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Introduction

Triplet photosensitizers (PSs) have attracted much attention recently, due to the significance of these compounds in both fundamental photochemistry studies,^{1–3} as well as in applications in photocatalysis,^{4–6} photodynamic therapy (PDT),^{7,8} photopolymerization,^{9–13} and triplet–triplet annihilation-based upconversion.^{14–18}

Triplet PSs are crucial for these applications, especially concerning the photo absorptivity, intersystem crossing (ISC) and triplet state lifetimes, *etc.* Recently, we developed different series of triplet PSs based on different ISC mechanisms,^{1,2} for instance, those based on the heavy atom effect of transition metals or halogen atoms, the electron spin–spin interactions by introducing a stable radical in the molecular structures,

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We prepared a series of amino-substituted 9,10-anthraquinone (AQ) derivatives to study the photophysical properties, especially the intersystem crossing (ISC) efficiency and the triplet excited states. Monoamino-substituted AQ derivatives show red-shifted absorption bands centered at 509 nm, as compared to the chloro-AQ derivatives ($\lambda_{abs} = 340$ nm). Interestingly, attaching an extra amino substituents on the AQ chromophore, *i.e.* the diamino substituted AQ derivatives show decent ISC efficiency (singlet oxygen quantum yield, Φ_{Δ} , is up to 33.3%), whereas the monoamino-AQ derivatives show negligible Φ_{Δ} values. Nanosecond transient absorption spectra indicate the formation of a triplet excited state lifetime is attributed to the n- π^* character of the T₁ states of the diamino substituted AQ derivatives, which is supported by DFT computations. We show that the bisamino-substituted AQs can be used as efficient photoinitiators for photopolymerization effect. The mechanism is supposed to be hydrogen abstraction by the photoinitiators at triplet excited states. These results indicate that compounds showing efficient ISC and T₁ state with n- π^* character can be developed as efficient photoinitiators for radical polymerization of alkene monomers.

electron spin converters, twisted molecular structures, matching of the S_1/T_n (n > 1) states, or by the spin-orbit charge transfer ISC (SOCT-ISC). One major approach we used in the design of the above mentioned triplet PSs is using a visible light-harvesting chromophore in the molecular structure; note the molecular structures have to be designed in such a way that the ISC is efficient, otherwise the singlet excited state energy, directly produced upon photoexcitation, is unable to be transformed into the triplet excited energy.^{19,20} Moreover, a balanced absorptivity, absorption wavelength, ISC efficiency and triplet state lifetimes have to be achieved, although the effects to realize these properties are counter constructive to each other.

Concerning the above aspects, aminoanthraquinone is in particular of interest.²¹ These kinds of compounds have been used as disperse dyes in the traditional pigment industry,^{22–24} or as electron acceptors in photochemistry, or have been used as electron acceptors in photochemistry studies, as molecular probes,²⁵ and in photopolymerization,^{26–28} yet the principal photophysical properties of the anthraquinone derivatives were rarely studied.^{29,30} However, the photophysical properties of the compounds for their applications, thus, it is significant to study the photophysical properties of the compounds.



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Scheme 1 Synthesis of the compounds. (a) Ethanolamine, dry triethylamine, dry toluene, 120 °C, reflux 24 h, yield: 23.0%. (b) Similar to step (a), yield: 20.0%. (c) Butylamine, dry DMF, 100 °C, reflux 3 h, yield: 9.0% for AQ-NH-8-Cl, 15.8% for AQ-1,8-NH. (d) Similar to step (c), yield: 10.6% for AQ-NH-5-Cl, 15.8% for AQ-1,5-NH.

Previously, it was found that native AQ or chloro-substituted AQ shows absorption in the UV wavelength range,^{31,32} clearly this is unsuitable for application with visible light excitation. On the other hand, amino substituents were found to induce red-shifted absorption, and the triplet excited state of some monoamino-substituted AQ or 1,5-diamino AQ derivatives was studied,^{29,30} and it was found that the electronic configuration of the triplet state (T₁) is dependent on the substituents. The excited state properties of alkylamino 1,5- and 1,8-AQ were not studied in detail, thus, herein we prepared the above derivatives (Scheme 1), and the steady state and time-resolved transient spectra of the compounds were studied. A preliminary study of photopolymerization with the dialkylamino AQ compounds as initiators was also carried out.

