Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Discrimination of aniline and benzaldehyde assisted with Fisher's base

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1. Supplemental Experimental Procedures

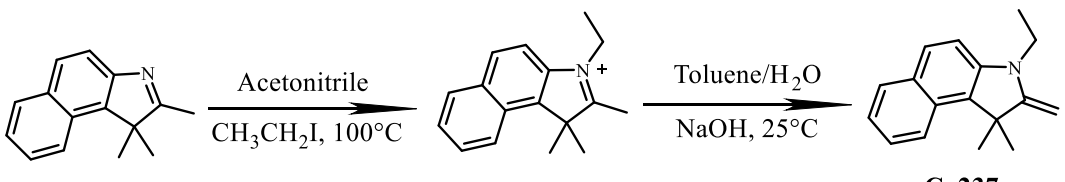
1.1. General methods and materials

All commercially available reagents were purchased from Sigma-Aldrich and used as received unless otherwise stated. Anhydrous solvents were purchased from Aladdin reagents and used without further purification.

Fluorescence spectra were obtained on a Hitachi F-7000 fluorescence spectrometer. UV-visible absorption spectra were acquired on a Shimadzu UV-3600 plus spectrometer. NMR spectra were acquired on a Bruker AVANCE III HD 500 (^{1}HNMR 500 MHz, ^{13}CNMR 126 MHz) spectrometer with TMS as the internal standard. High Resolution Mass spectrometry (HRMS) spectra were determined on Agilent 6540 quadrupole-time-of-flight (Q-TOF). High-performance liquid chromatography (HPLC) was performed on an Agilent 1260 Infinity II with UV-detector. Preparative Agilent 1260 Infinity II HPLC was used to purify compounds for NMR analysis. The light intensity was determined by a portable irradiance meter (DLY-1802, DELIXI). Lauda E100 circulating water pump was utilized to maintain constant temperature. The pH measurements were performed using a Mettler Toledo S210 pH meter.

1.2. The general synthesis procedure of Cy237

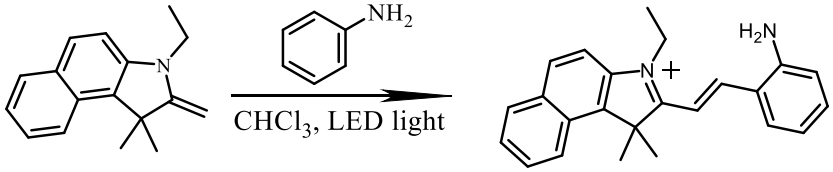
1,1,2-Trimethylbenz[e]indole (4.00 g, 19.13 mmol) was dissolved in dry acetonitrile, then CH_3I (3.10 mL, 38.76 mmol) was added, the solution was stirred at 100 °C for 12 h[1]. After the reaction was completed, the crude product was re-dissolved in dichloromethane and precipitated in diethyl ether, a grey powder Cy238 (6.45 g, 92.33%) was obtained. Cy238 (3.00 g, 8.22 mmol) and NaOH (2.00 g, 50 mmol) was dissolved in Toluene/H_2O (1:1, v/v, 40 mL), and stirred at room temperature for 30 min. The organic phase was washed with brine thrice and then was separated and evaporated under vacuum. The orange oil Cy237 (2.86 g, 95.79%) was yielded.



1,1,2-Trimethylbenz[e]indole **Cy238** **Cy237**

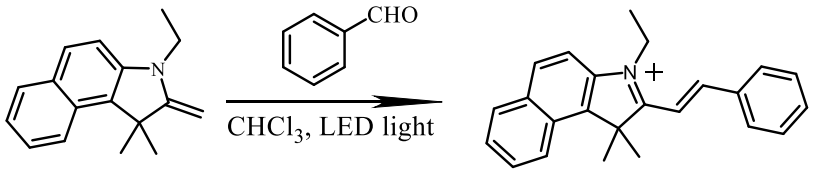
Cy237: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93, 7.72, 7.65, 7.36, 7.15, 6.94, 3.92, 3.62, 1.64, 1.19 (Figure S5). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.96, 143.12, 130.16, 129.72, 129.09, 128.88, 128.32, 126.92, 126.39, 121.53, 121.42, 108.72, 72.91, 46.23, 36.77, 29.85, 11.12 (Figure S6). ESI-MS (CH_3OH): Calcd. for Cy237 [Cy237+H^+] 238.1596, found 238.1613 (Figure S7).

1.3. LED light prompted synthesis of Cy341-O, Cy326 and Cy485



Cy237 **Cy341-O**

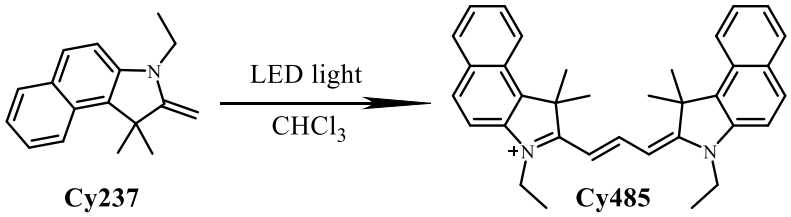
Cy341-O: Cy237 (1.00 g, 4.23 mmol) and aniline (5.00 mL, 5.38 mmol) was dissolved in chloroform (30 mL) and irradiated under 405 nm LED light (100 mW/cm^2) irradiation for 30 seconds. The solution was changed from yellow to deep green rapidly. Then the crude product was purified by basic alumina column chromatography (CH_2Cl_2/CH_3OH, v/v, 10:1), affording a dark green solid of Cy341-O 1.06 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67, 8.07, 7.91, 7.57, 7.41, 7.29, 7.20, 6.70, 4.10, 2.89, 1.96, 1.43 (Figure S8). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.18, 139.50, 131.78, 131.29, 130.53, 130.08, 129.61, 128.29, 127.61, 125.61, 124.39, 121.62, 119.20, 109.95, 93.07, 50.06, 39.01, 28.76, 12.14 (Figure S9). ESI-MS (CH_3OH): Calcd. for Cy341-O [Cy341-O] 341.2012, found 341.2072 (Figure S10).



Cy237 **Cy326**

Cy326: Cy237 (1.00 g, 4.22 mmol) and benzaldehyde (0.36 mL, 3.53 mmol) was dissolved in chloroform (30 mL) and irradiated under 405 nm LED light (100 mW/cm^2) irradiation for 30 seconds. The solution was changed from yellow to deep yellow rapidly. Then the crude product was purified by basic alumina column

chromatography (CH_2Cl_2/CH_3OH, v/v, 10:1), affording a dark yellow solid of Cy326 (1.20 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 16.3 Hz, 1H), 8.29 – 8.19 (m, 3H), 8.14 (d, *J* = 8.9 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.77 (dd, *J* = 15.9, 7.8 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.50 (m, 3H), 5.12 (q, *J* = 7.4 Hz, 2H), 2.14 (s, 6H), 1.69 (t, *J* = 7.4 Hz, 3H) (Figure S11). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.22, 153.82, 139.01, 137.59, 133.90, 133.87, 133.76, 131.99, 131.16, 130.35, 129.55, 128.77, 127.77, 127.30, 122.90, 112.40, 111.90, 44.81, 26.75, 14.62 (Figure S12). ESI-MS (CH_3OH): Calcd. for Cy326 [Cy326] 326.1903, found 326.1913 (Figure S13).



Cy237 **Cy485**

Cy485: Cy237 was dissolved in chloroform (30 mL) and irradiated under 405 nm LED light (100 mW/cm^2) for 30 seconds. The solution was changed from yellow to red immediately and then deep red along with irradiation time. Finally, the solution was purified by basic alumina column chromatography (CH_2Cl_2/CH_3OH, v/v, 40:1), affording a dark red solid Cy485 (0.47 g, 71.0%). ^{1}H NMR (500 MHz, DMSO) δ 8.59, 8.30, 8.15, 8.10, 7.82, 7.70, 7.54, 6.64, 4.33, 2.02, 1.40 (Figure S14). ^{13}C NMR (126 MHz, DMSO) δ 175.13, 149.02, 139.66, 133.61, 131.99, 131.02, 130.43, 128.34, 128.04, 125.48, 122.63, 111.93, 102.45, 55.37, 51.02, 27.50, 13.19 (Figure S15). ESI-MS (CH_3OH): Calcd. for Cy485 [Cy485] 485.2951, found 485.3007 (Figure S16).

1.4. Instrumentations and HPLC conditions

Liquid chromatography (LC) analysis was performed using an Agilent 1260 Series high-performance LC. This LC apparatus was consisted of a quaternary pump (model G71111A), an autosampler (model G7115A), a thermostatic column compartment (model G7116AA), a diode array detector (DAD) (model G7121A) and a fluorescence detector (model G7121A). Chromatographic separation was achieved on a Hypersil GOLD C18 column (250 × 4.6 mm, Thermo) with a binary gradient elution. Eluent A was 30 % acetonitrile in water, and B was acetonitrile. The elution conditions were as follows: 0-100 % B from 0 to 20 min. The flow rate was constant at 1 mL/min, the column temperature was kept at 30 ℃, and DAD wavelengths were set at 254 nm. The injection volume was 10 μL, and the column was pre-balanced with the mobile phase for 10 min before each analysis.

1.5. Determination of benzaldehyde in almond

10.0 g of finely ground and dried almonds was added in a flask, and added deionized water and ethanol (1:1) 50 mL and 5 mL of trifluoroacetic acid (2 mol/L). The flask was sealed and the solution was hydrolyzed at 90 ℃ for 2 h.[2] After that, the solution was extracted with $CHCl_3$ three times. The organic phase was concentrated until dry to obtain crude benzaldehyde. The crude product was re-dissolved with 1 mL of $CHCl_3$, and titrated with Cy237 (0.98 nmol/mL in chloroform) under 405 nm blue LED light (100 mW/cm^2) irradiation.

2. Supplemental Figures and Tables

Table S1. The yields of Cy485 synthesized from Cy237 under 405 nm LED light

Entry	Solvent	Yield (%)
1	Chloroform	65.1
2	Triethylamine	N.D.
3	Methanol	3.8
4	Pyridine	30.5
5	Aniline	N.D.
6	N,N-Dimethylformamide	31.7
7	Acetonitrile	28.3
8	Dimethyl sulfoxide	34.2
9	Acetone	20.5
10	Chloroform + Triethylamine	N.D.
11	Chloroform + Methanol	34.7
12	Chloroform + Methanol + $CuCl_2$	N.D.
13	Chloroform + Propylamine	N.D.
14	Chloroform + Aniline	N.D.
15	Chloroform + TEMPO	61.4
16	Chloroform + DMPO	N.D.

The concentration of Cy237 was 0.1 M and the concentration of free radical trapping agent was 0.2 M. The ratio of the mixed solvents was 1: 9 (other solvent: chloroform, v/v). 405 nm LED light (100 mW/cm^2) irradiation time was 30 s. N.D.: no detection. The yields was determined by HPLC analysis.

Table S2. Color changes of Cy237 and different equivalents of aniline in chloroform under 405 nm LED light

Entry	n_{Cy237} / $n_{aniline}$	Color
1	0.1 - 1	
2	1 - 2	
3	2 - 10	

The concentration of aniline was 0.1 M. The 405 nm LED light (100 mW/cm^2) irradiation time was 30 s.

