

Supplementary Material

**New long-wavelength D- π -A- π -D chalcone photoinitiator for visible light
polymerization with photobleaching and biocompatibility**

Yanyang Gao, and Jinqing Qu*

*School of Chemistry and Chemical Engineering, South China University of Technology,
Guangzhou 510640, China Information. Email: cejqqqu@scut.edu.cn*

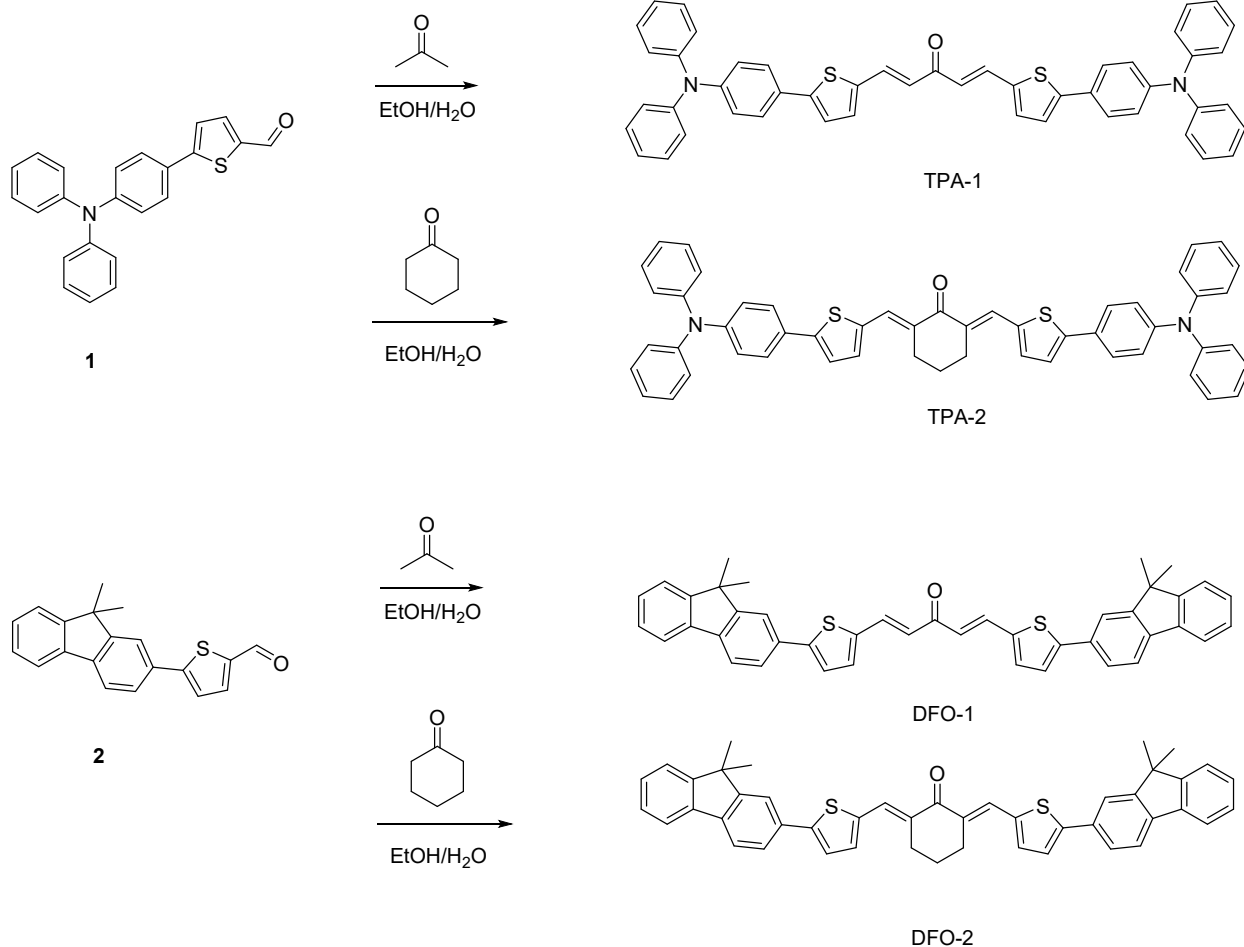
Corresponding Authors: Jinqing Qu cejqqqu@scut.edu.cn

1. Experimental

1.1 Materials.

4-(Diphenylamino)phenylboronic acid pinacol ester, 9,9-Dimethyl-2-boronic acid fluorene, 5-bromothiophene-2-carbaldehyde, tetrakis(triphenylphosphino)palladium, potassium carbonate, sodium hydroxide, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM), acetone, cyclohexanone, diphenyliodonium hexafluorophosphate (Iod) and diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO), tert-Butylbenzene and phenyl-N-tert-butyl nitron (PBN) were purchased from Adamas (Shanghai, China). ethyl 4-(dimethylamino)benzoate (EDAB) was obtained by Sigma-Aldrich. Polyethylene glycol diacrylate (PEGDA, Mn=400) is provided by J&K Technology Co., Ltd. (Shanghai, China). Trimethylolpropane triacrylate (TMPTA) and hydroxyethyl methacrylate (HEMA) were used as the benchmark monomers and obtained from Jiangsu Litian Chemical Co., Ltd. (Co., Ltd.). All chemicals are used without further purification.

