

Supporting Information

Photochlorination of Anthracene in Saline Ice under Simulated Solar Light

Text S1. QA/QC for ClANTs

Solvent blanks, which utilized methanol, were routinely run and found to contain negligible levels of 2-ClANT, 9-ClANT and 9,10-Cl₂ANT. Standard samples of the three types of ClANTs were prepared using HPLC grade methanol at a concentration of 1 mg/L. During the operation diode array detectors of HPLC for the detection, the retention time of 2-ClANT, 9-ClANT, and 9,10-Cl₂ANT were recorded at 8.91 min, 10.59 min, and 17.87 min, respectively. Following this, the standard solutions (0.01, 0.04, 0.08, 0.16 and 2 mg/L) were prepared for the quantitative analysis of ClANTs. The resulting standard curves were as follows: $y = 6.3 \times 10^{-5} x$ ($R^2 = 0.9982$) for 2-ClANT, $y = 6.2 \times 10^{-5} x$ ($R^2 = 0.9972$) for 9-ClANT, and $y = 3.2 \times 10^{-5} x$ ($R^2 = 0.9937$) for 9,10-Cl₂ANT.

Text S2. Materials and reagents

Anthracene (ANT, purity $\geq 99.0\%$), furfuryl alcohol (FFA, purity $\geq 98\%$), coumarin (COU, purity $\geq 98\%$), 3,5-dimethyl-1 H-pyrazole (DMPZ, purity $\geq 98\%$), 1,4-diazabicyclo[2.2.2]octane (DABCO), 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO, purity $\geq 98\%$), 2,4,6-trimethylphenol (TMP, purity $\geq 98\%$), fulvic acid (FA, purity $\geq 98\%$) and 1,3-diphenylisobenzofuran (DPBF, purity $\geq 98\%$) were purchased from McLean Biochemistry and Technology Co Ltd (Shanghai, China). Sodium chloride (NaCl, analytically pure), sodium thiocyanate (NaSCN, purity $\geq 98\%$) was purchased from Komeo Chemical Reagents Ltd (Tianjin, China). Sodium hydroxide (NaOH, analytically pure) was purchased from Tianli Chemical Reagent Co Ltd (Tianjin, China). Chromatography grade methanol, dichloromethane, and n-hexane were purchased from Bailiwick Technology Co Ltd (Beijing, China). Ultrapure water ($\geq 18.2 \Omega$) was manufactured by water purifier HK-MTYS-20 (Haokang, Chengdu, China).

Text S3. Methods of analysis

In this experiment, the quantitative analysis of the reacted ANT and its chlorinated products was carried out using a HPLC (LC-16, Shimadzu, Japan) configured with a diode array detector and a C18 column. The detection conditions were as follows:

mobile phase ratio V (methanol) : V (water) = 90:10, column temperature set at 40 °C, injection volume was 20 µL, flow rate was 1 mL/min, detection wavelength was 251 nm.

ROS ($\cdot\text{OH}$, $^1\text{O}_2$) involved in the reaction were investigated using electron paramagnetic resonance (EPR, Bruker E500, Germany). To detect the participation of O_2^- in the reaction, a fluorescence detector (FS5, Edinburgh, UK) was used (excitation wavelength 410 nm, emission wavelength 455 nm). DPBF, as a fluorescent probe for O_2^- , was added to the ice sample, and the generation of O_2^- during the reaction process was then determined by observing the change in the fluorescence intensity of DPBF as a function of illumination time.

The absorption spectra of ANT and FA were measured using a UV-visible spectrophotometer (Cary 5000, Agilent, USA) with a detection range of 200-800 nm.

The intermediate products produced by ANT in photochemical reactions were determined using a GC-MS (8890-5977B, Agilent, USA) using helium as the carrier gas, the flow rate was 1.1 mL/min. The mass spectrometry was performed in the electron collision ionization mode, and the electron energy was set at 70 eV. The column temperature was initial maintained at 100 °C for 2 min, then raised to 310 °C at a rate of 15 °C/min and held for 25 min. The temperatures of the injection port, ionization source and quadrupole mass spectrometer were set to 280, 230, 150 °C, respectively.

A nanosecond laser flash photolysis spectrometer (LF900, Edinburgh, UK) was utilized to conduct laser flash photolysis (LFP) experiments. A Nd: YAG pulse laser (355 nm) with a pulse duration of 6 ns as the excitation light source. These experiments were performed in a 1 cm quartz cell.

Raman spectroscopy and Raman microscope images of water ice, saline ice, and FA saline ice were measured utilized Raman imaging spectrometer (DRCi, Thermo fisher scientific, USA). The experimental conditions entailed the following parameters: Raman laser frequency was 18788.2617, exposure time was 0.50 s, Laser was 532 nm, laser power level was set at 8.0 maw, spectrograph aperture used a 50 µm pinhole. The results of the tests are depicted in Fig S3 and S4.

