Supplementary Material

for

Water-soluble bis-chalcone-based photoinitiators with long-wavelength absorption for radical polymerization and 3D printing

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1. Experimental

1.1 Characterization of bis-chalcones

The characteristic of ^{1}HNMR, ^{13}CNMR and HR-MS spectrum were shown in Fig.S1-Fig.S14.

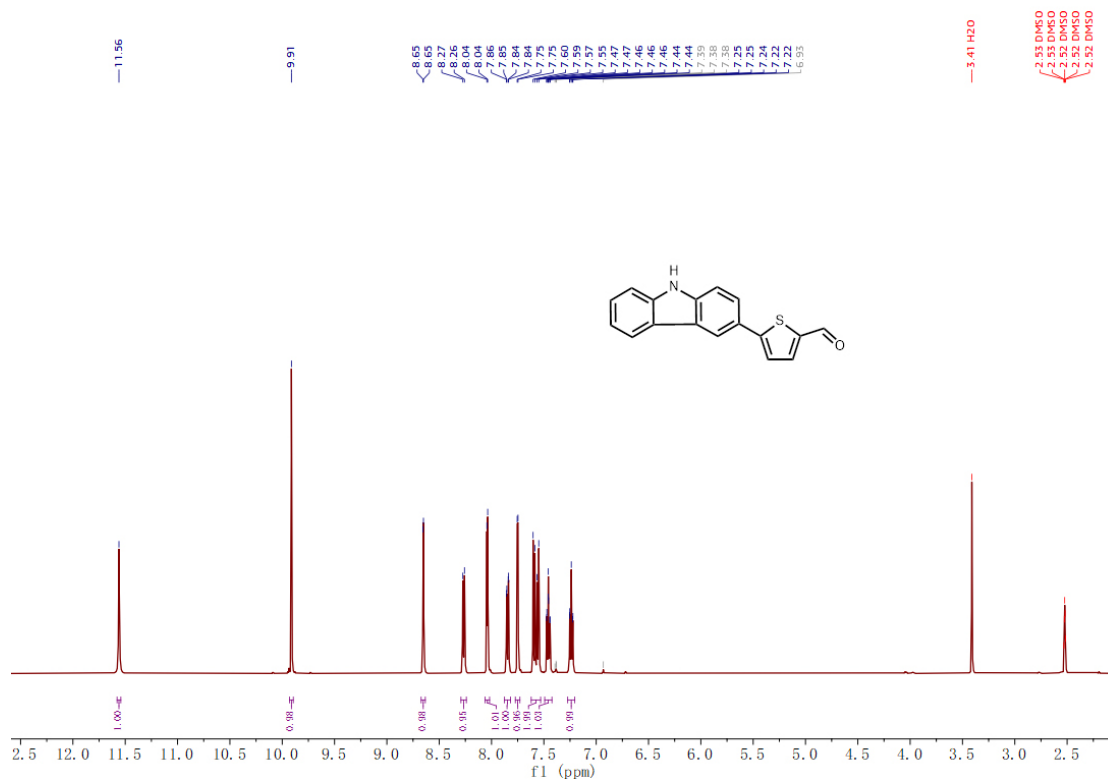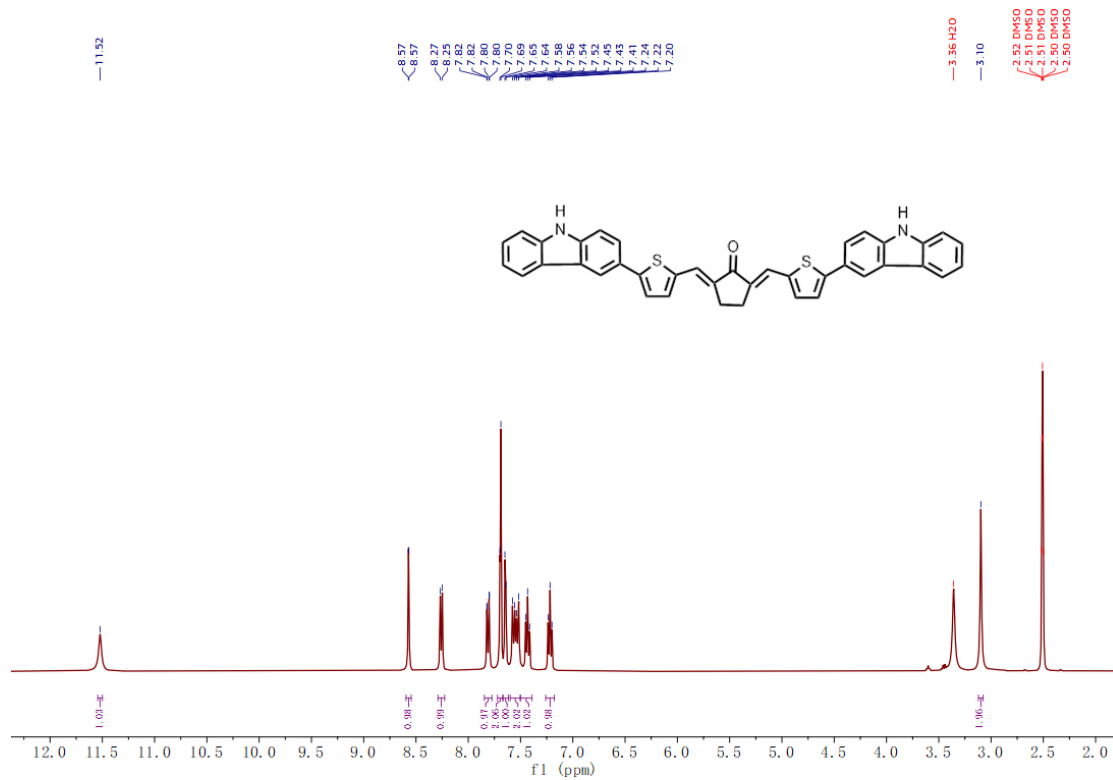Fig. S1 ^{1}H NMR spectrum of KS (NMR solvent: DMSO-d_6).