Table S3. Color changes of Cy237 with benzaldehyde in a mixed solvent of chloroform under 405 nm LED light irradiation

Entry	Solvent	Color
1	Chloroform	
2	Chloroform (50%) + Triethylamine (50%)	
3	Chloroform (50%) + Methanol (50%)	
4	Chloroform (50%) + Methylbenzene (50%)	
5	Chloroform (50%) + Pyridine (50%)	
6	Chloroform (50%) + DMSO (50%)	
7	Chloroform (50%) + DMF (50%)	
8	Chloroform (50%) + Acetone (50%)	
9	Chloroform (50%) + Acetonitrile (50%)	
10	Chloroform (20%) + Ethanol (40%) + H_2O (40%)	

The concentration of Cy237 and benzaldehyde was 0.1 M. The LED light (100 mW/cm^2) irradiation time was 30 s.

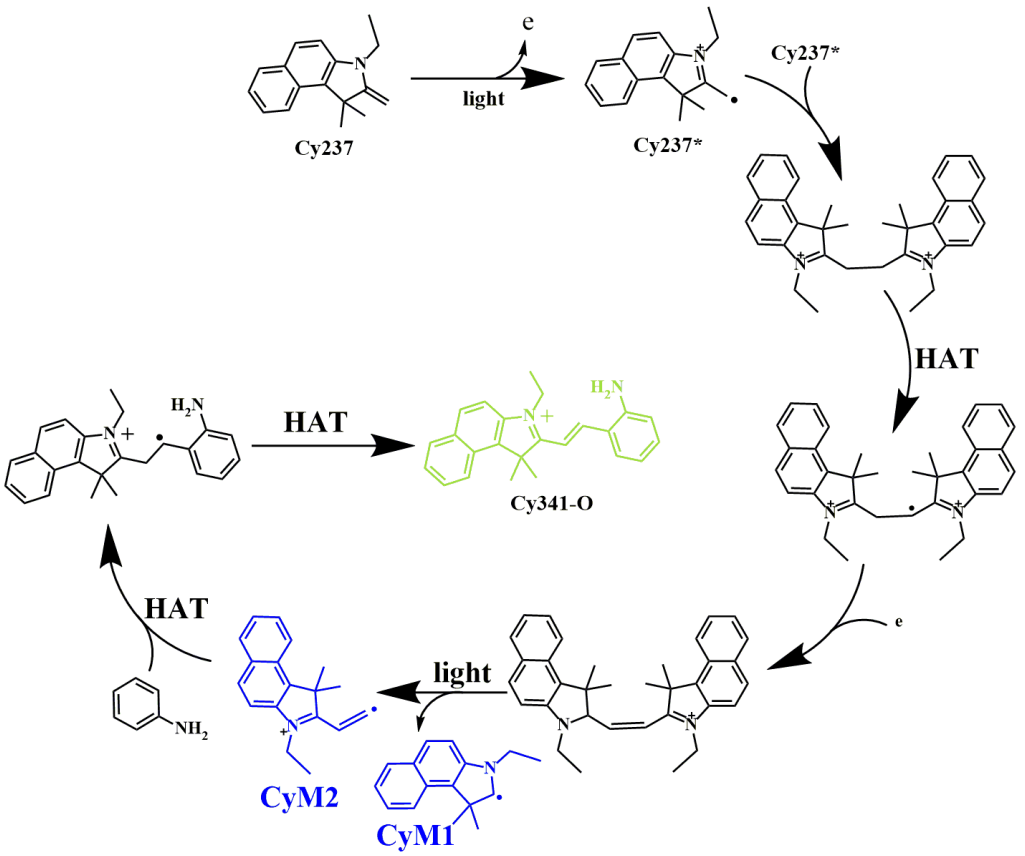
Table S4. The detection performance of Cy237 was compared with other probes for benzaldehyde

Sample	Method	Detection limit
Cy237 (This work)	Fluorescence detection	0.67 μM
TPMCN[3]	Fluorescence detection	2.17 μM
Cd-MOFs 1/2[4]	Fluorescence detection	24.27 μM / 3.14 μM
$[\{Ln(SIP)(H_2O)_4\}]_n$[5]	Fluorescence detection	1 μM
GA-AuNP@Tollens[6]	UV detection	0.12 μM
LMOF-341[7]	Fluorescence detection	64 ppm

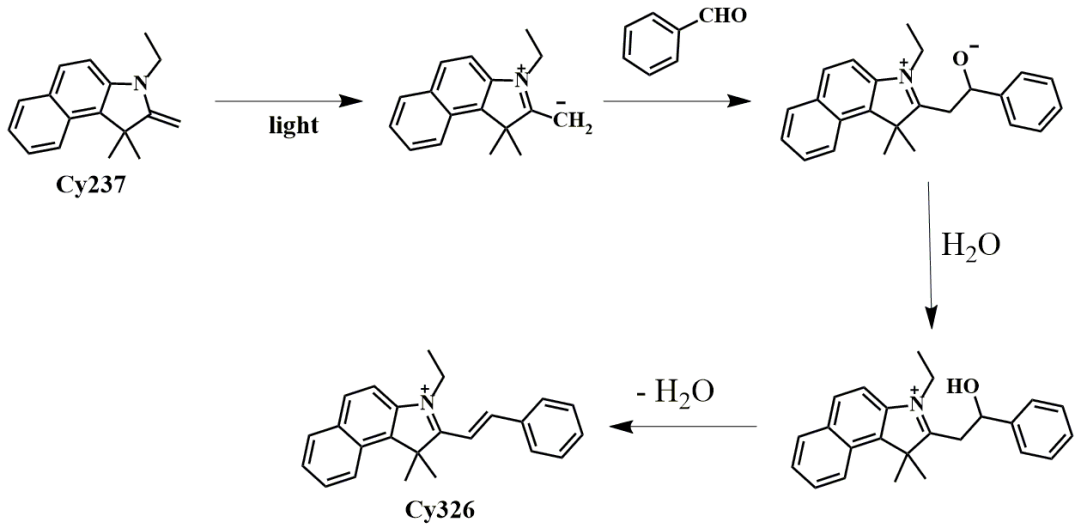
Table S5. Detection of benzaldehyde concentration in this work

Actual benzaldehyde concentration	This work	Percentage error
0 % (0 mg/mL)	/	/
1 % (10.4 mg/mL)	1 %	0 %
3 % (31.2 mg/mL)	2.9 %	3.3 %
5 % (52.0 mg/mL)	5.2 %	4 %
8 % (83.2 mg/mL)	8.1 %	1.25 %
10 % (104 mg/mL)	9.8 %	2 %
20 % (208 mg/mL)	19.5 %	2.5 %
30 % (312 mg/mL)	30.3 %	1 %
40 % (416 mg/mL)	40.8 %	2 %
50 % (520 mg/mL)	49.1 %	1.8 %
60 % (624 mg/mL)	62.1 %	3.5 %
70 % (728 mg/mL)	70.1 %	0.14 %
80 % (832 mg/mL)	78.8 %	1.5 %
90 % (936 mg/mL)	89.7 %	0.33 %
100 % (1040 mg/mL)	101.1 %	1.1 %

Detection device: 40 μM of Cy237 in chloroform in a bottle, power source: 405 nm LED light (100 mW/cm^2) irradiation.



Scheme S1. Proposed mechanism of the LED light irradiation-directed conversion of Cy237 and aniline in chloroform.



Scheme S2. Proposed mechanism for the generation of Cy326 from Cy237 and benzaldehyde in chloroform under LED light irradiation.

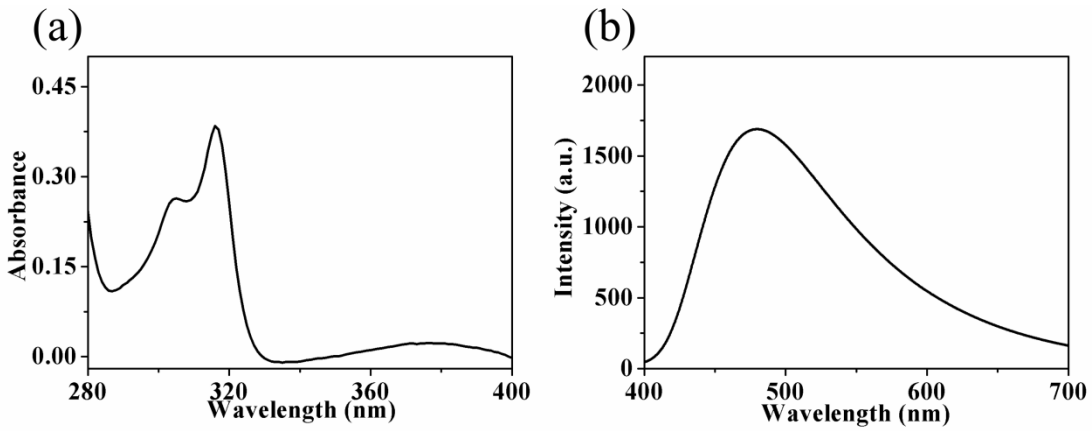


Figure S1. (a) UV-visible spectra of Cy237 in chloroform. (b) Fluorescence emission spectra of Cy237 in chloroform. The concentration of probes was 10 μM.

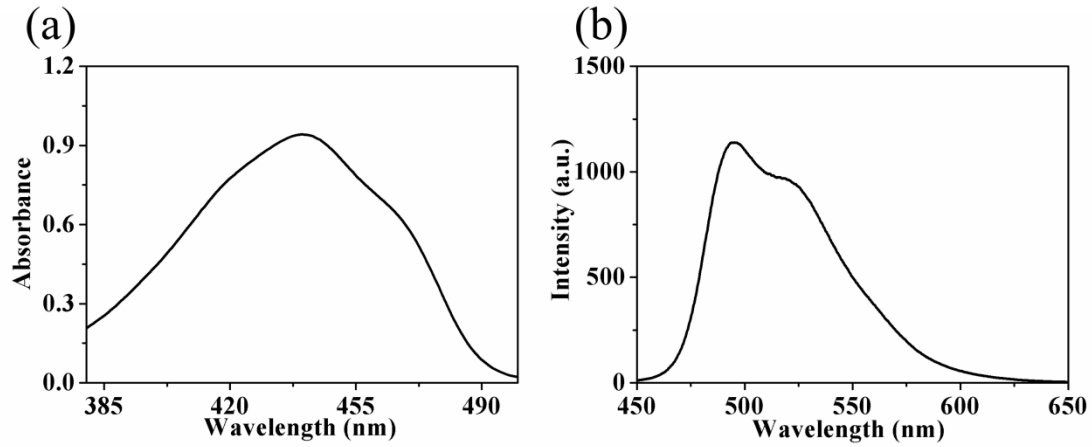


Figure S2. (a) UV-visible spectra of Cy341-O in chloroform. (b) Fluorescence emission spectra of Cy341-O in chloroform. The concentration of probes was 10 μM.