Abbreviations:

Full form	Abbreviation
polycyclic aromatic hydrocarbon	PAHs
chlorinated polycyclic aromatic hydrocarbons	ClPAHs
anthracene	ANT
singlet state ANT	¹ ANT*
triplet state ANT	³ ANT*
hydroxyl radical	·OH
chloride ions	Cl ⁻
chlorine radicals	·Cl
aryl hydrocarbon receptor	AhR
xenon	Xe
dissolved organic matter	DOM
sodium chloride	NaCl
coumarin	COU
singlet oxygen	¹ O ₂
superoxide radical	O ₂ ^{-·}
furfuryl alcohol	FFA
2,2,6,6-tetramethylpiperidine-1-oxy radical	TEMPOL
2,4,6-trimethylphenol	TMP
3,5-dimethyl-1 H-pyrazole	DMPZ
sodium thiocyanate	NaSCN
1,4-diazabicyclo[2.2.2]octane	DABCO
1,3-diphenylisobenzofuran	DPBF
ANT cationic radicals	ANT ⁺⁺
reactive oxygen radical	ROS
the triplet oxygen	³ O ₂
highest occupied molecular orbital	HOMO
lowest unoccupied molecular orbital	LUMO
frontier electron density	FED
high-performance liquid chromatography	HPLC
gas chromatography-mass spectrometry	GC-MS
selected ion monitoring	SIM
mass-to-charge ratios	m/z
fluorescence	FL
electron paramagnetic resonance	EPR

Table S1. The photodegradation rate constant (k) of ANT in saline ice at different NaCl concentrations.

NaCl concentration (mol/L)	k (min ⁻¹)	R ²
0	$(1.63 \pm 0.15) \times 10^{-2}$	0.9772
0.1	$(1.16 \pm 0.03) \times 10^{-2}$	0.9952
0.2	$(1.74 \pm 0.11) \times 10^{-2}$	0.9767
0.3	$(1.95 \pm 0.12) \times 10^{-2}$	0.9704
0.4	$(2.13 \pm 0.15) \times 10^{-2}$	0.9664
0.5	$(2.73 \pm 0.15) \times 10^{-2}$	0.9830

Table S2. Photodegradation rate of ANT and production of ClANTs under different exposure times.

exposure times (min)	C _t /C ₀ of ANT	production of ClANTs (μg/L)		
		2-ClANT	9-ClANT	9,10-Cl ₂ ANT
20	(64.32 ± 1.98)%	0.39 ± 0.011	0.32 ± 0.008	0.11 ± 0.006
40	(30.05 ± 3.92)%	0.41 ± 0.017	0.37 ± 0.011	0.21 ± 0.008
60	(23.24 ± 1.94)%	0.49 ± 0.008	0.40 ± 0.009	0.18 ± 0.013
90	(19.96 ± 1.51)%	0.54 ± 0.016	0.39 ± 0.016	0.27 ± 0.011
120	(15.08 ± 3.47)%	0.68 ± 0.020	0.44 ± 0.015	0.32 ± 0.009
240	(7.08 ± 0.83)%	0.44 ± 0.010	0.36 ± 0.012	0.27 ± 0.008

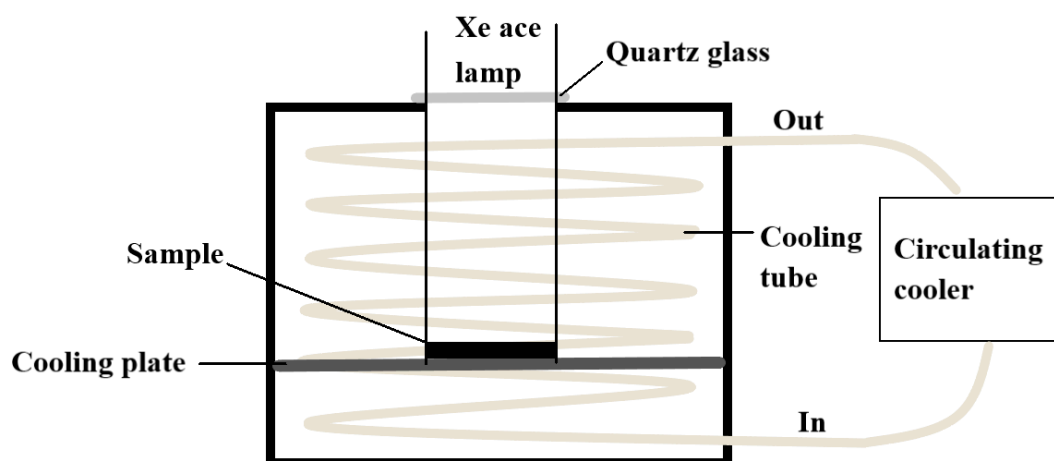


Figure S1 Schematic diagram of a homemade temperature-adjustable reaction chamber.

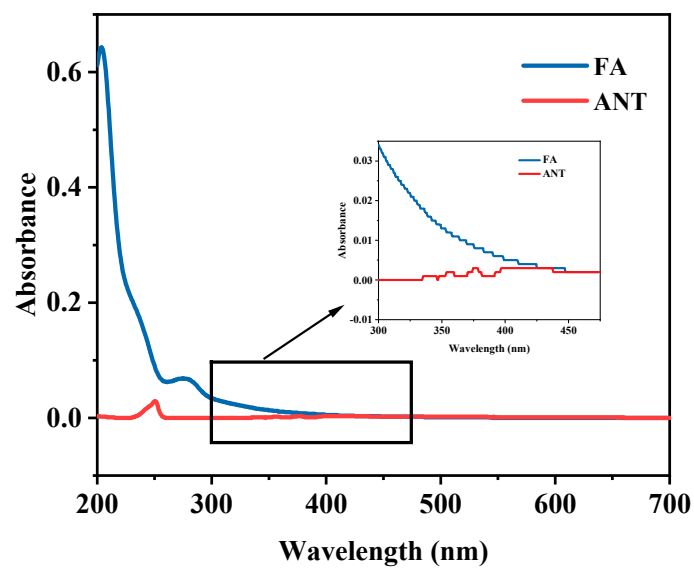


Figure S2. UV-Vis absorption spectra of ANT and FA. Reaction condition: $[ANT] = 0.5$ mg/L, $[FA] = 10$ mg/L.