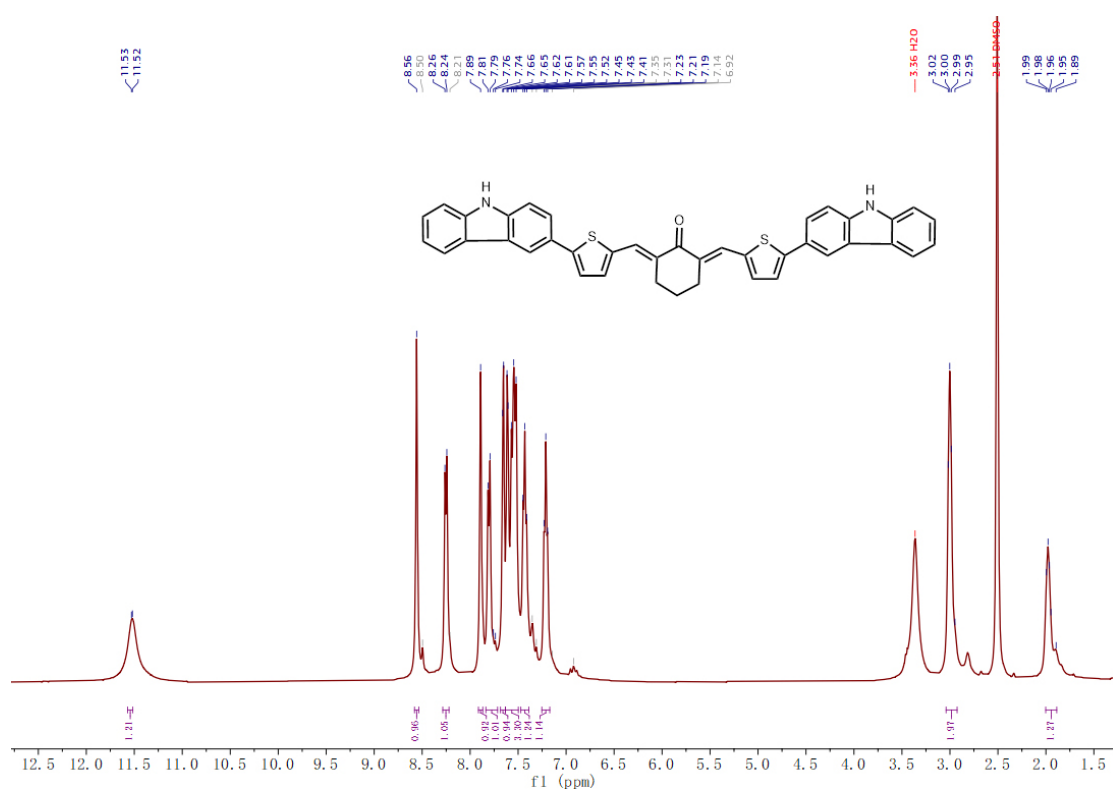Fig. S2 ^{1}H NMR spectrum of KSE (NMR solvent: DMSO-d_6).

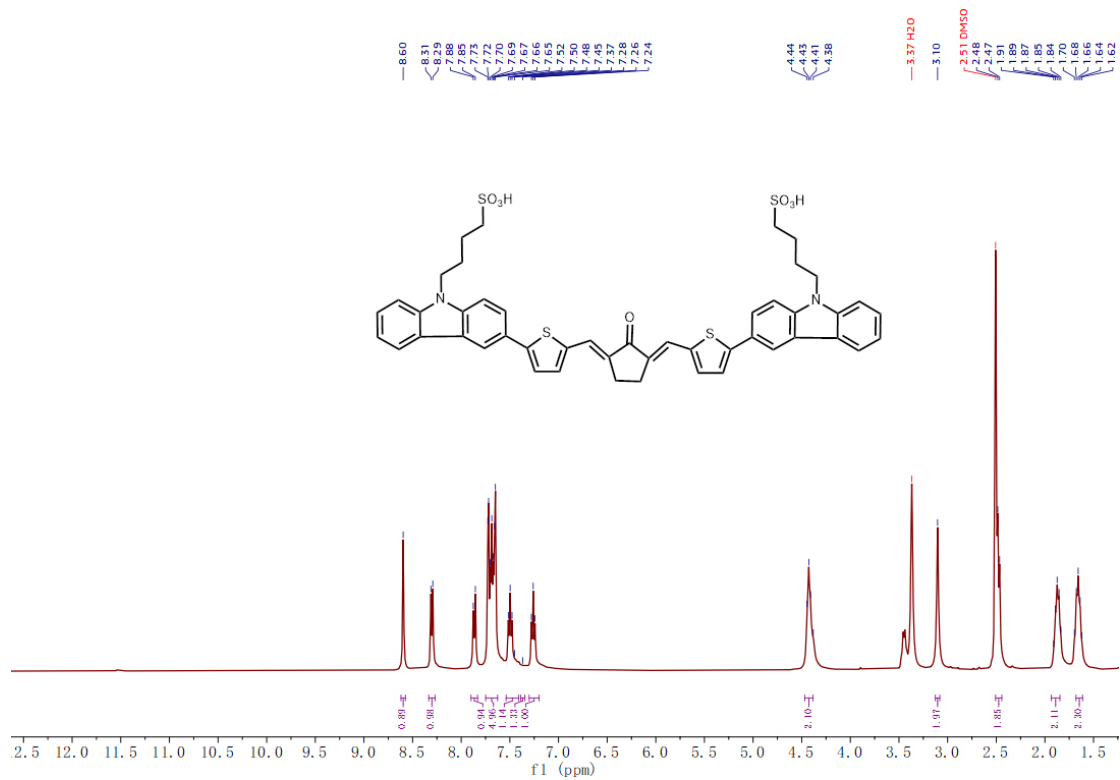
Fig. S3 ^{1}H NMR spectrum of KST (NMR solvent: DMSO-d_6).

Fig. S4 ^{1}H NMR spectrum of KSES (NMR solvent: DMSO-d_6).

Fig. S5 ^{1}H NMR spectrum of KSTS (NMR solvent: DMSO-d_6).

