

Electronic Supplementary Information (ESI) for
An in-situ, reversible fluorescent paper sensor for
selective detection of ambient CO₂

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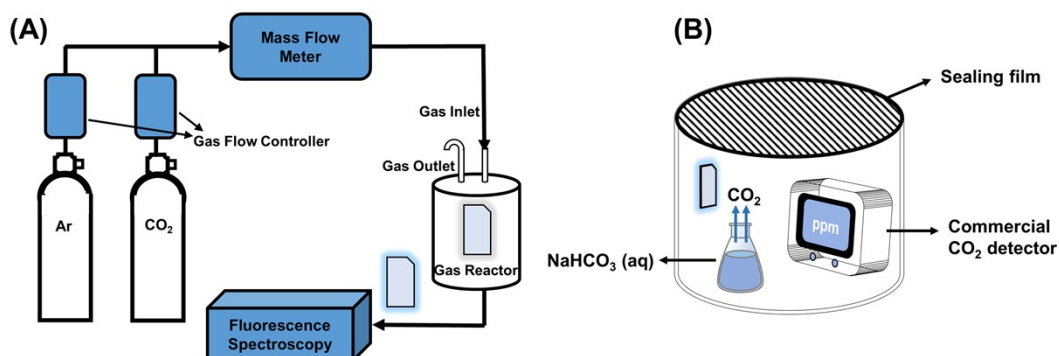
Experimental Section

Materials and instrumentation

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, #6674-22-2, purity 98%) was purchased from Meryer (Shanghai, China). Imidazole (#288-32-4, purity 98%) was purchased from Zancheng sales (Tianjin, China). Hydrobromic acid (#957452, 48.0% wt in H₂O) was purchased from J&K Scientific Co. Ltd. (Beijing, China). Anthracene (#A800676-25g, purity 98%), 1,3,5-trioxane (#T819525-100g, purity 99.5%), triphenylphosphine (#T818895-100g, purity 99%) were purchased from Macklin Inc. (Shanghai, China). High-purity carbon dioxide (#6039543, purity 99.999%) was purchased from AP Baif Gases Industry Co. Ltd. (Beijing, China). High-purity argon (#QT17, purity 99.999%) was purchased from Huanyu Jinghui Jingcheng Gas Technology Co., Ltd. (Beijing, China). Ethyl cellulose ether (#ISO9001, purity 98%) was purchased from Xlya Chemical Technology Co. Ltd. (Shandong, China). Concentrated ammonia solution (NH₃ solution, 25.0-28.0% wt in H₂O) and organic solvents of analytical purity were all purchased from Sinopharm Chemical Reagent Beijing Co. (Beijing, China). All chemicals were used as received without further purification.

All UV-Vis absorption spectra were measured on a JASCO V-550 UV-visible spectrometer (Tokyo, Japan). All IR spectra were measured on a PerkinElmer Spectrum 100 spectrometer (Waltham, United States). All fluorescence spectra were recorded using a JASCO FP-8600 fluorescence spectrometer (Tokyo, Japan). If not stated, the bandwidth of excitation and emission were set as 1 nm and 2 nm, respectively. All NMR spectra were recorded using a JOEL JNM-ECZ400S spectrometer (Tokyo, Japan) operated at 400 MHz. All mass spectra were recorded using an LCMS-IT/TOF mass spectrometer (Shimadzu, Japan). All the fluorescent photographs were taken by a Canon EOS 600D camera under a hand-held 254 UV lamp. The determination of fluorescence lifetime was carried out on an FLS 920 combined steady state and fluorescence lifetime spectrometer (Edinburgh, United Kingdom). The determination of fluorescence quantum yield was carried out on a Hamamatsu Photonics C9920-02 absolute PL quantum yield measurement system (Hamamatsu, Japan) under ambient conditions. The determination of CO₂ concentrations in the simulation experiments was carried out on a commercial C7E Airhug CO₂ detector purchased from YEETC (Beijing, China).

Additional figures and tables



Scheme S1 (A) Schematic experimental setup of gaseous CO₂ detection. CO₂ mixed with carrier gas argon (Ar) passes through the mass flow meter and then flows into the gas reactor. **(B)** Schematic experimental setup of the simulation of high concentrations of indoor CO₂.

