# Dysprosium-Doped Carbon Nitride Activating Sulfite for Synergistic Photocatalytic Degradation of Methylene Blue

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## Supplementary Material

**Text S1.**

### Materials and chemicals

Melamine ($C_3H_6N_6$, 99%), methylene blue ($C_{16}H_{18}N_3ClS$,99%), tert-Butanol (TBA, AR grade), p-benzoquinone (p-BQ, AR grade) were supplied by the Macklin Biochemical Co., Ltd. (Shanghai, China). Dysprosium nitrate pentahydrate (Dy $(NO_3)_3 \cdot 5H_2O$,99%), Sodium sulfite anhydrous ($Na_2SO_3$,98%), were obtained from Aladdin Biochemical Technology Co., Ltd. Methanol (MeOH, AR grade) were obtained from Guangzhou Chemical Reagent Factory. All experiments were conducted using deionized water. All the chemicals used here are analytical grade and are used as received, without any further purification.

### Characterization

Powder X-Ray Diffraction (P-XRD), BRUKER D8 ADVANCED, with Cu Kα radiation (1.54 Å), accelerating voltage 45 KV, electric current 35 mA and 2 theta ranging from 5° to 80° were used to analyze the crystalline phase and lattice parameters. Field Emission Scanning Electron Microscopy (FESEM), JEOL JSM 6390LV was used to record the surface morphologies and size of g-$C_3N_4$ and 0.3Dy-CN nanostructures. X-ray photoelectron

spectroscopy (XPS) was used to investigate binding energy and oxidation states of as prepared samples. Fourier Transform Infrared (FTIR) spectra of the photocatalysts were performed ranging from 4000–400 $cm^{-1}$ by Perkin Elmer SP65 and KBr was used as a reference material. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution of the samples were determined by $N_2$ adsorption-desorption at −196 °C using an autosorb IQ. The samples were degassed in a vacuum at 200 °C overnight before the tests. The specific surface area and pore size distribution were evaluated by the Brunauer-Emmett-Teller (BET) equation and the Barrett-Joyner-Halenda (BJH) method, respectively. UV–vis diffuse reflectance spectra (DRS) were obtained on a UV-vis spectrometer (Shimadzu UV-2600, Japan). Photoluminescence (PL) spectra were recorded with a fluorescence spectrometer (F-7000, Hitachi, Japan) with excitation wavelength of 365 nm at room temperature. The electrochemical impedance spectroscopy (EIS) was performed on a CHI660 electrochemical workstation (Chenghua, Shanghai, China) by applying an AC voltage of 10 mV amplitude in the frequency range of 105 Hz to 10−1 Hz with the initial potential (-0.3 V) in 0.5M $Na_2SO_4$.

**Analytical methods**

The residual concentration of MB was measured by UV-vis spectrophotometer (INESA Scientific Instrument Co., Ltd. Shanghai, China) at a wavelength of 664 nm. The reactive radicals were detected by electron paramagnetic resonance (EPR) on a Bruker EMS-plus instrument with DMPO and TEMP as a spin-trapping agent. LC-MS (PR-LCMS-2020) was used to detect MB removal intermediates. The transformation intermediates during the MB degradation process were detected by HPLC-MS (Waters2695, Waters ZQ2000, C18RRHD 4.6×50 mm, 5μm). The mobile phase A was made up by formic acid/water (0.1% formic acid) and mobile phase B was made up by formic acid/acetonitrile (0.1% formic acid), the column temperature was 30 ℃ and the flow rate was 0.2 mL/min.

**Text S2.Experimental procedures**

Catalyst activity of xDy-CN was performed for Methylene blue (MB) degradation in the presence of sulfite in aqueous solution in a 100 mL conical flask at 25 ℃. Typical experiments were carried out by dispersing the xDy-CN samples (0.4 g $L^{-1}$) in MB (20 mg $L^{-1}$, initial pH without adjustment) solution. A 20-min dark adsorption process was first conducted to ensure

that the adsorption-desorption equilibrium was basically achieved. Subsequently, a certain amount of sodium sulfite ($Na_2SO_3$) was added to initiate the reaction, and the reaction system was irradiated under a 25 W LED lamp with a wavelength cutoff at 400 nm ($\lambda > 400$ nm). At determined intervals, 5 mL of solution was withdrawn and immediately filtered by a 0.22 μm Millipore syringe filter to remove any solid particles[1]. All the experiments were performed three times, and the data of this study were the averages of the data of the three measurements. The standard deviations were determined to be less than 3 % in all the measurements.