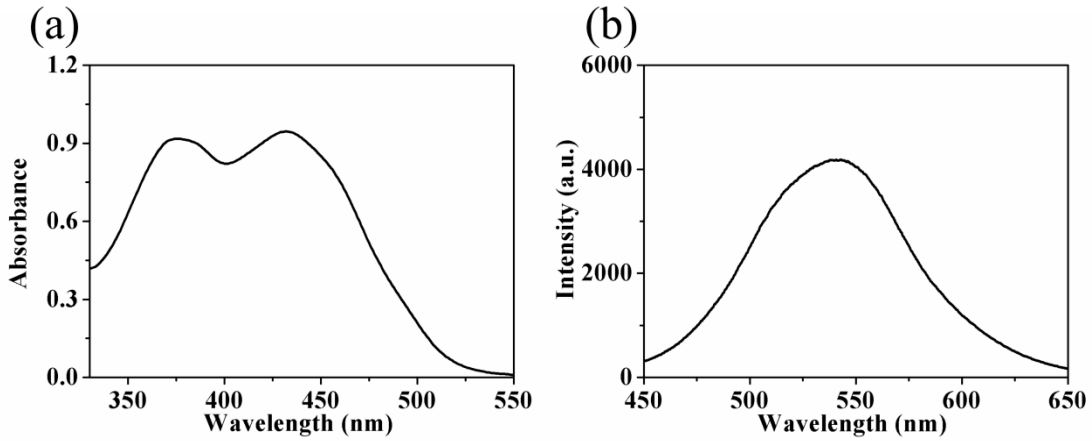


Figure S3. (a) UV-visible spectra of Cy326 in chloroform. (b) Fluorescence emission spectra of Cy326 in chloroform. The concentration of probes was 10 μM.

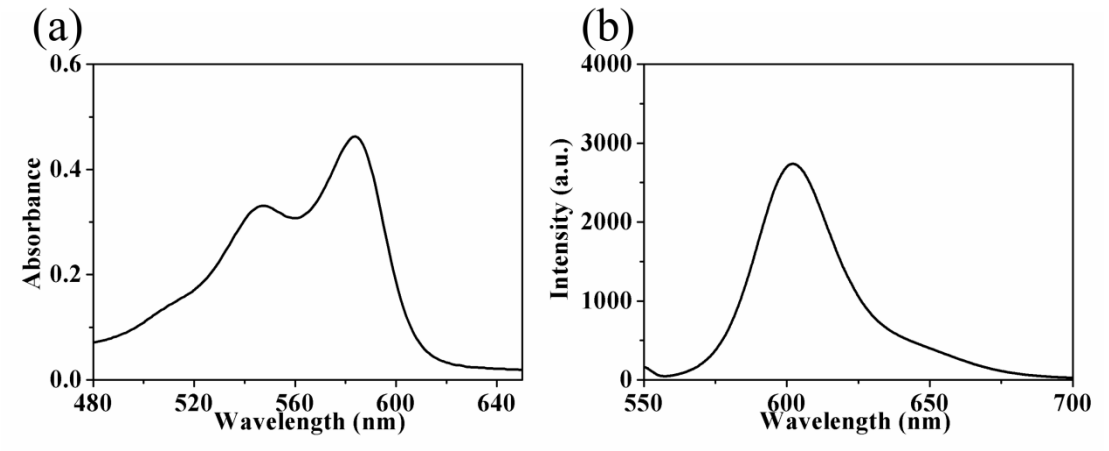


Figure S4. (a) UV-visible spectra of Cy485 in chloroform. (b) Fluorescence emission spectra of Cy485 in chloroform. The concentration of probes was 10 μM.

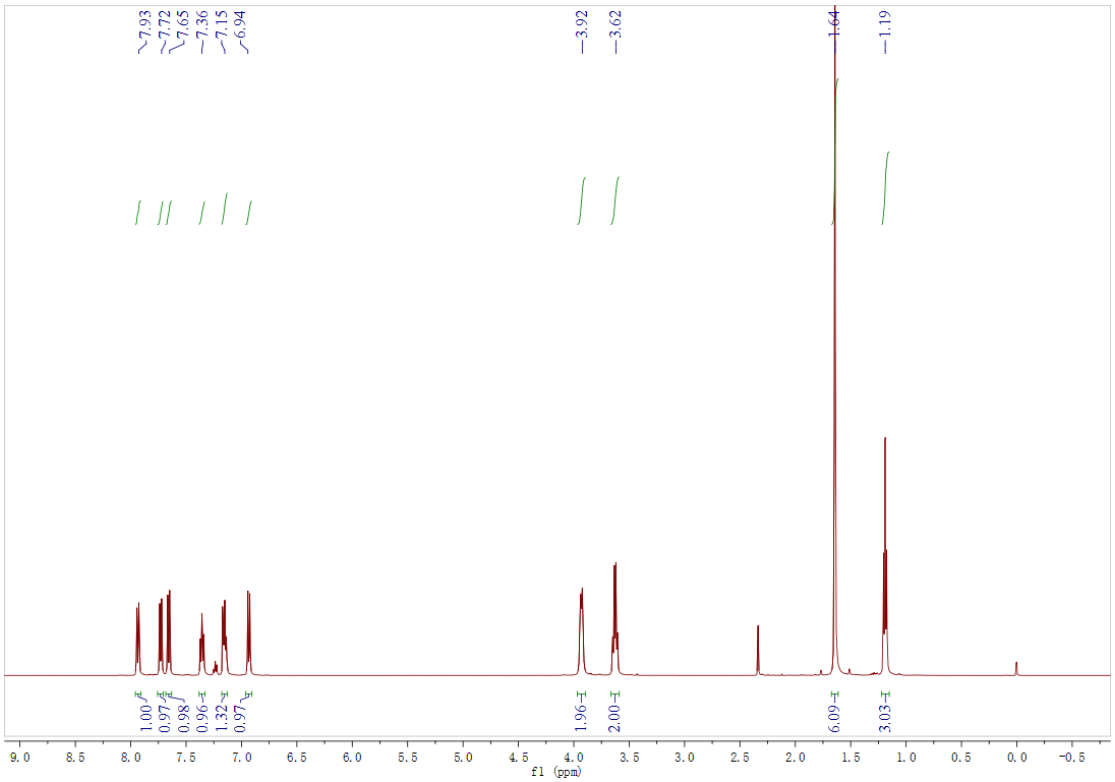


Figure S5. ^{1}H NMR spectrum of Cy237 in $CDCl_3$.

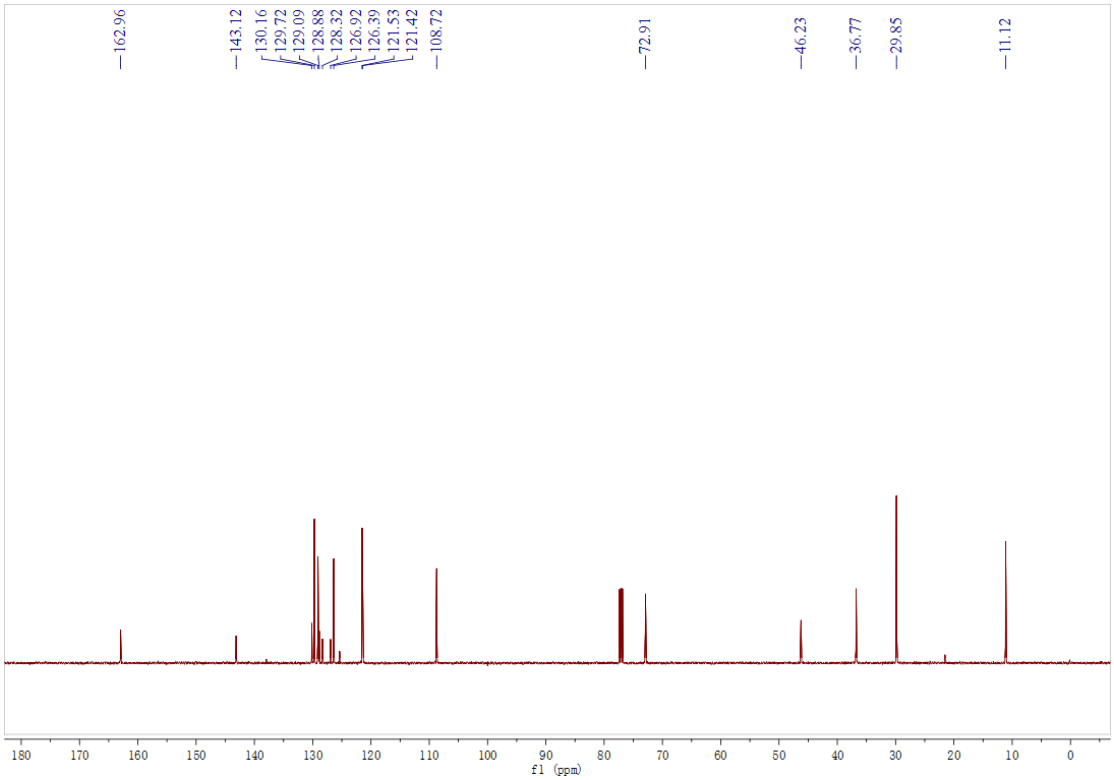


Figure S6. ^{13}C NMR spectrum of Cy237 in $CDCl_3$.

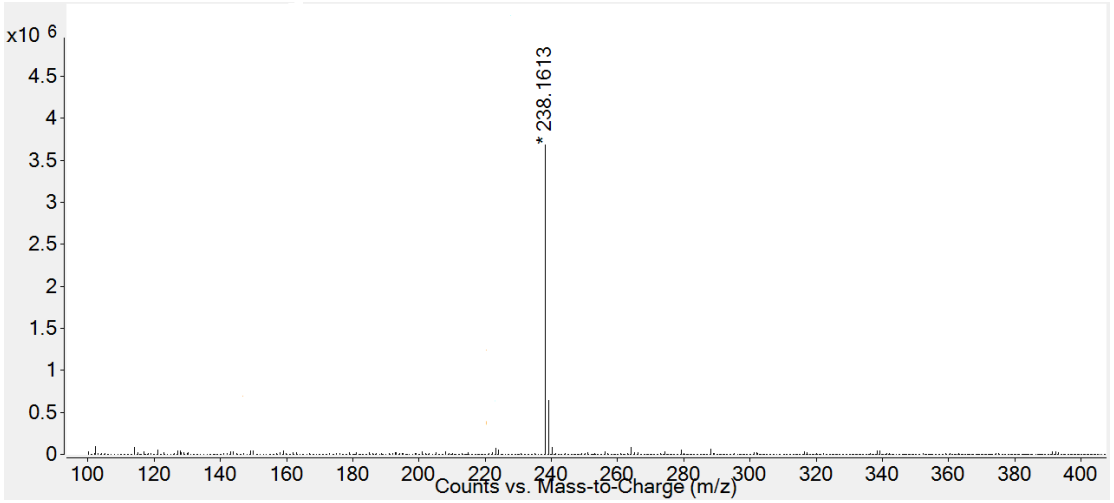


Figure S7. ESI-MS spectrum of Cy237.