1.2 Synthesis of chalcones



The synthesis route was shown in Scheme S1. 5-(4-(diphenylamino)phenyl)thiophene-2 carbaldehyde (1) and 5-(9,9-dimethyl-9,9a-dihydro-4aH-fluoren-7-yl)thiophene-2-carbaldehyde (2) were obtained according to literatures ^{1,2}.

Synthesis of (1E,4E)-1,5-bis(5-(4-(diphenylamino)phenyl)thiophen-2-yl)penta-1,4-dien-3-one (TPA-1)

A mixture of 2.25 mmol acetone, 4.50 mmol compound 1 and 60 mL ethanol were added into a 100 mL round-bottom flask, Then NaOH solution as catalyst was dropped into the above mixture. The process was reacted 60 °C and monitored by thin-layer chromatography (TLC). After the reaction, a product of TPA-1 (1.28 g, 78% yield) was obtained by recrystallization (ethanol, 3

times) ^1H NMR (400 MHz, Chloroform- d) δ 7.81 (d, J = 16.0 Hz, 2H), 7.53 – 7.43 (m, 4H), 7.32–7.26 (m, 10H), 7.19 (d, J = 4.0 Hz, 2H), 7.16 – 7.11 (m, 8H), 7.10–7.04 (m, 8H), 6.78 (d, J = 16.0 Hz, 2H). HRMS (ESI) : calcd for $\text{C}_{49}\text{H}_{36}\text{N}_2\text{OS}_2$ $[\text{M}^+\text{H}]^+$ 733.2347, found, 733.2342.

Synthesis of (2E,6E)-2,6-bis((5-(4-(diphenylamino)phenyl)thiophen-2-yl)methylene)cyclohexanone (TPA-2)

A mixture of 2.25 mmol cyclohexanone, 4.50 mmol compound 1 and 60 mL ethanol were added into a 100 mL round-bottom flask, Then NaOH solution as catalyst was dropped into the above mixture. The process was reacted 60 °C and monitored by thin-layer chromatography (TLC). After the reaction, a product of TPA-2 (1.31 g, 75% yield) was obtained by recrystallization (ethanol, 3 times). ^1H NMR (400 MHz, DMSO- d_6) δ 7.84 (s, 2H), 7.66 (d, J = 8.0 Hz, 3H), 7.57 (d, J = 16.0 Hz, 3H), 7.34 (d, J = 8.0 Hz, 10H), 7.08 (d, J = 8.0 Hz, 10H), 6.99 (d, J = 8.0 Hz, 6H), 2.93 (s, 4H), 1.24 (s, 2H). HRMS (ESI) : calcd for $\text{C}_{52}\text{H}_{40}\text{N}_2\text{OS}_2$ $[\text{M}^+\text{Na}]^+$ 795.2479, found, 795.2474.

Synthesis of (1E,4E)-1-(5-(9,9-dimethyl-9,9a-dihydro-4aH-fluoren-7-yl)thiophen-2-yl)-5-(5-(9,9-dimethyl-9H-fluoren-3-yl)thiophen-2-yl)penta-1,4-dien-3-one (DFO-1)

A mixture of 2.25 mmol acetone, 4.50 mmol compound 2 and 60 mL ethanol were added into a 100 mL round-bottom flask, Then NaOH solution as catalyst was dropped into the above mixture. The process was reacted 60 °C and monitored by thin-layer chromatography (TLC). After the reaction, a product of DFO-1 (1.04 g, 73% yield) was obtained by recrystallization (ethanol, 3 times). ^1H NMR (400 MHz, Chloroform- d) δ 7.88 (s, 1H), 7.84 (s, 1H), 7.78 – 7.72 (m, 4H), 7.70 – 7.67 (m, 2H), 7.64 (dd, J = 7.9, 1.6 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.39 – 7.32 (m, 8H), 6.88 (s,

1H), 6.84 (s, 1H), 1.55 (s, 12H). HRMS (ESI) : calcd for $C_{43}H_{35}N_2OS_2 [M^+H]^+$ 631.2129, found, 631.2124.