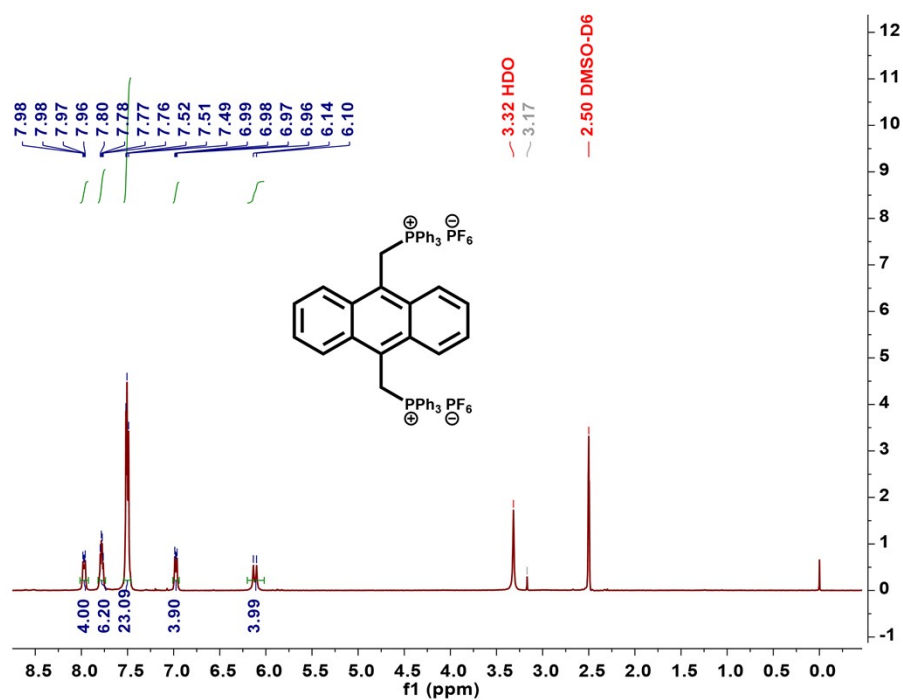


Figure S1 ¹H-NMR spectrum of ANT-PPh₃. (Solvent: DMSO-*d*₆)

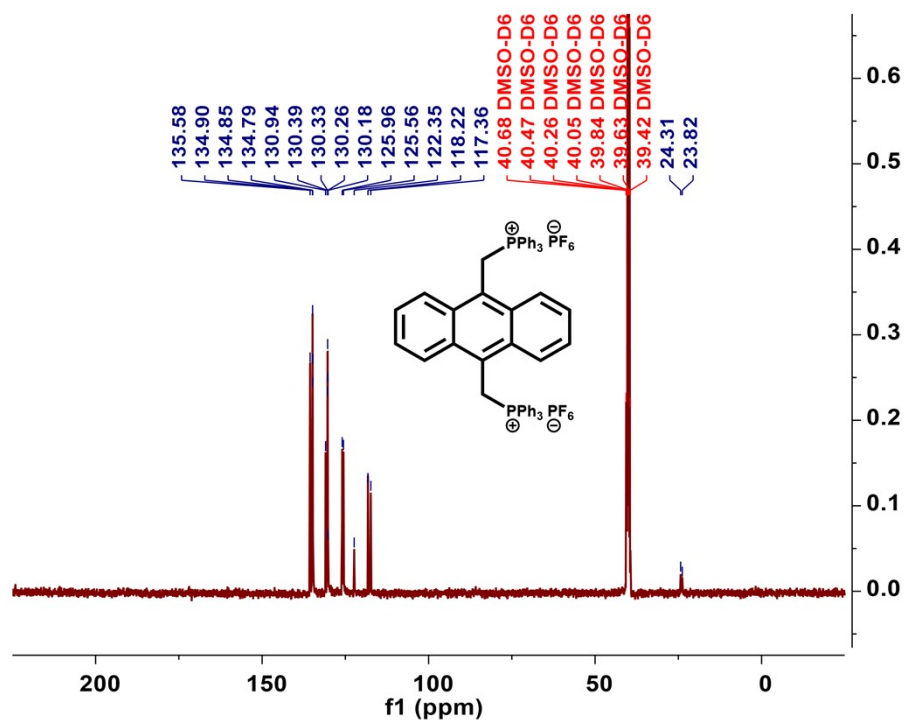


Figure S2 ¹³C-NMR spectrum of ANT-PPh₃. (Solvent: DMSO-*d*₆)

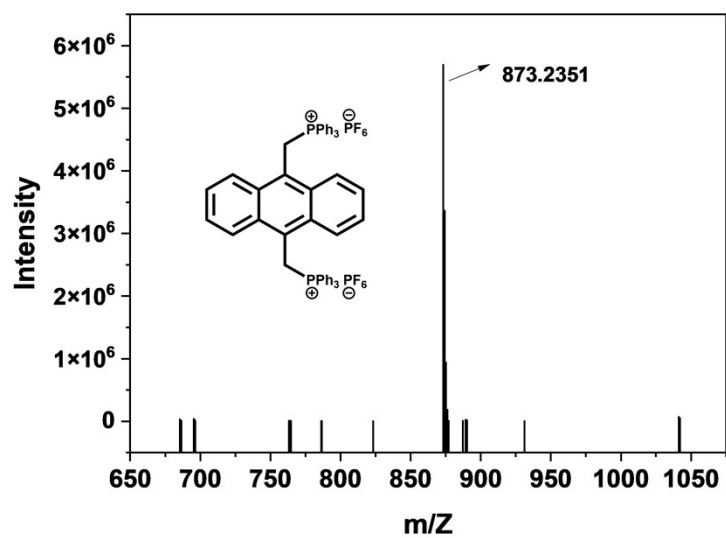


Figure S3 ESI-MS spectrum of ANT-PPh₃. (Positive mode)

