Supporting Information

# Phototherapeutic applications of benzophenone-containing NIR-emitting photosensitizers based on different receptor modulations

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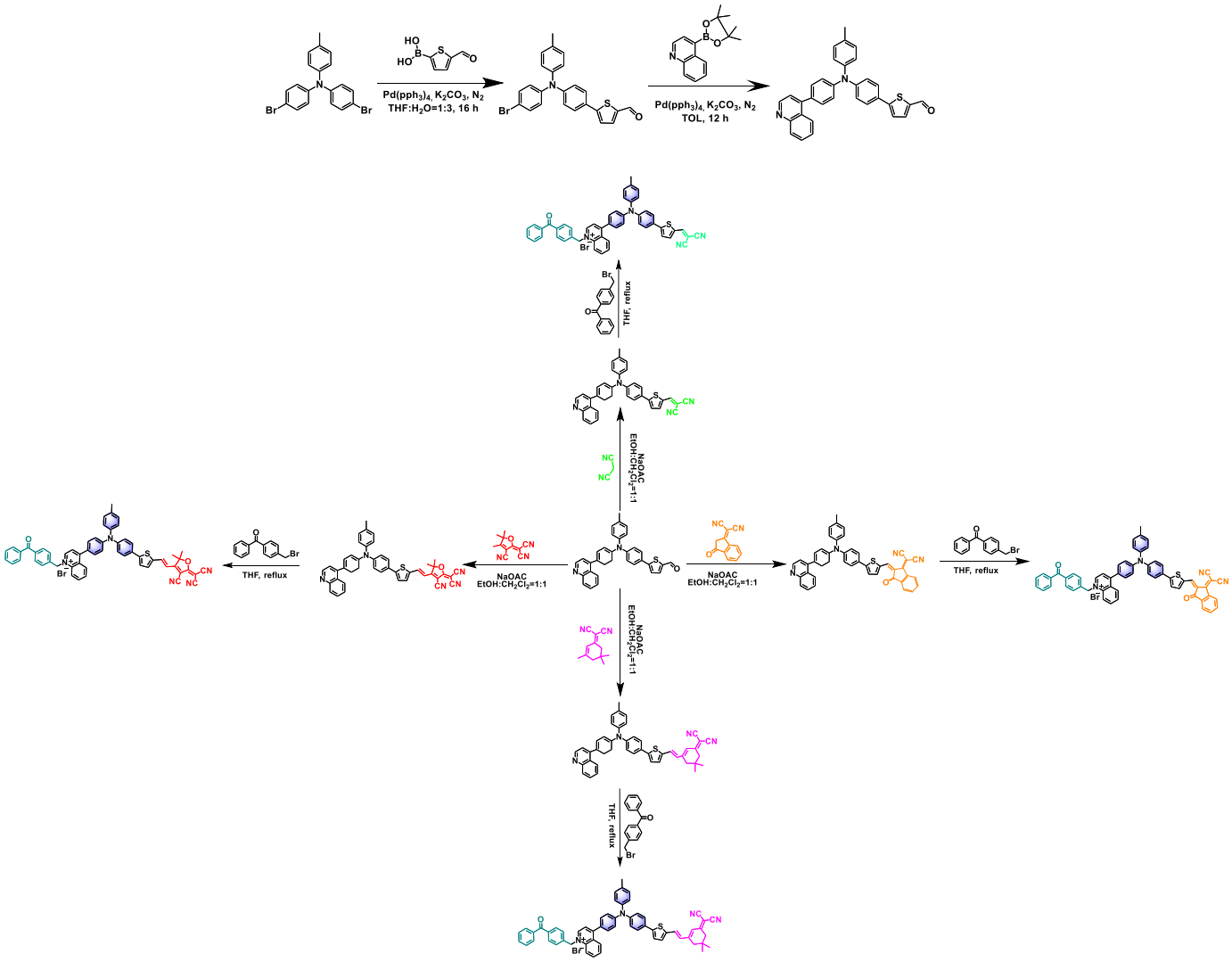
## 1. Synthesis




