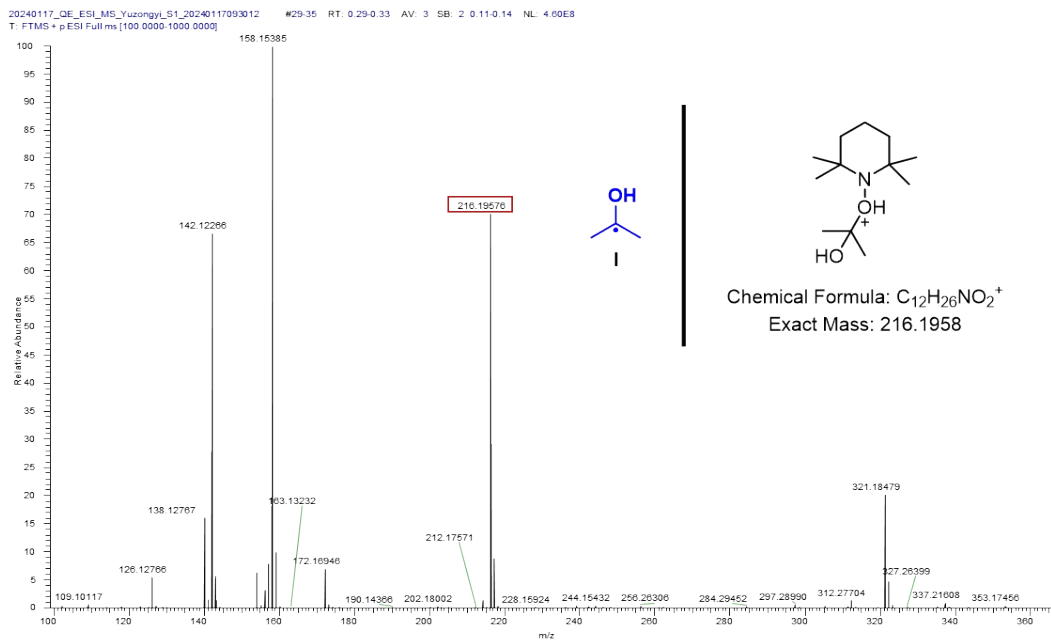


Fig. S4 The HRMS spectrum of the intermittent I adduction with TEMPO in the photocatalytic process. HRMS (m/z): (ESI) calcd. for C₁₂H₂₆NO₂⁺ [M + H]⁺: 216.1958, found: 216.19576.

Detection of superoxide radical anion (O₂^{-·}) by EPR test.

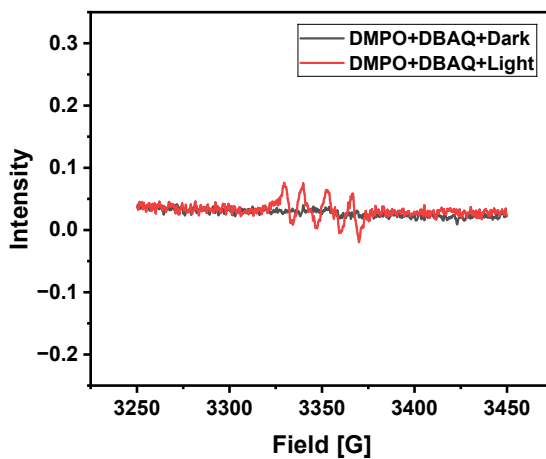


Fig. S5 EPR test of the photocatalytic system to detect the generation of superoxide radical anion (O₂^{-·}) under the irradiation.

Table S8. Summary of the photocatalytic production of H₂O₂ photocatalysts.

