Supporting Information

Thioxanthone based one-component polymerizable visible light photoinitiator for free radical polymerization

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Scheme S1  Synthesis of TX-PA and TX-Ac
**Experimental section**

**Materials and instrumentation**

2-Benzyl(methyl)amino-9H-thioxanthen-9-one (TX-B), 1 2-methylamino-9H-thioxanthen-9-one\(^1\) and 4-(hydroxymethyl)phenyl benzoate\(^2\) were prepared following the literature methods. \(N, N\)-Dimethylformamide (DMF) and methylene chloride (\(\text{CH}_2\text{Cl}_2\)) were dried and purified according to the standard laboratory methods. 1, 6-hexamendifoldiacrylate (HDDA, 90%) was obtained from Aladdin. All reagents and solvents were also obtained from Aladdin and used as received without further purification. \(^1\)H (300 MHz) and \(^{13}\)C (75 MHz) NMR spectra were determined at room temperature on a VARIAN Mercury 300 spectrometer of the Spectropole. Mass spectrometry was carried out using a Varian 320-MS triple quadrupole mass spectrometer operated in the electrospray ionization (ESI) modes.

**Synthesis of 4-(chloromethyl)phenyl benzoate**

Thionyl chloride (7.25 mL) was added dropwisely to the solution of 4-(hydroxymethyl)phenyl benzoate (11.40 g, 50 mmol) in anhydrous \(\text{CH}_2\text{Cl}_2\) (100 mL). Then, the solution was stirred for an additional hour at room temperature and the substances with low boiling point were removed under reduced pressure. Two milliliter of \(\text{CH}_2\text{Cl}_2\) was added into the residue. The solution was poured into 50 mL of petroleum ether. The precipitate was filtered off and dried under vacuum to give a white powder (11.07 g, 90%). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) ppm: 4.62 (s, 2H, -CH\(_2\)), 7.19-7.25 (m, 2H, Ar-H), 7.40-7.55 (m, 4H, Ar-H), 7.61-7.68 (m, 1H, Ar-H),
8.20 (d, 2H, Ar-H, J = 7.2 Hz).  $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ ppm: 165.0 (C=O), 150.8 (ArC), 135.0 (ArC), 133.7 (ArCH), 130.2 (ArC), 129.8 (ArCH), 129.3 (ArCH), 128.6 (ArCH), 122.0 (ArCH), 45.6 (-CH$_2$).

**Synthesis of 4-((methyl(9-oxo-9H-thioxanthen-2-yl)amino)methyl)phenyl benzoate**

A mixture of 2-methylamino-9H-thioxanthen-9-one (7.32 g, 30.0 mmol), sodium iodide (0.15g, 1.0 mmol), 4-(chloromethyl)phenyl benzoate (7.75 g, 31.5 mmol), K$_2$CO$_3$ (8.28 g, 60.0 mmol) and 100 mL of anhydrous DMF was stirred at 50 °C until the absence of 2-methylamino-9H-thioxanthen-9-one which was monitored by TLC. And then, the mixture was cooled down and the yellow precipitate was collected by filtration. The solid was dissolved in 20 mL of CH$_2$Cl$_2$, and then the solution was added into 200 mL of petroleum ether which afforded a yellow precipitate. The solid was collected by filtration and dried under high vacuum to give a yellow powder (12.45 g, 92%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ ppm: 3.18 (s, 3H, -NCH$_3$), 4.67 (s, 2H, -NCH$_2$), 7.18 (d, 3H, Ar-H, J = 7.8 Hz), 7.31 (d, 2H, Ar-H, J = 8.1 Hz), 7.46 (d, 2H, Ar-H, J = 4.2 Hz), 7.51 (t, 2H, Ar-H, J = 8.1 Hz), 7.56-7.65 (m, 3H, Ar-H), 8.00 (d, 1H, Ar-H, J = 2.4 Hz), 8.19 (d, 2H, Ar-H, J = 8.4 Hz), 8.63 (d, 1H, Ar-H, J = 8.1 Hz).  $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ ppm: 180.0 (C=O), 165.2 (COO), 149.9 (ArC), 148.1 (ArC), 137.7 (ArC), 135.7 (ArC), 133.6 (ArCH), 131.6 (ArCH), 130.1 (ArCH), 129.8 (ArC), 129.4 (ArCH), 128.5 (ArC), 127.7 (ArCH), 126.9 (ArC), 125.9 (ArCH), 125.6 (ArCH), 124.3 (ArCH), 121.9 (ArCH), 118.8 (ArCH), 110.4 (ArCH), 55.9
Synthesis of 2-[(4-hydroxybenzyl)(methyl)amino]-9H-thioxanthen-9-one (TX-HB)