The relevant parameters of the LED lamp are shown in Table S1.

**Tab.S1 Parameter of LED**

| Parameter | Numerical value |
|---|---|
| Main wavelength | 490 nm |
| Peak wavelength | 443.3 nm |
| Luminous flux | 98.42 lm |
| Light effect | 101.92 lm/W |
| Output power | 25 W |

**Text S3. ROS identifying and catalysts reusability experiments.**

On the basis of the results of MB degradation experiments, the optimum conditions for MB degradation were determined as: 20 mg/L MB, 0.4 g/L catalyst, 0.5 mM $Na_2SO_3$ at the initial pH without adjustment, under which the ROS quenching test and catalyst recycling assay were carried out as well. To investigate the mechanism of MB degradation in Dy-CN/$SO_3^{2-}$/vis system, quenching experiments were performed to identify the main active free radicals for MB degradation. Ammonium oxalate (AO), p-benzoquinone (p-BQ), methanol (MeOH), tert-butanol (TBA), and L-histidine (L-his) were respectively added to the reaction system. As a trap for hole($h^+$), superoxide anions ($O_2^{\bullet-}$), hydroxyl radicals (•OH) and sulfate radicals ($SO_4^{\bullet-}$), hydroxyl radicals (•OH), and singlet oxygen ions ($^1O_2$) generated during the reaction process. The recycling test consisted of four cycles in total. The conditions of each cycle were same.

After each cycle, the catalyst was collected by centrifugation followed by rinsing with ethanol and water for 3 times, eventually drying at 85 ℃ in an oven all the night long. Then the recovered catalysts were reused for the next cycle.

**Text S4. EPR measurement.**

To further identify the reactive oxygen species (ROS) in the 0.3Dy-CN/$SO_3^{2-}$/vis system, DMPO and TEMP were used as the spin trapping agents for radicals and nonradicals, respectively, and the signal of ROS was tested by EPR. The specific test methods are as follows: (1) Capture and determination of •OH and $SO_4^{\bullet-}$: dissolve MB with deionized water as solvent one days in advance. Add 2 mg of catalyst and 5 μM of $Na_2SO_3$ to 5 mL of 20 mg/L MB solution, and then add DMPO, the active oxygen trapping agent, at a ratio of 100 mM. Shake for 5 min and then take a certain amount of liquid for EPR measurement with a capillary glass tube. (2) Capture and determination of $O_2^{\bullet-}$: replace deionized water with MeOH in method (1), and the rest of the procedure is the same. (3) Capture and measurement of $^1O_2$: replace DMPO with TEMP in method (1), and the other steps are the same.

**Text S5. Kinetic model of degradation process.**

Percentage of the MB dye degradation was premeditated by using the equation (1),

$$Photodegradation\ rate = \left(1 - \frac{c}{c_0}\right) * 100\% \quad (1)$$

The photocatalytic activity of the as prepared photocatalysts were evaluated by the rate equation, the rate constant ($k$) was calculated by using equation (2),

$$ln\left(\frac{c}{c_0}\right) = -kt \quad (2)$$

Where '$c_0$' is the primary concentration of MB dye solution, while '$c$' is the concentration of the remaining MB dye solution at time '$t$' each irradiated time interval.