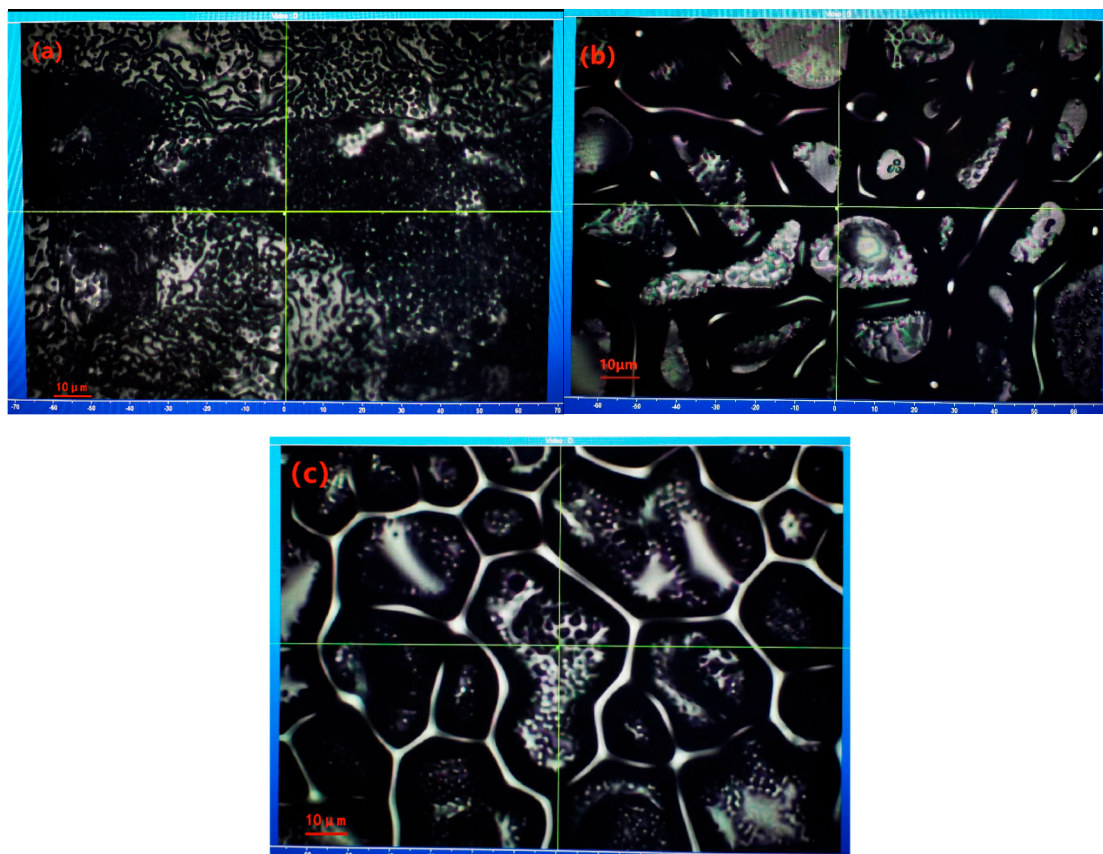


Figure S3. Raman micrographs of ANT in (a) water ice, (b) saline ice, and (c) FA saline ice. Reaction condition: $[ANT] = 0.5$ mg/L, $[NaCl] = 0.5$ mol/L, $[FA] = 10$ mg/L.

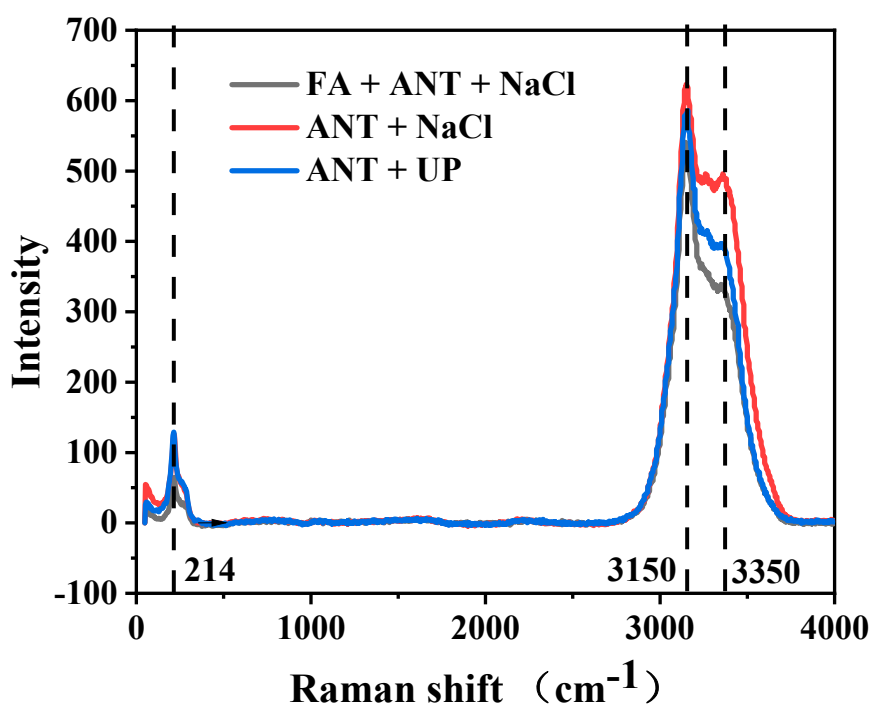


Figure S4. Raman spectra of ANT in water ice (blue line), saline ice (red line), and FA saline ice (blank line). Reaction condition: $[\text{ANT}] = 0.5 \text{ mg/L}$, $[\text{NaCl}] = 0.5 \text{ mol/L}$, $[\text{FA}] = 10 \text{ mg/L}$.

