Thioxanthone Hydroquinone-*O,O′*-diacetic Acid: Photoinitiator or Photostabilizer?

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Ⓢ *Supporting Information*

ABSTRACT: A photoinitiator for free-radical polymerization based on a thioxanthone chromophore containing two acetic acid functions was synthesized and characterized. Photophysical studies such as fluorescence, phosphorescence, and laser flash photolysis in addition to photopolymerization of acrylates were performed to elucidate the radical generation mechanism involving intramolecular electron transfer from the triplet state followed by decarboxylation. We found that the position of the acetic acid substituent is critical for the photoreactivity. In most solvents and acrylic monomers, if the acetic acid functionality is at the 1-position, the singlet excited states are deactivated rapidly before electron transfer can occur, resulting in negligible photoreactivity. The excited-state deactivation probably involves intramolecular H-bonding deactivation. The intramolecular H-bonding is disrupted by solvents that support intermolecular H-bonding, such as DMF and DMSO, leading to efficient intramolecular photoreaction.
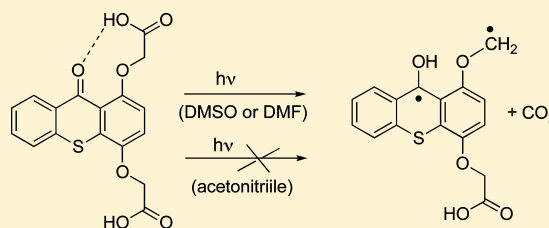
INTRODUCTION

Photoinitiated free-radical polymerization is a widely used technology that finds many industrial applications for coatings.[1−3] An important component in these coating formulations is the photoinitiator, which generates free radicals upon photolysis.[4] Among the many commercially used photoinitiators, thioxanthone (TX) derivatives have the advantage of excellent light absorption characteristics with molar absorptivities of ~5000 M^{-1} cm^{-1} in the 350−400 nm spectral region. Most TX derivatives generate the initiating free radical by reaction of the TX triplet state (generated by photoexcitation) and a coinitiator. We recently showed that an acetic acid derivative of TX (TX-Ma) can generate free radicals without the need of a coinitiator and proposed a decarboxylation mechanism initiated by intermolecular electron transfer from the triplet state (eq 1).[5,6] We also showed
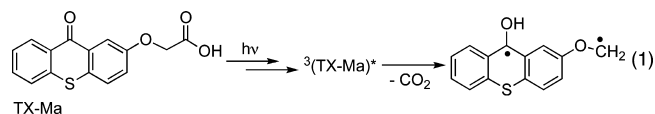
that the efficiency of this photoinitiator can be increased by incorporating a second acetic acid substituent (TX-Ct in Chart 1).[5] Here we report on the importance of the positions of the acetic acid substituents on the TX phenyl rings. We show that changing the substitution from the 2-position (in TX-Ct) to the 1-position (in TX-Hq) switches off the photoreactivity in most solvents.

RESULTS AND DISCUSSION

The absorption spectra of TX-Hq and TX-Ct are shown in Figure 1. These two TX derivatives show similar absorbance

Chart 1. Structures of TX Derivatives Investigated in This Study
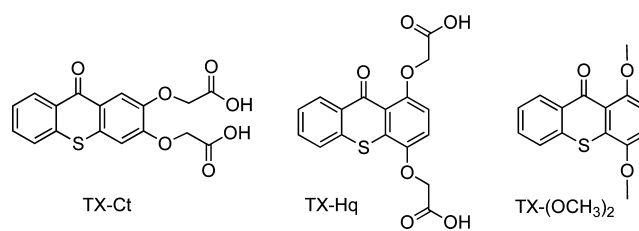
with high molar absorptivities between 350 and 400 nm. However, TX-Hq shows a slight bathochromic shift relative to TX-Ct, which should make TX-Hq attractive as photoinitiator for applications of pigmented formulations.