Results and discussion

Molecular structure designing rationales

Previously, the 2-amino AQ derivatives were studied for their triplet state properties by using nanosecond transient absorption spectra,³³ yet 1-amino-substituted AQ was not studied in detail, although the ISC yield, ($\Phi_{\rm ISC} = 100\%$ in CCl₄), the triplet state absorption and lifetime were studied.²⁹

1,8-Diaminoanthraquinone ligands were prepared as the antenna for lanthanide complexes, but the triplet state property was not studied.³⁴ Previously, 1,8-diaminoanthraquinone derivatives were studied for their antitumor activity, but the triplet state property was not studied.²¹

All the compounds were prepared by the routine substitution reaction of chloroAQ (Scheme 1).^{21,34} The molecular structures were fully verified using ¹H NMR, and HR MS methods (see the Experimental section).

With 1,8- and 1,5-dichloro AQ as the starting materials, we introduced alkylamino substituents on the AQ chromophore (Scheme 1). Although 1,5-diamino AQ was studied for its triplet

state absorption and lifetimes,³⁰ it was found that the photophysical properties of the AQ derivatives can be affected by the substituents on the N atom.³¹

UV-vis absorption and fluorescence emission studies

The amino-substituted compounds show absorption bands centred at *ca.* 509 nm (Fig. 1). It is interesting that the monoamino- and diamino-substituted AQ derivatives show a similar absorption wavelength. For instance, **AQ-NH-8-Cl** gives absorption maxima at 509 nm, whereas compound **AQ-1,8-NH** gives similar absorption maxima at 524 nm. Compared with the absorption wavelength of 1amino anthraquinone, the absorption wavelength of 1-(ethylamino)anthraquinone shows a red shift, indicating that the introduction of the alkyl chain on the amino group will cause a red shift of the absorption wavelength. 1-(2-Aminoethylamino)anthraquinone and 1-(ethylamino) anthraquinone show the similar absorption wavelength, indicating that an extra amino group does not induce further red-shift.³¹ Previously, it was found that 1,4-diaminosubstituted AQ derivatives gave rise to a maximal absorption band centered at *ca.* 630 nm,²⁶ whereas the analogues with 1,5- and 1,8-diamino



Fig. 1 UV-vis absorption spectra of the compounds in methanol (MeOH), with $c = 1.0 \times 10^{-5}$ M at 20 °C.



Fig. 2 (a) Fluorescence emission spectra of compounds in cyclohexane (CHX). (b) Fluorescence emission spectra of **AQ-1,8-NH** in different solvents. Optically matched solutions were used, with A = 0.1 at $\lambda_{ex} = 500$ nm, at 20 °C.

substituents gave rise to maximal absorption at *ca.* 524 nm. In comparison, the introduction of an amino group on naphthalimide (NI) does cause a red shift of the absorption wavelength. It is interesting that the mono-amino and diamino-substituted NI derivatives show a similar absorption wavelength, which is similar to that of the above-mentioned amino-substituted AQ compounds.^{35,36}

The red-shifting of the absorption wavelengths of the aminosubstituted AQ and NI chromophores can be attributed to the intermolecular charge transfer (ICT) effect. It should be noted that for the mono- and bis- amino-substituted AQ compounds studied herein, the compounds show similar maximal absorption wavelengths, which indicates that the ICT effect is not additive or synergetic.³⁷

In order to study the S_1 excited state properties, the fluorescence of the compounds was studied (Fig. 2). All the compounds show an emission band centred at *ca.* 580 nm (Fig. 2a), either with mono- or diamino-substituents. Interestingly, for the diamino-AQ derivatives, the emission bands are more structured. The fluorescence emission wavelengths are similar to the scenario of the UV-vis absorption character of the compounds (Fig. 1).

In order to study the ICT character of the emissive S_1 state of the compounds, the fluorescence of **AQ-1,8-NH** in solvents with different polarity was studied (Fig. 2). **AQ-1,8-NH** shows much red-shifted and weaker emission bands in polar solvents as those in non-polar solvents, and the same pattern was observed in the other five anthraquinone amino derivatives (Fig. S13 and S14, ESI†). We attributed the emission of **AQ-1,8-NH** to an S_1 state with ICT character, especially in polar solvents. This is similar to amino-substituted NI, in which the luminescence of mono-substituted NI derivatives reduced and the wavelength is redshifted in large polar solvents.³⁶