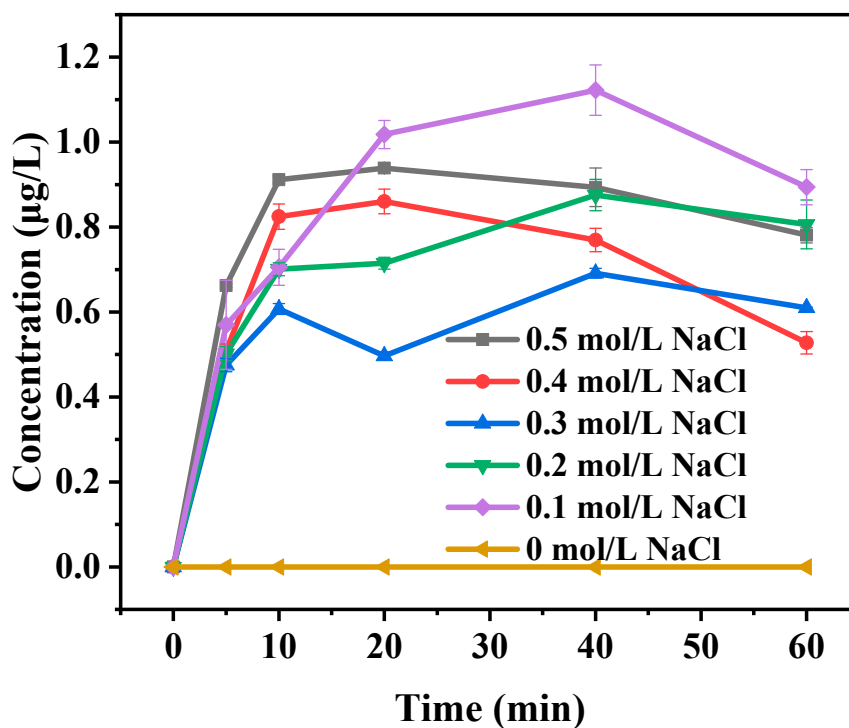


Figure S5. The formation of total CIANTs at varying concentrations of NaCl after illumination. Reaction condition: $[\text{ANT}]_{\text{initial}} = 0.5 \text{ mg/L}$, temperature: -15°C .

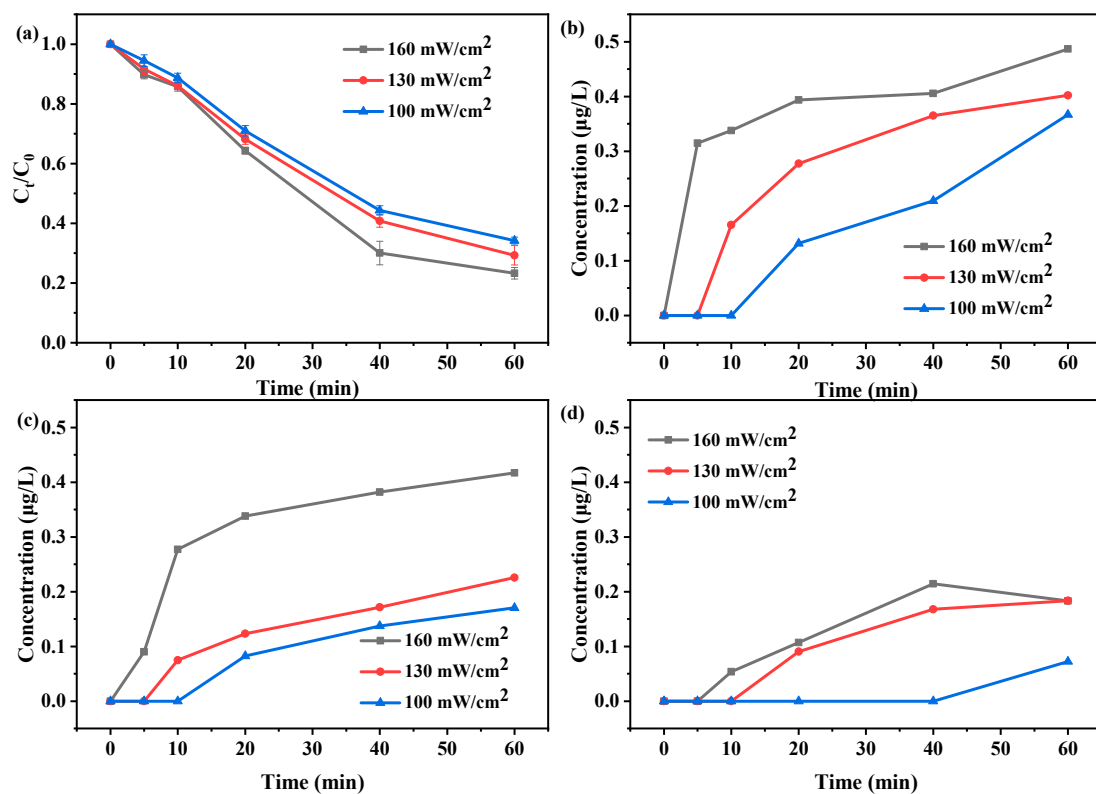


Figure S6. Phototransformation kinetics of (a) ANT and its chlorinated products (b) 2-ClANT, (c) 9-ClANT, and (d) 9, 10-Cl₂ANT at varying light intensities. Reaction condition: [ANT]_{initial} = 0.5 mg/L, pH = 6, temperature: -15 °C.