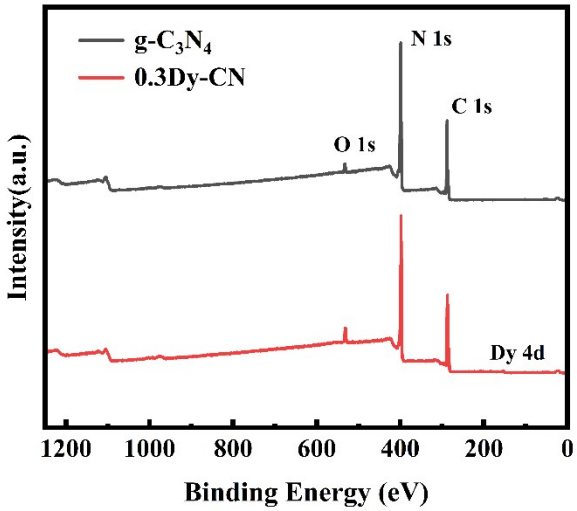



**Fig.S1 survey of XPS spectra**

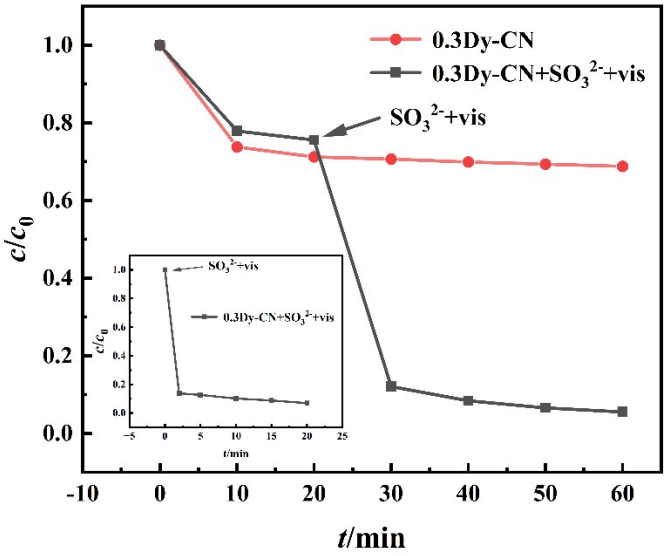



**Fig.S2 The adsorption performance of 0.3Dy-CN and its degradation performance under different conditions**

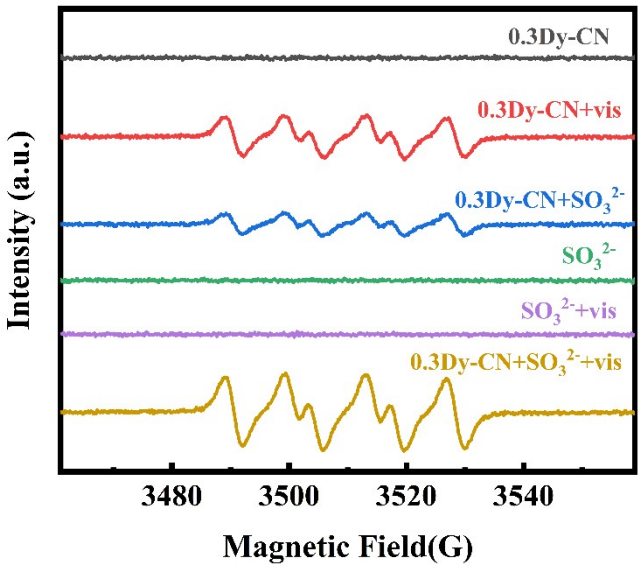



**Fig.S3 A single-control EPR experiment of $O_2^{\bullet-}$**

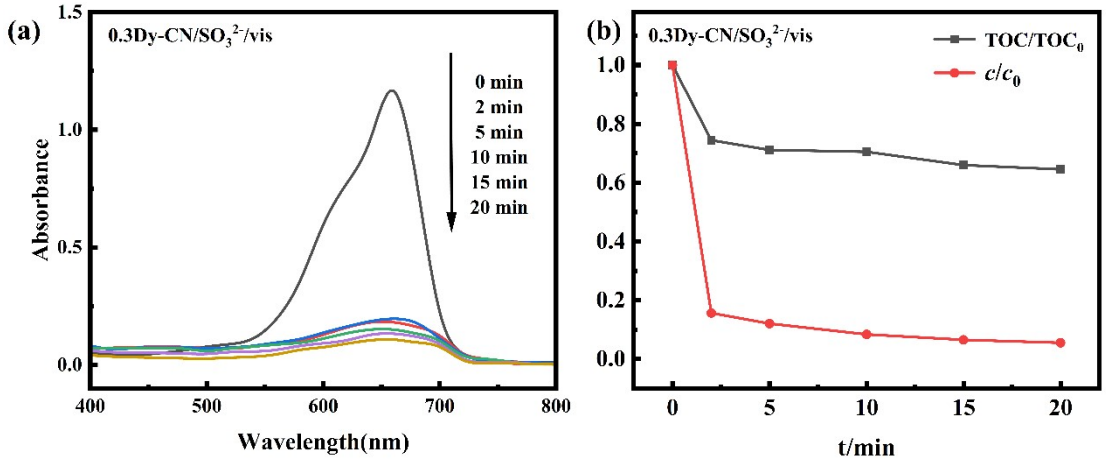



**Fig.S4 Ultraviolet-visible spectral changes of MB solution during the degradation process(a), TOC during the degradation of MB in the 0.3Dy-CN/$SO_3^{2-}$/vis system(b)**