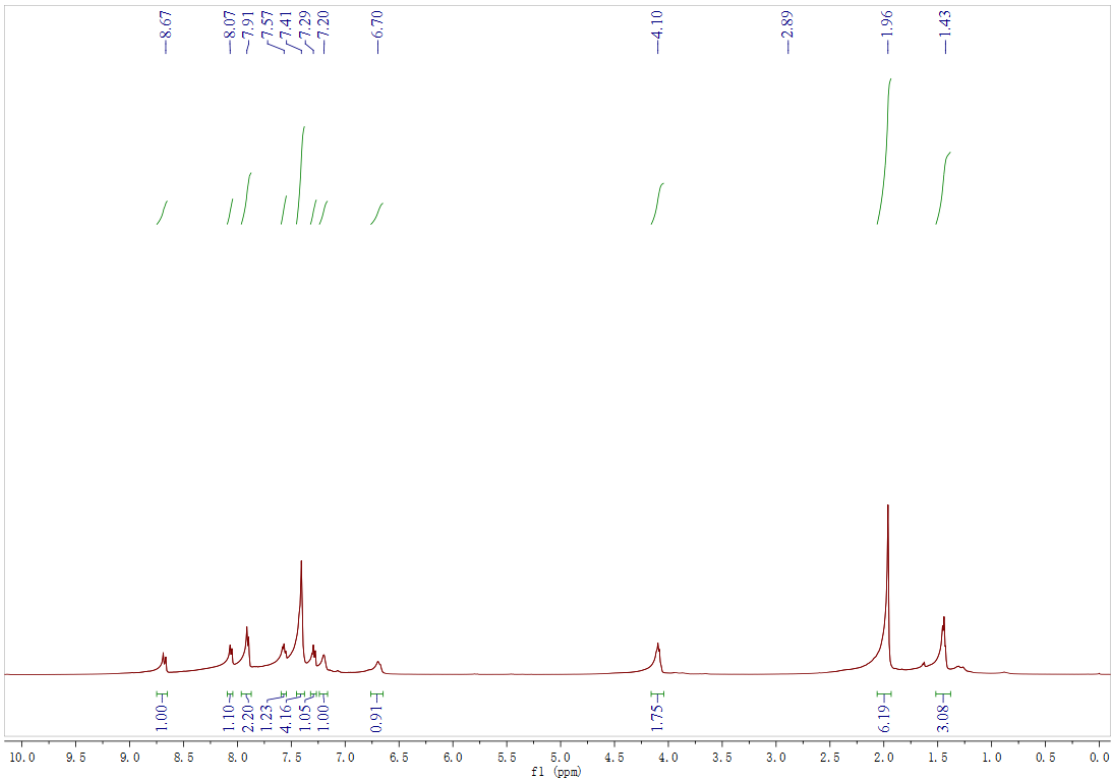


Figure S8. ^{1}H NMR spectrum of Cy341-O in $CDCl_3$.

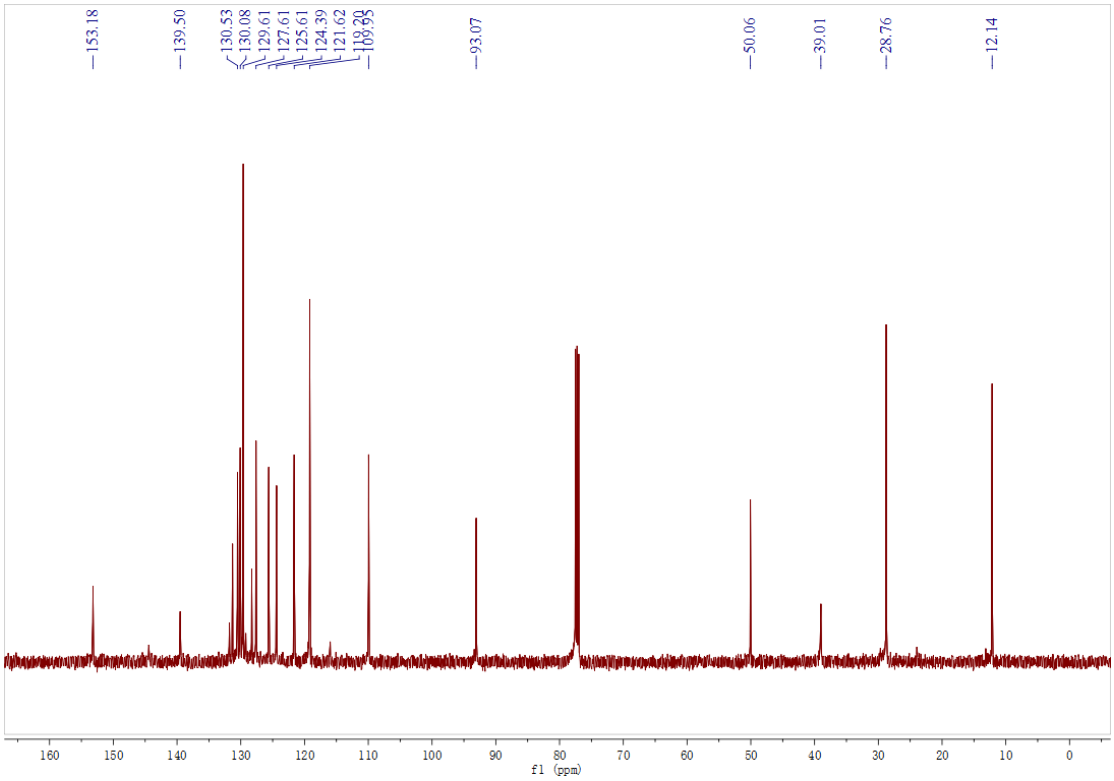


Figure S9. ^{13}C NMR spectrum of Cy341-O in $CDCl_3$.

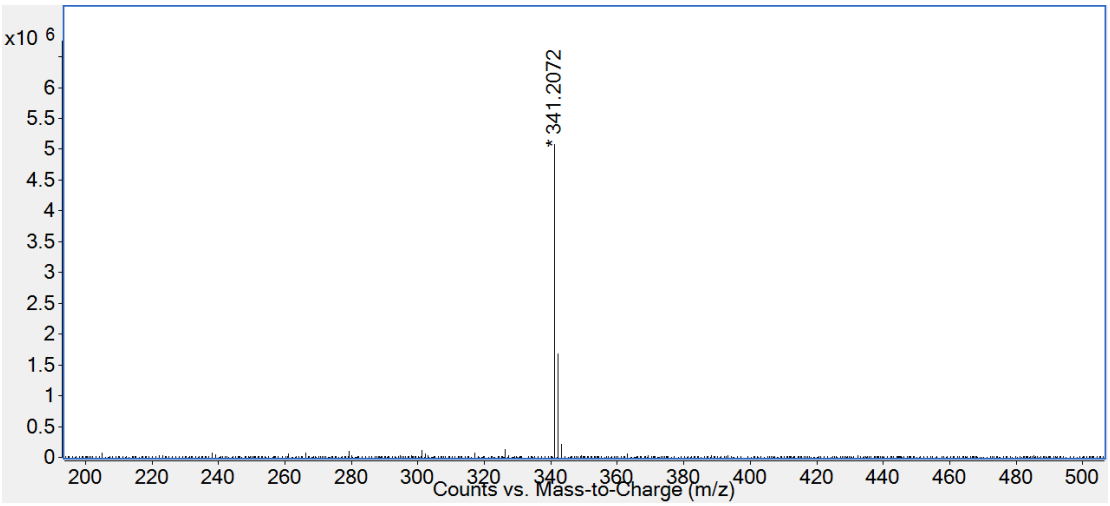


Figure S10. ESI-MS spectrum of Cy341-O.

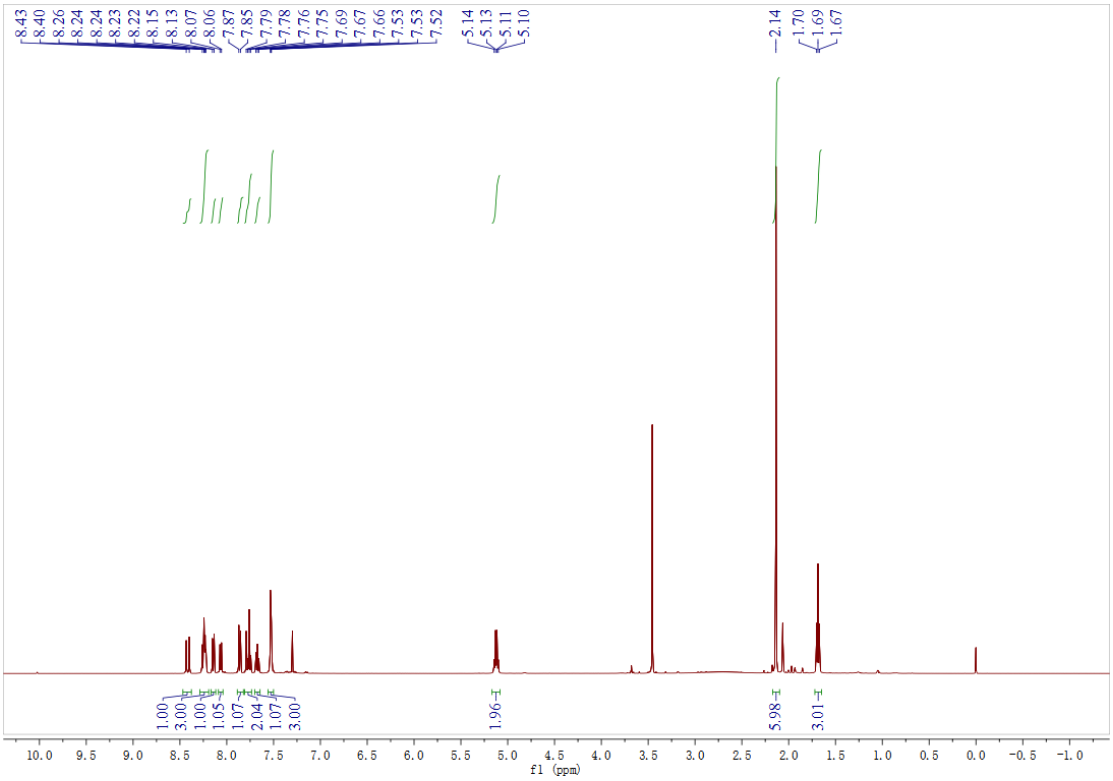


Figure S11. ^{1}H NMR spectrum of Cy326 in $CDCl_3$.