A mixture of 4-((methyl(9-oxo-9H-thioxanthen-2-yl)amino)methyl)phenyl benzoate (13.53 g, 30.0 mmol), 100 mL of methanol, and 0.10 g anhydrous K$_2$CO$_3$ was stirred under reflux conditions for 2 h. Then it was cooled down to room temperature and then was filtered to remove solids. After the methanol was stripped off under a reduced pressure, 5 mL of THF was added to the residue. Then the solution was added into 200 mL of petroleum ether which afforded a red precipitate. The solid was collected by filtration and dried under high vacuum to give a red powder (7.33 g, 70%), m.p. 182-184 °C. $^1$H NMR (DMSO-d$_6$, 300 MHz) δ ppm: 3.05 (s, 3H, -NCH$_3$), 4.52 (s, 2H, -NCH$_2$), 6.72 (d, 2H, Ar-H, J = 8.1 Hz), 7.03 (d, 2H, Ar-H, J = 8.1 Hz), 7.24-7.27 (m, 1H, Ar-H), 7.45-7.54 (m, 2H, Ar-H), 7.64-7.71 (m, 3H, Ar-H), 8.42 (d, 1H, Ar-H, J = 7.5 Hz), 9.33 (s, 1H, -OH). $^{13}$C NMR (DMSO-d$_6$, 75 MHz) δ ppm: 184.1 (C=O), 161.8 (ArC), 153.3 (ArC), 142.4 (ArC), 137.6 (ArCH), 134.5 (ArCH), 133.6 (ArC), 133.4 (ArC), 133.3 (ArCH), 132.6 (ArC), 131.8 (ArCH), 131.4 (ArC), 128.1 (ArCH), 124.7 (ArCH), 120.8 (ArCH), 114.6 (ArCH), 60.2 (-NCH$_2$), 43.9 (-NCH$_3$). MS, m/z (ESI) 348.1 ([M+H]$^+$, 100%).

Synthesis of 4-((methyl(9-oxo-9H-thioxanthen-2-yl)amino)methyl)phenyl acrylate (TX-PA)

TX-HB (0.69 g, 2.0 mmol), triethylamine (0.28 mL, 4.0 mmol), and 50 mL of CH$_2$Cl$_2$
were added into a 250 mL of three-necked round bottom flask fitted with a thermometer and a pressure-equalized funnel. Under cooling (0-5 °C), the solution of acryloyl chloride (0.34 mL, 4.0 mmol) and 10 mL of CH₂Cl₂ was added dropwise into the flask within 1 h. The mixture was stirred at room temperature for another hour. Then, the low-boiling point substances were stripped off under vacuum. After that, 50 mL of CH₂Cl₂ was added. The mixture was washed with water, and dried overnight with anhydrous sodium sulfate. After evaporated the low-boiling point substances, additional 2 mL of CH₂Cl₂ was added and the mixture was dropped into 50 mL of petroleum ether. After the precipitates were filtered off and dried under vacuum, 0.64 g of yellow product was collected with 80% yield, m.p. 102-104 °C. ¹H NMR (CDCl₃, 300 MHz) δ ppm: 3.16 (s, 3H, -NCH₃), 4.65 (s, 2H, -NCH₂), 6.00-6.05 (m, 1H, -CH=CH₂), 6.27-6.42 (m, 1H, -CH=CH₂), 6.58-6.64 (m, 1H, -CH=CH₂), 7.09-7.15 (m, 3H, Ar-H), 7.26-7.29 (m, 2H, Ar-H), 7.41-7.48 (m, 2H, Ar-H), 7.57-7.59 (m, 2H, Ar-H), 7.97 (d, 1H, Ar-H, J = 2.7 Hz), 8.64 (d, 1H, Ar-H, J = 8.1 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ ppm: 179.9 (C=O), 164.5 (OC=O), 149.6 (ArC), 148.1 (ArC), 137.7 (ArC), 135.7 (ArC), 132.5 (-CH=CH₂), 131.6 (ArCH), 129.8 (ArCH), 128.7 (ArCH), 127.8 (ArC), 127.6 (-CH=CH₂), 126.9 (ArC), 125.9 (ArCH), 125.5 (ArC), 124.3 (ArCH), 121.7 (ArCH), 118.8 (ArCH), 110.5 (ArCH), 55.8 (-NCH₂), 38.7 (-NCH₃). MS, m/z (ESI) 402.0 ([M+H]+, 100%).