**Tab.S2 The content of XPS functional group of g-$C_3N_4$and 0.3Dy-CN**

| element | | g-$C_3N_4$ (at%) | 0.3Dy-CN (at%) | 0.3Dy-CN-used (at%) |
|---|---|---|---|---|
| C | C-C | 15.5 | 20.9 | 33.2 |
| | C-N | 3.0 | 3.0 | 8.8 |
| | N-C=N | 76.9 | 72.4 | 55.2 |
| | $\pi$-$\pi^*$ | 4.6 | 3.7 | 2.8 |
| N | C=N-C | 74.2 | 73.8 | 73.8 |
| | $N-C_3$ | 11.4 | 13.0 | 12.5 |
| | C-N-H | 9.0 | 7.9 | 9.4 |
| | $\pi$-excitation | 5.4 | 5.3 | 4.3 |
| O | O-H | 81.4 | 78.8 | 64.4 |
| | $H_2O/CO_2$ | 18.6 | 21.2 | 35.6 |

**Tab.S3 Atomic percentages of catalysts**

| Samples | C (at%) | N (at%) | O (at%) | Dy (at%) |
|---|---|---|---|---|
| g-$C_3N_4$ | 44.25 | 53.08 | 2.67 | 0 |
| 0.3Dy-CN | 45.18 | 50.22 | 4.47 | 0.14 |
| 0.3Dy-CN-used | 66.94 | 21.64 | 11.33 | 0.09 |

**Tab.S4 Nitrogen sorption results of 0.3Dy-CN and g-$C_3N_4$ composites**

| Samples | BET surface area（$m^2/g$） | Pore volume（$cm^3/g$） | Average pore size（nm） |
|---|---|---|---|
| g-$C_3N_4$ | 8.58 | 0.0648 | 38.89 |
| 0.3Dy-CN | 24.87 | 0.1981 | 7.79 |

**Tab.S5 Experiment on photocatalytic degradation of MB by photocatalyst**

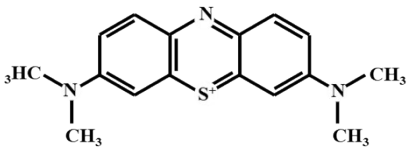
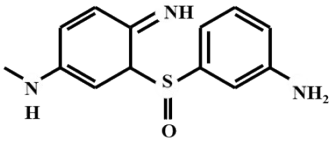
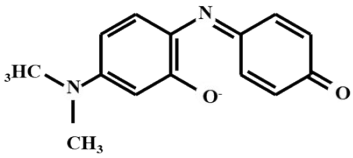
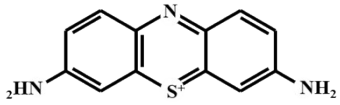
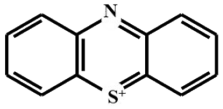
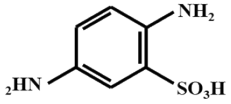
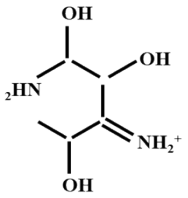
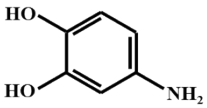
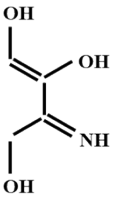
| Catalysts | Pollutants | Pollutant concentration | Mass (mg) | Light source wavelength [nm] | pH | Type/dosage of oxidant | Degradation time/efficiency | Reaction rate constant (*k*) | Ref |
|---|---|---|---|---|---|---|---|---|---|
| CuO:Dy | Methylene blue | 3 mg $L^{-1}$ | - | Sunlight | 7 | - | 180 min/82% | 0.0088 $min^{-1}$ | 2 |
| α-$Fe_2O_3$/g-$C_3N_4$ | Methylene blue | 10 mg $L^{-1}$ | 1 g $L^{-1}$ | 6 W UV lamp (≥ 254) | 7 | $H_2O_2$/1 mM | 90 min/97% | 0.0367 $min^{-1}$ | 3 |
| MCA-CN/$WO_3$ | Methylene blue | 20 mg $L^{-1}$ | 0.15 g $L^{-1}$ | 25 W LED lamp (≥ 400) | 7 | $H_2O_2$/1 mM | 30 min/98% | 0.1121 $min^{-1}$ | 4 |
| Dy-doped ZnO | Methylene blue | 3 mg $L^{-1}$ | 0.1 g $L^{-1}$ | Sunlight | 7 | - | 120 min/92% | 0.0181 $min^{-1}$ | 5 |
| $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+}$ | Methylene blue | 10 mg $L^{-1}$ | - | 6 W UV lamp (≥ 365) | 7 | - | 300 min/77% | - | 6 |
| Mg-Zn-g-$C_3N_4$ | Methylene blue | 0.1 mM | 0.2 g $L^{-1}$ | 60W LED lamp (≥ 400) | 7 | - | 90 min/98% | 0.0295 $min^{-1}$ | 7 |
| $ZrMo_2O_8$/g-$C_3N_4$ | Methylene blue | $10^{-4}$ M | 0.6 g $L^{-1}$ | 50 W LED lamp (⩾ 400) | 7 | - | 120 min/95% | 0.0290 $min^{-1}$ | 8 |
| Dy-doped-$SnO_2$ | Methylene blue | 5 mg $L^{-1}$ | | 100 W LED lamp (≥ 400) | 7 | - | 240 min/86% | 0.0375 $min^{-1}$ | 9 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0.3Dy-CN | Methylene blue | 20 mg $L^{-1}$ | 0.4 g $L^{-1}$ | 25 W LED lamp (≥ 400) | 7-11 | $Na_2SO_3$/0.5 mM | 10 min/95% | 0.0551 $min^{-1}$ | Our study |