Fig. S6 ^{13}C NMR spectrum of KS (NMR solvent: DMSO-d_6).
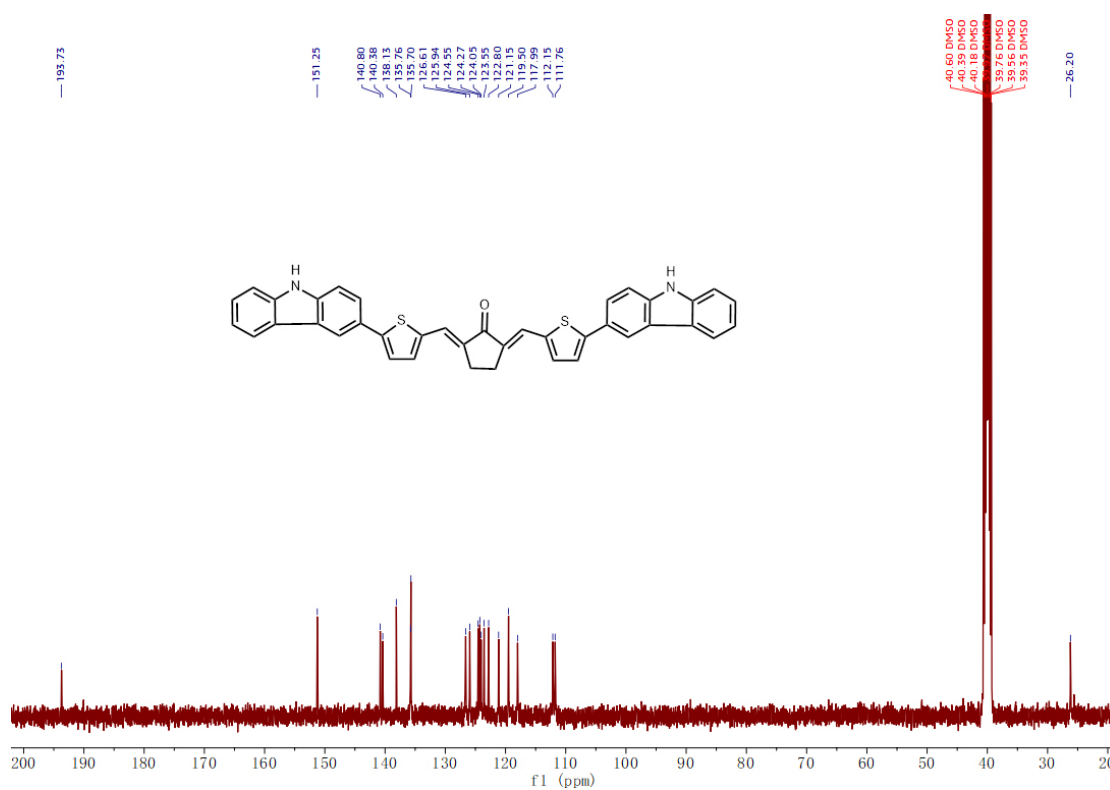
Fig. S7 ^{13}C NMR spectrum of KSE (NMR solvent: DMSO-d_6).
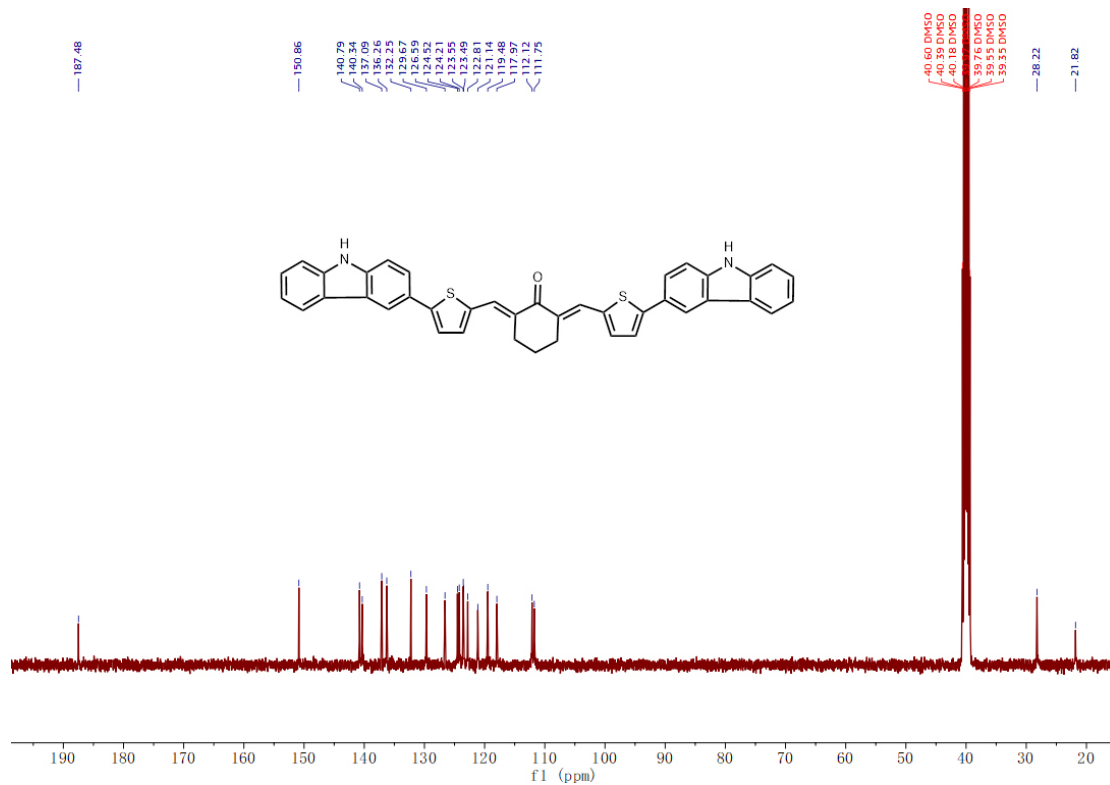
Fig. S8 ^{13}C NMR spectrum of KST (NMR solvent: DMSO-d_6).
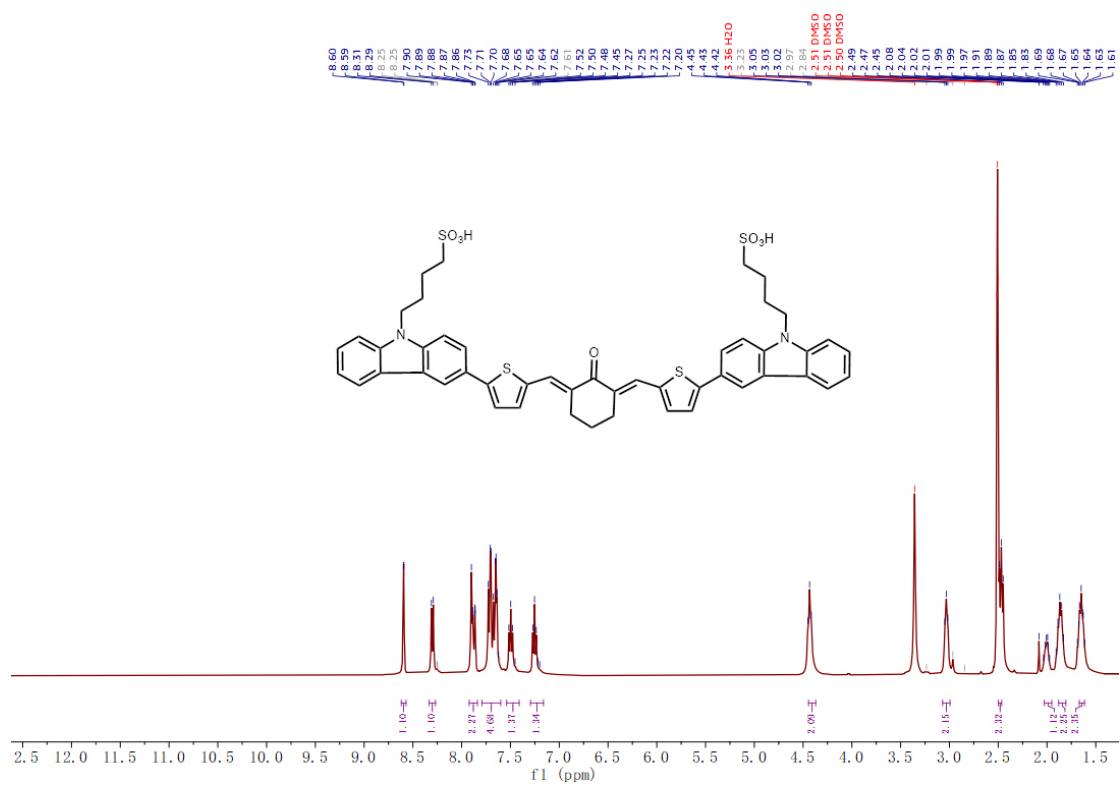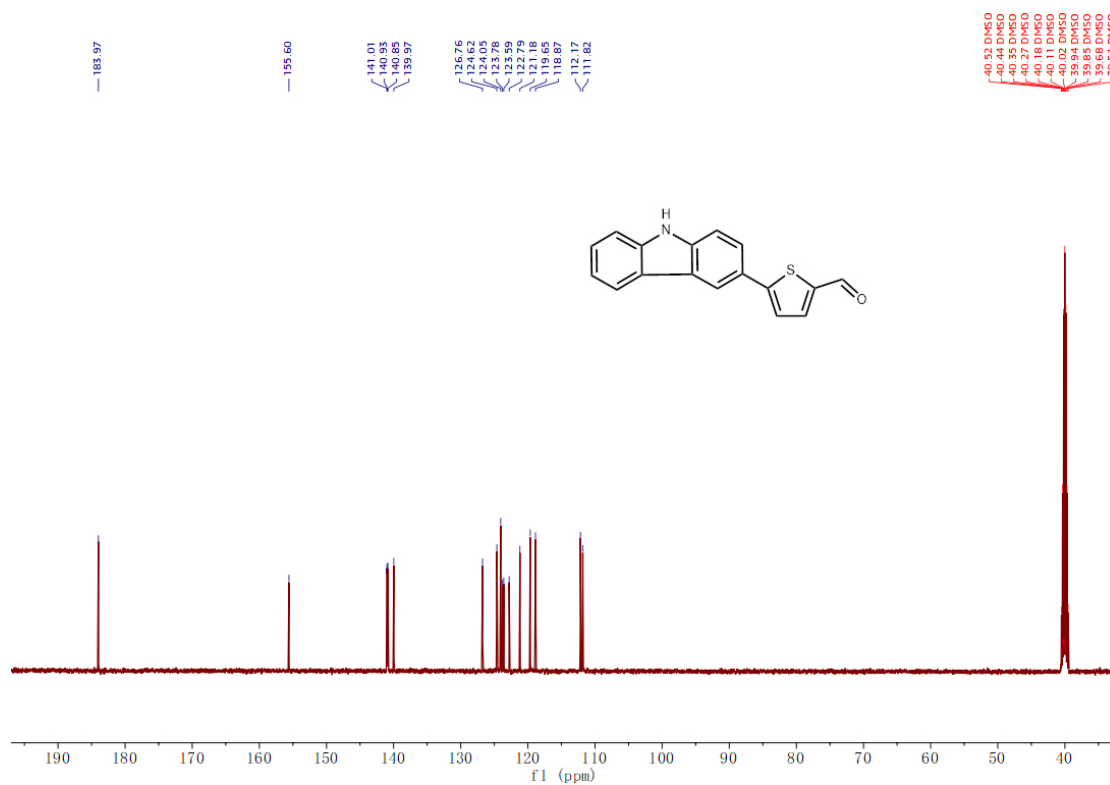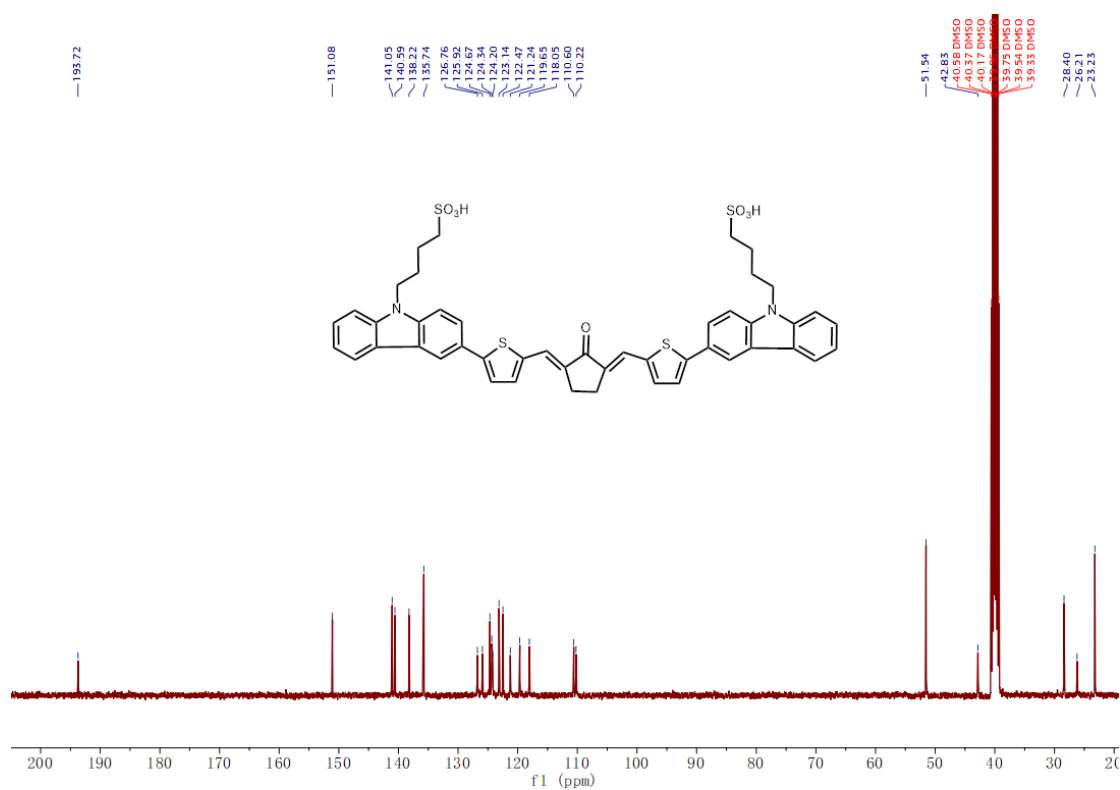