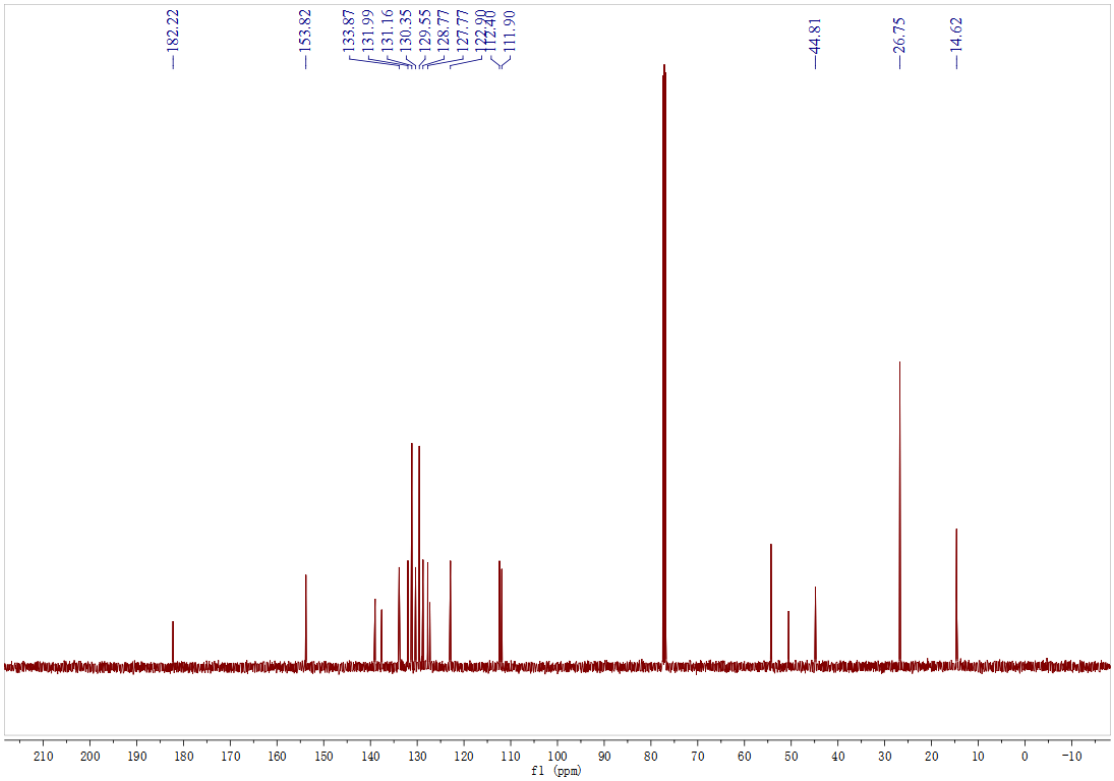


Figure S12. ^{13}C NMR spectrum of Cy326 in $CDCl_3$.

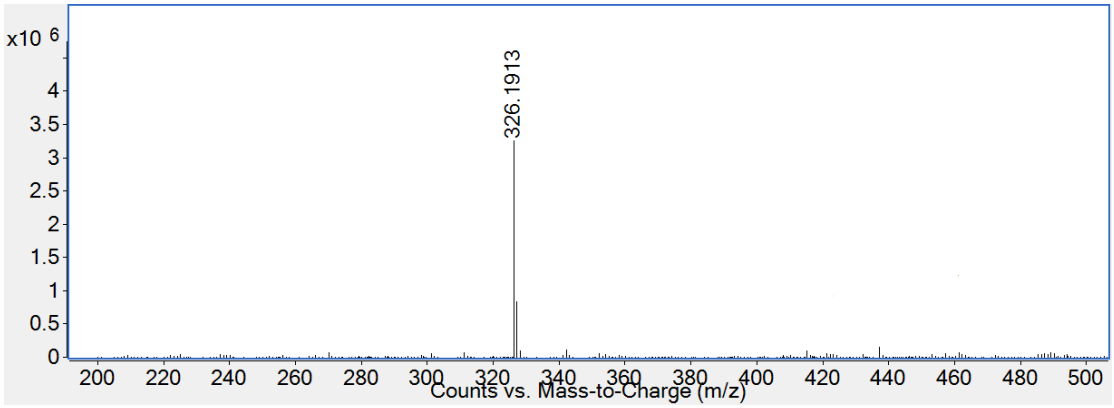


Figure S13. ESI-MS spectrum of Cy326.

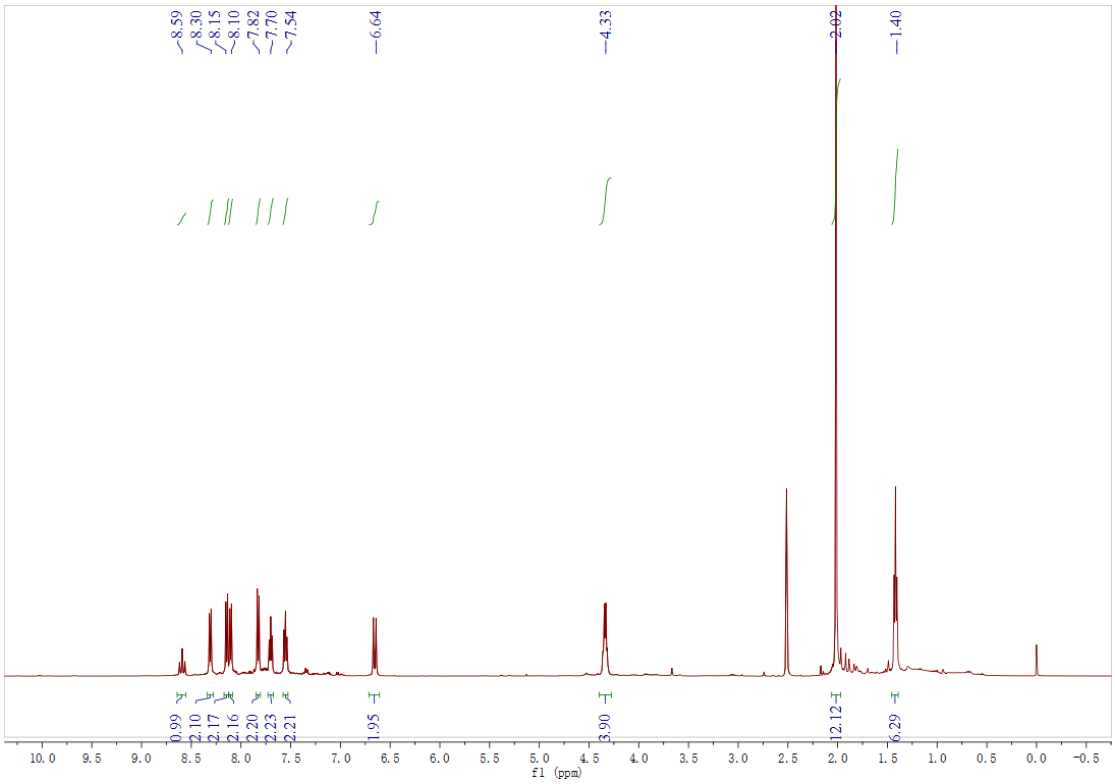


Figure S14. ^{1}H NMR spectrum of Cy485 in $CDCl_3$.

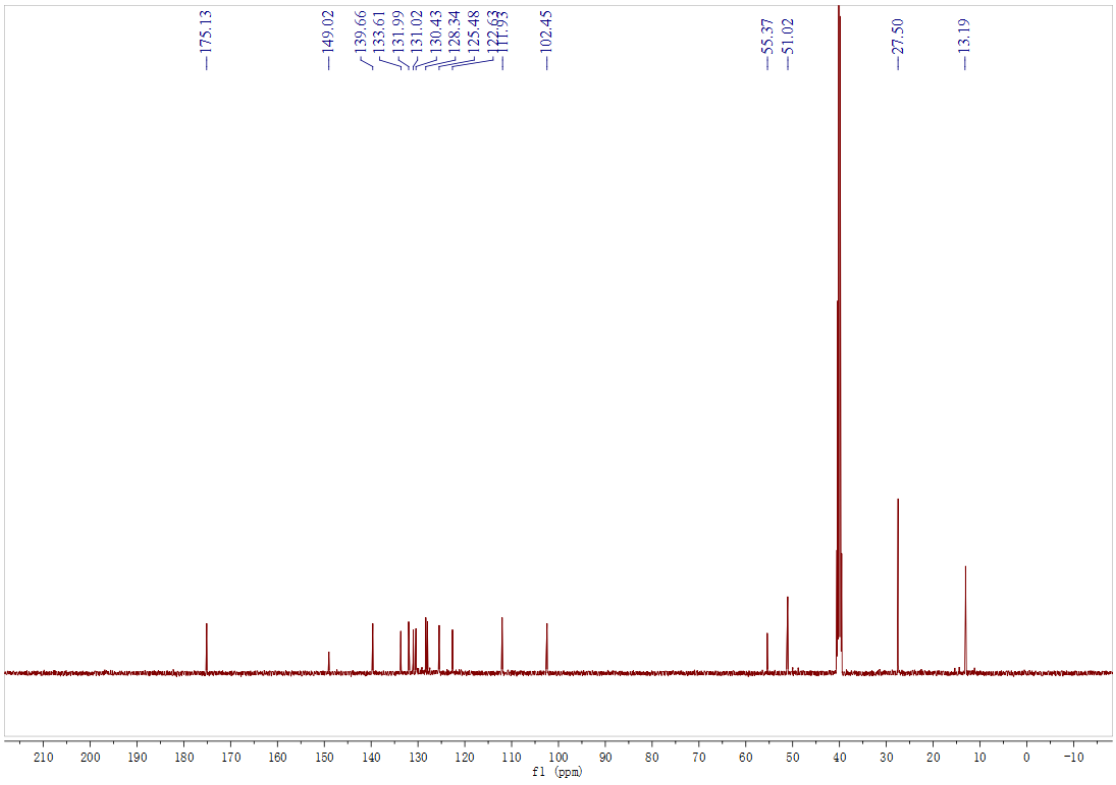


Figure S15. ^{13}C NMR spectrum of Cy485 in $CDCl_3$.

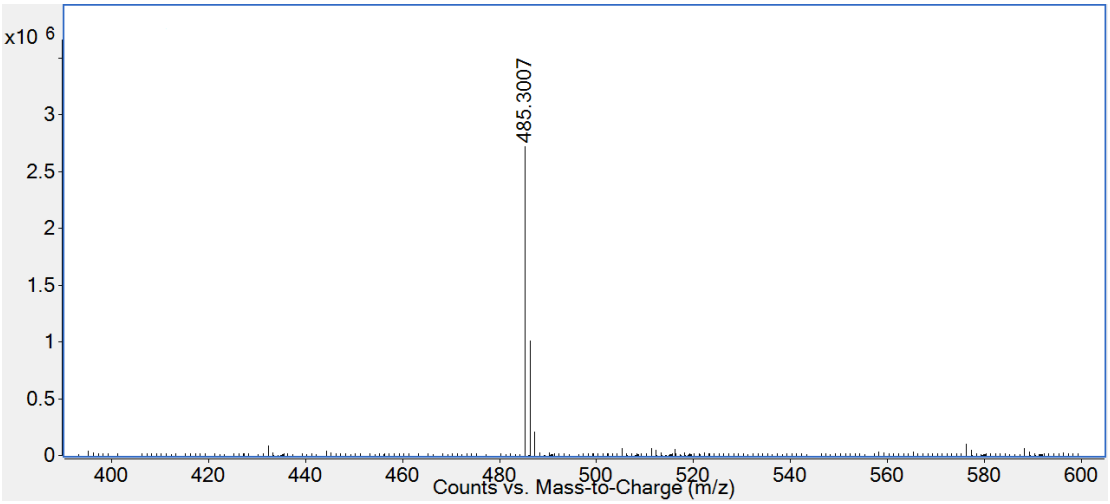


Figure S16. ESI-MS spectrum of Cy485.