Catalyst	Reaction solution	Wave length	Light source & power	H ₂ O ₂ yield
TiO ₂ ⁶	benzyl alcohol	λ>280 nm	300W Xe Lamp	3.3 mM/h
CQD/TiO ₂ ⁷	ethanol	λ>420 nm	300 W Xe Lamp	1.7 mM/h
CoPi/rGO/TiO ₂ ⁸	2-propanol	λ>320 nm	200 W mercury lamp	1.5 mM/h
KH ₂ PO ₄ /g-C ₃ N ₄ ⁹	ethanol	λ>420 nm	300 W Xe Lamp	0.5 mM/h
g-C ₃ N ₄ -carbon ¹⁰	water + 2-propanol	λ>280 nm	200 W Xe Lamp	0.3 mM/h
AQ-augmented g-C ₃ N ₄ ¹¹	2-propanol	AM 1.5G	150 W Xenon Arc Lamp	0.4 mM/h
Au/BiVO ₄ ¹²	water + EtOH	λ>420 nm	2000 W Xe lamp	4.0 mM/h
Silica/graphene oxide/CdS ¹³	ethanol	λ=635 nm	300 W Xe Lamp	90.0 μM/h
Graphene oxide ¹⁴	water	λ>420 nm	300W Xe Lamp	33.3 μM/h
CdS-graphene ¹⁵	water + methanol	AM 1.5G	300W Xe Lamp	10.7 μM/h
rGO/Cd ₃ (TMT) ₂ ¹⁶	water + methanol	λ>420 nm	300W Xe Lamp	0.3 mM/h
Ni/MIL-125-NH ₂ ¹⁷	benzyl alcohol	λ>420 nm	500W Xe Lamp	1.0 mM/h
AQ Polymers ¹⁸	water	λ>400 nm	300W Xe Lamp	3.2 mM/h
Phenanthrenequinone Polymer s ¹⁹	water	λ>400 nm	300W Xe Lamp	3.0 mM/h
Resins ²⁰	water	λ>420 nm	500 W Xe lamp	4.1 μM/h
2-Ethylanthraquinone ²¹	Mesitylene+ trioctyl phosphate	AM 1.5G	300W Xe Lamp	15.2 mM/h
2-Ethylanthraquinone ²²	ethanol	AM 1.5G	300W Xe Lamp	25.2 mM/h
2-tert-Butylanthraquinone ²³	toluene	395 nm	50W LED	28.0 mM/h
²⁴	benzyl alcohol	λ< 400 nm	300W Xe Lamp	176.4 mM/h
This work	isopropanol	427 nm	40W LED	621.2 mM/h

7. DFT-Calculation details

All the BDFE of HADs were calculated by Gaussian 09W, Opt+Freq was used to obtain the optimized configuration^{25, 26}. The detailed settings of the calculation process are shown in **Fig. S6**

Method:

Basis Set: (,)