Fig. S9 ^{13}C NMR spectrum of KSES (NMR solvent: DMSO-d_6).
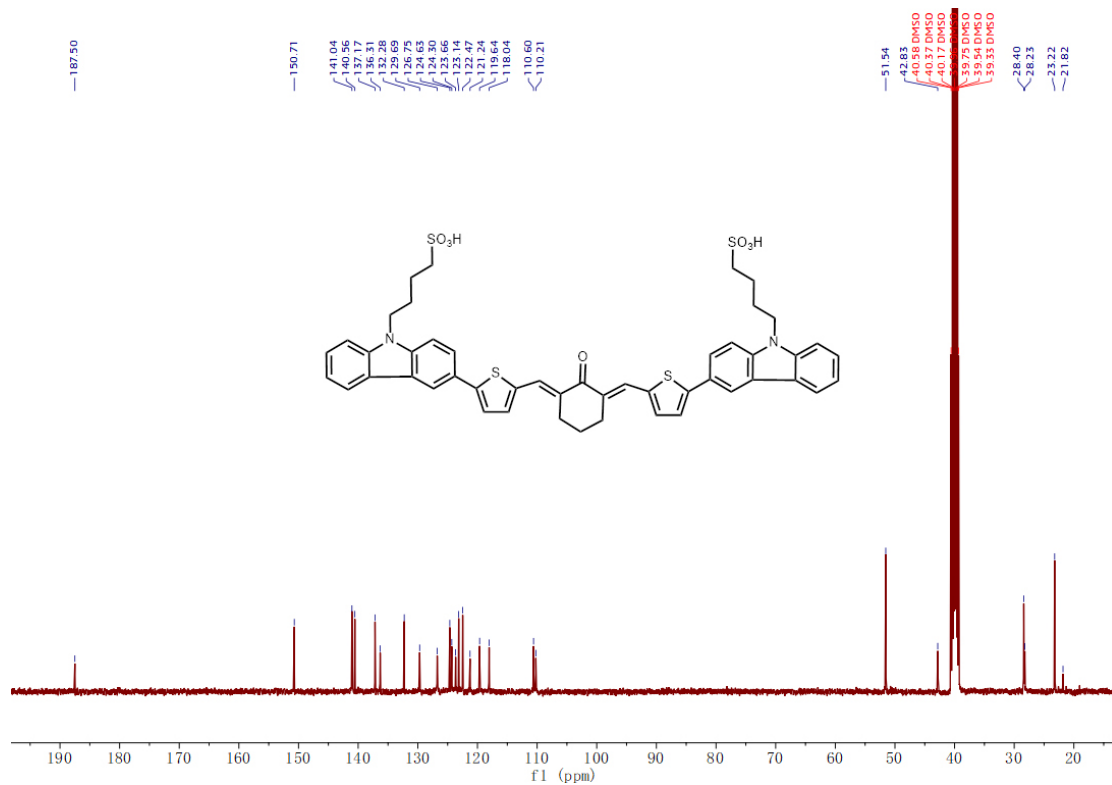
Fig. S10 ^{13}C NMR spectrum of KSTS (NMR solvent: DMSO-d_6).
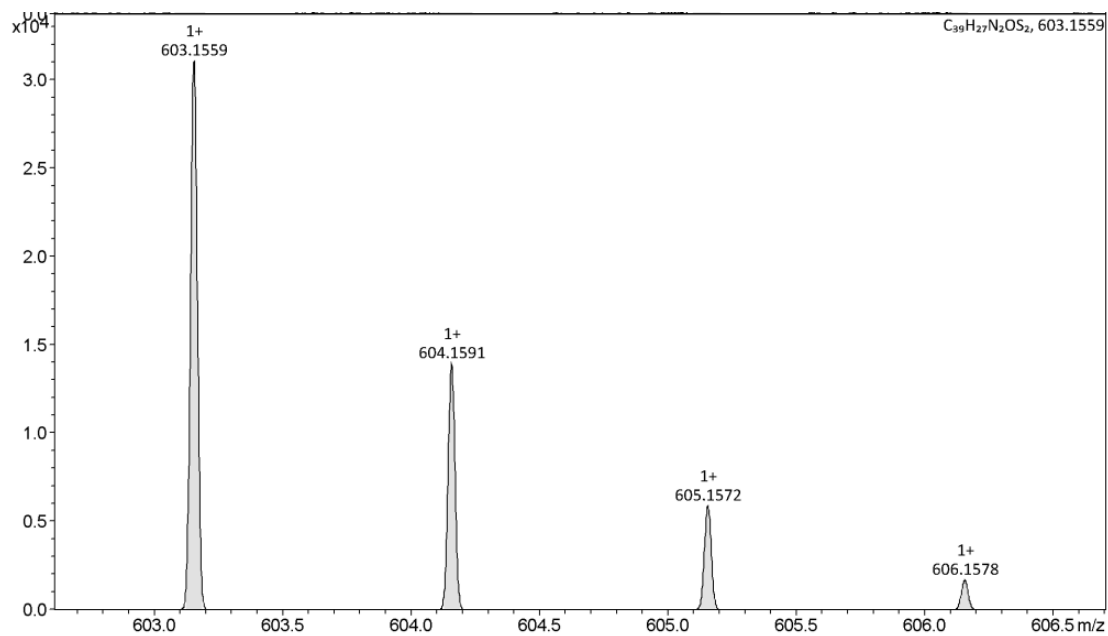
Fig. S11 HR-MS spectrum of KSE.