Photopolymerization experiments were performed using photo-differential scanning calorimetry (photo-DSC) and isobornyl acrylate as the monomer. The experiments were performed in the presence of a small amount of solvent (15% acetonitrile or DMF) (Figure 2). Using TX-Ct as the initiator, good conversions of acrylate monomer into polymer were observed during photolysis. Surprisingly, when TX-Hq was used as the photoinitiator, polymerization was observed only in the presence of DMF, and no polymerization in the presence of acetonitrile was detectable. The lack of polymerization in the presence of acetonitrile was surprising because the light absorption properties of the two initiators in the two solvents are
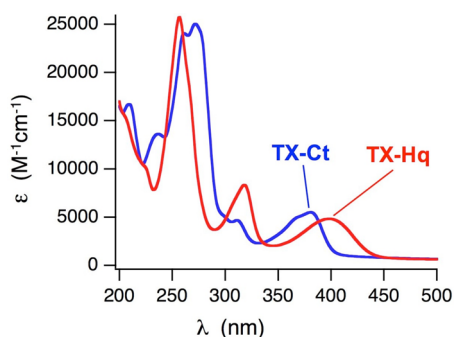
Figure 1. Absorbance spectra of TX-Hq (red) and TX-Ct (blue) in acetonitrile solution.
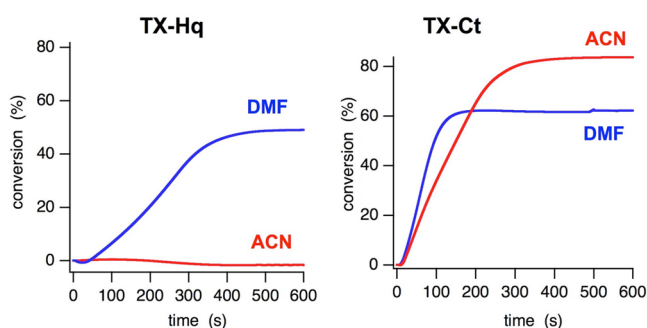

Figure 2. Conversion of monomers to polymer vs photolysis time as measured by photo-DSC. Polymerization of isobornyl acrylate using (left) TX-Ct or (right) TX-Hq (0.1% w/w) in the presence of acetonitrile (ACN) (15%, red lines) or DMF (15%, blue lines). Light intensity: 60 mW/cm^2.

similar. In addition, acetonitrile is considered to be an inert solvent in reactions involving radicals.

To investigate the cause of the different polymerization efficiencies for the two TX derivatives, their photophysical properties were measured. Photoexcitation generates singlet excited states, which are conveniently studied by fluorescence spectroscopy. In addition, a TX-Hq derivative without the photolabile acetic acid functionality [TX-(OCH$_3$)$_2$; Chart 1] was investigated. Figure 3 shows the fluorescence spectrum of
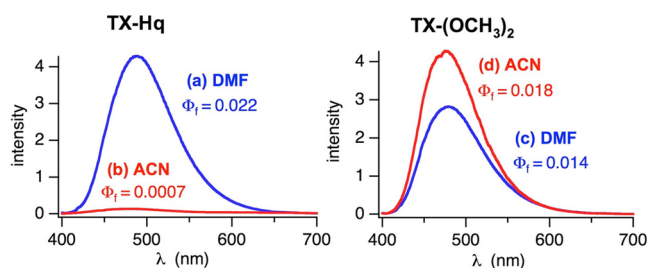

Figure 3. Fluorescence spectra of TX-Hq and TX-(OCH$_3$)$_2$ in acetonitrile (ACN) and DMF solutions.

TX-Hq. The fluorescence of TX-Ct was characterized previously.[5] Both TX derivatives exhibit weak fluorescence with quantum yields below 0.1 (Figure 3). The low fluorescence quantum yields suggest efficient intersystem crossing into the triplet state. The properties of the triplet state were determined by phosphorescence spectroscopy in an ethanol matrix at 77 K (Figure S1 in the Supporting Information). The phosphorescence spectra of ketones with a nπ^* electronic configuration

of the lowest triplet state are usually structured because of the vibrational progression of the C=O vibration, and $\pi\pi^*$ triplets are mostly unstructured.[7,8] In addition, phosphorescence lifetimes for nπ^* triplets are significantly shorter (several milliseconds) than those of $\pi\pi^*$ triplets (more than 100 ms).[8,9] Therefore, the observed broad unstructured phosphorescence of TX-Hq together with the long phosphorescence lifetime at 77 K (249 ms) indicates a $\pi\pi^*$ configuration of the lowest triplet state.