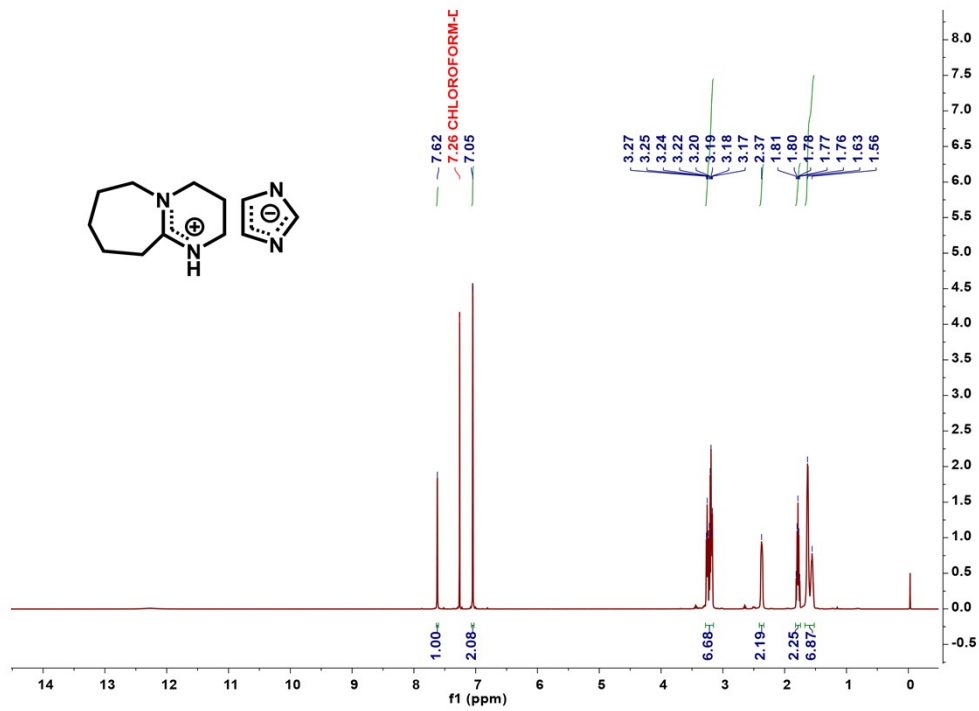


Figure S4 ¹H-NMR spectrum of [DBUH]⁺[Im]⁻. (Solvent: Chloroform-d)

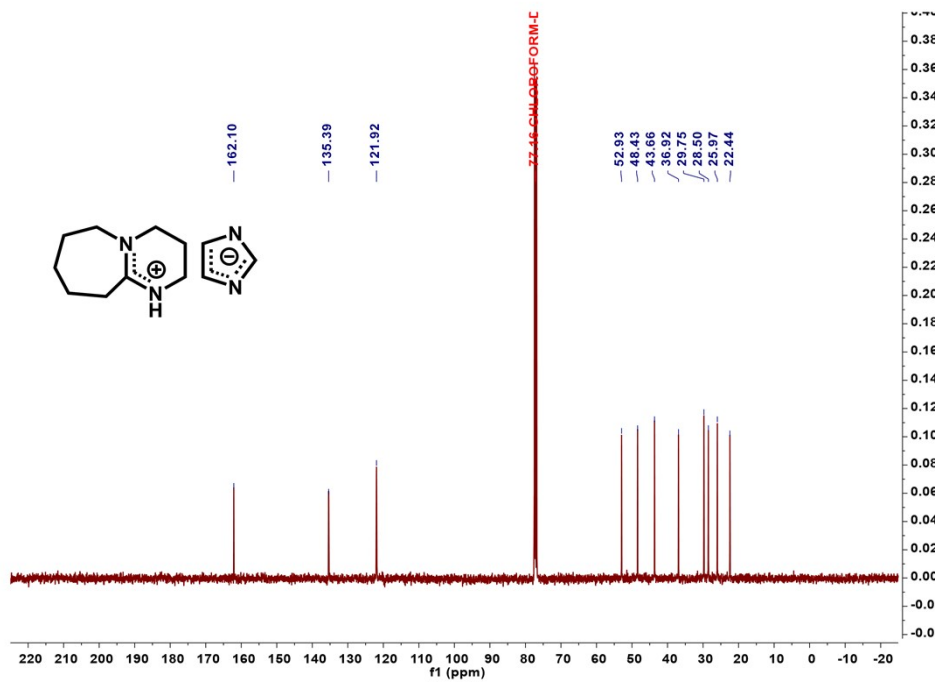


Figure S5 ¹³C-NMR spectrum of [DBUH]⁺[Im]⁻. (Solvent: Chloroform-d)

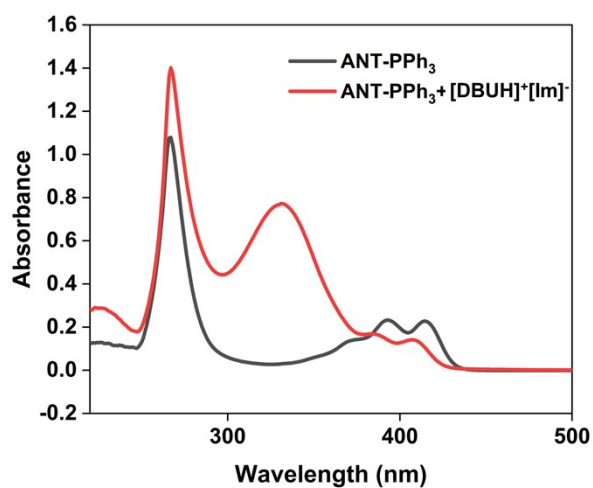


Figure S6 Absorption spectra of ANT-PPh₃ in DMSO with or without [DBUH]⁺[Im]⁻. [ANT-PPh₃]= 20 μM, V_{[DBUH]⁺[Im]⁻} = 10 μL.