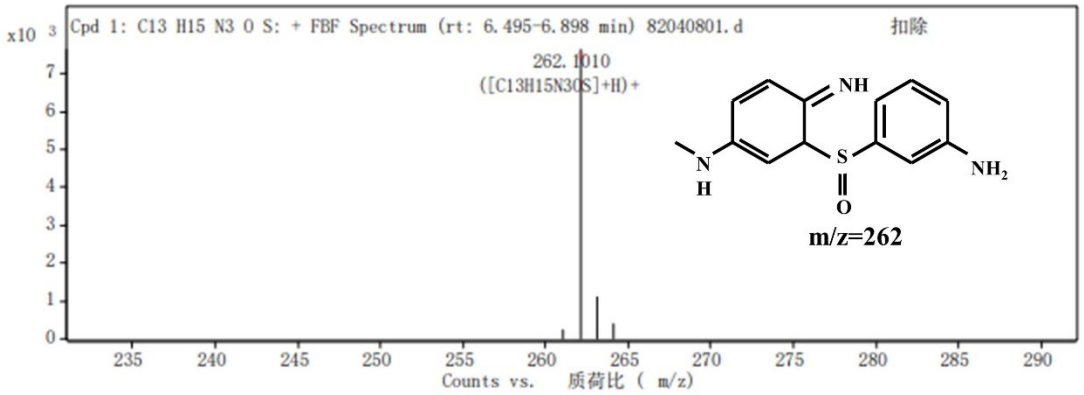
**Tab.S6 Band gap (Eg), relative conduction band ($E_{CB}$) and valence band ($E_{VB}$) of the as-prepared samples.**

| Samples | $E_g$/eV | $E_{VB}$/eV | $E_{CB}$/eV |
|---|---|---|---|
| g-$C_3N_4$ | 2.58 | 1.51 | -1.07 |
| 0.3Dy-CN | 2.41 | 1.425 | -0.985 |

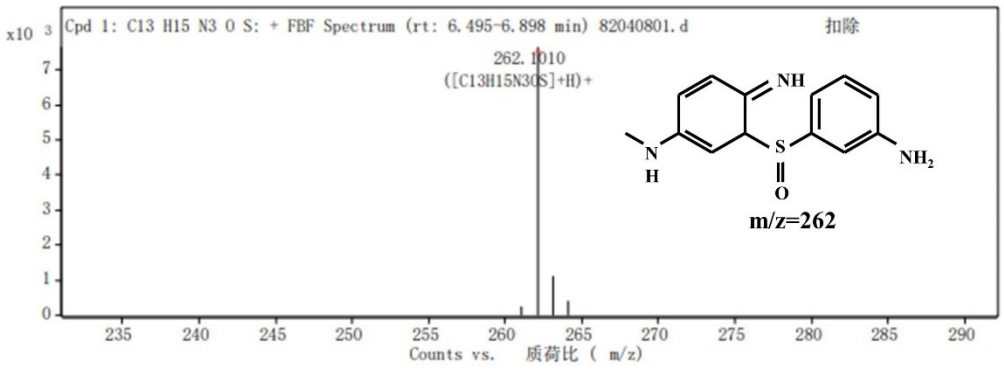
**Tab.S7. Intermediate products during MB degradation.**