Synthesis of (2E,6E)-2-((5-(9,9-dimethyl-9,9a-dihydro-4aH-fluoren-7-yl)thiophen-2-yl)methylene)-6-((5-(9,9-dimethyl-9H-fluoren-3-yl)thiophen-2-yl)methylene)cyclohexanone (DFO-2)

A mixture of 2.25 mmol cyclohexanone, 4.50 mmol compound 2 and 60 mL ethanol were added into a 100 mL round-bottom flask, Then NaOH solution as catalyst was dropped into the above mixture. The process was reacted 60 °C and monitored by thin-layer chromatography (TLC). After the reaction, a product of DFO-2 (1.13 g, 75% yield) was obtained by recrystallization (ethanol, 3 times). 1H NMR (400 MHz, Chloroform-d) δ 8.00 (s, 2H), 7.78 – 7.61 (m, 8H), 7.48 – 7.33 (m, 10H), 3.05 (t, J = 5.5 Hz, 4H), 2.11 – 2.01 (m, 2H), 1.55 (s, 12H). HRMS (ESI) : calcd for $C_{46}H_{38}N_2OS_2 [M^+Na]^+$ 795.2479, found, 795.2474.

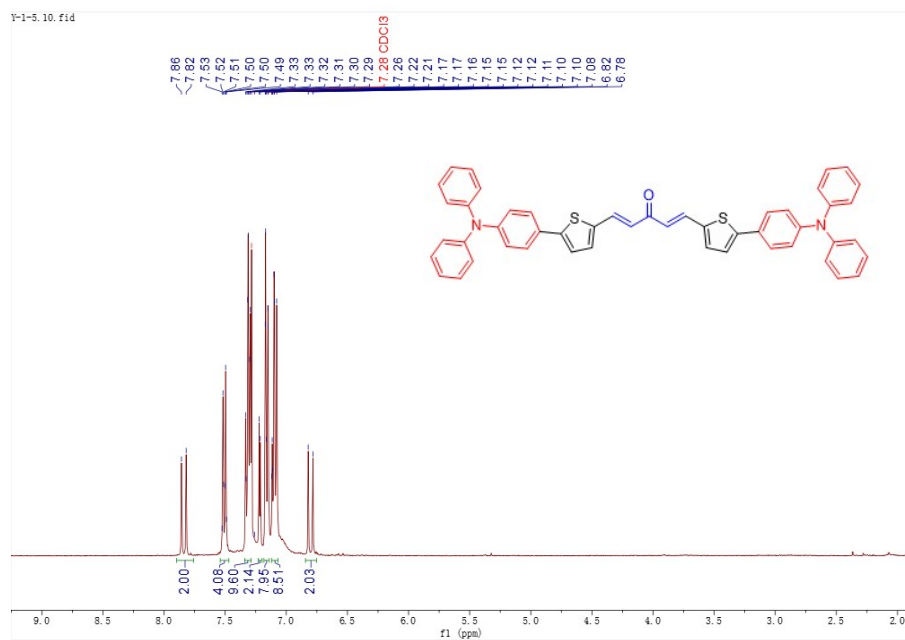


Figure S1. ^1H NMR spectrum of TPA-1 (NMR solvent: $\text{CDCl}_3\text{-d}_1$).

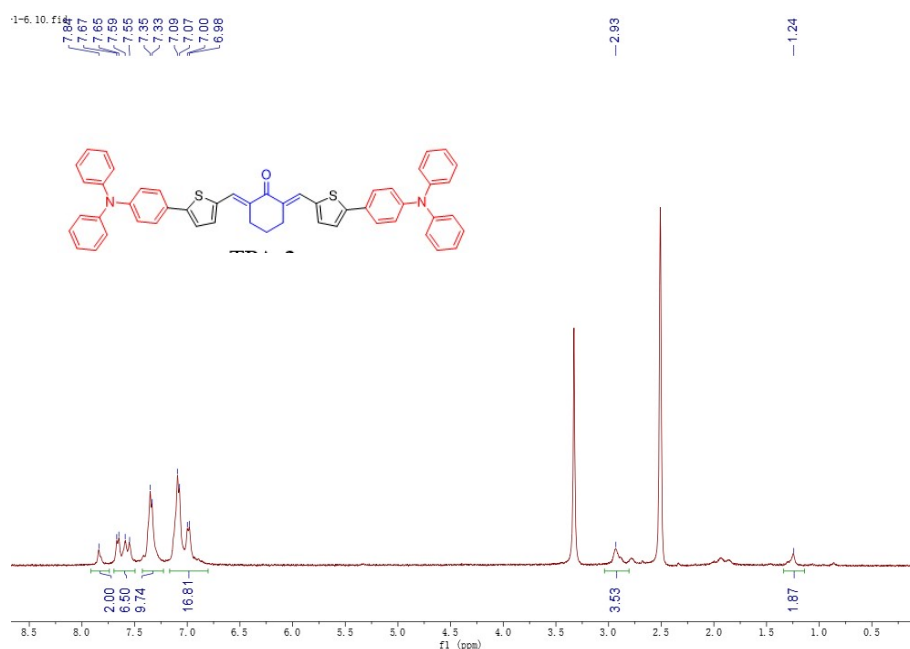


Figure S2. ^1H NMR spectrum of TPA-2 (NMR solvent: DMSO-d_6).

