

Supporting information

Cleavable Coumarin-based Oxime Esters with Terminal Heterocyclic Moieties: Photobleachable Initiators for Deep Photocuring Under Visible LED Light Irradiation

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1. Synthesis of the precursors

- 1.1. Synthesis of 7-(diethylamino)-2H-chromen-2-one (**1**)
- 1.2. Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde (**2**)
- 1.3. Synthesis of (E)-7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (**3**)
- 1.4. Synthesis of furan-3-carbonyl chloride (**4a**)
- 1.5. Synthesis of thiophene-3-carbonyl chloride (**4b**)

2. Photolysis study

1. Synthesis of the precursors

1.1. Synthesis of 7-(diethylamino)-2H-chromen-2-one (**1**)

4-Diethylaminosalicylaldehyde (2.013 g, 10.4 mmol) was dissolved in 20 mL anhydrous ethanol. Diethyl malonate (3 mL, 19.8 mmol) and piperidine (1 mL, 10.9 mmol) were added. Then the mixture was stirred and refluxed for 6 h. All volatiles were evaporated under reduced pressure, concentrated HCl (20 mL) and glacial acetic acid (20 mL) were added for hydrolysis and stirred for another 6 h at reflux temperature. The reaction solution was cooled to room temperature and poured into 100 mL of ice water. 20% NaOH solution was added dropwise to adjust the pH to ~6 whereby a precipitate formed immediately. After stirring for 1 h, the solid was filtered, washed with water, and dried to give 2.01 g desired product in 89% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 9.4 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 1H), 6.73 (d, 1H), 6.61 (s, 1H), 6.11 (d, *J* = 9.3 Hz, 1H), 3.45 (q, *J* = 7.1 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H).

1.2. Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde (**2**)

Dried DMF (2 mL) was added dropwise to POCl₃ (2 mL) at room temperature with N₂ atmosphere and stirred for 30 minutes to yield a pink solution. Compound **1** (1.543 g, 7.1 mmol, dissolved in 8 mL DMF) was added dropwise to the solution. The mixture was stirred at 60°C for 12 h and then poured into 100 mL of ice water. 20% NaOH solution was added dropwise to adjust the pH of the mixture to yield large amount of precipitate. The crude product was filtered, washed with water and recrystallized from ethanol to give 1.392 g of compound **2** in 80% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.30 (s, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 6.76 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 3.51 (q, *J* = 7.1 Hz, 4H), 1.29 (t, *J* = 7.2 Hz, 6H).

1.3. Synthesis of (E)-7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (**3**)

Compound **2** (1.591 g, 6.5 mmol), hydroxylamine hydrochloride (690 mg, 10.0 mmol) and anhydrous sodium acetate (815 mg, 9.9 mmol) were dissolved in 50 mL. The mixture was stirred at reflux temperature for 1 h. After the solution cooling to room temperature, the solvent was evaporated under reduced pressure, and the crude product was recrystallized from ethanol to give yellow solid with a yield of 97%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.32 (s, 1H), 8.16 (s, 1H), 7.99 (s, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 6.74 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 3.46 (q, *J* = 7.0 Hz, 4H), 1.13 (t, *J* = 7.0 Hz, 6H).

1.4. Synthesis of furan-3-carbonyl chloride (**4a**)

3-Furoicacid (1.009 g, 9.0 mmol) was added to a round bottom flask equipped with a reflux condenser. Then the thionyl chloride (5 mL) was added. The reaction mixture was allowed to reflux for 3 h under N₂ atmosphere. After the solution cooling to room temperature, the excess thionyl chloride was evaporated under reduced pressure and dried on a vacuum to yield gray crystals (1.105 g, 85%), which was used for the next step without further purification.

1.5. Synthesis of thiophene-3-carbonyl chloride (**4b**)

3-thiophenecarboxylic acid (1.101 g, 8.6 mmol) was added to a round bottom flask equipped with a reflux condenser. Then the thionyl chloride (5 mL) was added. The reaction mixture was allowed to reflux for 3 h under N₂ atmosphere. After the solution cooling to room temperature, the excess thionyl chloride was evaporated under reduced pressure and dried on a vacuum to yield gray crystals (1.113 g, 88%), which was used for the next step without further purification.

2. Photolysis study

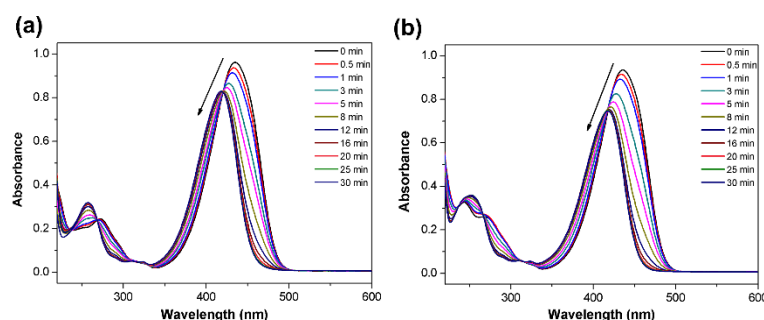


Fig. S1 UV-vis absorption evaluation of as-synthesized oxime esters (a) **3-O** and (b) **3-S** in real-time photodecomposition in acetonitrile using irradiation of 200 mW/cm², 450 nm LED light.

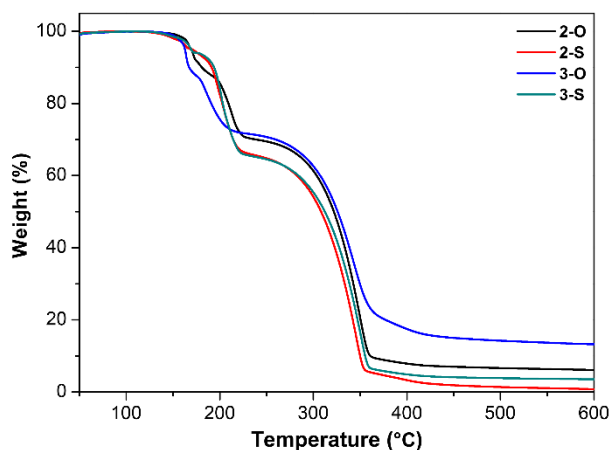


Figure S2. TG curves of novel oxime ester PIs