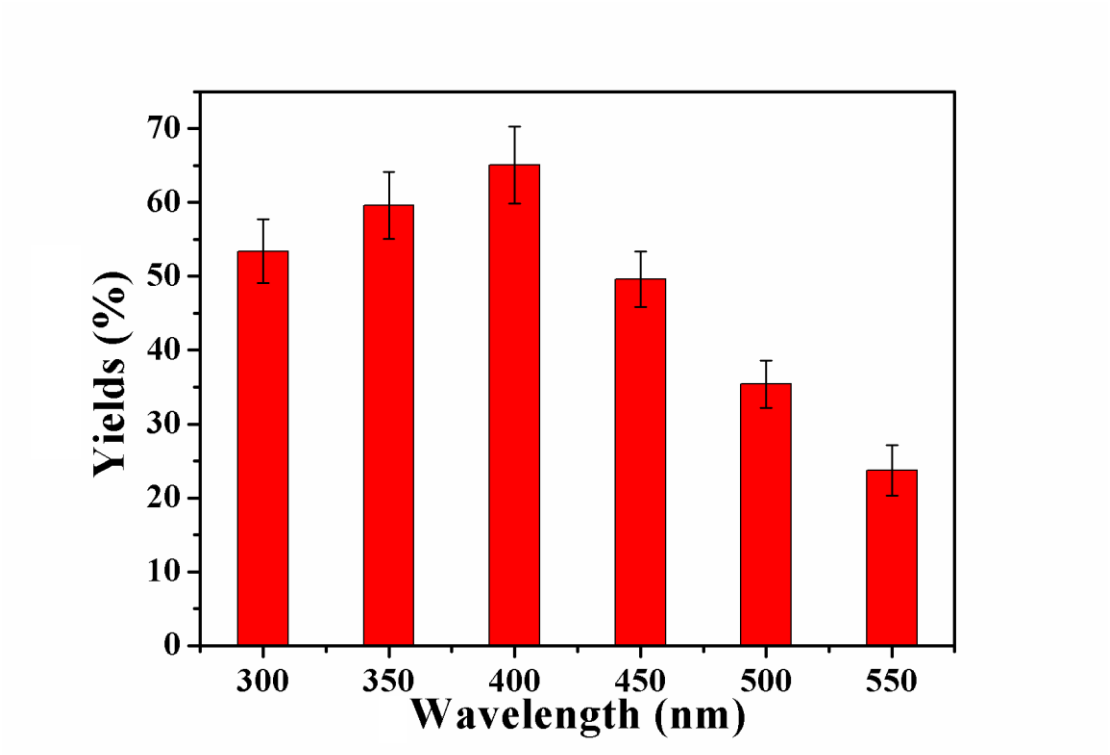


Figure S17. The yields of Cy485 generated from Cy237 under LED light (100 mW/cm^2) irradiation at different wavelengths.

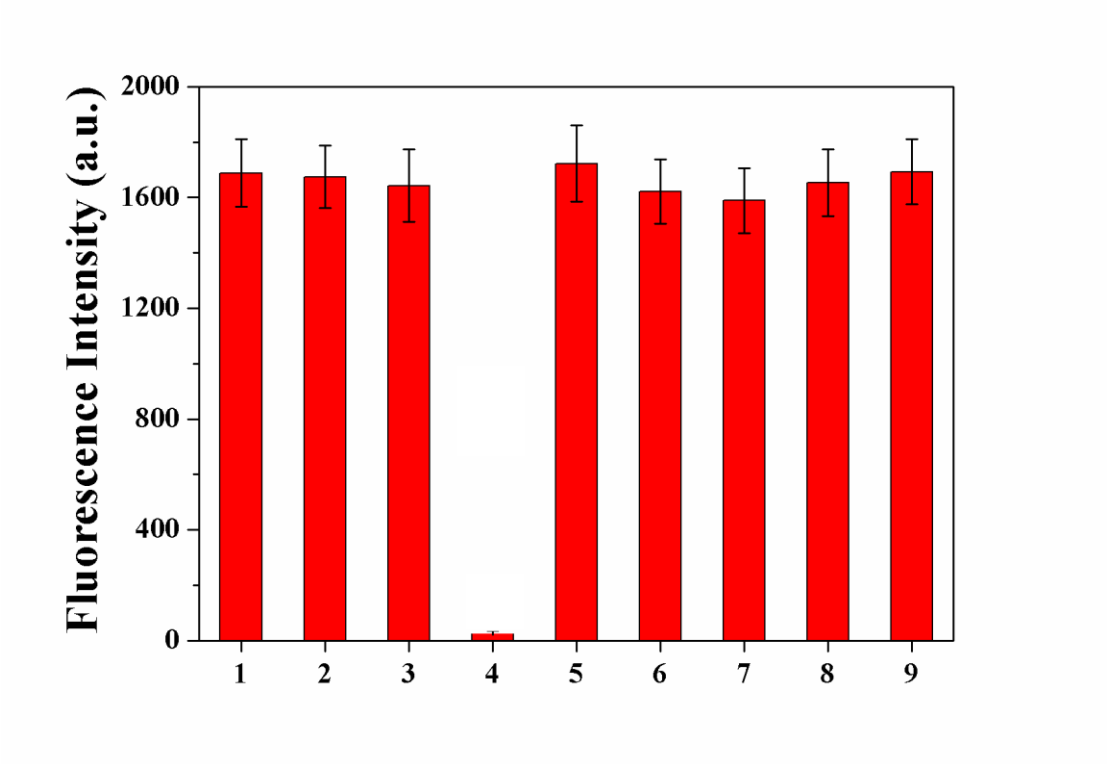


Figure S18. The effect of different cations and anions on photosynthesis of Cy341-O from Cy237 (40 μM) and benzaldehyde (40 μM) in mixed solution (Chloroform: Ethanol: H_2O = 2/4/4, v/v/v). Fluorescence intensity is recorded at the emission peak of 540 nm. 1. Blank. 2. Na^+ (NaCl). 3. K^+ (KCl). 4. Cu^{2+} ($CuCl_2$). 5. NH_4^+ (NH_4Cl). 6. NO_3^- ($NaNO_3$). 7. SO_4^{2-} (Na_2SO_4). 8. CO_3^{2-} (Na_2CO_3). 9. I^- (KI).

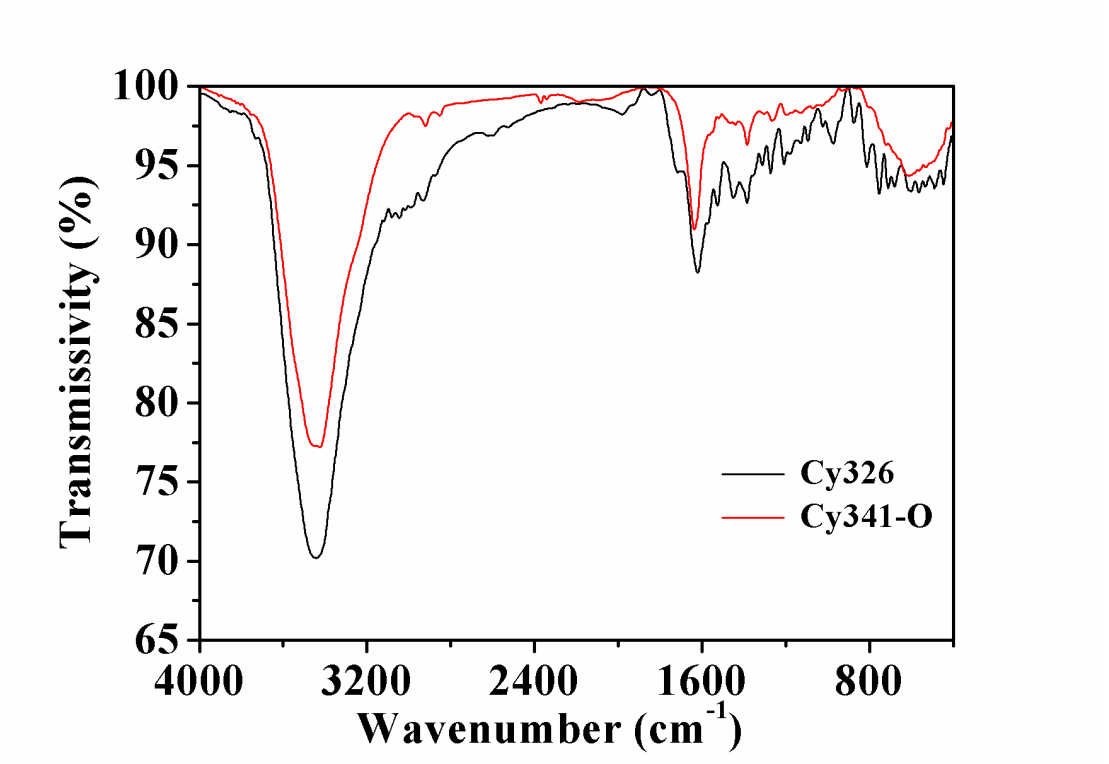


Figure S19. The FT-IR spectroscopy of Cy326 and Cy341-O.

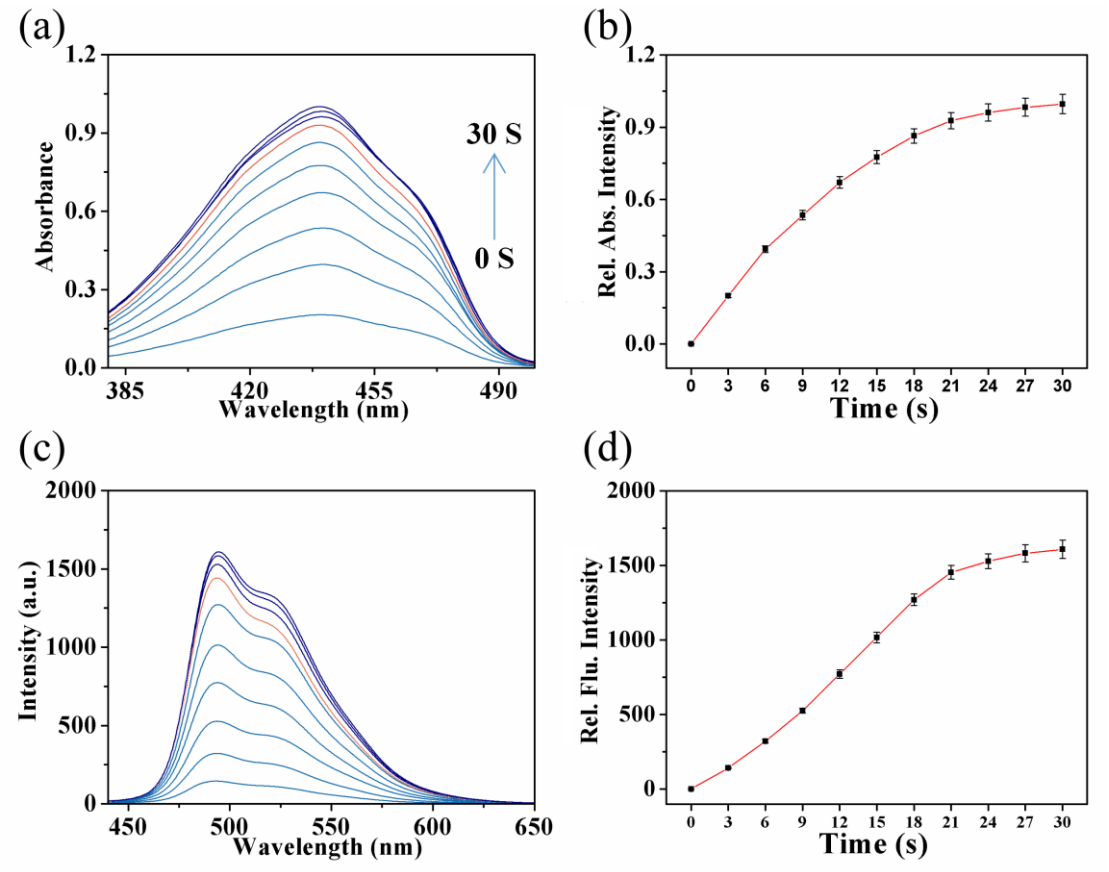


Figure S20. (a) The UV-visible spectra of Cy237 (10 μM) and aniline (10 μM) in chloroform under irradiation from 0 second to 30 seconds. (b) The absorbance intensity of Cy237 (10 μM) and aniline (10 μM) in chloroform under irradiation from 0 second to 30 seconds. Peak of absorption: 440 nm. (c) The fluorescence spectra of Cy237 (10 μM) and aniline (10 μM) in chloroform under irradiation from 0 second to 30 seconds. (d) The fluorescence intensity of Cy237 (10 μM) and aniline (10 μM) in chloroform under irradiation from 0 second to 30 seconds. Peak of emission: 500 nm. Irradiation: 405 nm LED light (100 mW/cm^2). The samples were first treated with LED light and then measured.