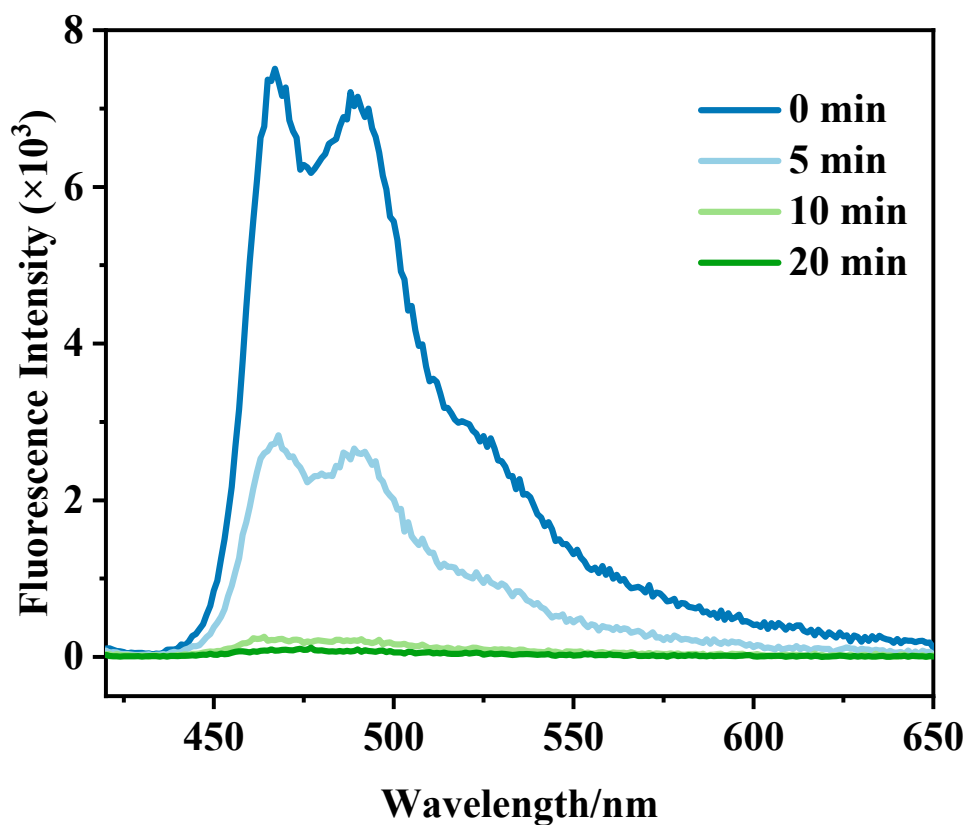


Figure S7. Fluorescence spectra of reactive ice samples with the addition of DPBF as

a function of time of exposure to Xe lamps.

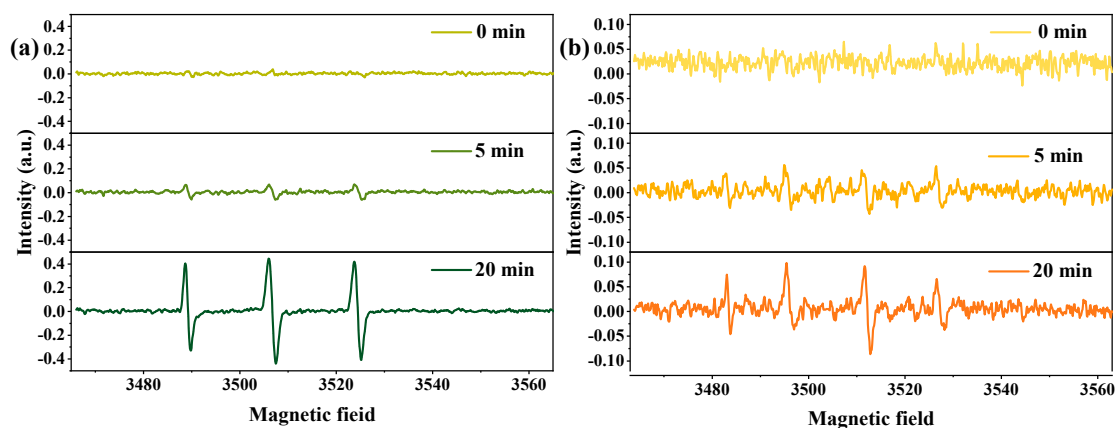


Figure S8. EPR spectra of the adducts formed between the spin-trapping agents (a) TEMP and (b) DMPO in irradiated saline ice samples. Experimental conditions: [DMPO] = 0.15 mol/L, [TEMP] = 0.1 mol/L.