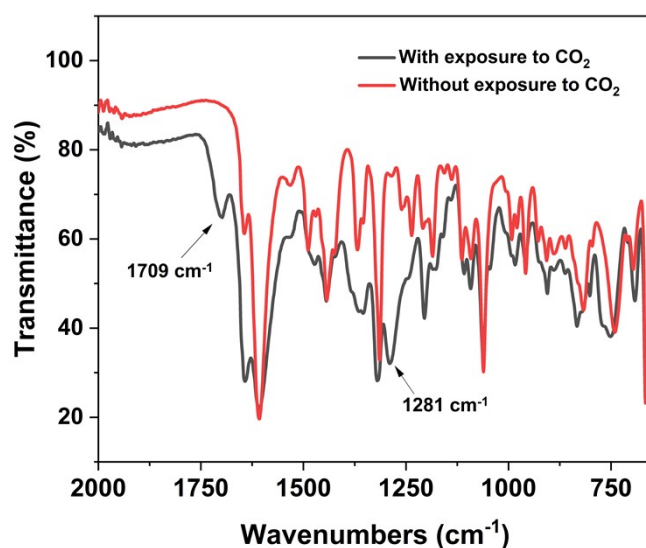


Figure S7 IR spectra of [DBUH]⁺[Im]⁻ before and after reaction of gaseous CO₂.

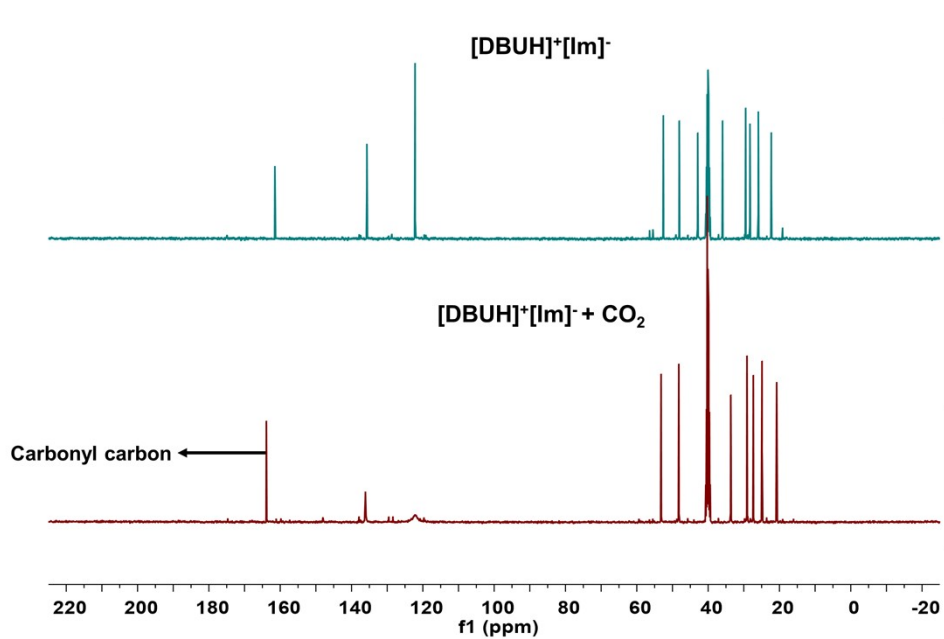


Figure S8 ^{13}C -NMR spectra of $[\text{DBUH}]^+[\text{Im}]^-$ before and after exposure to gaseous CO_2 . (Solvent: $\text{DMSO}-d_6$)

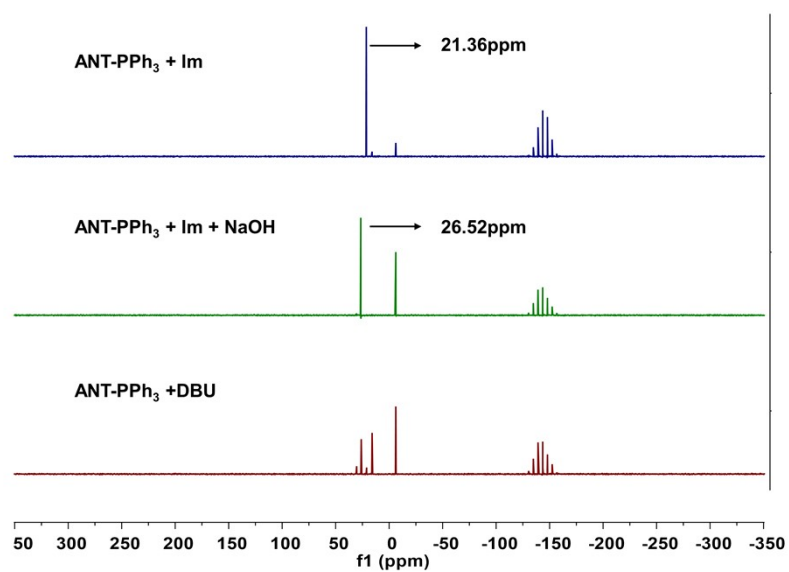


Figure S9 ^{31}P -NMR spectra of ANT-PPh_3 in the presence of excess imidazole, imidazole + NaOH , and DBU .