Electrochemical properties of the compounds

In order to study the redox potentials of the compounds, the cyclic voltammetry graphs of the compounds were recorded (Fig. 3). For AQ-1,5-Cl₂, a reversible reduction wave at -1.30 V was observed, and a similar reduction potential was observed for AQ-1,8-Cl₂. However, no oxidation wave was observed in the potential window applied in the studies (Table 2). For all the



Fig. 3 Cyclic voltammogram of (a) AQ-1,5-Cl₂, AQ-NH-OH-5-Cl, AQ-NH-5-Cl and AQ-1,5-NH and (b) AQ-1,8-Cl₂, AQ-NH-OH-8-Cl, AQ-NH-8-Cl and AQ-1,8-NH in deaerated DCM containing 0.10 M Bu₄NPF₆ as the supporting electrode and with the Ag/AgNO₃ reference electrode. Scan rate: 100 mV s⁻¹. $c = 1.0 \times 10^{-3}$ M. Ferrocene (Fc) was used as the internal reference at 20 °C.

amino-substituted AQ derivatives, anodically shifted reduction potentials indicate that the amino-substituted AQ derivatives are more difficult to be reduced because of the attachment of the electron-donating amino group. For the diamino-substituted AQ derivatives, the compounds have slightly more negative reduction potentials, for instance, the E_{Red} values of **AQ-1,5-NH** and **AQ-1,8-NH** are -1.55 V and -1.52 V (*vs.* Fc/Fc⁺), respectively. This is in agreement with the similar UV-vis absorption wavelengths of the mono- and diamino-substituted AQ derivatives. Slightly lower oxidation potentials were observed for the diamino-substituted AQ derivatives, indicating their stronger electron donating ability. Moreover, with molecular orbital analysis (see DFT computation), we propose that the oxidation of the amino AQ derivatives is not due to the amino moiety; to a large extent, it is due to that the amino-AQ derivative molecular structure as a whole unit.



Fig. 4 Nanosecond transient absorption spectra of (a) **AQ-1,5-NH** and (b) **AQ-1,8-NH** in deaerated TOL. The corresponding decay traces monitored at 450 nm are presented in (c) **AQ-1,5-NH** and (d) **AQ-1,8-NH**, respectively. $c = 5.0 \times 10^{-5}$ M, $\lambda_{ex} = 506$ nm, at 20 °C.

Nanosecond transient absorption spectra

In order to study the triplet excited states of the compounds, we measured the nanosecond transient absorption (ns-TA) spectra (Fig. 4). We studied the diamino-substituted AQ, i.e. AQ-1,5-NH and AQ-1,8-NH, because other compounds show negligible singlet oxygen photosensitizing ability (Table 1). For AQ-1,5-NH, excited state absorption (ESA) bands centred at 340 nm and 460 nm were observed, and a ground state bleaching (GSB) band centred at 530 nm was also observed (Fig. 4a). The triplet state lifetime was determined as 2.4 µs (Fig. 4c). Similar results were observed for AQ-1,8-NH, and the triplet state lifetime was determined as 2.7 µs. Note that these triplet state lifetimes are much shorter than those of the organic chromophores. It was proposed that the $n-\pi^*$ character of the T_1 state of the AQ derivatives contributes to the unusually short T₁ state lifetimes of the AQ derivatives. Triplet lifetime of 1-chloroanthraquinone in toluene is 17.9 µs; for 1,5-dichloroanthraquinone in toluene, the triplet state lifetime is 2.4 µs, on the other hand, the triplet lifetime of 1,8-dichloroanthraquinone in toluene is 3.8 µs.³⁸ The triplet state lifetime of other related compounds like 1,5diaminoanthraquinone is $\tau_{\rm T}$ = 3.4 µs in toluene, and in 1-bromoanthraquinone and 2-bromoanthraquinone, it is $\tau_{\rm T}$ = 5 µs in benzene.³⁰ Similar results were observed for 2-(2-ethyl)hexylamidoanthraquinone ($\tau_{\rm T}$ = 1.37 μs in acetonitrile), 2-(octadecyl-8ene)amidoanthraquinone ($\tau_{\rm T}$ = 2.07 µs in acetonitrile), 2-ethoxyamidoanthraquinone ($\tau_{\rm T}$ = 2.64 µs in acetonitrile),³³ and 1-acetylaminoanthraquinone ($\tau_{\rm T}$ = 3.5 µs in toluene).²⁹

DFT computation

The molecular orbitals were obtained (Fig. 5). For the HOMO of the compounds, we found that the diamino-substituted derivatives, such as AQ-1,5-NH and AQ-1,8-NH, are symmetrically distributed on the molecular frameworks. On the other hand,