C₄₀H₂₈N₂NaOS₂, 639.1535

| 1+ | 1+ | 1+ | 1+ |
| 639.1535 | 640.1567 | 641.1550 | 642.1555 |
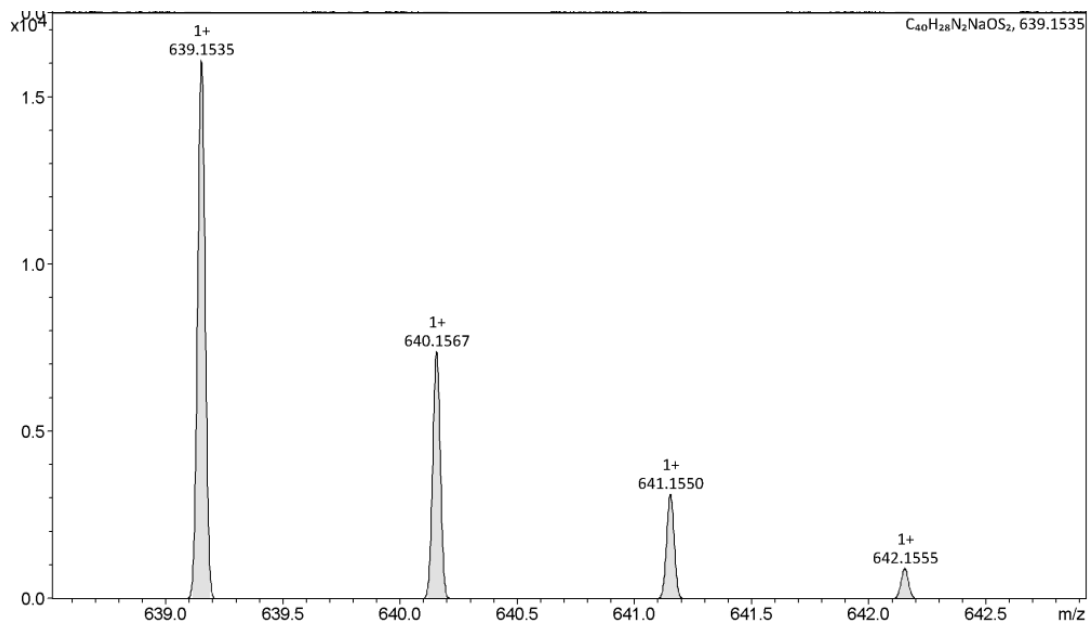
Fig. S12 HR-MS spectrum of KST.