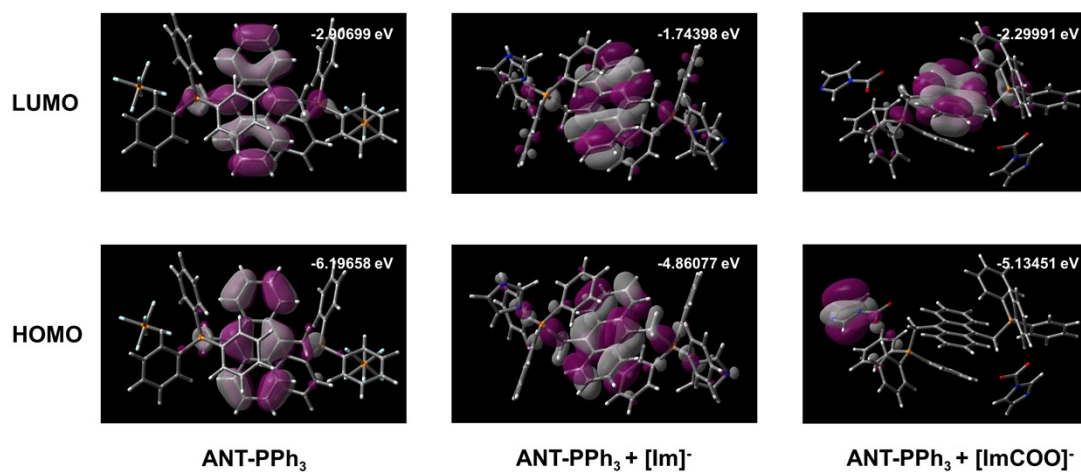


Figure S10 FMOs (Frontier Molecular Orbital) of ANT-PPh₃, ANT-PPh₃ + [Im]⁻ adduct and ANT-PPh₃ + [ImCOO]⁻ adduct using the DFT/B3LYP-d3 method.

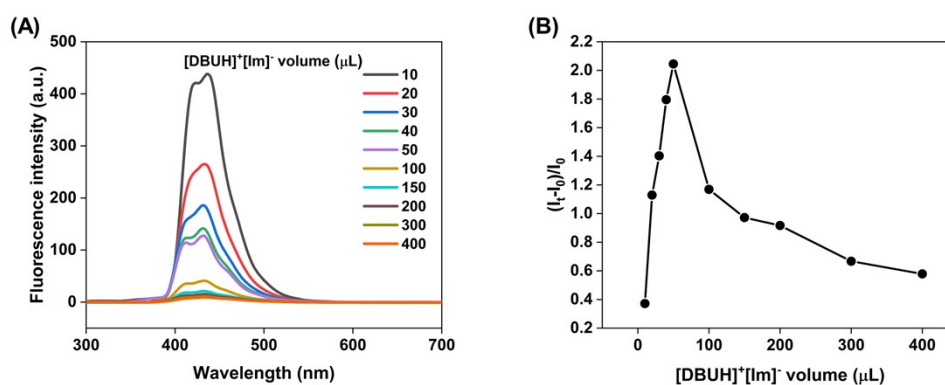


Figure S11 (A) Fluorescence spectra of ANT-PPh₃ with the addition of different amounts of [DBUH]⁺[Im]⁻. **(B)** Fluorescence enhancement ratios ((I_t - I₀) / I₀) of ANT-PPh₃ with different amounts of [DBUH]⁺[Im]⁻ after injection of 5 mL CO₂. [ANT-PPh₃] = 20 μM, in DMSO.

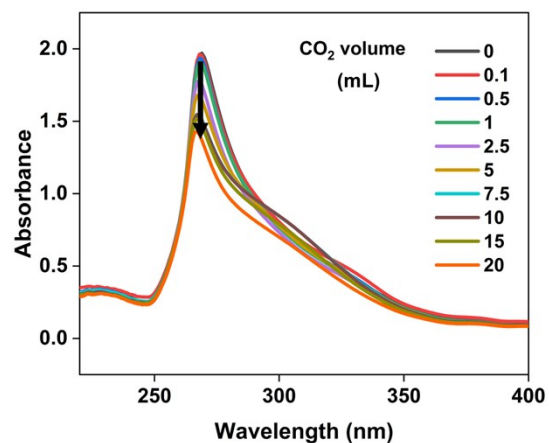


Figure S12 UV-VIS absorption spectra of ANT-PPh₃ + [DBUH]⁺[Im]⁻ in DMSO solution after the injection of different amounts of CO₂. [ANT-PPh₃]= 20 μM, V_{[DBUH]⁺[Im]⁻} = 50 μL.