Table 1 Photophysical parameters of the compounds ^a						
Compounds	Solvents	$\lambda_{abs}{}^a/nm$	ε^{b}	$\lambda_{\rm em}{}^{c}/{\rm nm}$	$\Phi_{\Delta}{}^d$ /%	
AQ-NH-OH-5-Cl	CHX	492	0.7	586	1.1	
-	DCM	506	0.7	615	1.1	
	ACN	505	0.7	640	0.5	
AQ-NH-OH-8-Cl	CHX	490	0.5	583	1.0	
	DCM	506	0.5	615	1.1	
	ACN	505	0.7	640	0.5	
AQ-NH- 5-Cl	CHX	500	0.8	582	0.9	
	DCM	514	0.8	628	1.0	
	ACN	508	0.8	639	0.8	
AQ-NH- 8-Cl	CHX	500	0.7	585	0.9	
	DCM	513	0.8	628	1.0	
	ACN	509	0.7	639	0.8	
AQ-1,5-NH	CHX	506	1.7	574	20.9	
	DCM	525	1.6	604	33.3	
	ACN	519	1.6	617	19.6	
AQ-1,8-NH	CHX	506	1.5	571	24.5	
	DCM	522	1.5	605	30.9	
	ACN	520	1.4	617	17.8	

^{*a*} Maximal UV-vis absorption wavelength, $c = 1.0 \times 10^{-5}$ M at 20 °C. ^{*b*} Molar absorption coefficient at absorption wavelength, ϵ : 10^4 M⁻¹ cm⁻¹. ^{*c*} Fluorescence emission wavelength, $\lambda_{ex} = 500$ nm. ^{*d*} Singlet oxygen (¹O₂) quantum yield with 2,6-didiiodo-Bodipy as the standard ($\Phi_{\Delta} = 87\%$ in dichloromethane (DCM)) and $\lambda_{ex} = 500$ nm.

 Table 2
 Electrochemical redox potentials of the compounds^a

	$E_{\rm OX}/{\rm V}$	$E_{\rm RED}/{ m V}$
AQ-1,5-Cl ₂	b	-1.30, -1.91
AQ-1,8-Cl ₂	b	-1.30, -1.91
AQ-NH-OH-5-Cl	0.91	-1.40, -1.84
AQ-NH-OH-8-Cl	0.91	-1.40, -1.84
AQ-NH- 5-Cl	0.93	-1.43, -1.99
AQ-NH- 8-Cl	0.94	-1.43, -2.01
AQ-1,5-NH	0.77	-1.55, -2.07
AQ-1,8-NH	0.78	-1.52, -2.07

 a Cyclic voltammetry in $\rm N_2$ -saturated solvents DCM containing 0.10 M Bu_4NPF_6. The Pt electrode as the counter electrode, glassy carbon electrode as the working electrode, ferrocene (Fc/Fc⁺) as the internal reference (set as 0 V in the cyclic voltammograms), and Ag/AgNO_3 couple as the reference electrode. b Not observed.

the distribution of the electron density of the HOMO of the mono-amino substituted AQ derivatives is uneven, it is mole localized on the AQ part at which amino is present.

Interestingly, this trend was not observed for the LUMOs. The energy of the calculated MOs agrees well with the electrochemical studies. For instance, the HOMO energy of the monoamino AQ derivatives is generally lower than that of the diamino-substituted AQ derivatives, such as **AQ-1,5-NH** and **AQ-1,8-NH** by *ca.* 0.4 eV. This trend corresponds to the lower oxidation potentials observed in the electrochemistry studies. A similar trend was observed for the LUMOs.

The triplet state spin density surfaces were studied (Fig. 6). For both **AQ-1,5-NH** and **AQ-1,8-NH**, the oxygen and nitrogen atom contribute significantly to the T_1 state, indicating the T_1 state has $n-\pi^*$ character. The energy of the electronic ground state and excited state were examined (Fig. 7). For both **AQ-1,5-NH**, and **AQ-1,8-NH**, there is slightly lower T_2 state than the S_1 state, as compared to other compounds. This could be the reason for the efficient ISC of **AQ-1,5-NH** and **AQ-1,8-NH**.