Laser flash photolysis experiments were performed to investigate the triplet-state reactivity at room temperature. Figure 4a shows the transient absorption spectrum of
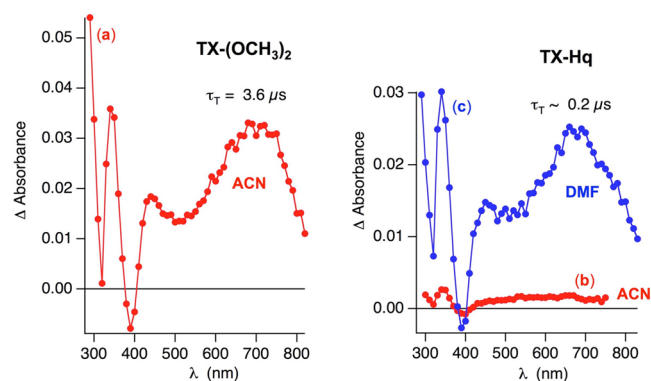

Figure 4. Transient absorption spectra of (a) TX-(OCH$_3$)$_2$ and (b, c) TX-Hq in argon-saturated (a, b) acetonitrile and (c) DMF recorded at the end of the laser pulse (355 nm, 5 ns).

TX-(OCH$_3$)$_2$ directly after the laser pulse. Three maxima were observed at 290, 340, and 700 nm, which were quenched by molecular oxygen with rate constants of 5.7×10^9 M^{-1} s^{-1} (Figure S2 in the Supporting Information), consistent with a triplet or radical nature of the transient. The transient at 700 nm decayed monoexponentially with a lifetime of 3.6 μs in acetonitrile solution. The transient peak of TX-(OCH$_3$)$_2$ is slightly broader than that of the previously studied TX-Ct[5] and was assigned to the triplet–triplet absorption on the basis of the following quenching experiments with naphthalene. Naphthalene, which does not absorb at 355 nm, the excitation wavelength for TX-(OCH$_3$)$_2$, has a triplet-state energy (255 kJ/mol) similar to that of TX-(OCH$_3$)$_2$ (255−240 kJ/mol, estimated from the broad phosphorescene spectrum at 77 K). Therefore, quenching of TX-(OCH$_3$)$_2$ triplets by naphthalene should generate naphthalene triplet states, which are known to show a distinct absorption at 412 nm.[10] Laser flash photolysis experiments of TX-(OCH$_3$)$_2$ in the presence of 3 mM naphthalene showed a buildup of transient absorption at 412 nm (naphthalene triplet) over a period of 1 μs with a simultaneous decrease of the transient absorption at 700 nm [consistent with the TX-(OCH$_3$)$_2$ triplet] (Figure S3 in the Supporting Information). The bimolecular quenching rate constant was determined to be 1.2×10^9 M^{-1} s^{-1} by varying the naphthalene concentration (Figure S4 in the Supporting Information). This value of the rate constant, which is lower than the diffusion-controlled value, is typical for triplet–triplet energy transfer for energy donors having similar or slightly lower triplet energies than the acceptor.[11] From the quenching experiments with oxygen and naphthalene, we conclude that the observed broad transient at 700 nm is correctly assigned to the triplet absorption of TX-(OCH$_3$)$_2$.

The structurally similar TX-Hq was expected to show triplet absorption similar to that of TX-(OCH$_3$)$_2$. Surprisingly, only

negligible transient absorption was observed for TX-Hq in acetonitrile solution (Figure 4b). However, when DMF was used as the solvent, the triplet absorption of TX-Hq (Figure 4c) was similar to that of TX-$(OCH_3)_2$ (Figure 4a). The TX-Hq triplets decayed with a lifetime of 0.2 μs, suggesting that an intramolecular fragmentation analogous to eq 1 occurs. The lack of observable triplet absorption by TX-Hq in acetonitrile (Figure 4b) is consistent with the absence of polymer in the presence of acetonitrile (Figure 1 left, red).