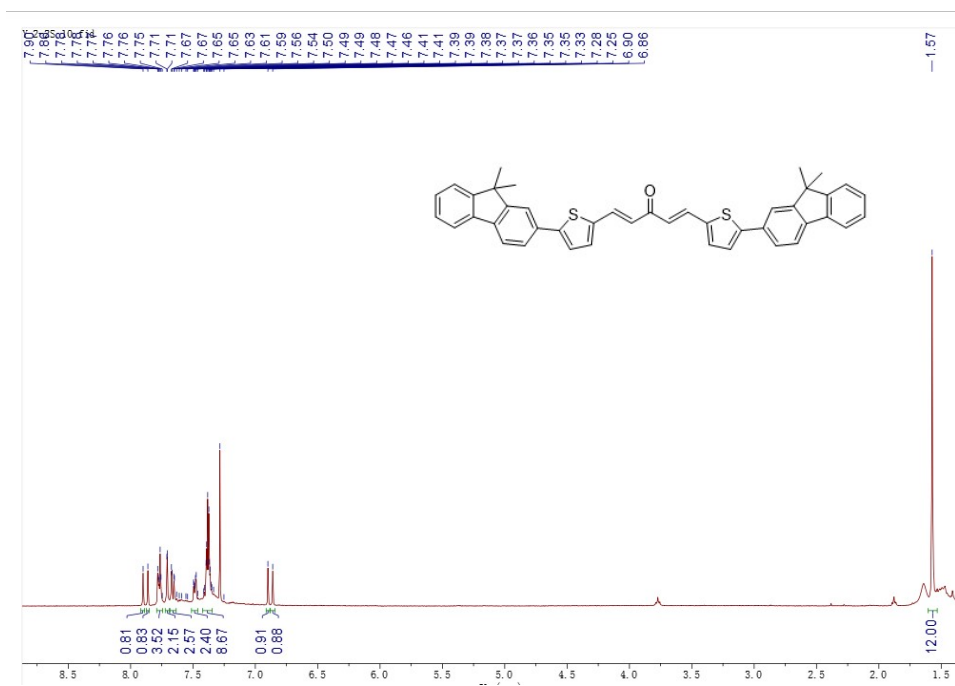


Figure S3. ¹H NMR spectrum of DFO-1 (NMR solvent: CDCl₃-d₁).

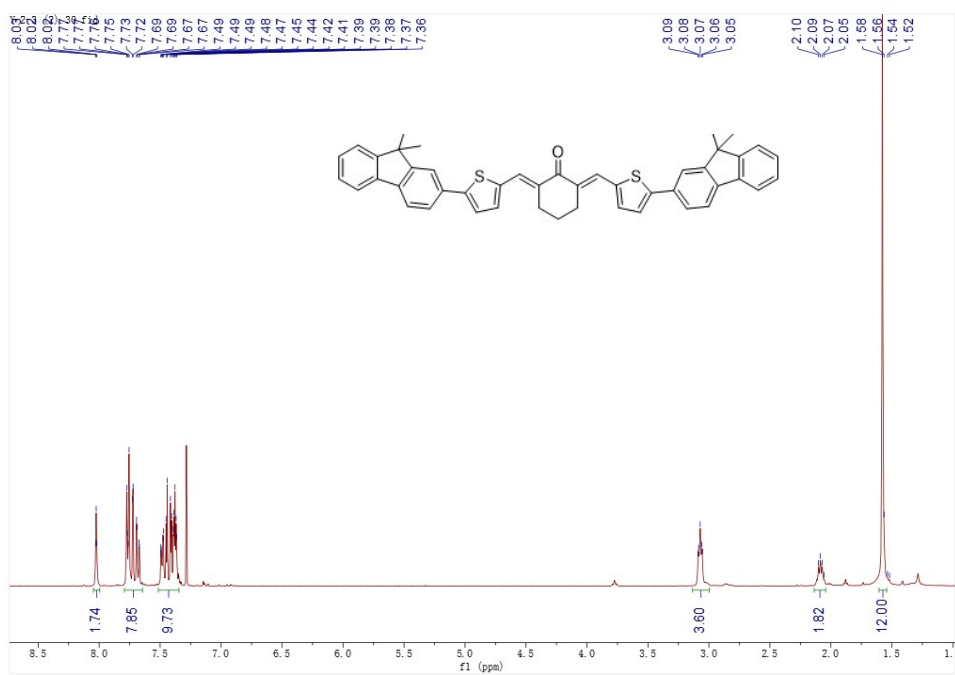


Figure S4. ¹H NMR spectrum of DFO-2 (NMR solvent: CDCl₃-d₁).