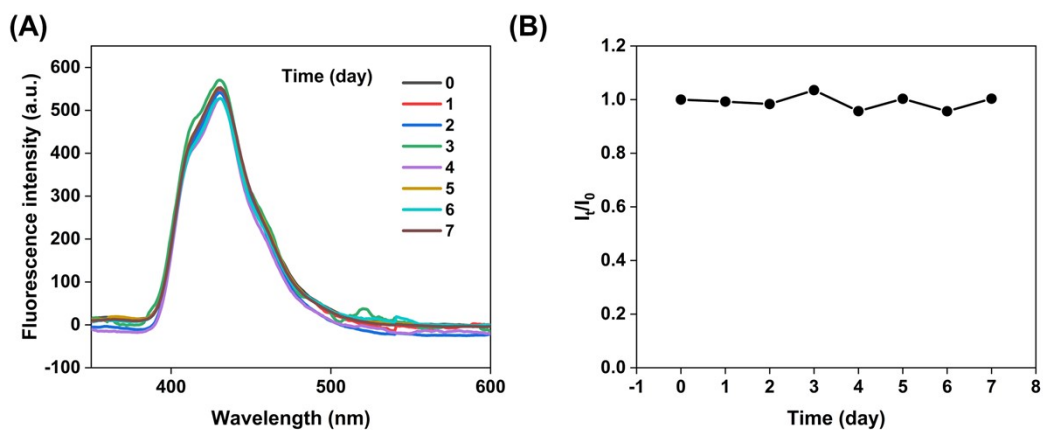


Figure S13 (A) Fluorescence spectra of CO₂ paper sensor in a sealed dish under ordinary room light at different times. **(B)** Fluorescence intensities at 430 nm of CO₂ paper sensor in **(A)**.

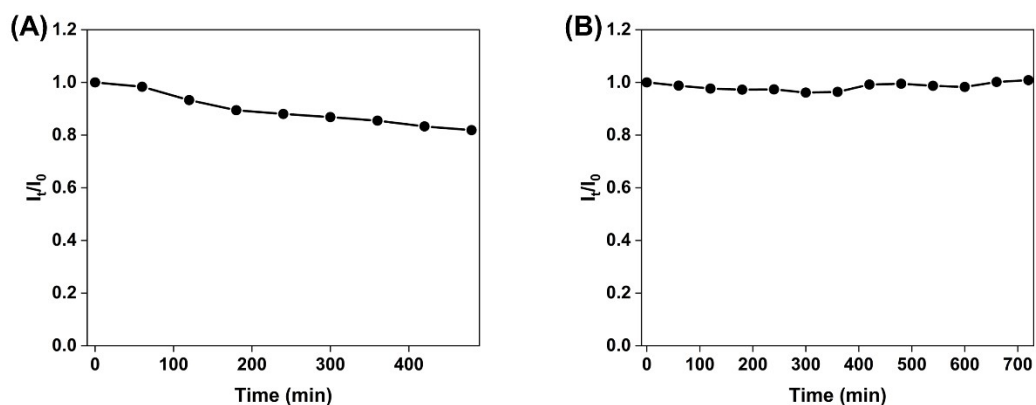


Figure S14 (A) I_t/I_0 at 430 nm of CO_2 paper sensor with exposure to 254 nm UV at different times. (B) I_t/I_0 at 430 nm of CO_2 paper sensor with exposure to white LED at different times.

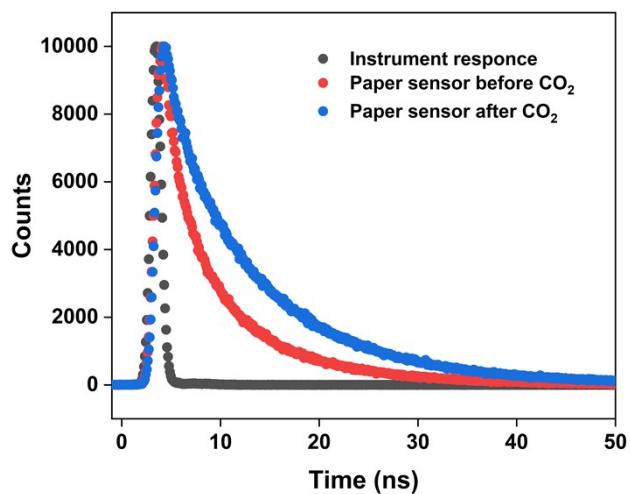


Figure S15 Fluorescence decay curve of CO_2 paper sensor before and after exposure to high purity CO_2 for 1 min.

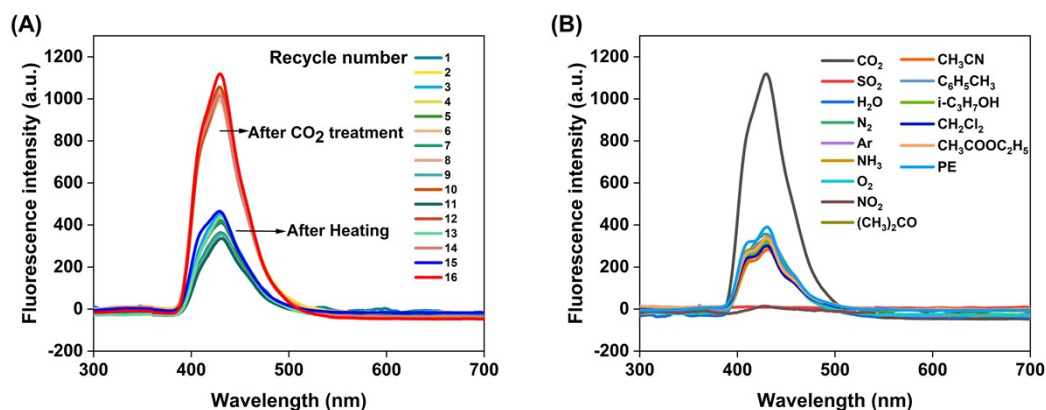


Figure S16 (A) Fluorescence spectra of CO₂ paper sensor after CO₂ treatment and 30 min heating alternatively. **(B)** Fluorescence spectra of CO₂ paper sensor after 15 min exposure to different gases (O₂, N₂, Ar, CO₂: >99 vol %, SO₂, NO₂: 2 vol %) or saturated vapors. ((CH₃)₂CO: acetone; CH₃COOC₂H₅: ethyl acetate; CH₃CN: acetonitrile; C₆H₅CH₃: toluene; PE: petroleum ether; CH₂Cl₂: dichloromethane; i-C₃H₇OH: isopropanol)