C₄₇H₄₃N₂O₇S₄, 875.1948

| 1+ | 1+ | 1+ | 1+ | 1+ |
| 875.1948 | 876.1978 | 877.1955 | 878.1962 | 879.1948 |
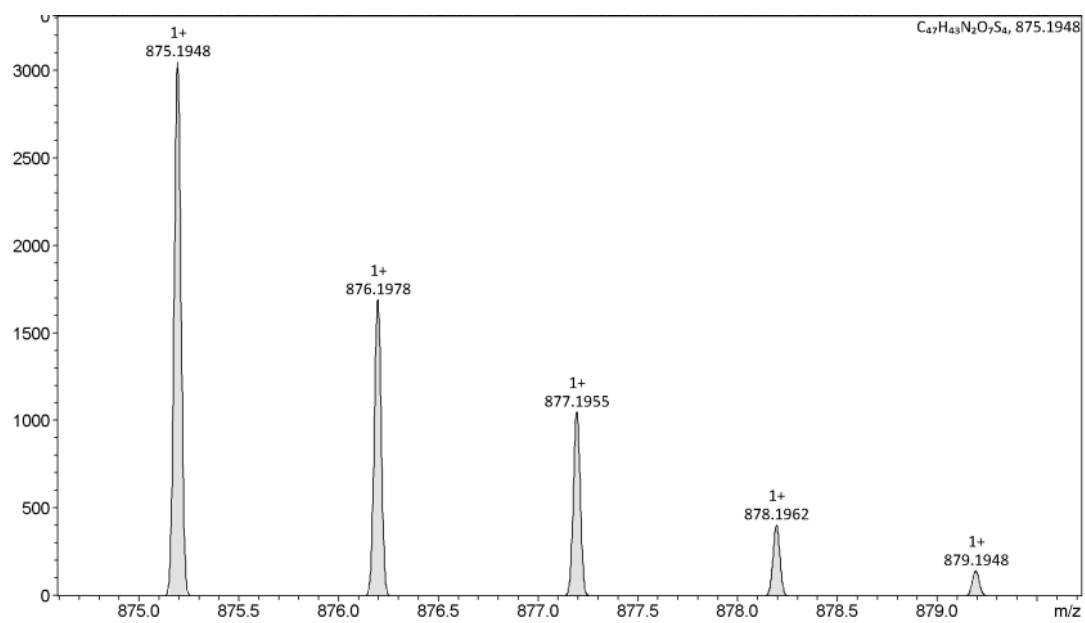
Fig. S13 HR-MS spectrum of KSES.
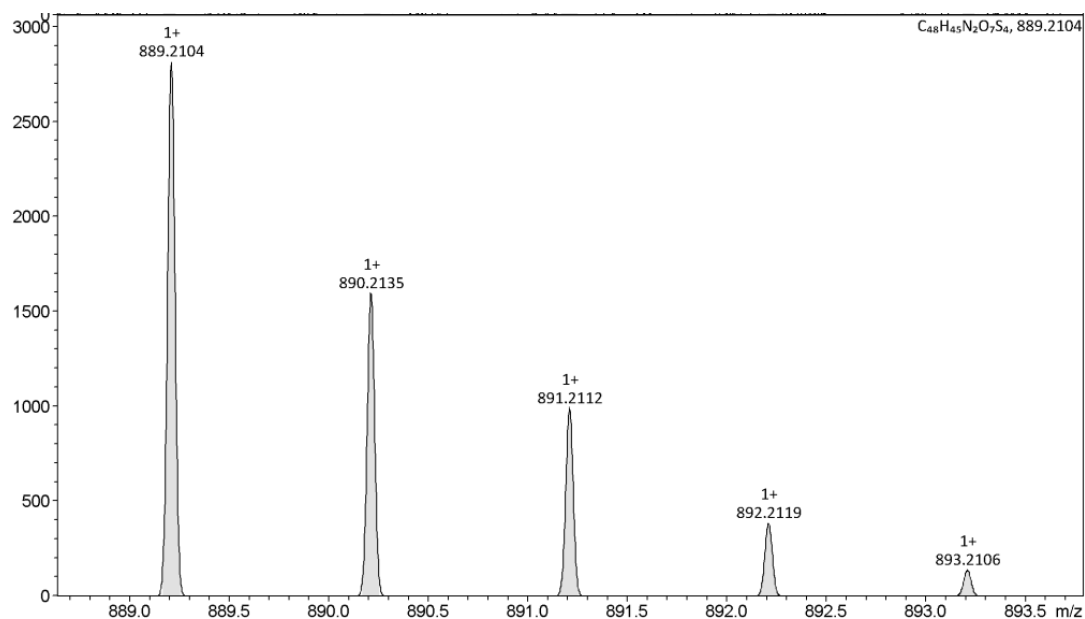
Fig. S14 HR-MS spectrum of KSTS.

KS: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.56 (s, 1H), 9.91 (s, 1H), 8.65 (d, J = 1.9 Hz, 1H), 8.27 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 3.9 Hz, 1H), 7.85 (dd, J = 8.5, 1.9 Hz, 1H), 7.75 (d, J = 4.0 Hz, 1H), 7.58 (dd, J = 18.7, 8.3 Hz, 2H), 7.46 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 7.27 – 7.20 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.97, 155.60, 141.01, 140.93, 140.85, 139.97, 126.76, 124.62, 124.05, 123.78, 123.59, 122.79, 121.18, 119.65, 118.87, 112.17, 111.82.

KSE: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.57 (d, J = 1.9 Hz, 1H), 8.26 (d, J = 7.8 Hz, 1H), 7.81 (dd, J = 8.5, 1.9 Hz, 1H), 7.69 (d, J = 3.8 Hz, 2H), 7.64 (d, J = 4.0 Hz, 1H), 7.55 (dd, J = 15.5, 8.3 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 3.10 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.73, 151.25, 140.80, 140.38, 138.13, 135.76, 135.70, 126.61, 125.94, 124.55, 124.27, 124.05, 123.55, 122.80, 121.15, 119.50, 117.99, 112.15, 111.76, 26.20. HRMS (ESI): calcd for $C_{39}H_{27}N_2OS_2$ [M$^+$H]$^+$ 603.1566, found, 603.1559.

KST: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.56 (s, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.89 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 3.8 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.43 (t, J = 7.7 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 2.99 (q, J = 15.4, 10.8 Hz, 2H), 2.00 – 1.89 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.48, 150.86, 140.79, 140.34, 137.09, 136.26, 132.25, 129.67, 126.59, 124.52, 124.21, 123.55, 123.49, 122.81, 121.14, 119.48, 117.97, 112.12, 111.75, 28.22, 21.82. HRMS (ESI): calcd for $C_{40}H_{28}N_2NaOS_2$ [M$^+$Na]$^+$ 639.1541, found, 639.1535.

KSES: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (s, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.75 – 7.63 (m, 5H), 7.50 (t, J = 7.7 Hz, 1H), 7.37 (s, 1H), 7.26 (t, J = 7.4 Hz, 1H), 4.43 (t, J = 7.1 Hz, 2H), 3.10 (s, 2H), 2.47 (d, J = 7.6 Hz, 2H), 1.87 (t, J = 7.7 Hz, 2H), 1.65 (q, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.72, 151.08, 141.05, 140.59, 138.22, 135.74, 126.76, 125.92, 124.67, 124.34, 124.20, 123.14, 122.47, 121.24, 119.65, 118.05, 110.60, 110.22, 51.54, 42.83, 28.40, 26.21, 23.23. HRMS (ESI): calcd for $C_{47}H_{43}N_2O_7S_4$ [M$^+$H]$^+$ 875.1954, found, 875.1948.

KSTS: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (d, J = 1.8 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.79 – 7.60 (m, 5H), 7.50 (t, J = 7.7 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 4.42 (d, J = 7.3 Hz, 2H), 3.03 (t, J = 6.1 Hz, 2H), 2.48 (d, J = 7.6 Hz, 2H), 2.00 (dd, J = 9.0, 4.2 Hz, 1H), 1.86 (d, J = 7.7 Hz, 2H), 1.65 (t, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 187.50, 150.71, 141.04, 140.56, 137.17, 136.31, 132.28, 129.69, 126.75, 124.63, 124.30, 123.66, 123.14, 122.47, 121.24, 119.64, 118.04, 110.60, 110.21, 51.54, 42.83, 28.40, 28.23, 23.22, 21.82. HRMS

(ESI): calcd for $C_{48}H_{45}N_2O_7S_4$ $[M^+H]^+$ 889.2110, found, 889.2104.

1.2 UV-vis spectra and photodecomposition experiment

The photoinitiators KSE, KST, KSES and KSTS were dissolved in DMSO solution and configured into 2×10^{-5} mol/L solution, then UV-vis spectra experiments were recorded on a UV-2600 spectrophotometer at room temperature. The optical path of the cuvette used is 1 cm, and the molar extinction coefficient of the photoinitiator at the maximum absorption wavelength was calculated according to the Lambert-Beer formula.

For photodecomposition experiments, photoinitiators was firstly dissolved in DMSO, then deoxidized with nitrogen for 10 min and irradiated for different times under 480 nm LED light (30 W/cm^2).