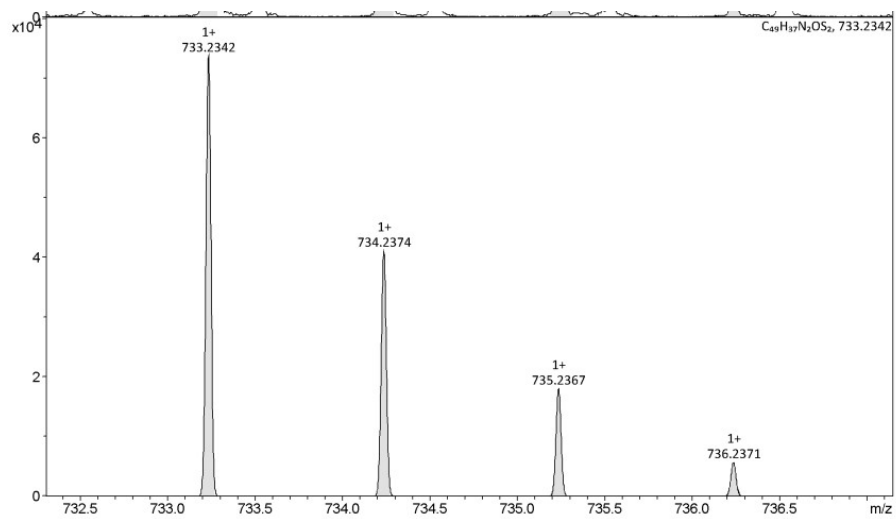


Figure S5. HR-MS spectrum of TPA-1

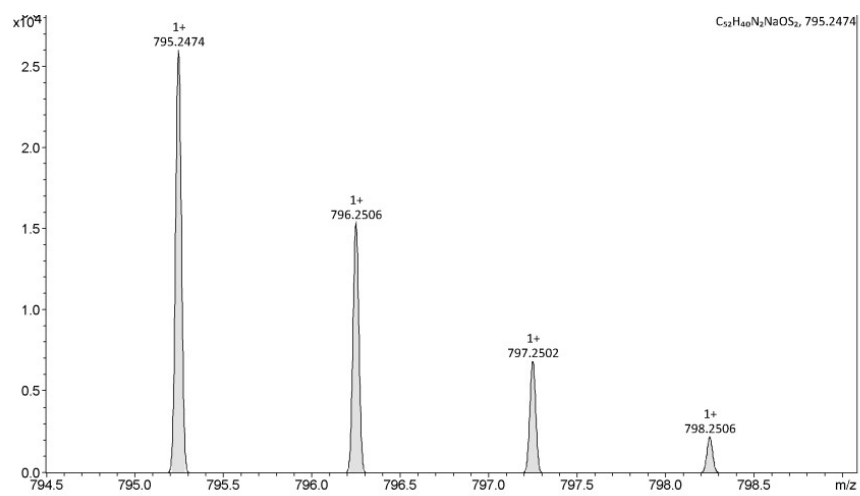


Figure S6. HR-MS spectrum of TPA-2

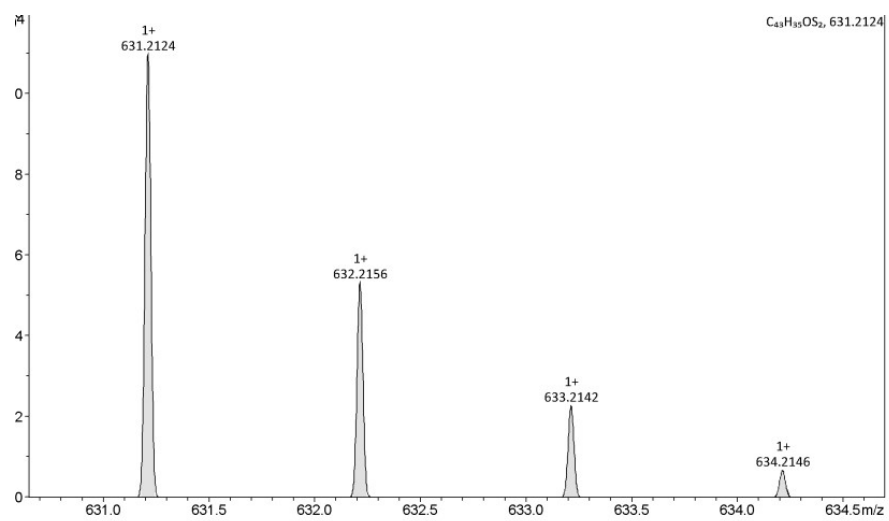


Figure S7. HR-MS spectrum of DFO-1

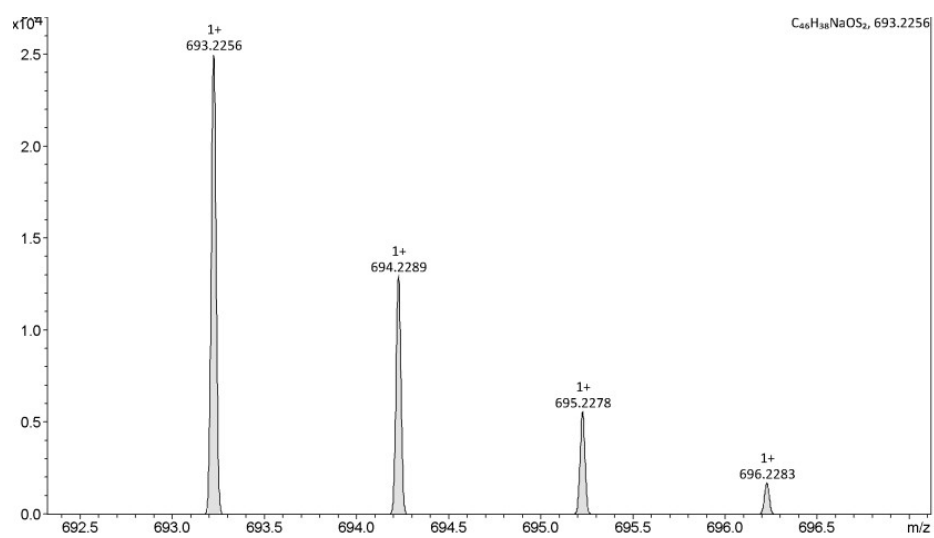


Figure S8. HR-MS spectrum of DFO-2

1.3 UV–visible spectroscopy and photolysis experiments

The absorption spectra of the photoinitiator were determined with a U-2450 spectrophotometer. For photolysis experiments, chalcone was firstly dissolved in DMSO, then irradiated with LED light (30 w/cm²) at the maximum absorption wavelength at different irradiation times, the detection wavelength was set from 300 nm to 650 nm, and the test temperature was maintained at 25 °C.

1.4 Real-time photopolymerization experiments

the photopolymerization ratio with the change of time was detected by Real-Time Fourier transform infrared spectrometer (Nicolet 5700), The homogeneous liquid including chalcones coinitiators and monomers were spread evenly between two polyvinyl chloride (PVC) films to eliminate the effect of oxygen. The change of double band conversion rate (DC) over time was determined by monitoring the change of C=C tensile vibration absorption peak area of 790 cm⁻¹. The formula was as follows:

$$C = \frac{A_0 - A_t}{A_0} \times 100 \%$$

where C was the conversion at t time, A₀ and A_t were the peak area of function group before irradiation and at t time.

1.5 Fluorescence and cyclic voltammetry experiments