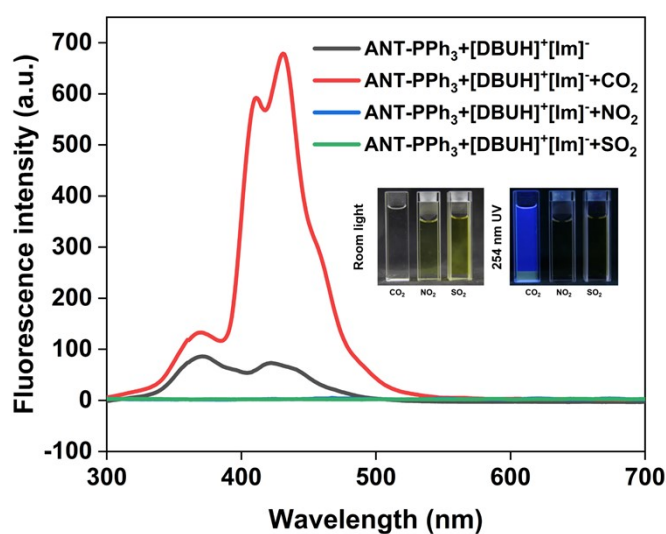


Figure S17 Fluorescence spectra of ANT-PPh₃ + [DBUH]⁺[Im]⁻ after bubbling excessive CO₂, NO₂, and SO₂ in DMSO. [ANT-PPh₃] = 20 μM, V_{[DBUH]⁺[Im]⁻} = 50 μL. Inset: Photographs of the same set of samples. Fluorescent pictures were taken under 254 nm UV light.

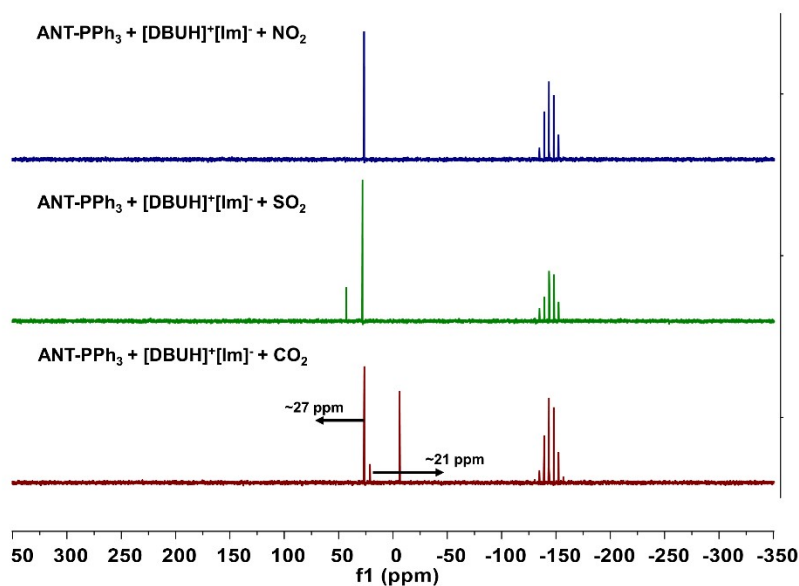


Figure S18 ^{31}P -NMR spectra of ANT-PPh₃ + [DBUH]⁺[Im]⁻ after bubbling excessive NO₂, SO₂ and CO₂ in DMSO-*d*₆.

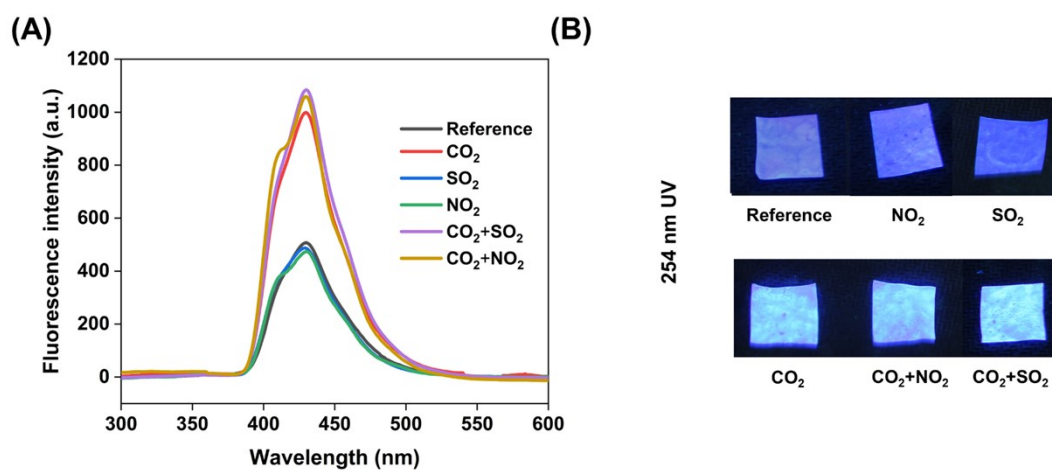


Figure R19 (A) Fluorescence spectra of paper sensor after 3 h exposure to different gases of lower concentrations (SO₂: 200 ppm, NO₂: 200 ppm, CO₂: 5500 ppm). **(B)** Fluorescence pictures of CO₂ paper sensors in **(B)**. Pictures were taken under 254 nm UV.