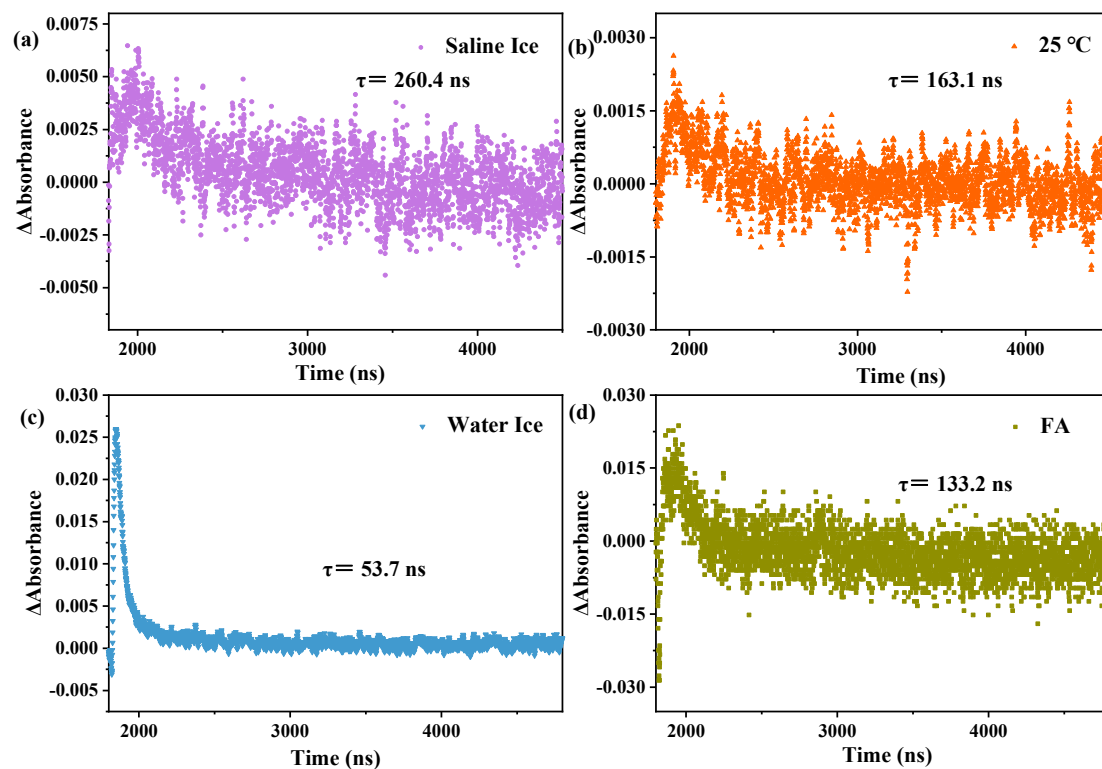


Figure S9. Transient lifetimes of $^3\text{ANT}^*$ in (a) saline ice, (b) normal temperature saline solution, (c) water ice, and (d) FA saline ice.

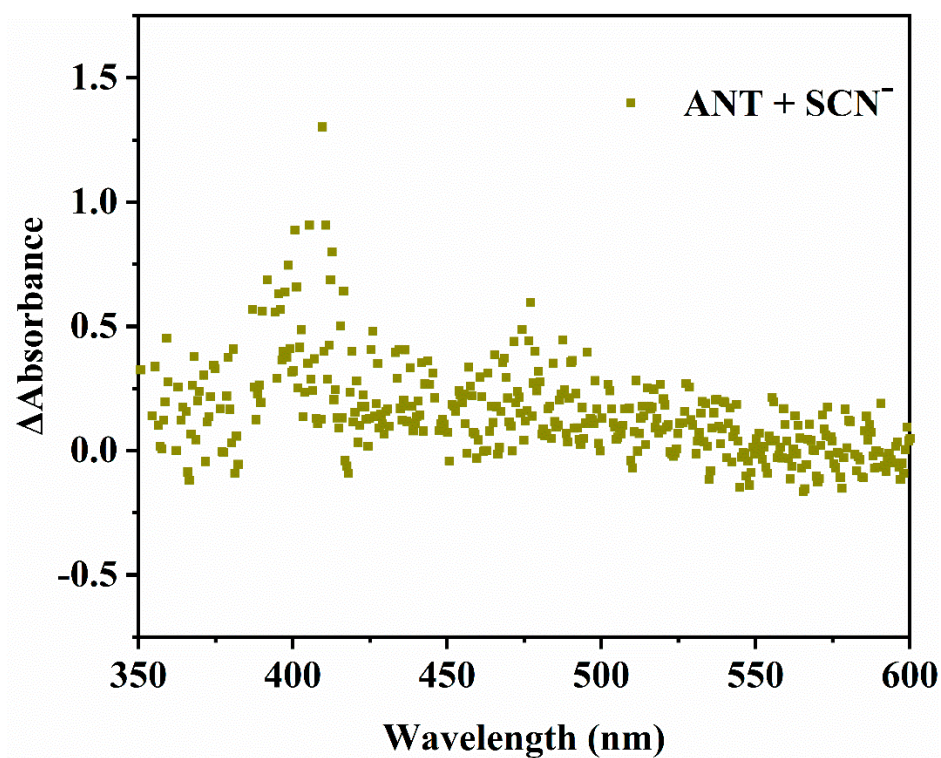


Figure S10. Laser flash photolysis images of ANT saline ice with added NaSCN. The excitation spectrum is 355nm