The fluorescence properties of chalcones were studied by JASCO FP-6200 fluorescence spectrometer. In addition, the fluorescence quenching experiments between Iod and chalcone were performed in DMSO. The redox potential of different chalcones was measured by cyclic voltammetry in dichloromethane with tetrabutylammonium hexafluorophosphate (Aldrich) 0.1 M as the supporting electrolyte. A platinum electrode was used as the working electrode, and the

platinum auxiliary electrode and Ag/AgNO₃ were used as the reference electrode. Experiments were performed at 25 °C, in nitrogen-degassed DCM. Ferrocene was used as internal standard.

The Gibbs free energy change of charge transfer between chalcones and Iod was calculated by the RW equation.

$$\Delta G_{et} = E_{OX} - E_{red} - E_{S1} - C$$

where E_{ox} and E_{red} were the oxidation potential of the electron donor and the reduction potential of the electron acceptor, respectively; E_{S1} was the energy of the first excited state, corresponding to the energy at the intersection wavelength of the normalized absorption spectrum and the emission spectrum. The constant C was the electrostatic energy and was negligible. The reduction potential of iodonium was −0.2 eV according to the literature data ³.

1.6 Theoretical calculations

The optimized chalcone molecular structure was obtained by the Chem3D program. According to the density functional theory (DFT) method, the electrostatic potential map was obtained at the B3LYP/6-31G(d) theoretical level. Gaussian 09 software program was used for molecular orbital calculations, including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Gauss View 5.0 program was applied to visualize leading molecular orbitals. In addition, the harmonic frequencies were calculated under the same computational conditions to verify the lowest energy state of the molecular geometry.