Synthesis of 4-((methyl(9-oxo-9H-thioxanthen-2-yl)amino)methyl)phenyl acetate (TX-Ac)
Following the method of 4-((methyl(9-oxo-9H-thioxanthen-2-yl)amino)methyl)phenyl acrylate was synthesized.  $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ ppm: 2.29 (s, 3H, -COCH$_3$), 3.15 (s, 3H, -NCH$_3$), 4.64 (s, 2H, -CH$_2$), 7.04 (d, 2H, Ar-H, $J = 7.8$ Hz), 7.11 (d, 1H, Ar-H, $J = 7.8$ Hz), 7.24 (m, 1H, Ar-H), 7.43 (d, 2H, Ar-H, $J = 8.1$ Hz), 7.57 (s, 2H, Ar-H), 7.95 (s, 1H, Ar-H), 8.62 (d, 1H, Ar-H, $J = 8.1$ Hz).

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ ppm:  179.8 (C=O), 169.4 (OC=O), 149.5 (ArC), 148.0 (ArC), 137.6 (ArC), 135.6 (ArC), 131.5 (ArCH), 129.6 (ArCH), 128.5 (ArCH), 127.5 (ArC), 126.8 (ArC), 125.8 (ArCH), 125.4 (ArCH), 124.2 (ArCH), 121.7 (ArCH), 118.6 (ArCH), 110.2 (ArCH), 55.7 (-NCH$_2$), 38.6 (-NCH$_3$), 21.0 (-CH$_3$).

MS, m/z (ESI) 390.0 ([M+H]$^+$, 100%).
$^1$H (300 MHz) /$^{13}$C (75 MHz) NMR Spectra

Fig. S1  $^1$H NMR spectrum of TX-B and TX-PA in CDCl$_3$.

Fig. S2  $^1$H NMR spectrum of TX-Ac in CDCl$_3$. 
Fig. S3  $^{13}$C NMR of TX-B and TX-PA in CDCl$_3$.

Fig. S4  $^{13}$C NMR of TX-Ac in CDCl$_3$. 
ESI-MS Analysis

Fig. S5  Mass spectrometry of TX-HB.
Fig. S6  Mass spectrometry of TX-PA.
Fig. S7  Mass spectrometry of TX-Ac.
**Fig. S8**  UV-vis absorption spectra of (1) TX-B and (2) TX-PA in THF solution [2 × 10^{-4} mol L^{-1}].

**Fig. S9**  Fluorescence excitation and emission spectra of TX-B and TX-PA in THF solution [8 × 10^{-6} mol L^{-1}].
Fig. S10  The fluorescence emission of TX-PA in THF solution [8 × 10^{-6} mol L^{-1}] with different concentration of MDEA.

Fig. S11  The fluorescence emission of TX-PA in THF solution [8 × 10^{-6} mol L^{-1}] with different concentration of DMA.
Fig. S12  Stern-Volmer plot of the quenching of (1) TX-B and (2) TX-PA [8 × 10⁻⁶ mol L⁻¹] by DMA in THF.

Fig. S13 UV-vis absorption spectra of (1) TX-B and (2) TX-PA in acetone solution.
Notes and references