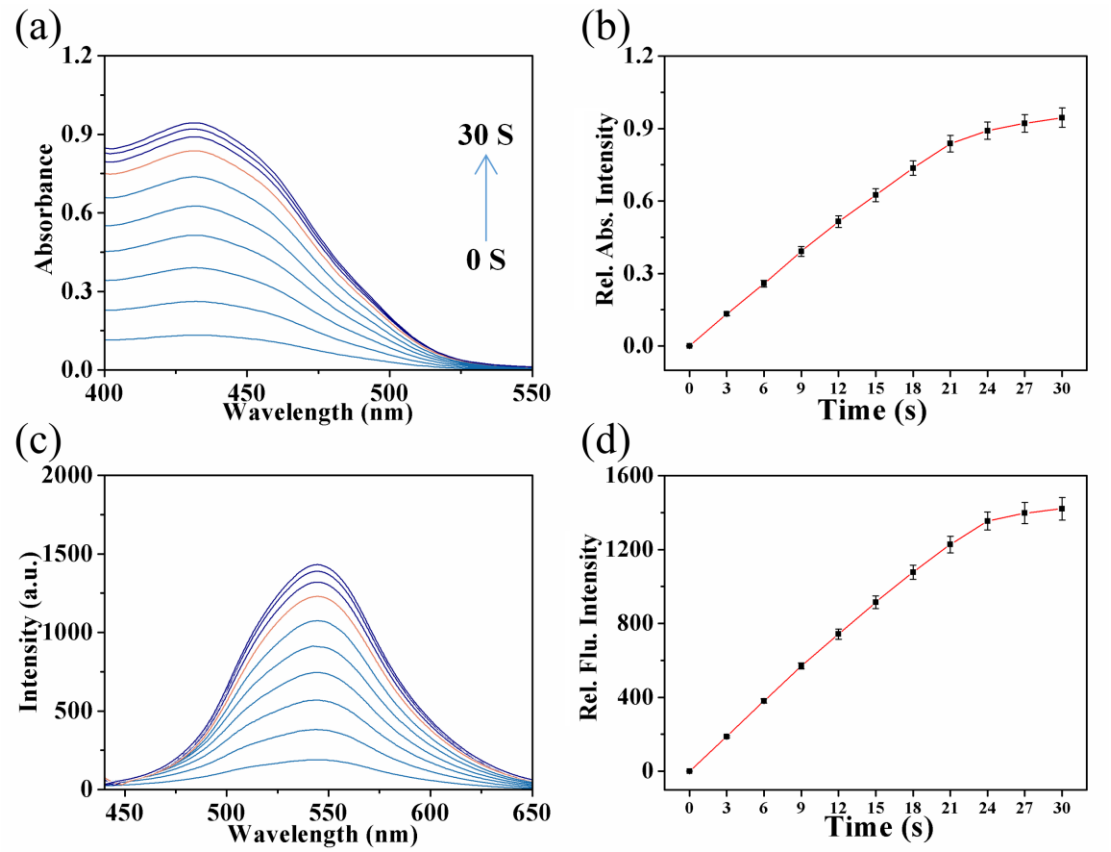


Figure S21. (a) The UV-visible spectra of Cy237 (10 μM) and benzaldehyde (10 μM) in chloroform under irradiation from 0 second to 30 seconds. (b) The absorbance intensity of Cy237 (10 μM) and benzaldehyde (10 μM) in chloroform under irradiation from 0 second to 30 seconds. Peak of absorption: 440 nm. (c) The fluorescence spectra of Cy237 (10 μM) and benzaldehyde (10 μM) in chloroform under irradiation from 0 second to 30 seconds. (d) The fluorescence intensity of

Cy237 (10 μM) and benzaldehyde (10 μM) in chloroform under irradiation from 0 second to 30 seconds. Peak of emission: 540 nm. Irradiation: 405 nm LED light (100 mW/cm^2). The samples were first treated with light and then measured.

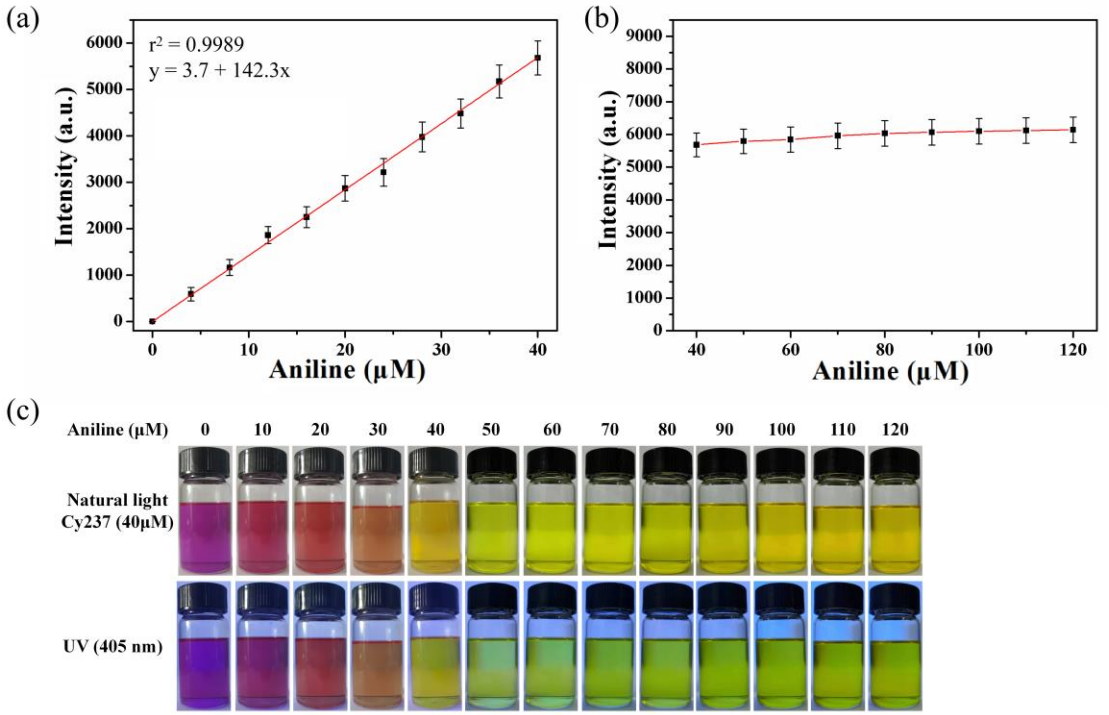


Figure S22. (a) Fluorescence responses of detection device with aniline (0 - 40 μM). r^2 = 0.9989. (b) Fluorescence responses of detection device with aniline (40 - 120 μM). (c) Color changes of detection device with aniline (0 - 120 μM) under natural light and 405 nm LED light after 30 seconds of irradiation with 405 nm LED light (100 mW/cm^2). Peak of emission: 500 nm. Detection device: 40 μM of Cy237 in chloroform in a bottle.

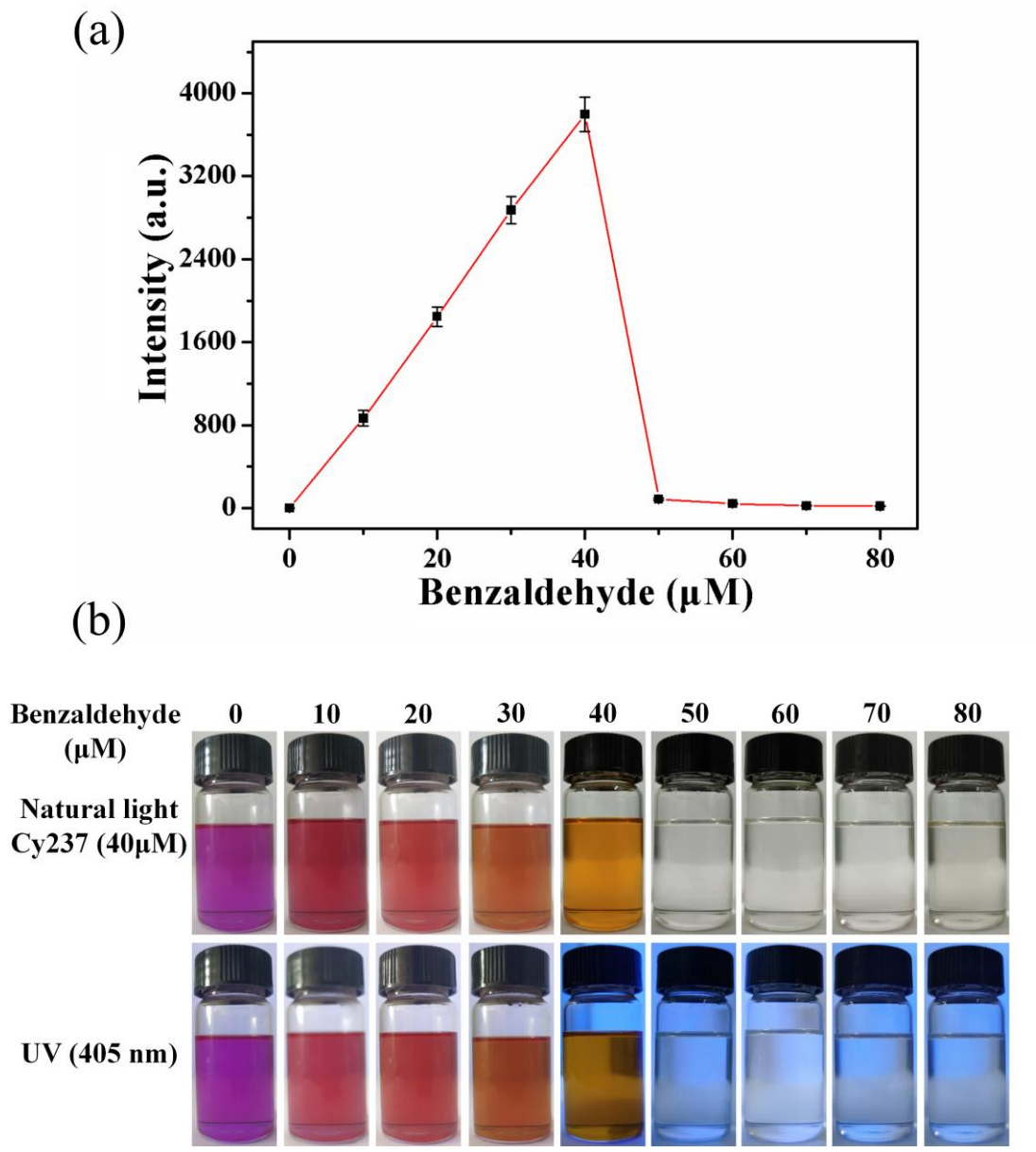


Figure S23. (a) Fluorescence responses of detection device with benzaldehyde (0 - 80 μM). (b) Color change of detection device with benzaldehyde (0 - 80 μM) under natural light and 405 nm LED light after 30 seconds of irradiation with 405 nm LED light (100 mW/cm^2). Peak of emission: 540 nm. Detection device: 40 μM of Cy237 in chloroform in a bottle.