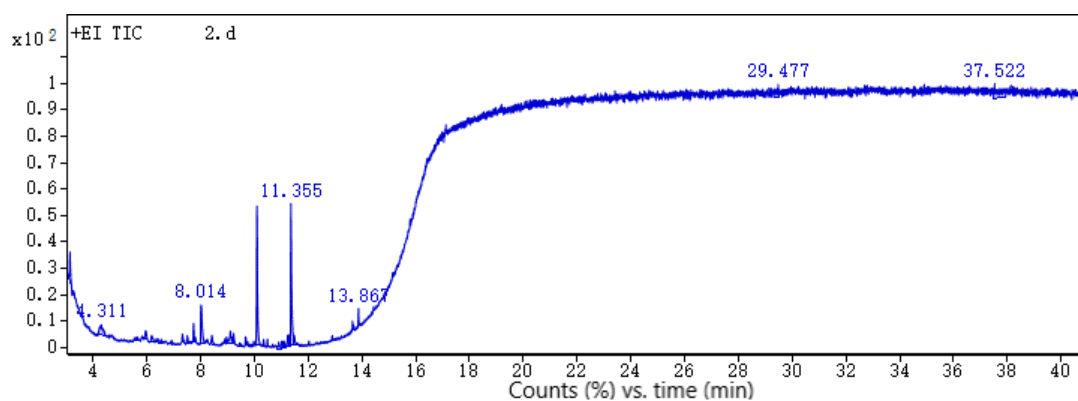
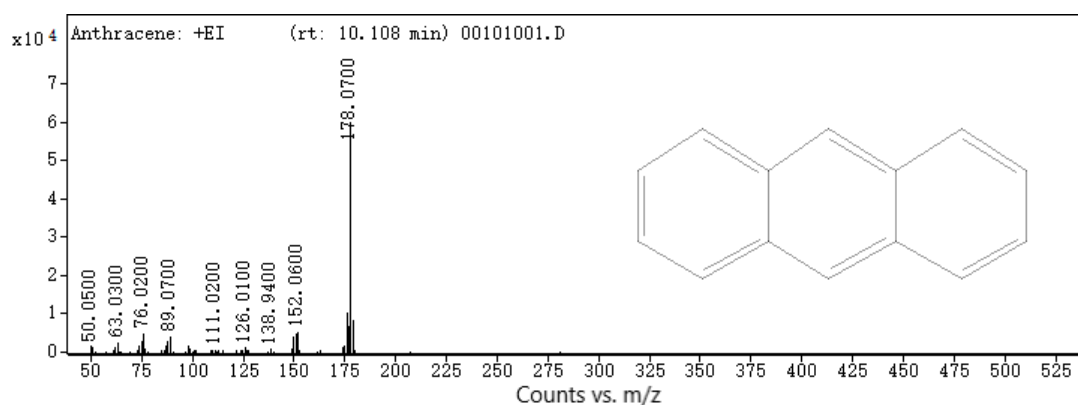
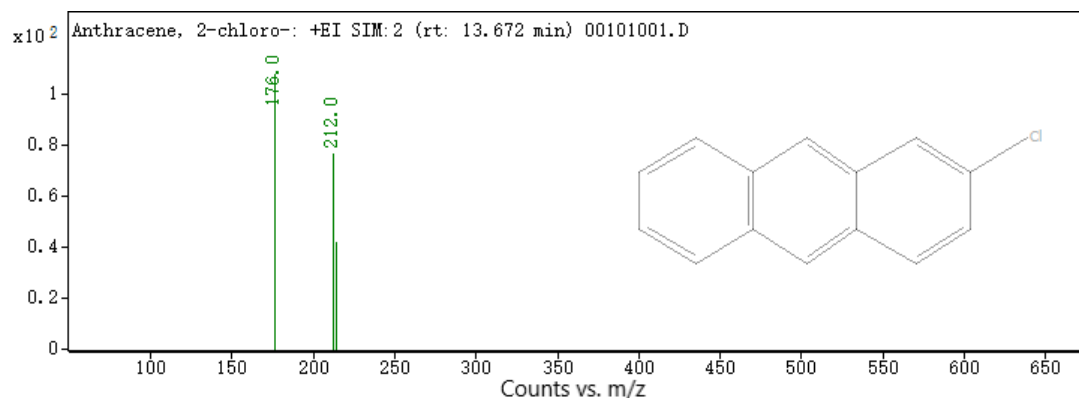
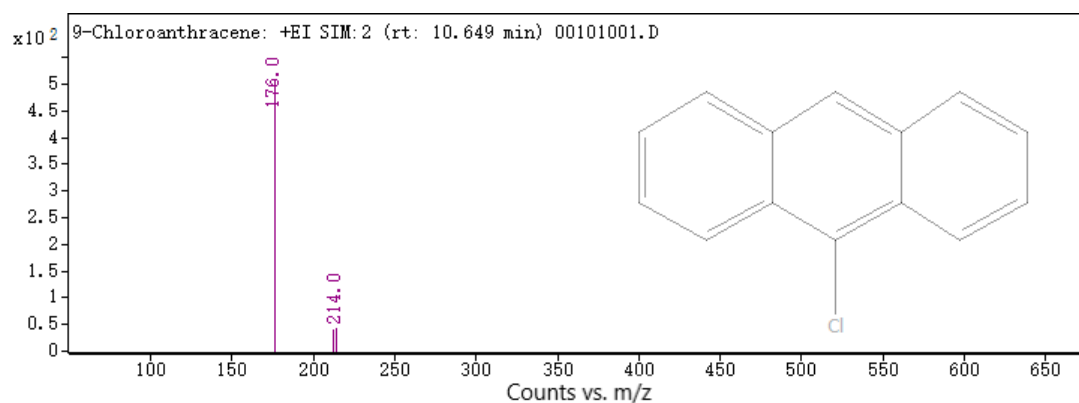
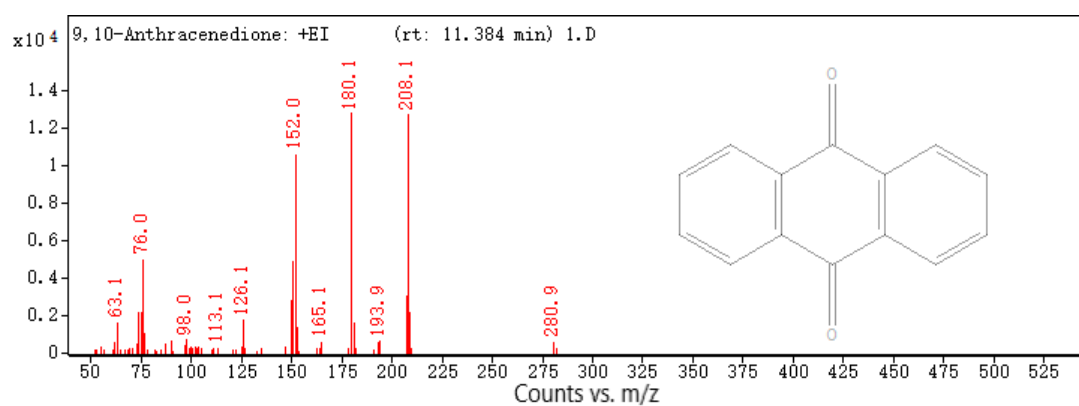
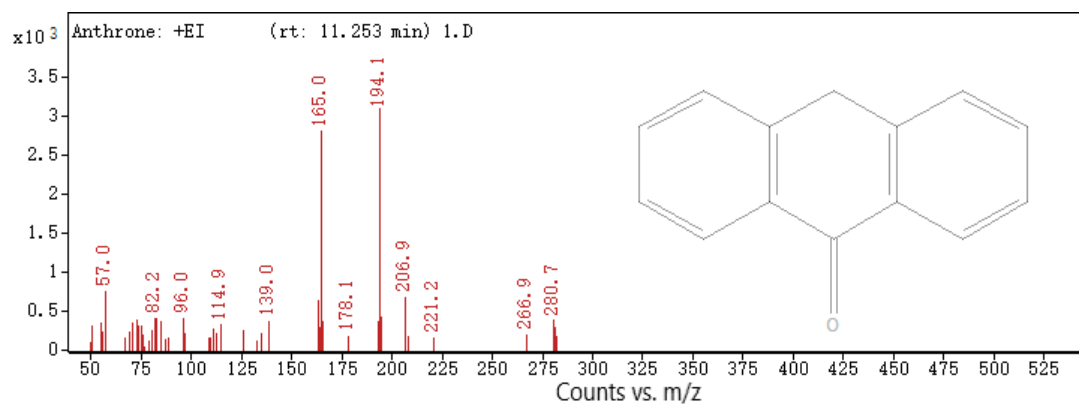