1.7 Electron spin resonance spin-trapping (ESR-ST) experiment

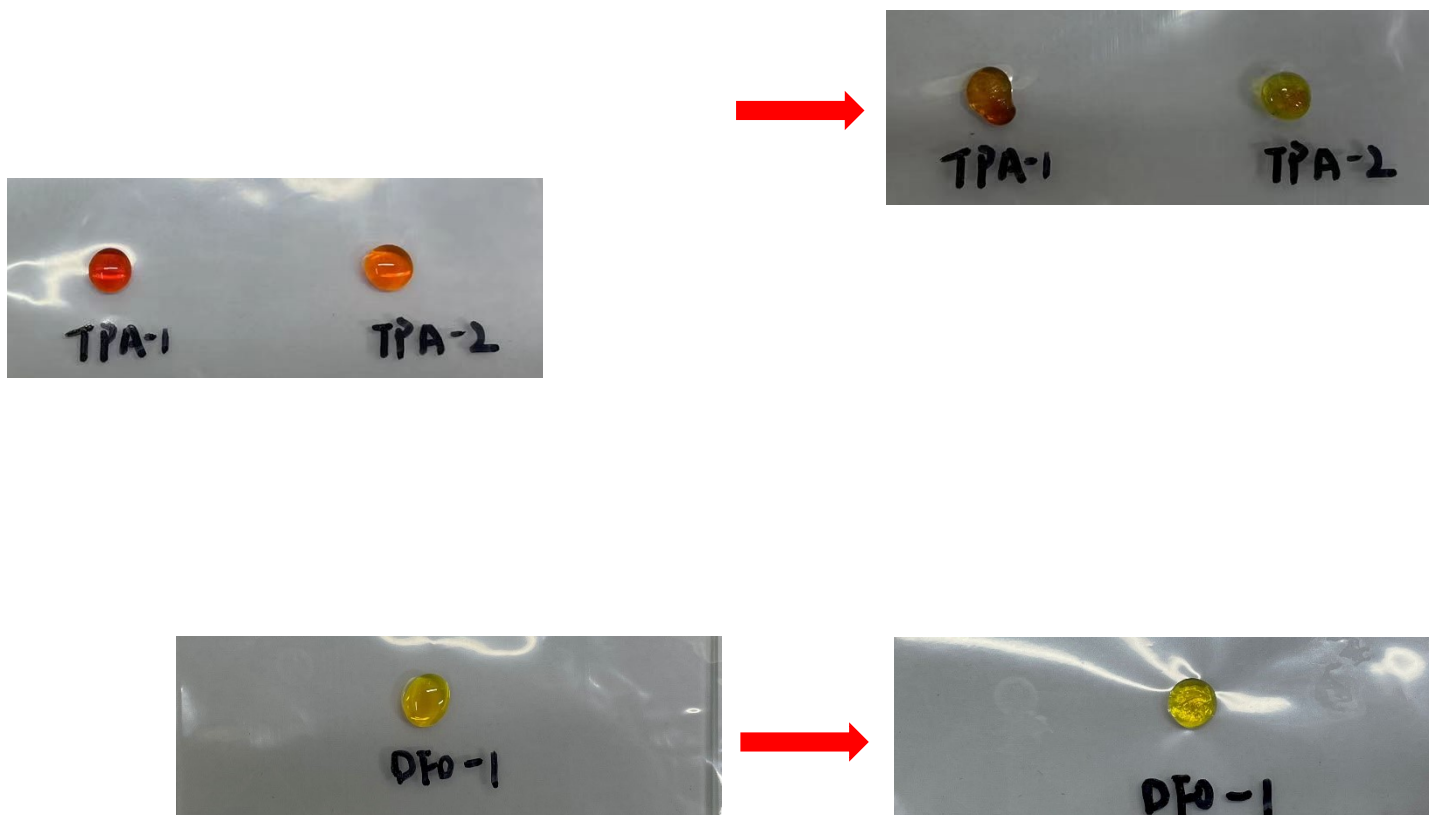
the ESR-ST experiments were carried out by Bruker ELEXSYS-II E500 CW-EPR. The chalcones, Iod, and phenyl-N-tert-butyl nitron as radicals trap dissolved in tert-butylbenzene, and then, blue LEDs were used as irradiation sources that excite free radical generation at 25 °C, in a nitrogen atmosphere.

1.8 Cytotoxicity test

Photo-induced cytotoxicity was tested by MTT colorimetry. The cells were cultured in PRMI-1640 medium containing 10 % fetal bovine serum, penicillin (100 U/mL), and streptomycin (100 U/mL). The ambient temperature was constant at 37 °C, maintaining a CO₂ concentration of 5 %. Hela cells with a cell density of 6.5×10^3 cells/well were seeded in 96-well plates and cultured overnight. Then 200 μ L of medium containing different sample concentration gradients (10 μ M, 20 μ M, 30 μ M, 40 μ M, and 50 μ M) were added to the well and cultured for 24 h. Cytotoxicity data were obtained by using an enzyme plate analyzer (BioTek ELX80).

2. Results and discussion

2.1 The photobleaching of chalcones



Before irradiation

After irradiation

Figure S9. Photobleaching properties of chalcones (0.1 wt% chalcones, 1.0 wt% Iod, 405 nm LED).