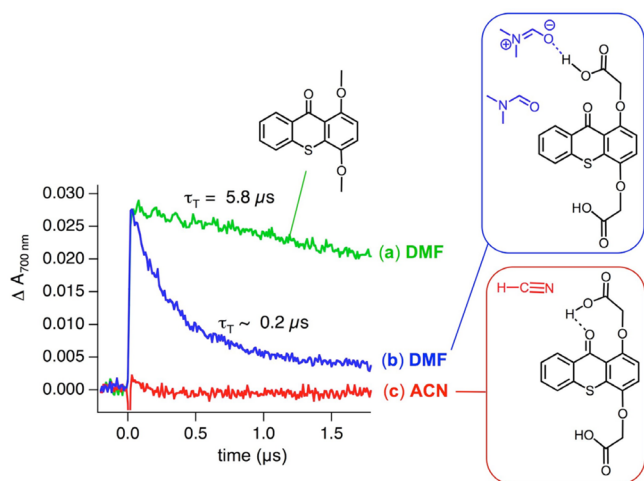Figure 5 shows transient decay traces of TX-$(OCH_3)_2$ and TX-Hq with matching absorbances at the excitation wave-

Figure 5. Transient decay traces monitored at 700 nm following pulsed laser excitation (355 nm) of (a) TX-$(OCH_3)_2$ and (b, c) TX-Hq in argon-saturated (a, b) DMF and (c) acetonitrile.

length (355 nm), monitoring the triplet absorption kinetics at 700 nm. In DMF solution, at the end of the laser pulse, (a) TX-$(OCH_3)_2$ and (b) TX-Hq showed nearly identical absorbances at 700 nm, which indicates that the yields of triplet formation for the two compounds were similar in DMF. In acetonitrile solution, however, TX-Hq showed only negligible transient absorption (Figure 5c). Therefore, TX-Hq triplets are deactivated rapidly or not formed in acetonitrile solution. Because the fluorescence quantum yield of TX-Hq is ~30 times smaller in acetonitrile than in DMF (Figure 3 left), rapid quenching of the singlet excited state in acetonitrile is suggested.

Intramolecular H-bonding deactivation of excited states of aromatic ketones has been known for many decades. For example, excited states of 2-hydroxybenzophenone are rapidly quenched through intramolecular H-bonding.[12] This excited-state quenching is so efficient that 2-hydroxybenzophenone and its derivatives are used as UV absorbers in sunscreens.[13−15] A similar intramolecular H-bond deactivation mechanism can be envisioned for TX-Hq (Figure 5c inset). The ~30 times lower fluorescence quantum yield of TX-Hq in acetonitrile relative to DMF (Figure 3 left) suggests that quenching of the singlet excited state by intramolecular H-bonding deactivation is so efficient that intersystem crossing into the triplet state cannot compete. In addition, the generated triplet states could also undergo rapid quenching by intramolecular H-bonding deactivation before electron transfer and fragmentation into initiator radicals can occur.

Solvents such as DMF and DMSO are known to disrupt solute intramolecular H-bonds by forming intermolecular

H-bonds with the solute.[16] Because increased fluorescence intensity (Figure 3 left), increased triplet absorption (Figure 5b), and efficient initiation of free-radical polymerization (Figure 2 left) were observed in DMF, we conclude that the intramolecular H-bonds in TX-Hq are disrupted by DMF (Figure 5b inset). Similar to DMF, laser flash photolysis experiments of TX-Hq in DMSO also showed an intense triplet absorption (Figure S5 in the Supporting Information).

Laser flash photolysis experiments were performed in acetonitrile solution with increasing amounts of DMF and DMSO to further investigate the disruption of intramolecular H-bonds by DMF and DMSO. Figure 6 shows the observed
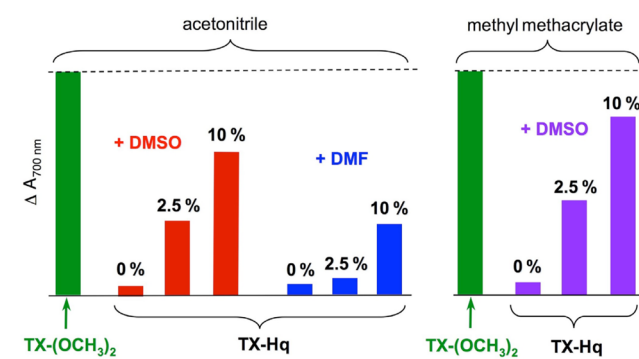