**Scheme S1.** Synthetic routes of CN-TPAQ-BP, ICN-TPAQ-BP, FCN-TPAQ-BP and ACN-TPAQ-BP.

## 1. $^{1}H$ and $^{13}C$ NMR spectra

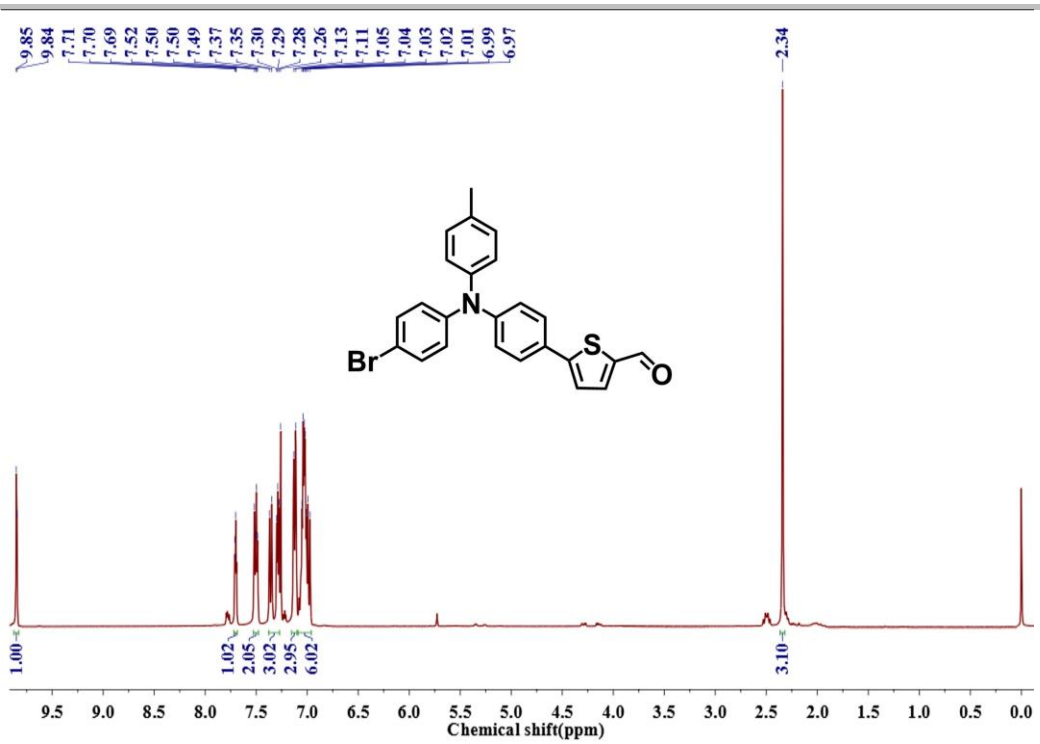



**Fig. S1** $^{1}H$ NMR spectrum of TPA-T in $CDCl_3$.