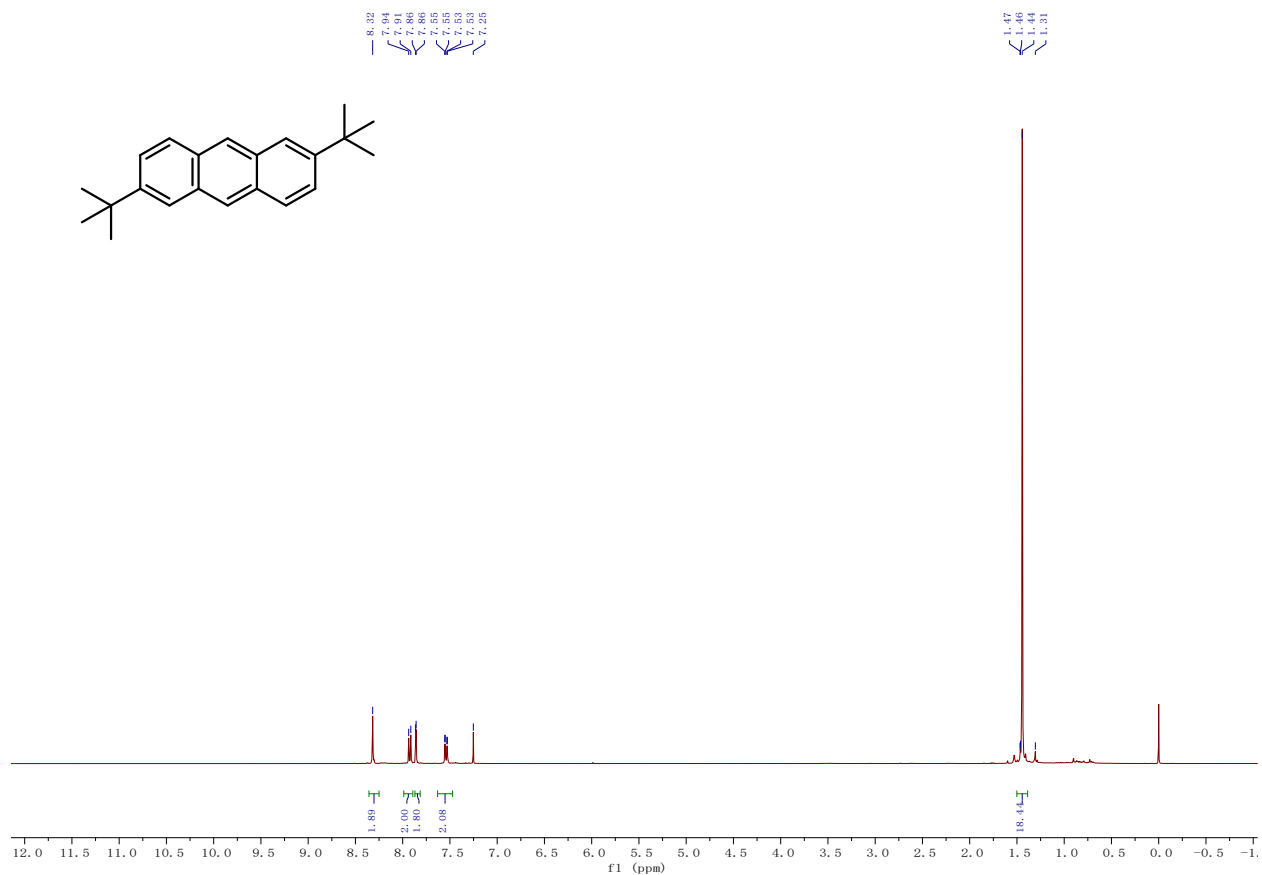
Charge: Spin:

Fig. S6 Detailed settings of the DFT calculation.

8. NMR spectrum

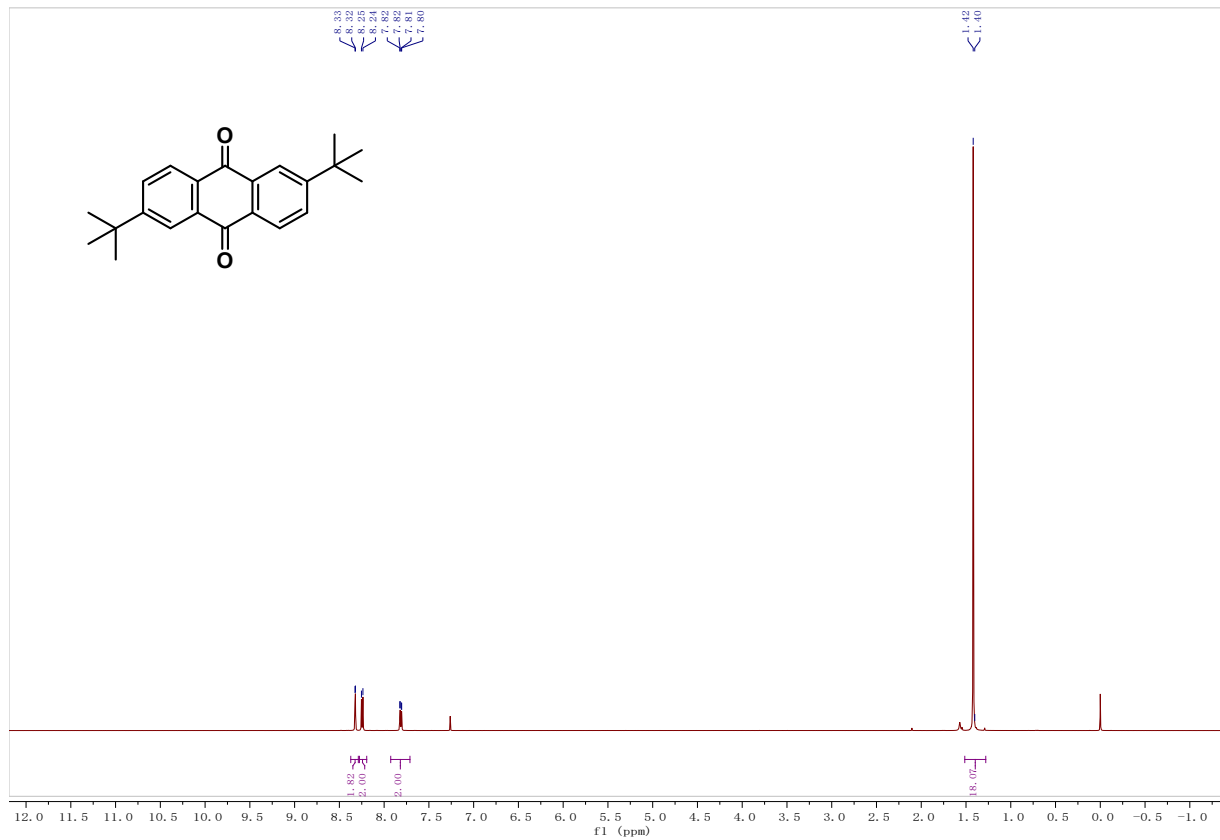
¹H-NMR spectra of 2,6-Di-tert-butylanthracene.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 2H), 7.93 (d, $J = 8.9$ Hz, 2H), 7.86 (d, $J = 1.9$ Hz, 2H), 7.54 (dd, $J = 8.9, 2.0$ Hz, 2H), 1.44 (s, 18H).