2.1 The photobleaching of DKEs

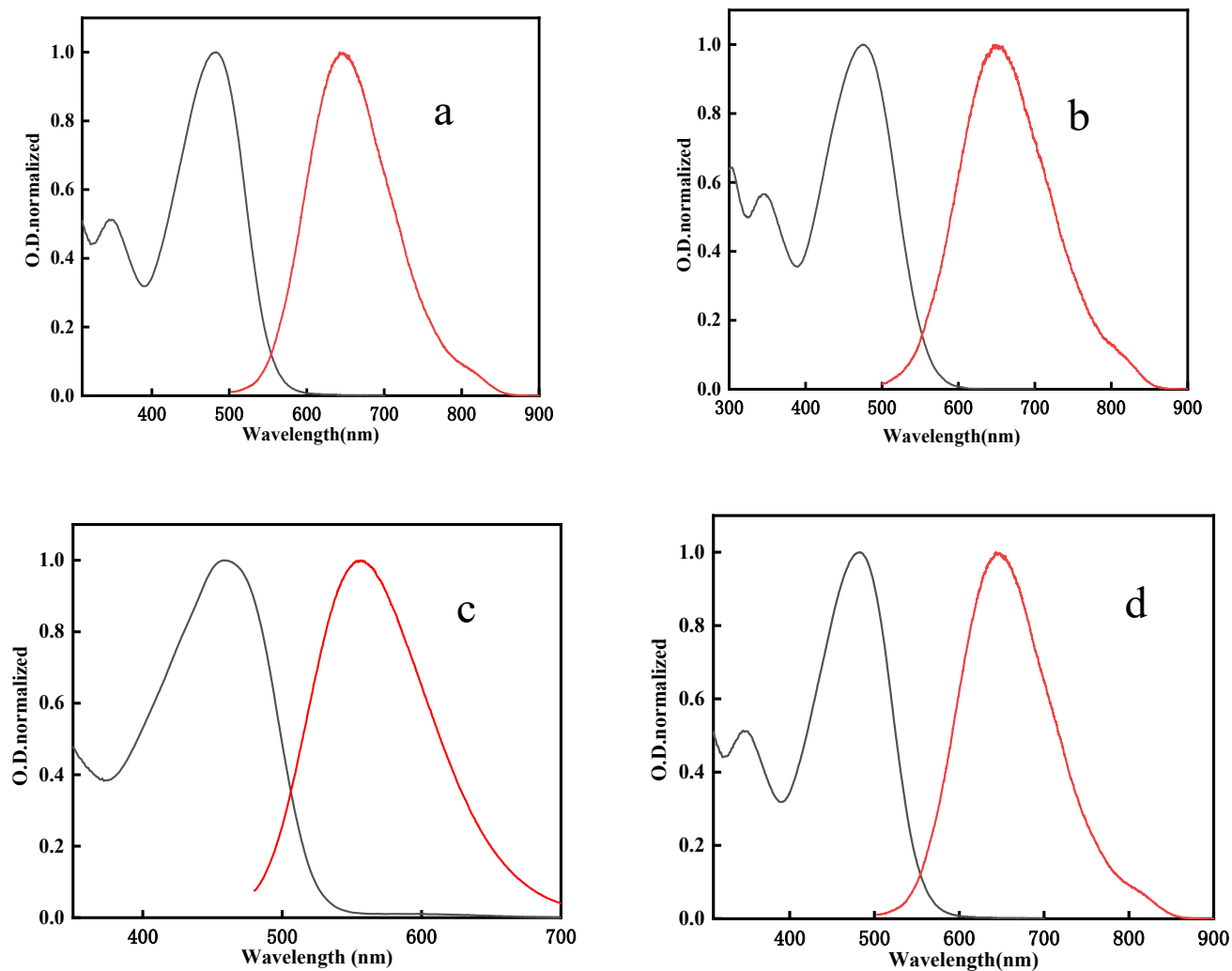


Figure S10. Singlet state energy determination in acetonitrile of (a)TPA-1; (b) TPA-2; (c) DFO-1 and (d) DFO-2

1. Zhang, G. Q.; Gao, Z.; Zhang, J.; Ou, H.; Gao, H.; Kwok, R. T. K.; Ding, D.; Tang, B. Z., A wearable AIEgen-based lateral flow test strip for rapid detection of SARS-CoV-2 RBD protein and N protein. *Cell Rep Phys Sci* **2022**, 3 (2), 100740.
2. Deng, K.; Wang, L.; Xia, Q.; Liu, R.; Qu, J., A nucleic acid-specific fluorescent probe for nucleolus imaging in living cells. *Talanta* **2019**, 192, 212-219.
3. Podsiadły, R.; Strzelczyk, R., N-substituted quinoxalinobenzothiazine/iodonium salt systems as visible photoinitiators for hybrid polymerization. *Dyes and Pigments* **2013**, 97 (3), 462-468.