Electronic Supplementary Information

Photophysical properties, singlet oxygen generation efficiency and cytotoxic effects of aloe emodin as a blue light photosensitizer for photodynamic therapy in dermatological treatment

I. Fluorescence quantum yield of AE

In the measurement, a relative spectrophotometric method was applied. R6G was used as the referencewith quantum yield of 0.93 in methanol (S1). The relationshipbetween Φ_F of AE and R6G luminescence was described by the following equation (S2):

$$\boldsymbol{\Phi}_{\mathrm{F}} = \boldsymbol{\Phi}_{\mathrm{F}}^{\mathrm{r}} \left(\frac{I}{A}\right) \left(\frac{A^{\mathrm{r}}}{I^{\mathrm{r}}}\right),\tag{E1}$$

where $\Phi_{\rm F}^{\rm r}$ and $\Phi_{\rm F}$ are the luminescence quantum yields of R6G and AE in methanol. $A^{\rm r}$ and A are the absorption of excitation light (473 nm laser) by R6G and AE, which is related to the concentrations and extinction coefficients. $I^{\rm r}$ and I are the integrated emission intensities of R6G and AE, respectively. To obtain the absorption (A) of the excitation light in Eq. (E1), the following equation was used:

$$A = \int I_{473} \left(\lambda \right) \times \left(1 - e^{-\varepsilon(\lambda)CL} \right) d\lambda, \qquad (E2)$$

where I_{473} (λ) is the normalized emission spectrum of the 473 nm laser, $\varepsilon(\lambda)$ is the absorption coefficient of each substance, *C* represents the concentration and *L* is the light pathlength in the cuvette.

Fig. S1 shows the normalized fluorescence spectra of AE and R6G under the

same excitation of 473 nm laser, the inset figure of which shows the amplified fluorescence spectrum of AE. *A* and *I* for R6G and AE can be obtained from Eq. (E2) and Fig. S1. Based on these results and fluorescence quantum yield of R6G (0.93), the fluorescence quantum yield of AE was calculated to be 0.021 ± 0.001 from Eq. (E1). The experimental conditions and calculated fluorescence quantum yield of AE in methanol are shown in Tab. S1. Φ (0.021) of AE fluorescence is high enough for application in spectroscopic analysis.



Fig. S1. The normalized fluorescence spectra of AE and R6G, inset figure: the amplified fluorescence spectrum of AE.

Photosensitizers	Concentrations (µM)	λ _{exc} (nm)	Ι	A(mW/cm²)	${oldsymbol{\varPhi}}_{\mathrm{F}}$
R6G	5	473	946650.7	1.44	0.93*
AE	60	473	49412.2	3.39	0.021

Table S1.Chemicals, concentrations, intensity integral *I*, absorption *A* and calculated Φ_{Δ} .

*Data from ref.S1.

II. Choosing of appropriate excitation light for the measurement of ${oldsymbol{\varPhi}}_{\Delta}$

To choose appropriate excitation light in the measurement of singlet oxygen quantum

yield of AE, typical UV-visible absorption spectra of DPBF, AE and RB were measured and shown in Fig. S2. It can be seen that there is a significant overlap between absorption spectra of AE and DPBF from 350 to 450 nm. Although laser centered at 430 nm is well matched with the absorption of AE, it causes photobleaching of DPBF. The absorption spectra of RB and AE have overlap from 460 to 480 nm while there is no absorption for DPBF in this spectral region. Therefore, the solid laser centered at 473 nm was used as the excitation light, emission spectrum of which is also shown in Fig. S2.



Fig. S2. Normalized absorption spectra of RB (black solid), AE (black dash), DPBF (black dot) as well as the emission spectrum (red solid) of the laser centered at 473 nm.

III. The photostability of DPBF

Fig. S3 shows the absorption spectra of DPBF (15 μ M) alone at different irradiation time by 473 nm laser. It can be seen that the absorption spectra of DPBF alone remained unchanged in 14 min under the irradiation of 473 nm laser.



Fig. S3. The absorption spectra of DPBF (15 $\mu M)$ alone at different irradiation time by 473 nm laser

IV. The measurement of singlet oxygen quantum yield for AE

A relative spectrophotometric method (S3, S4) was used for the measurement of Φ_{Δ} . based on Eq. (E3).

$$\frac{\boldsymbol{\Phi}_{\Delta}A}{k} = \frac{\boldsymbol{\Phi}_{\Delta}^{\mathrm{r}}A^{\mathrm{r}}}{k^{\mathrm{r}}},$$
 (E3)

where *k* is the degradation rate of the singlet oxygen trap DPBF; *A* represents the absorption of excitation light by each substance (S4), which is related to the concentrations and extinction coefficients. To obtain the absorption (*A*) of the excitation light in Eq. (E3), Eq. (E2) was used. Data needed in this analysis include: Φ_{Δ} of the reference reagent, the absorption of excitation light, and the photodegradation rates of singlet oxygen trap in mixtures with each photosensitizer. Three samples were prepared: DPBF 15 μ M; DPBF 15 μ M, RB 5 μ M; DPBF 15 μ M, AE 25 μ M. Each sample of 3 ml was put in a quartz cuvette of 1 cm length and irradiated with a solid state laser centered at 473 nm. The consumption of DPBF was monitored with UV-visible absorption spectra of DPBF at different irradiation times.

The degradation rate of DPBF (k) was determined according to the decrease of absorption peak at 410 nm with time.

To obtain the degradation rate of DPBF (k) in the mixture with AE under the irradiation of 473 nm laser, the absorption spectra of DPBF at different irradiation time in the mixture with AE were measured and shown in Fig. S3. The absorption spectra of DPBF (15 μ M) alone remained unchanged in 14 min as shown in Fig. S2. It can be seen from Fig. S4 that DPBF was consumed in the mixture with AE under the irradiation, which demonstrated the generation of singlet oxygen.



Fig. S4. The absorption spectra of DPBF (15 μ M) alone at different irradiation time by 473 nm laser.

Table S2. Chemicals, concentrations and calculated degradation rates k, absorption I_{abs} and Φ_{Δ} .

Photosensitizers	Concentrations (µM)	$\lambda_{ m exc}$ (nm)	k (min ⁻¹)	A (mW/cm ²)	${oldsymbol{\varPhi}}_{\Lambda}$
RB	5	473	0.083	2.73	0.79*
AE	25	473	0.028	1.28	0.57

*Data from ref. S5.

References

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