Photobleaching and photopolymerization

In order to study the application potentials of the compounds, especially those showing efficient ISC, *i.e.* **AQ-1,5-NH** and **AQ-1,8-NH**, we made a preliminary investigation of photopolymerization of alkene monomers with the AQ derivatives as photoinitiators. We selected diphenyliodonium hexafluorophosphate (DPI) as a coinitiator.^{26,39}

The supposed photoinitiation mechanism is outlined in Fig. 8.⁴⁰⁻⁴² Upon photoexcitation, the AQ derivatives act as electron donors, such as **AQ-1,8-NH**, $*E_{\text{ox}} = E_{\text{ox}} - E_{00} = -1.02 \text{ V} (E_{00} \text{ is the triplet excited state energy}), whereas the diaryliodonium salts act as electron acceptors (<math>E_{\text{Red}} = -1.0 \text{ V}$, *vs.* Fc/Fc⁺). Phenyl radicals will be produced, as a result of the intermolecular electron transfer (shown in Fig. 9) and photopolymerization of the monomers is initiated.

Fig. 10 shows anthraquinone amino derivatives alone can induce photopolymerization of pentaerythritol (PETA). Moreover, PETA can undergo photopolymerization in the presence of triethylamine (TEA) or DPI, and the combination of photosensitizers and TEA or DPI can promote the polymerization of PETA (Fig. S18 and S19, ESI[†]).



Fig. 5 Selected frontier molecular orbitals of compounds calculated by DFT (B3LYP/6-31G (d)) in a vacuum with Gaussian 09, isovalue = 0.02, based on the optimized ground state geometry. The energy levels of the orbits are presented (in eV).



Fig. 6 Electron spin density surfaces of the triplet state of (a) AQ-1,5-NH and (b) AQ-1,8-NH calculated by DFT (B3LYP/6-31G(d)) in gas phase with Gaussian 09. Isovalue = 0.0004.

In order to confirm the above postulated mechanisms, firstly we did the steady state photolysis of the mixtures of the potential photoinitiators and the coinitiator DPI (Fig. 9).²⁶

The results show that significant photobleaching was observed for the two AQ derivatives showing efficient ISC, *i.e.* **AQ-1,5-NH** and **AQ-1,8-NH**. On the other hand, in the absence of DPI, no bleaching was observed for the photoinitiators alone upon photoirradiation (Fig. S16, ESI[†]). These results show that there is an electron transfer between the photoinitiator and coinitiator DPI. For those AQ derivatives that show poor ISC, the bleaching in the presence of DPI is much weaker.

Next, we studied the photopolymerization of a typical monomer of pentaerythritol triacrylate (PETA). We found that with the photoinitiator/coinitiator DPI, efficient photopolymerization was observed (Fig. 11). The formulations of the photoinitiating system are similar to those reported in the previous literatures.^{26,28} On the other hand, for those AQ derivatives showing poor ISC, the photopolymerization needs much longer photoirradiation time. This result infers that the ISC capability of the AQ compounds is critical for initiating photopolymerization. Interestingly, we found that **AQ-1,5-NH** and **AQ-1,8-NH** alone are efficient photoinitiators for photopolymerization, in the absence of DPI or TEA. Considering the $n-\pi^*$ character of the T_1 states of these compounds, we suppose that the initiating mechanism under this circumstance could be hydrogen atom abstraction by the photoinitiators at triplet excited state, and the radical formed by the H donor may initiate the subsequent polymerization. This is the typical initiating mechanism of the conventional photoinitiators such as benzophenone, and ketocoumarin.⁴³ These results indicate that **AQ-1,5-NH** and **AQ-1,8-NH** can be developed as new, efficient photoinitiators for the photopolymerization of olefin monomers.

Conclusion

In summary, we prepared a series of 9,10-anthraquinone (AQ) derivatives, with different chloride and alkylamino substituents attached. We found that the amino-substituted AQ derivatives give rise to absorption bands centred at *ca*. 509 nm, which are red shifted by *ca*. 169 nm as compared to those of chloro AQs. We found that addition of an extra amino group does not induce a further red-shift of the absorption band. The amino-substituted AQ derivatives show much red-shifted and weaker emission bands in polar solvents as those in non-polar solvents, indicating the intramolecular charge transfer character of the emissive S_1 state. The intersystem crossing (ISC) efficiency of the bisamino-substituted AQ derivatives is moderate

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Fig. 7 States energy level diagram of (a) AQ-1,5-NH, (b) AQ-1,8-NH, (c) AQ-NH-5-Cl, (d) AQ-NH-8-Cl, (e) AQ-NH-OH-5-Cl and (f) AQ-NH-OH-8-Cl after TD-DFT calculation at the B3LYP/6-31G(d) level using Gaussian 09.