| Compounds | Molecular formula | m/z | Proposed structure |
|---|---|---|---|
| MB | $C_{16}H_{18}N_3ClS$ | 284 |  |
| A | $C_{13}H_{15}N_3OS$ | 262 |  |
| B | $C_{14}H_{13}N_2O_2^-$ | 241 |  |
| C | $C_{12}H_{10}N_3S^+$ | 228 |  |
| D | $C_{12}H_7NS^+$ | 198 |  |
| E | $C_6H_8N_2O_3S$ | 188 |  |
| F | $C_4H_{10}O_3N_2$ | 149 |  |
| G | $C_6H_7NO_2$ | 125 |  |
| H | $C_4H_7O_3N$ | 117 |  |

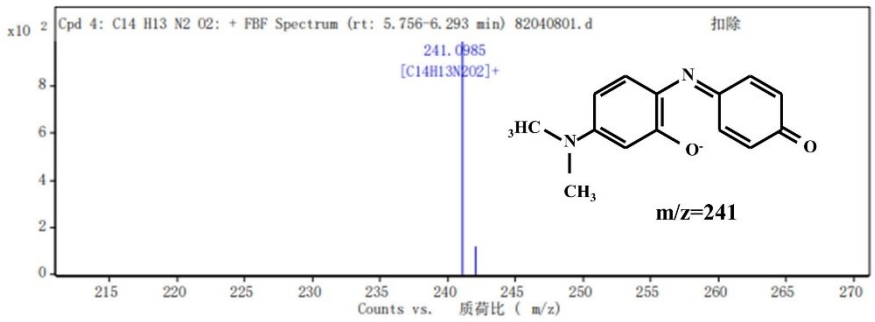
**(a)**


Cpd 1: C13 H15 N3 O S: + FBF Spectrum (rt: 6.495-6.898 min) 82040801.d
扣除
262.1010
([C13H15N3OS]+H)+
NH
S
NH2
N
H
O
m/z=262
Counts vs. 质荷比 ( m/z)

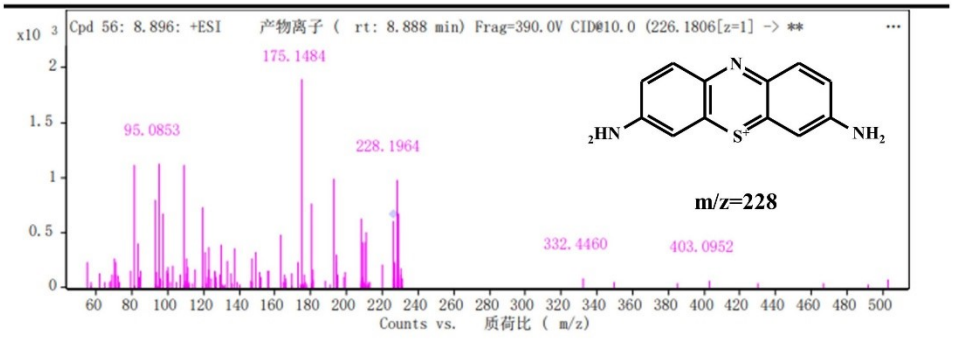
**(b)**


Cpd 1: C13 H15 N3 O S: + FBF Spectrum (rt: 6.495-6.898 min) 82040801.d
扣除
262.1010
([C13H15N3OS]+H)+
NH
S
NH2
N
H
O
m/z=262
Counts vs. 质荷比 ( m/z)

**(c)**


Cpd 4: C14 H13 N2 O2: + FBF Spectrum (rt: 5.756-6.293 min) 82040801.d
扣除
241.0985
[C14H13N2O2]+
N
3HC
N
CH3
O-
O
m/z=241
Counts vs. 质荷比 ( m/z)