Figure 6. Transient absorbance monitored at 700 nm at the end of the laser pulse (355 nm) for argon-saturated (left) acetonitrile and (right) methyl methacrylate solutions of TX-$(OCH_3)_2$ (green) or TX-Hq in the presence of different amounts of DMF or DMSO.

amounts of triplet states at the end of the laser pulse. TX-$(OCH_3)_2$ serves as the benchmark of maximum generatable triplet states. Only negligible amounts of TX-Hq triplets were observable in acetonitrile. Addition of small amounts of H-bond-disrupting solvent (i.e., DMF or DMSO) generated a significant increase in the amount of triplet states. For example, 10% DMSO in acetonitrile disrupted 66% of the intramolecular H-bonding quenching in TX-Hq. When the polymerizable monomer methyl methacrylate was used as the solvent, only negligible amounts of TX-Hq triplet states were observed. However, when 10% DMSO was added, 79% of the triplet states were restored (Figure 6 right). The generated triplet states of TX-Hq can undergo decarboxylation analogous to eq 1 to generate radicals to initiate free-radical polymerization of the acrylic monomer. This is consistent with the polymerization experiments (Figure 2 left), where good polymerization yields were observed in the presence of the H-bond-disrupting solvent DMF but negligible polymer yields were obtained in acetonitrile.

Laser flash photolysis showed that radical generation from TX-Hq triplet states can be initiated by intramolecular electron transfer with a rate constant of ~5 × 10^6 s^{-1}. However, at high TX-Hq concentrations, intermolecular electron transfer involving a TX-Hq molecule in the ground state could compete with the intramolecular mechanism (Scheme 1). To determine the concentrations of TX-Hq at which the intermolecular mechanism is competitive, the bimolecular rate constant k_q was estimated. Because the direct determination of k_q for TX-Hq was experimentally difficult, model compounds were used instead. To increase the triplet-state lifetime, TX-$(OCH_3)_2$ was chosen to generate triplet states, and 2-phenoxyacetic acid was selected as the electron donor because it contains the basic structure of the electron-donor moiety of TX-Hq and is

Scheme 1. Proposed Mechanism of Photoinduced Radical Generation
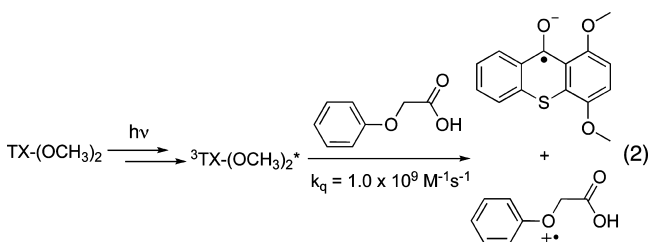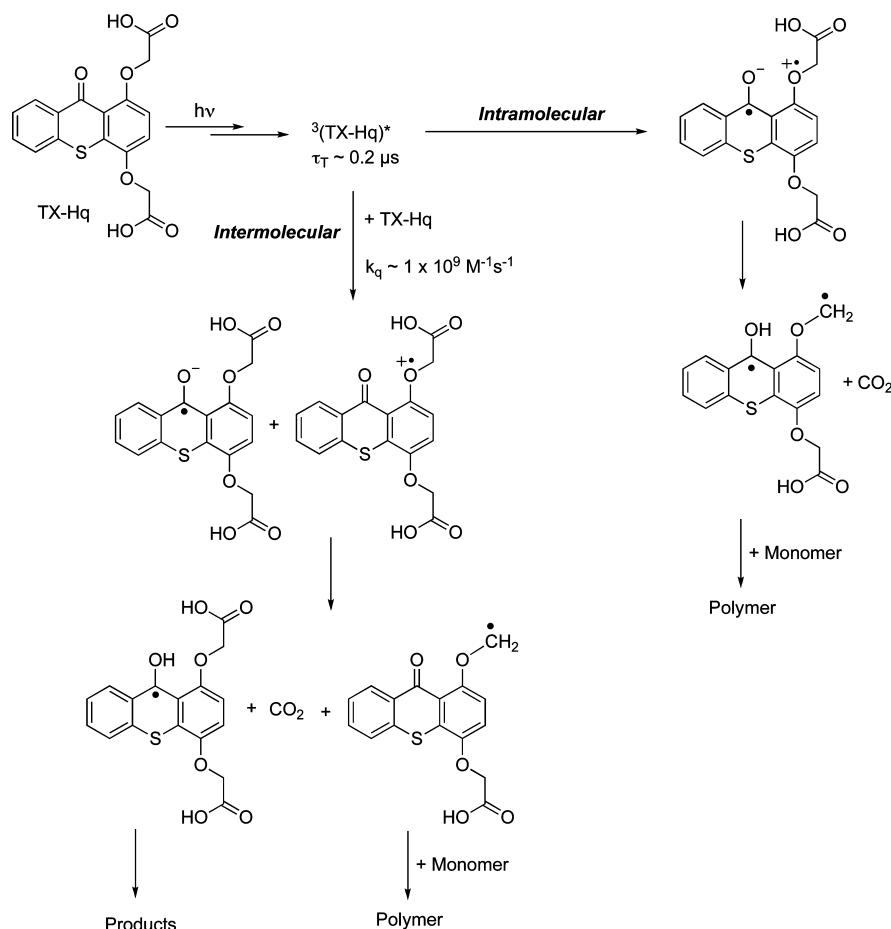
transparent at the excitation wavelength (355 nm) (eq 2). Determination of the triplet lifetime of $TX-(OCH_3)_2$ in the presence of various concentrations of 2-phenoxyacetic acid and pseudo-first-order analysis led to a bimolecular rate constant of 1.0×10^9 M^{-1} s^{-1} (Figure S6 in the Supporting Information). This rate constant serves as an estimate of the contribution from the intermolecular pathway involving the reaction of triplet TX-Hq with ground-state TX-Hq (Scheme 1). For a triplet lifetime of ~200 ns at a TX-Hq concentration of ~5 mM, half of the TX-Hq triplets would react via the intermolecular pathway.