Fig. 8 Photochemical mechanisms of the generation of radicals for the Ps/DPI system upon photoexcitation.



(singlet oxygen quantum yields are 17-33%), whereas the ISC of the mono amino AQ derivatives is negligible. Nanosecond transient absorption spectra confirmed the production of triplet excited states for the bisamino AQ derivatives, and the triplet state lifetimes were determined to be 2.4-2.7 µs, This unusually short triplet excited state lifetime is attributed to the $n-\pi^*$ character of the T₁ states of two compounds, and this is supported by the theoretical computation of the compounds. Preliminary studies of photopolymerization with the AQ derivatives as photoinitiators show that the bisamino AQ derivatives are efficient photoinitiators, even in the absence of typical coinitiators such as diphenyliodonium hexafluorophosphate (DPI) and triethylamine (TEA). The initiating mechanism is supposed to be hydrogen atom abstraction of the ³AQ state, which is typical for photoinitiators with the T_1 state of $n-\pi^*$ character. In the presence of DPI, intermolecular electron transfer and phenyl radical is produced, which initiates the radical polymerization. These highly efficient bisaminoanthraquinone-based photoinitiating systems will be useful in lithography and 3D printing.

Fig. 9 Photobleaching of the compounds in the presence of electron acceptors upon white light irradiation, monitored by the evolution of the absorbance of **AQ-NH-OH-5-Cl/DPI**, **AQ-NH-OH-8-Cl/DPI**, **AQ-NH-5-Cl/DPI**, **AQ-NH-8-Cl/DPI**, **AQ-NH-8-Cl/DPI**, **AQ-1,8-NH/DPI** at 520 nm vs. irradiation time upon exposure to a 35 W xenon lamp (unfiltered white light intensity: 30 mW cm⁻²) in deaerated acetonitrile, *c* [photosensitizer] = 5.0×10^{-5} M, *c* [DPI] = 30 mM.

Experimental section

General method

All the chemicals used in synthesis are analytically pure and were used as received without purification. UV-vis absorption spectra were recorded on a UV-2550 spectrophotometer (Shimadzu Ltd, Japan). Fluorescence emission spectra were recorded using the FS5 spectrofluorometer (Edinburgh instruments Ltd, UK).

Nanosecond transient absorption spectroscopy

The nanosecond transient absorption spectra (ns-TA) were recorded on a LP920 laser flash-photolysis spectrometer (Edinburgh Instruments, Ltd, UK). All samples were studied under N_2 conditions. The sample solution was purged with N_2 for 15 min



Fig. 10 The photopolymerization of PETA under N₂ before irradiation using a 35 W xenon lamp (unfiltered white light intensity: 200 mW cm⁻²) with different photoinitiators. (a), (e), (i), (m), (q) and (u) In the absence of the photosensitizer, only PETA. In the presence of (c) AQ-1,5-NH, (g) AQ-1,8-NH, (k) AQ-NH-5-Cl, (o) AQ-NH-8-Cl, (s) AQ-NH-OH-5-Cl and (w) AQ-NH-OH-8-Cl. The photopolymerization of PETA after irradiation using a 35 W xenon lamp (unfiltered white light intensity: 200 mW cm⁻²). (b), (f), (j), (n), (r) and (v) In the absence of the photosensitizer, only PETA. In the presence of (d) AQ-1,5-NH, (h) AQ-1,8-NH, (l) AQ-NH-5-Cl, (p) AQ-NH-8-Cl, (t) AQ-NH-OH-5-Cl and (x) AQ-NH-OH-8-Cl. Photosensitizer: 0.3 wt%. The photopolymerization activity is shown in the gelation of liquid blends upon photoirradiation.

and the cuvette was sealed for measurement. The sample was excited by a 506 nm nanosecond pulsed laser. The data (kinetic decay traces and spectra) were analyzed using L900 software.

Cyclic voltammetry

Cyclic voltammetry curves were recorded on a CHI610D electrochemical workstation (CHI Inc., Shanghai China), in N2-purged DCM solution containing 0.10 M Bu₄NPF₆ as the supporting electrolyte, platinum as the counter electrode, the glassy carbon electrode as the working electrode and Ag/AgNO₃ (0.1 M in ACN) couple as the reference electrode. DCM was used as the solvent and ferrocene was used as an internal reference.