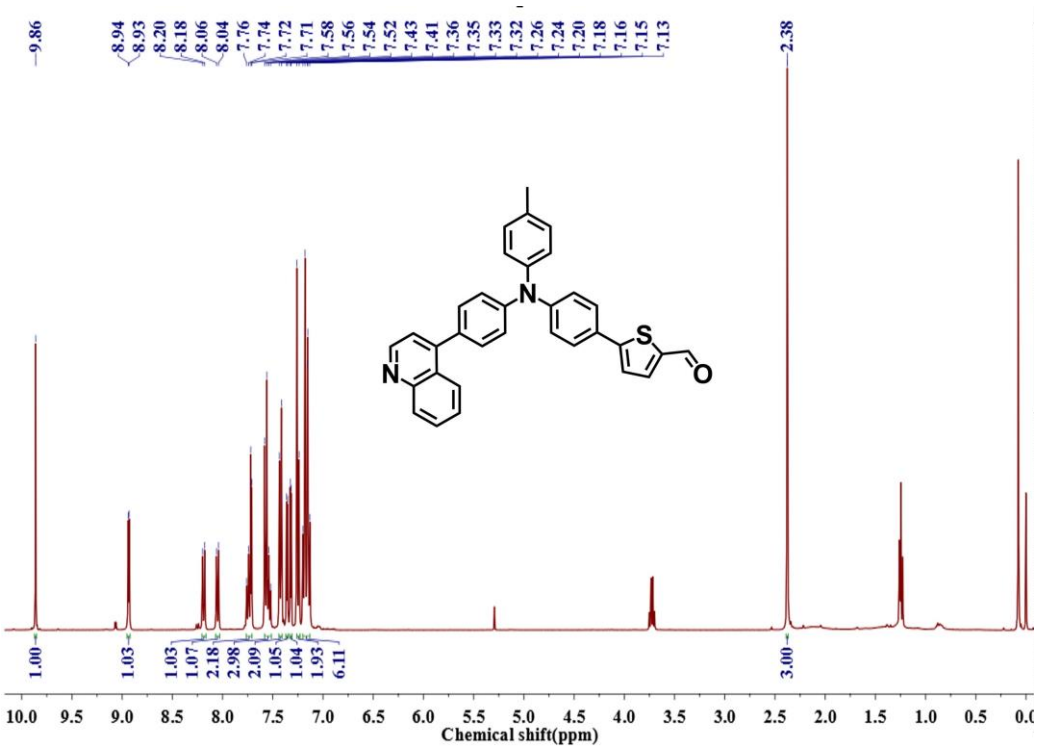



**Fig. S2** $^{1}H$ NMR spectrum of TPAQ-T in $CDCl_3$.

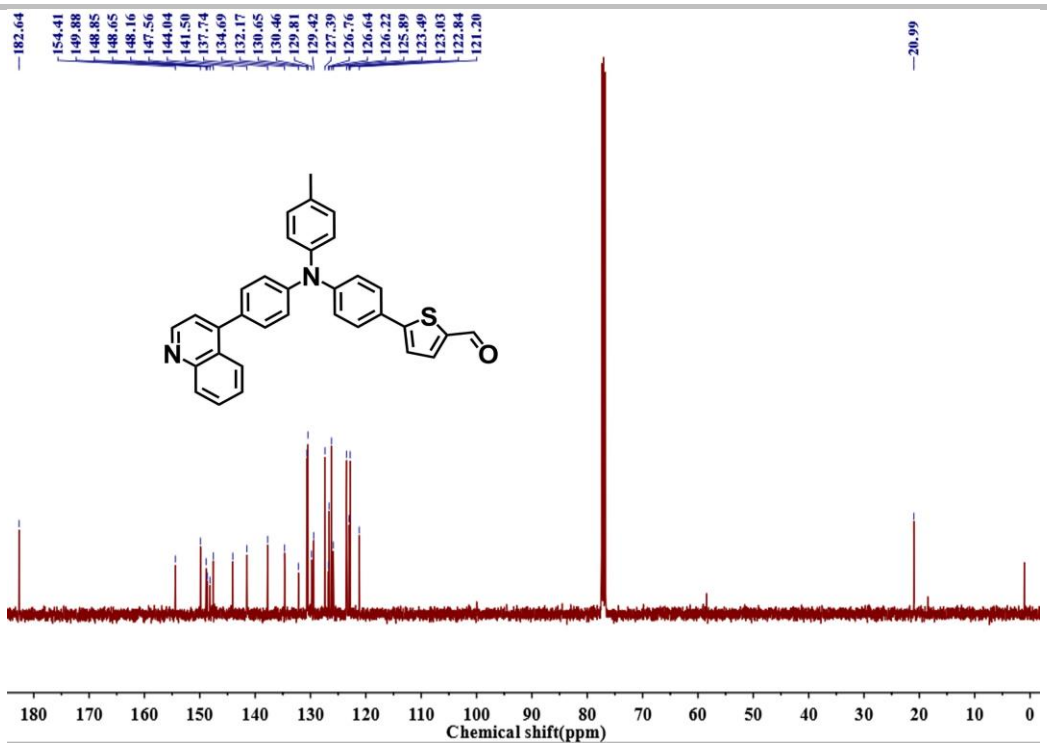



**Fig. S3** $^{13}C$ NMR spectrum of TPAQ-T in $CDCl_3$.