Figure S11. The total ion flow diagram of GC-MS after 30 min of illumination.





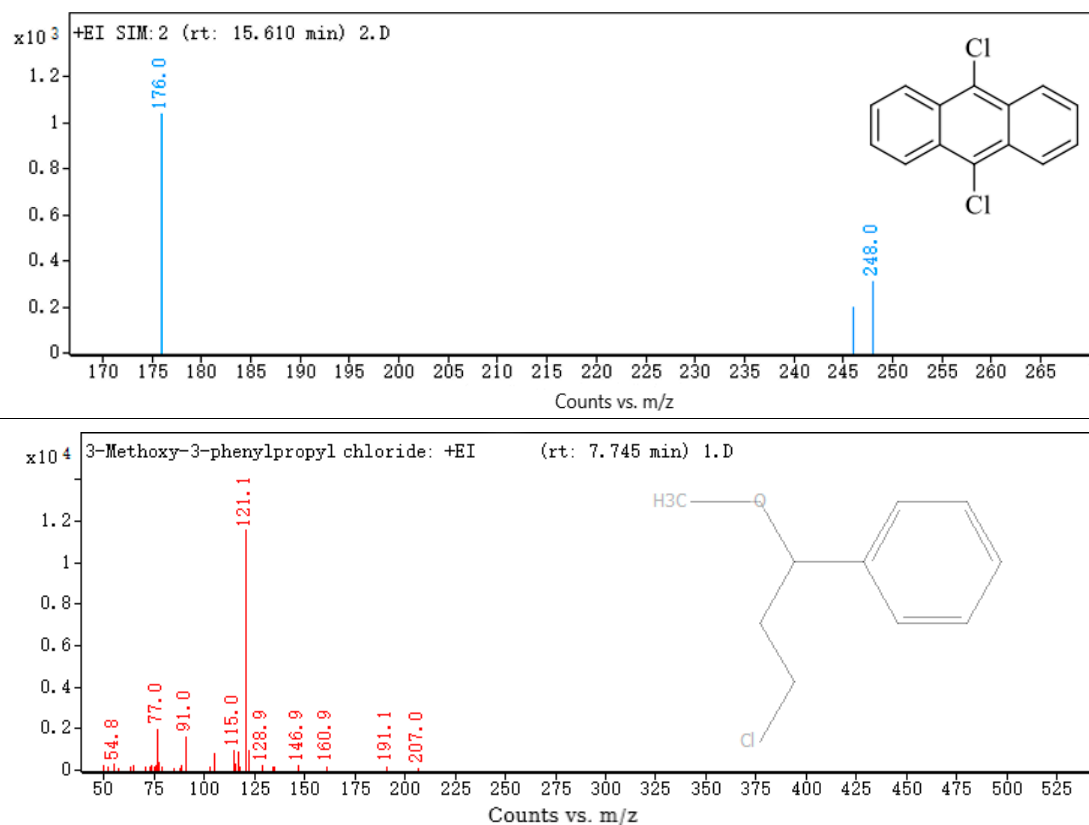


Figure S12. MS spectra of the degradation intermediates of ANT by GC-MS analysis.