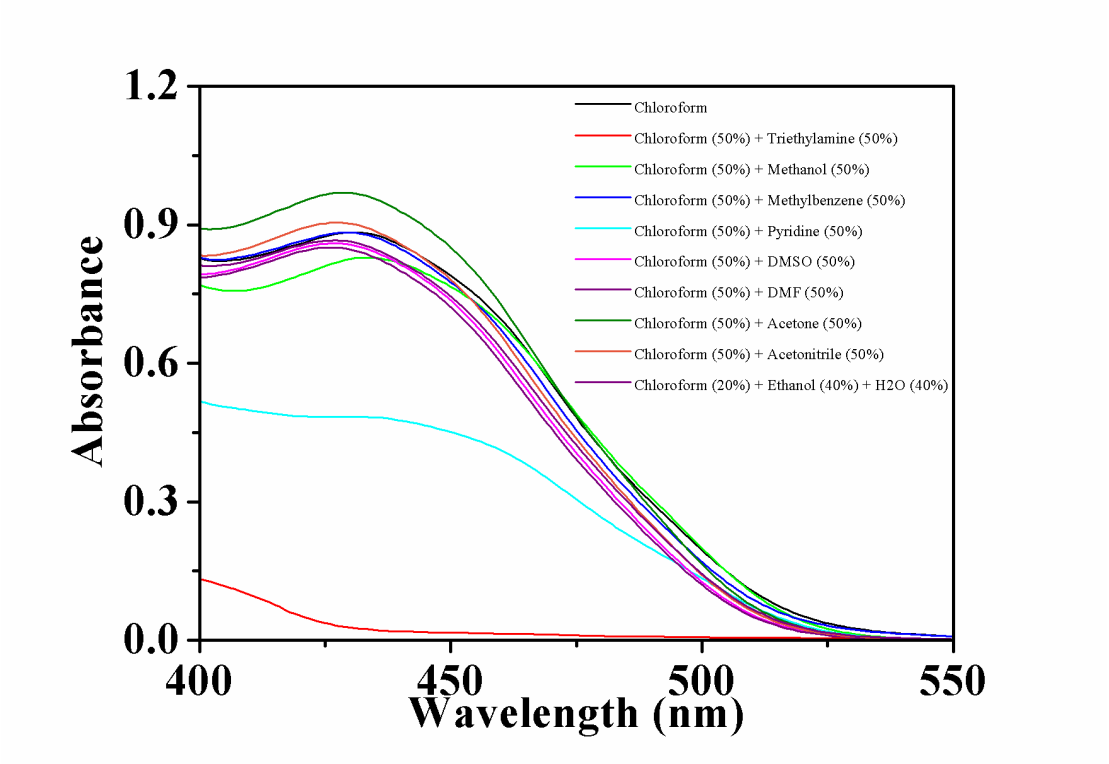


Figure S24. The UV-visible spectra of Cy237 with benzaldehyde in a mixed solvent of chloroform under 405 nm LED light (100 mW/cm^2). The concentration of Cy237 and benzaldehyde was 0.1 M. The LED light irradiation time was 30 s.

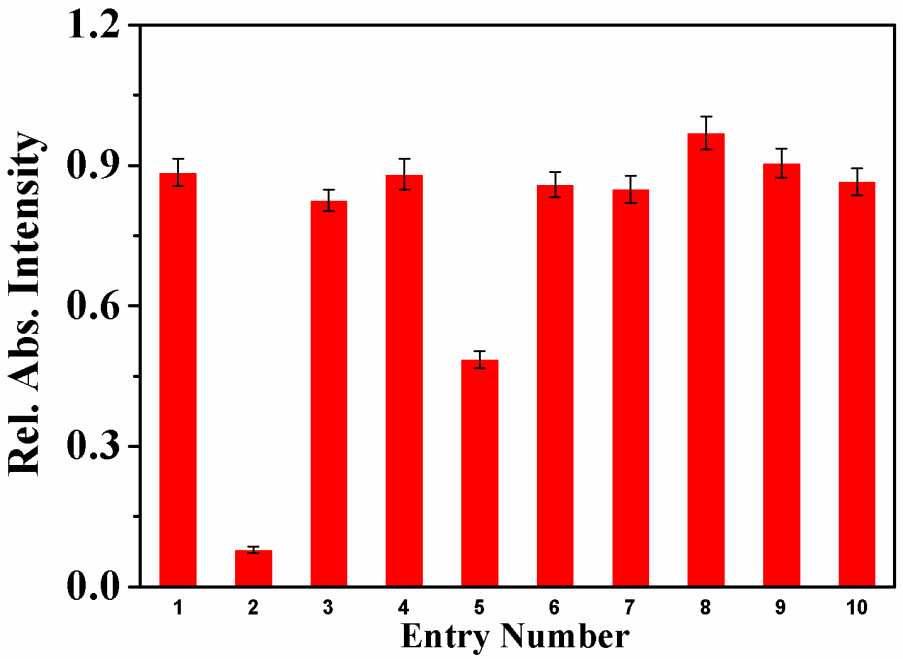


Figure S25. The absorbance intensity of Figure S24. Entry Number 1 - 10: Chloroform; Chloroform (50%) + Triethylamine (50%); Chloroform (50%) + Methanol (50%); Chloroform (50%) + Methylbenzene (50%); Chloroform (50%) + Pyridine (50%); Chloroform (50%) + DMSO (50%); Chloroform (50%) + DMF (50%); Chloroform (50%) + Acetone (50%); Chloroform (50%) + Acetonitrile (50%); Chloroform (20%) + Ethanol (40%) + H_2O (40%). The concentration of Cy237 and benzaldehyde was 0.1 M. The LED light (100 mW/cm^2) irradiation time was 30 s. Peak of emission: 540 nm.

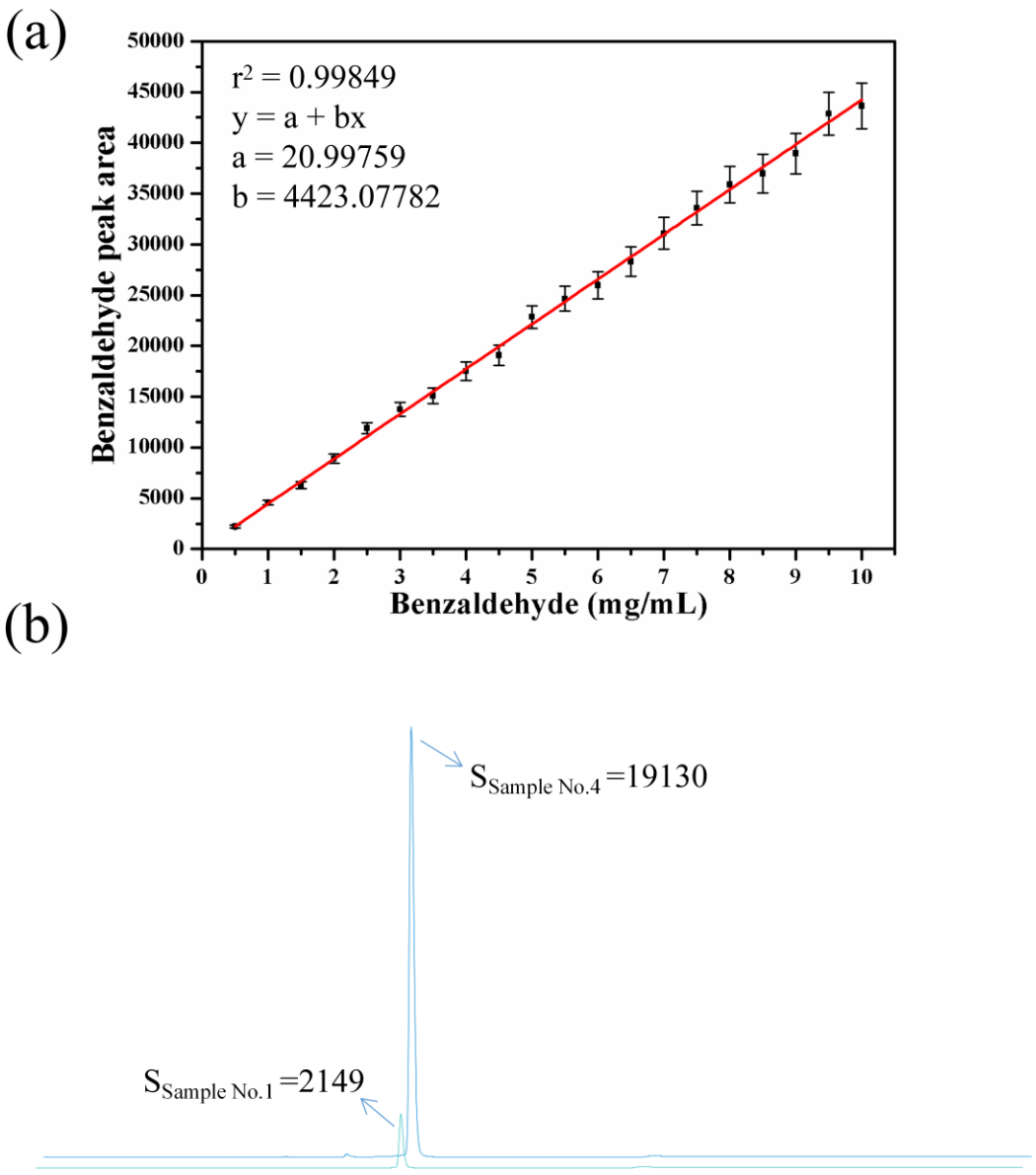


Figure S26. (a) Linear fitting curve of benzaldehyde content and chromatographic integral area by HPLC. (b) The benzaldehyde peak area of sample No.1 (sweet almond) and sample No.4 (bitter almond) by HPLC.

3. Supplemental References

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