**(d)**


Cpd 56: 8.896: +ESI 产物离子 ( rt: 8.888 min) Frag=390.0V CID@10.0 (226.1806[z=1] -> **
175.1484
95.0853
228.1964
332.4460
403.0952
N
2HN
S+
NH2
m/z=228
Counts vs. 质荷比 ( m/z)

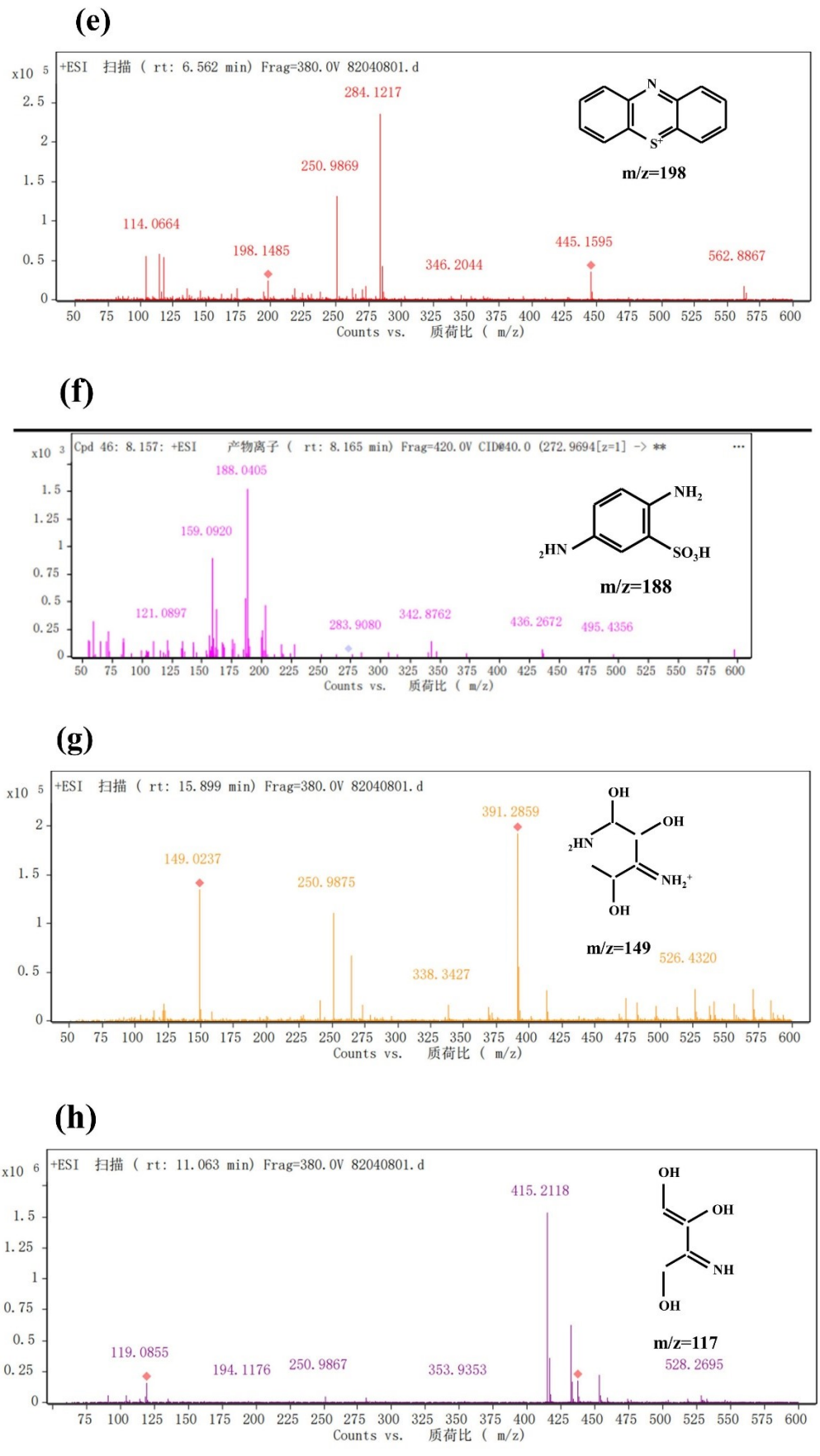



**Fig.S5 The mass spectrum of the intermediates of MB degradation**

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