CONCLUSIONS

Acetic acid derivatives of thioxanthone have been shown to generate carbon-centered radicals upon photolysis by intramolecular electron transfer followed by decarboxylation. We have shown that the position of the acetic acid substituent is critical for the photoreactivity. In most solvents and acrylic monomers, if the acetic acid functionality is at the 1-position (as in TX-Hq), the singlet excited states are deactivated rapidly

before electron transfer can occur, resulting in negligible photoreactivity. The excited-state deactivation probably involves intramolecular H-bonding. If the acetic acid functionality is shifted to the 2-position (as in TX-Ct), intramolecular H-bonding is sterically not favorable, and rapid photoreaction to generate carbon-centered radicals is observed. The intramolecular H-bonding in TX-Hq can be disrupted by solvents that support intermolecular H-bonding, such as DMF and DMSO. We observed that photoreactivity and radical generation in TX-Hq were restored by the addition of small amounts of DMF or DMSO. Therefore, when TX-Hq is used as photoinitiator for free-radical polymerization, small amounts of DMF, DMSO, or an analogous compound should be added.

EXPERIMENTAL SECTION

Materials. Thiosalicylic acid (97%), hydroquinone-O,O'-diacetic acid (97%), 1,4-dimethoxybenzene (98%), and sulfuric acid (H_2SO_4, 98%) were used as received. N,N'-Dimethylformamide (DMF, 99%) was distilled from CaH_2 under reduced pressure. Ethanol (HPLC grade), and acetonitrile (HPLC grade) were used as received. Isobornyl acrylate was used after removal of the inhibitor by passage through a column containing basic alumina.

Synthesis of (4-Carboxymethoxy-9-oxo-9H-thioxanthen-1-yloxy)acetic Acid (Thioxanthone Hydroquinone-O,O'-diacetic Acid; TX-Hq). Thiosalicylic acid (0.32 g, 2.0 mmol) was slowly added to concentrated sulfuric acid (15 mL) in an ice bath, and the mixture was stirred for 5 min to ensure thorough mixing. Hydroquinone-O,O'-diacetic acid (1.35 g, 6.0 mmol) was added slowly with stirring over a period of 30 min. After the addition, the reaction mixture was stirred at room temperature for 3 days, after which it was left to stand at room temperature overnight. The resulting mixture was poured carefully into