Computations

The conformation of the ground state (S_0) was calculated using density functional theory (DFT) with the B3LYP functional and 6-31G(d) basis set. The energy of singlet or triplet states was computed using time-dependent (TD)-DFT at B3LYP/6-31G(d)



Fig. 11 Photopolymerization's time of PETA under N₂ in the presence of anthraquinone derivative-based PISs (photosensitizer: 0.3 wt%; DPI or TEA: 6.2 wt%) obtained upon exposure to a 35 W xenon lamp, unfiltered white light intensity = 200 mW cm^{-2} .

levels based on the optimal ground-state geometry. All these computations were performed using Gaussian 09W software.44

Synthesis of AQ-NH-OH-8-Cl. Under a N₂ atmosphere, 1,8dichloroanthraquinone (2.0 g, 7.2 mmol), ethanolamine (2.0 g, 32.0 mmol), and anhydrous triethylamine (4.5 mL, 32.0 mmol) were mixed in dry toluene (15 mL). The mixture was refluxed for 24 h at 120 °C. After cooling, the reaction mixture was mixed with crushed ice. The precipitate was collected by filtration, washed thoroughly with water and further purified by column chromatography (silica gel, DCM: MeOH = 50:1, v/v). AQ-NH-OH-8-Cl was obtained as a red solid (500 mg, yield 23.0%). M.p.: 193.0–194.0 °C. ¹H NMR (400 MHz, DMSO- d_6): δ 9.70 (s, 1H), 8.25 (dd, J = 7.3, 1.7 Hz, 1H), 7.92–7.80 (m, 2H), 7.66 (dd, J = 8.5, 7.5 Hz, 1H), 7.38 (d, J = 6.8 Hz, 1H), 7.27 (d, J = 8.6 Hz, 1H), 4.95 (s, 1H), 3.70 (t, J = 5.5 Hz, 2H), 3.45 (dd, J = 10.7, 5.3 Hz, 2H). HRMS (ESI): calcd for $C_{16}H_{12}ClNO_3 [M + H^+]$, m/z 302.0546; found m/z 302.0574; calcd for $C_{16}H_{12}ClNO_3$ [M + Na⁺], m/z324.0404; found *m*/*z* 324.0392.

Synthesis of AQ-NH-OH-5-Cl. The synthesis of AQ-NH-OH-5-Cl was similar to AQ-NH-OH-8-Cl. The crude product was purified by column chromatography (silica gel, DCM: MeOH = 50:1, v/v). AQ-NH-OH-5-Cl was obtained as a red solid (350 mg, yield 20.0%). M.p.: 196.0–197.0 $^\circ \mathrm{C}.$ $^1\mathrm{H}$ NMR (400 MHz, DMSO- d_6) δ 9.71 (s, 1H), 8.25 (dd, J = 7.3, 1.6 Hz, 1H), 7.91–7.80 (m, 2H), 7.66 (dd, J = 8.5, 7.5 Hz, 1H), 7.38 (d, J =7.0 Hz, 1H), 7.27 (d, J = 8.6 Hz, 1H), 4.99 (s, 1H), 3.70 (t, J = 5.5 Hz, 2H), 3.45 (dd, J = 10.4, 5.2 Hz, 2H). HRMS (ESI): calcd for $C_{16}H_{12}ClNO_3 [M + H^+], m/z 302.0546; found m/z 302.0576; calcd$ for $C_{16}H_{12}ClNO_3$ [M + Na⁺], m/z 324.0404; found m/z 324.0394.

Synthesis of AQ-1,8-NH and AQ-NH-8-Cl. Under a N2 atmosphere, 1,8-dichloroanthraquinone (1.0 g, 3.6 mmol) and butylamine (0.6 g, 8.0 mmol) were mixed in dry DMF (20 mL). The mixture was refluxed for 3 h at 100 °C. After cooling, the reaction mixture was mixed with crushed ice. The precipitation was collected by filtration and washed with plenty of water. The crude