¹H-NMR spectra of 2,6-Di-tert-butylantraquinone (DBAQ)

¹H NMR (500 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 2.1 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 2H), 7.82 (dd, *J* = 8.2, 2.1 Hz, 2H), 1.42 (s, 18H).



9. Reagents used in the experimental section

Table S9. List of reagents used in the experimental section.

Name of reagent ^a	Purity	Manufacturer information
2,6-Di-tert-butylantraquinone	99%	Homemade, batch number [YZY20230112]
2-Methylantrone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
2-Dert-butylantraquinone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
2-Ethylantrone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
2-Tert-pentanylantraquinone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
Anthraquinone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
2-Brochantraquinone	98%	Shanghai Anji Medical Chemical Co., Ltd
1,5-dichloroanthraquinone	98%	Shanghai Anji Medical Chemical Co., Ltd
2-Chlorantrone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
2,6-Dibromantraquinone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
9-Thiotonone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
1,8-Dichlorananquinone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
2-Hydroxyantrone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
Alizarin	98%	Shanghai Anji Medical Chemical Co., Ltd
Emodin	98%	Shanghai Anji Medical Chemical Co., Ltd
2,6-Diaminoanthraquinone	98%	Shanghai Aladdin Biochemical Technology Co., Ltd
Alcohol	AR	Tianli Chemical Reagents Co., Ltd
Isopropanol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
n-Butyl alcohol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
2-Butanol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
1,3-Propylene glycol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
1,3-Butanediol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Cyclohexanol	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Cyclohexane	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Cyclohexylamine	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Methylbenzene	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Benzil alcohol	AR	Shanghai Aladdin Biochemical Technology Co., Ltd
1-Benzoethanol	AR	Shanghai Aladdin Biochemical Technology Co., Ltd
2-Benzoethanol	AR	Shanghai Aladdin Biochemical Technology Co., Ltd
1-Phenylpropanol	AR	Shanghai Aladdin Biochemical Technology Co., Ltd
p-Xylene	AR	Tianjin Fuyu Fine Chemical Co., Ltd
Oxygen	99.99%	Dalian Guangming Special Gas Co., LTD
Nitrogen	99.99%	Dalian Guangming Special Gas Co., LTD
Air	99.99%	Dalian Guangming Special Gas Co., LTD

^a Unless otherwise specified, the reagents used in the experiments were either provided by the aforementioned manufacturers or self-prepared and without further purified.

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