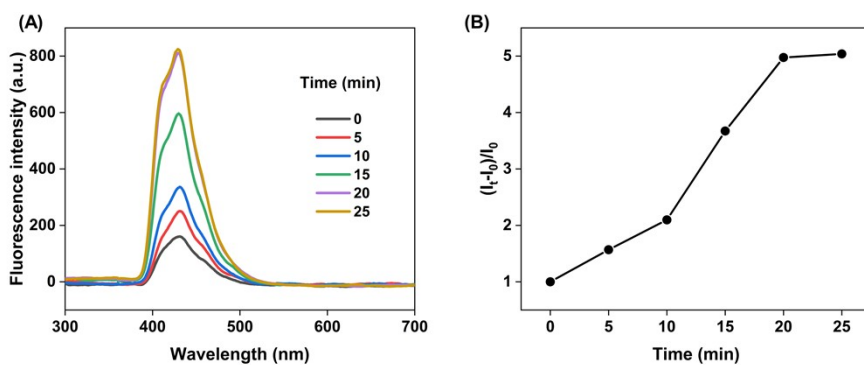


Figure S20 (A) Fluorescence spectra of CO₂ paper sensor in a sealed dish after exposure to human breath at different times. **(B)** Fluorescence enhancement ratios $((I_t - I_0)/I_0)$ at 430 nm of CO₂ paper sensor in **(A)**.

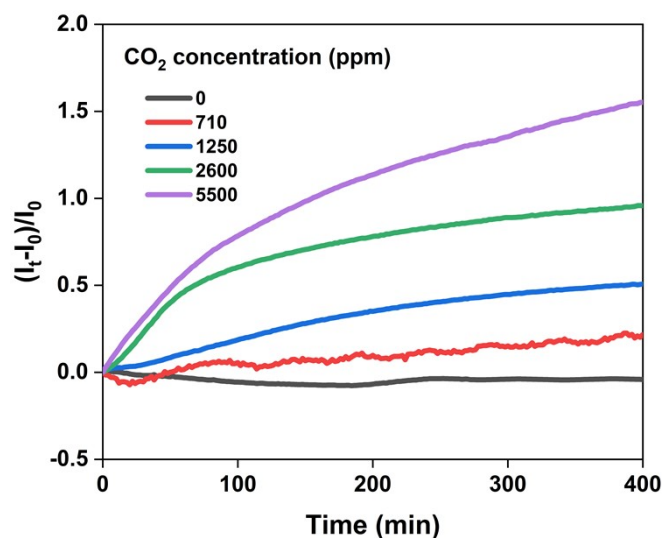


Figure S21 Fluorescence enhancement ratios of CO₂ paper sensor after exposure to different concentrations of ambient CO₂. The CO₂ concentrations were determined by a commercial CO₂ detector.

Sensor type	Selectivity	Sensitivity	Reversibility	Mechanism	Reference
Paper	Affected by acidic gases	5.7 ppm	Reusable after N ₂ treatment	Ratiometric, pH response	1
Organogels	Affected by acidic gases	4.5 ppm	Non-reusable	Quenching, PET	2
Solution	Not mentioned	Not mentioned	Reusable after N ₂ /heat treatment	Ratiometric, polarity response	3
Solution	Affected by acidic vapor	Not mentioned	Non-reusable	Enhancement, AIE	4
Solution	Not affected by common gases	0.031 vol %	Reusable after NaOH treatment	Quenching, AIE	5
Solution	Not mentioned	Not mentioned	Non-reusable	Enhancement, AIE	6
Solution	Not mentioned	Not mentioned	Non-reusable	Quenching, ICT	7
Paper	Not affected by common gases and acidic gases	0.183 vol %	Reusable after heat treatment	Enhancement, PET	This work

Table S1 Comparison of fluorescence-based optical sensors for gaseous CO₂.

Category	τ (ns)
ANT-PPh ₃ ^a	7.8
ANT-PPh ₃ + [DBUH] ⁺ [Im] ⁻ ^b	4.0
ANT-PPh ₃ + [DBUH] ⁺ [Im] ⁻ +CO ₂ ^c	8.5
Paper sensor without CO ₂	6.9
Paper sensor with CO ₂	10.0

a: [ANT-PPh₃] = 20 μ M, in DMSO.

b: [ANT-PPh₃] = 20 μ M, V_{[DBUH]⁺[Im]⁻} = 50 μ L, in DMSO.

c: [ANT-PPh₃] = 20 μ M, V_{[DBUH]⁺[Im]⁻} = 50 μ L, CO₂ bubbling for 1 min, in DMSO.

Table S2 Fluorescence lifetimes of ANT-PPh₃ in different chemical environments.

References

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