1.3 Real-time infrared spectroscopy

The photopolymerization performance of KSE, KST, KSES and KSTS was monitored 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 test time was set to 240 s and the infrared spectrum recording range was 4000~600 cm^{-1}. The change of double band conversion (DC) over time was determined by monitoring the change of C=C tensile vibration absorption peak area of 810 cm^{-1}. The formula was as follows:

$$DC = \frac{A0 - At}{A0} \times 100\%$$

where DC was the conversion at t time, A0 and At were the peak area of function

group before irradiation and at t time.

1.4 Theoretical calculations

The optimized bis-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.

1.5 Fluorescence quenching experiment

The fluorescence properties of bis-chalcones were studied by F-7000 fluorescence spectrometer. The chalcone solution to be tested was configured with the concentration of 1×10^{-5} mol/L in DMSO. In addition, the fluorescence quenching experiments between Iod and chalcone were performed in DMSO. The scanning speed was 1200 nm/min and the slit width was 2.5 nm. Fluorescence quantum yield (Φ_{eT}) was determined using the absorbance at the wavelength and fluorescence intensity according to the following equation.

$$\Phi eT = \frac{\Phi s \times Fu \times As}{Fs \times Au}$$

where Φs was the fluorescence quantum yield of reference material, Fu and Fs were the integrated fluorescence intensity of test material and reference material, Au and As were the absorbance of the test material and reference material.

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

The ESR-ST experiments were carried out by Bruker ELEXSYS-II E500 CW-EPR. The bis-chalcones, Iod, and phenyl-N-tert-butylnitrone as radicals trap dissolved in DMSO, and then inject nitrogen for 10 min to remove oxygen from the solution. The 480 nm LED lamp was used as irradiation sources that excite free radical generation.

1.7 Solubility of KSE, KST, KSES and KSTS

Adding bis-chalcone (1 mg), solvent (1ml) or monomer (1g) into the centrifuge tube, testing the solubility of KSE, KST, KSES and KSTS at room temperature. Indicating "++" for those that are completely dissolved by simple shock, and "+" for those that can be completely dissolved by ultrasonic oscillations and high-speed shock. After the above treatment, a small part of the undissolved is indicated by "-", and after the above treatment, most of the undissolved is indicated by "--".

1.8 The surface drying time of cured films

To research the surface drying time of the coating films, a series of curing films with different formulations were prepared. The specific operations were as follows: a certain amount of KSE, KST, KSES and KSTS, co-initiator (Iod, TEOA), water and PEGDA were prepared into uniform mixture liquid, and the thickness was about 20 μm. The film was cured under different light source. According to the national standard method (GB/T 1728-2020), the surface drying time of the coating was tested and characterized.

1.9 Migration properties of photoinitiators

The carbazolyl photoinitiator (0.1 wt %), coinitiator (1.0 wt % Iod, 1.0 wt %

TEOA) and PEGDA or PEGDA/water (80%/20%, wt) as monomer were mixed and stirred evenly according to the mass ratio, respectively. After standing, the film was prepared and cured. About 0.5 g of cured coating was placed in 25 mL DMSO solvent and soaked at room temperature for 24 h. After filtration, the absorbance of the maximum absorption peak of the photoinitiator was measured with a UV-visible spectrophotometer, and the migration extraction amount of the photoinitiator was quantitatively calculated according to Lamberbier's law. The formula is as follows:

$$\text{migration ratio} = \frac{25 \times A \times M}{\varepsilon \times 1 \times m_0} \times 100\%$$

Where A is the absorption, M is molecular weight of KSE, KST, KSES and KSTS, ε is the molar absorption coefficient of the photoinitiator in the solution, l is the length of the optical path, and m_0 is the mass of the solid film.

1.10 Cytotoxicity test

Photo-induced cytotoxicity was tested by CCK-8 colorimetry. The cells were cultured in DMEM 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 CO_2 concentration of 5 %. 3T3 cells with a cell density of 5×10^3 cells/well were seeded in 96-well plates and cultured overnight. Then 200 μL of medium containing different sample concentration gradients (10 μM, 20 μM, 30 μM, 40 μM, and 50 μM) were added to the well and cultured for 24 h. Cytotoxicity data were obtained by using an enzyme plate analyzer (BioTek ELX80).

1.11 3D Printing experiment

The carbazolyl photoinitiator (0.1 wt %), coinitiator (1.0 wt % Iod, 1.0 wt %

TEOA) and PEGDA or PEGDA/water (80%/20%, wt) as monomer were mixed and stirred evenly for 3D printing. Printing was carried out with a slice thickness of 0.05 mm on an LCD 3D printer (YIHERO, MS Pro) for LED@405 nm (5.0 mW/cm^2), the printout was washed with ethanol and air dried.

2. Results and discussion

2.1 Photophysical properties

Table S1 λ_{max} and ε_{max} of KSE, KST, KSES and KSTS in DMSO or H$_2$O.

Sample	KSE	KST	KSES	KSTS	KSES	KSTS
Solvent	DMSO	DMSO	DMSO	DMSO	H$_2$O	H$_2$O
λ_{max} (nm)	498	474	500	474	514	469
ε_{max} (L·mol^{-1}·cm^{-1})	53998	45702	40456	24989	28784	16787

2.2 Solubility of KSE, KST, KSES and KSTS

Table S2 The solubility of photoinitiators in different solvents and monomers

PI	DMSO	CHCl$_3$	CH$_2$Cl$_2$	EA	THF	DMF	H$_2$O	PEGDA
KSE	++	--	--	--	+	++	--	-
KST	++	-	-	-	++	++	--	+
KSES	++	--	---	--	--	++	++	--
KSTS	++	--	--	--	--	+	++	--

Note: can be completely dissolved after simple oscillation are expressed as "++"; can be completely dissolved after ultrasonic and high-speed oscillation are indicated by "+". After the above treatment, a small part of the undissolved is indicated by "-", and after the above treatment,

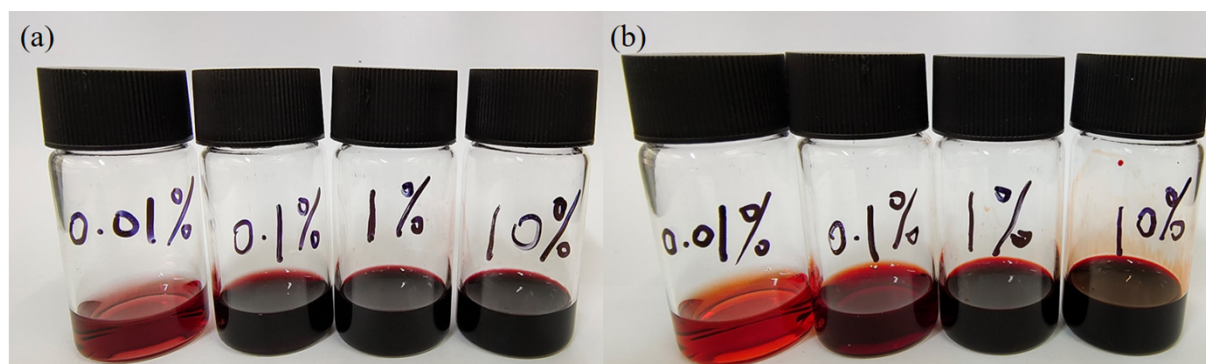most of the undissolved is indicated by "--".