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product was purified by column chromatography (silica gel, AcOEt: PE = 1:11, v/v). **AQ-1,8-NH** was obtained as a purple solid (200 mg, yield 15.8%). M.p.: 139.0–140.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.70 (s, 2H), 7.60 (dd, *J* = 7.4, 1.1 Hz, 2H), 7.56–7.51 (m, 2H), 7.06 (dd, *J* = 8.4, 0.9 Hz, 2H), 3.33 (t, *J* = 7.1 Hz, 4H), 1.81–1.70 (m, 4H), 1.52 (dd, *J* = 14.6, 7.3 Hz, 4H), 1.00 (t, *J* = 7.3 Hz, 6H). HRMS (ESI): calcd for C₂₂H₂₆N₂O₂ [M + H⁺], *m/z* 351.2067; found *m/z* 351.2070. **AQ-NH-8-Cl** was obtained as a red solid (100 mg, yield 9.0%). M.p.: 112.0–113.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.62 (s, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.56 (s, 2H), 7.10–7.04 (m, 1H), 3.35 (t, *J* = 6.9 Hz, 2H), 1.76 (dd, *J* = 7.3 Hz, 2H), 1.53 (dd, *J* = 14.8, 7.2 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). HRMS (ESI): calcd for C₁₈H₁₆ClNO₂ [M + H⁺], *m/z* 314.0942; found *m/z* 314.0945.

Synthesis of AQ-1,5-NH and AQ-NH-5-Cl. Under a N2 atmosphere, 1,5-dichloroanthraquinone (1.0 g, 3.6 mmol) and butylamine (0.6 g, 8.0 mmol) were mixed in dry DMF (20 mL). The mixture was refluxed for 3 h at 100 °C. After cooling, the reaction mixture was mixed with crushed ice. The precipitation was collected by filtration and washed with plenty of water. The crude product was purified by column chromatography (silica gel, AcOEt: PE = 1:11, v/v). AQ-1,5-NH was obtained as a purple solid (200 mg, yield 15.8%). M.p.: 146.0-147.0 °C. ¹H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 2H), 7.59–7.49 (m, 4H), 7.01 (d, J = 8.3 Hz, 2H), 3.32 (t, J = 6.9 Hz, 4H), 1.80-1.70 (m, 4H), 1.58-1.46 (m, 4H), 1.00 (t, I = 7.3 Hz, 6H). HRMS (ESI): calcd for $C_{22}H_{26}N_2O_2$ [M + H⁺], m/z351.2067; found m/z 351.2062. AQ-NH-5-Cl was obtained as a red solid (120 mg, yield 10.6%). M.p.: 115.0-116.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 1H), 8.30 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.58 (d, J = 4.3 Hz, 2H), 7.15–7.07 (m, 1H), 3.35 (t, J = 7.0 Hz, 2H), 1.84–1.71 (m, 2H), 1.59– 1.45 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H). HRMS (ESI): calcd for $C_{18}H_{16}ClNO_2 [M + H^+], m/z 314.0942; found m/z 314.0945.$

Photobleaching experiments

In the experiment, two groups of controlled experiments were conducted. In the first group, the aminoanthraquinone compound ($c = 5.0 \times 10^{-5}$ M) was added into 3 mL of deaerated acetonitrile to record its absorption spectra upon photoirradiation. A xenon lamp (unfiltered white light intensity: 30 mW cm⁻²) was used to irradiate the mixture for a certain time, and then the absorption spectra were recorded to prove whether the compound alone has a photobleaching effect. The second experiment: the aminoanthraquinone compound ($c = 5.0 \times 10^{-5}$ M) and DPI (30 mM) were added into 3 mL of deaerated acetonitrile to record the absorption spectra, and then a xenon lamp (unfiltered white light intensity: 30 mW cm^{-2}) is used to irradiate the mixture. After irradiating the mixture for a certain time, the absorption curve was measured to prove that photobleaching could occur in the aminoanthraquinone compound in the presence of coinitiator DPI.

Photopolymerization

In the experiment, four controlled experiments were conducted. Monomer PETA (1.5 g); PETA (1.5 g) and photosensitizer (4.0 mg); PETA (1.5 g) and DPI or TEA (100 mg); PETA (1.5 g), DPI or TEA (100 mg) and photosensitizer (4.0 mg) were added into deaerated acetonitrile (100 mg), respectively. Then, under the unfiltered white light irradiation of a xenon lamp (unfiltered white light intensity: 200 mW cm⁻²), the time required for the solidification of the fluid mixture was recorded as the time required for photopolymerization.

Author contributions

R. W. and H. C. conducted the experiments, analysed the data and wrote part of the manuscript. J. Z. conceived the research, supervised the research and finalized the manuscript; F. Y. designed some of the compounds, analysed part of the photophysical data and wrote parts of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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