cold water with stirring and then washed several times with cold water, and a dark-yellow product was obtained (eq 3). Yield: 0.57 g (80%).
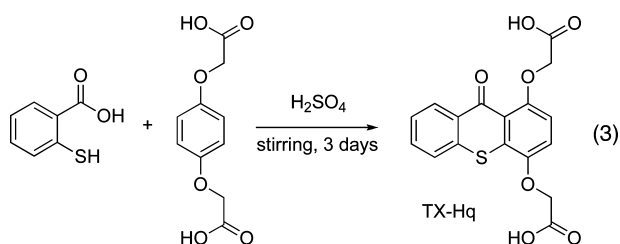
Mp: 230 °C. ^{1}H NMR (DMSO, 250 MHz) δ: 4.77 (s, 2H), 4.90 (s, 2H), 6.99−7.03 (d, J = 12.5 Hz, 1H), 7.27−7.32 (d, J = 12.5 Hz, 1H), 7.49−7.56 (m, 1H), 7.66−7.82 (m, 2H), 8.24−8.28 (d, J = 10 Hz, 1H) (Figure S7 in the Supporting Information). ^{13}C NMR (DMSO, 50 MHz) δ: 179.28, 170.1, 169.6, 153.9, 146.5, 134.7, 132.2, 130.6, 128.5, 127.9, 126.7, 126.2, 119.8, 115.7, 112.2, 66.7, 65.7 (Figure S8 in the Supporting Information). FT-IR: 3436, 1776, 1734, 1700, 1593 cm^{-1}. HRMS (FAB+) m/z: exact mass calcd for $C_{17}H_{13}O_7S$ [M + H]$^+$, 361.0382; found, 361.0379.

Synthesis of 1,4-Dimethoxy-9H-thioxanthen-9-one [1,4-Dimethoxythioxanthone; TX-(OCH$_3$)$_2$]. Thiosalicylic acid (0.64 g, 4.0 mmol) was slowly added to concentrated sulfuric acid (15 mL), and the mixture was stirred for 5 min to ensure thorough mixing. 1,4-Dimethoxybenzene (0.55 g, 12 mmol) was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was stirred at room temperature for 1 h and then at 80 °C for 3.5 h, after which it was left to stand at room temperature overnight. The resulting mixture was poured carefully with stirring into a 10-fold excess of boiling water and was further boiled for 5 min. The solution was cooled and filtered. The residue was recrystallized from dioxane/water, and a dark-yellow product was obtained. Yield: 0.87 g (80%). Mp: 194 °C. ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 3.90 (s, 3H), 3.92 (s, 3H), 6.83−6.85 (d, J = 9 Hz, 1H), 7.00−7.02 (d, J = 9 Hz, 1H), 7.19−7.39 (m, 1H), 7.48−7.50 (m, 2H), 8.40−8.42 (d, J = 9 Hz, 1H) (Figure S9 in the Supporting Information). GC-MS (70 eV) m/z: 272 (Figure S10 in the Supporting Information). FT-IR: 1640, 1593, 1250 cm^{-1}.

Laser Flash Photolysis. The laser flash photolysis experiments employed pulses from a Nd:YAG laser (266 nm, 5 ns) and a computer-controlled system, as described previously.[17] Acetonitrile solutions containing TX-Hq or TX-(OCH$_3$)$_2$ were prepared at concentrations that gave an absorbance of 0.3 at 266 nm (1 cm optical path length). The sample solutions were deoxygenated by argon purging.

Photoinitiated Polymerization. The photoinitiated polymerization of isobornyl acrylate was performed by photo-differential scanning calorimetry (Photo-DSC) using a medium-pressure mercury arc lamp that provided a light intensity of 60 mW/cm^2 as measured with a UV radiometer capable of broad UV range coverage. The masses of the samples were ~2.0 mg, and the measurements were carried out in an isothermal mode at room temperature under a nitrogen atmosphere (nitrogen flow rate: 50 mL/min).

Fluorescence Quantum Yields. The fluorescence quantum yields were determined using 9,10-diphenylanthracene as a standard.[18] Solutions with matching absorbances at the excitation wavelength were used, and the quantum yields were corrected for the refractive index of the solvent.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra for TX-Hq, ^{1}H NMR spectra and GC-MS data for TX-(OCH$_3$)$_2$, and additional flash photolysis and low-temperature phosphorescence results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.
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