Fig. S15 Images of different mass ratios of bis-chalcone dissolved in water: (a) KSES;
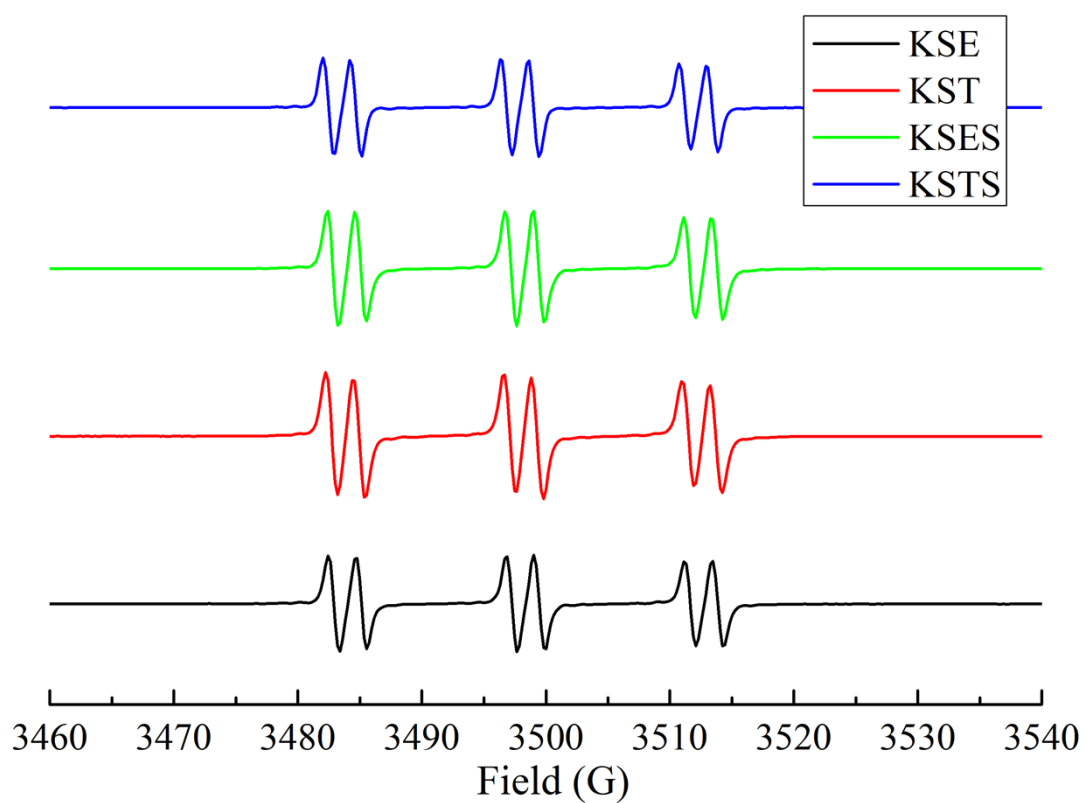
(b) KSTS.

2.3 ESR-ST spectrum

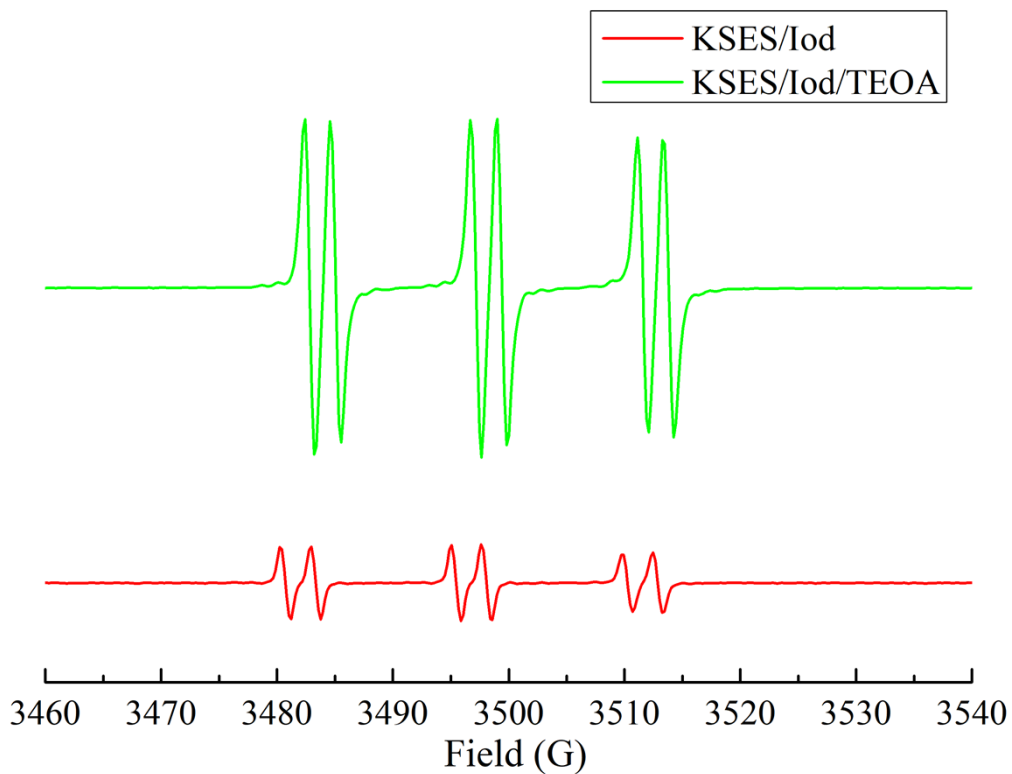Fig. S16 ESR-ST spectrum of bis-chalcone/Iod/TEOA system.

Fig. S17 ESR-ST spectrum of KSES/Iod system and KSES/Iod/TEOA system.

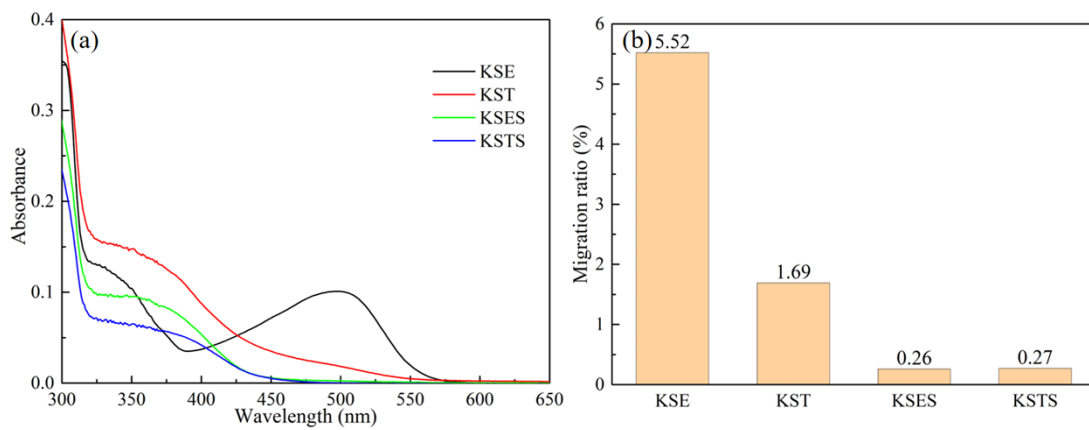## 2.4 Migration properties of KSE, KST, KSES and KSTS

Fig. S18 (a) UV absorption spectra in DMSO; (b) The migration ratio of four bis-chalcones