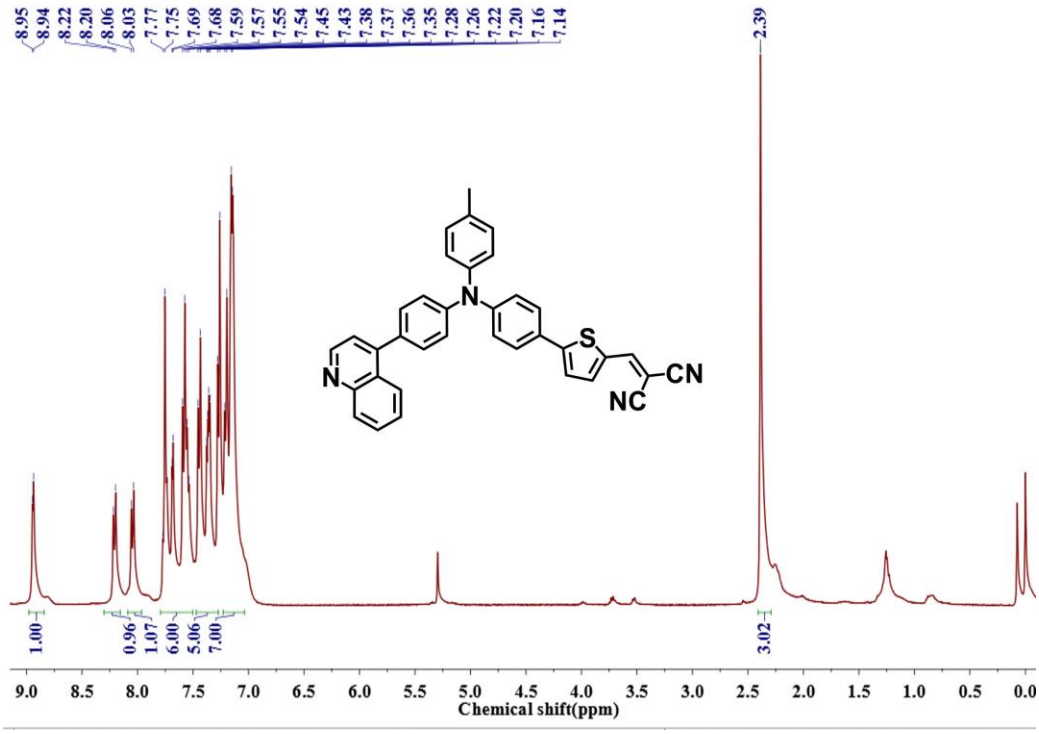



**Fig. S4** $^{1}H$ NMR spectrum of CN-TPAQ in $CDCl_3$.

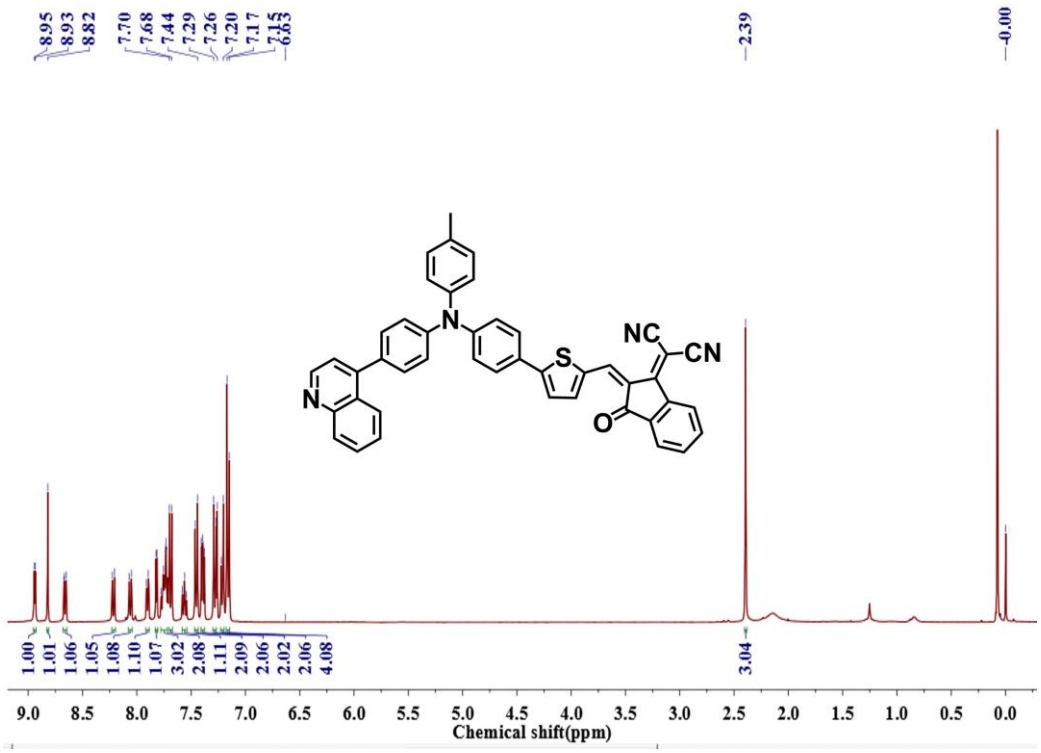



**Fig. S5** $^{1}$H NMR spectrum of ICN-TPAQ in $CDCl_3$.

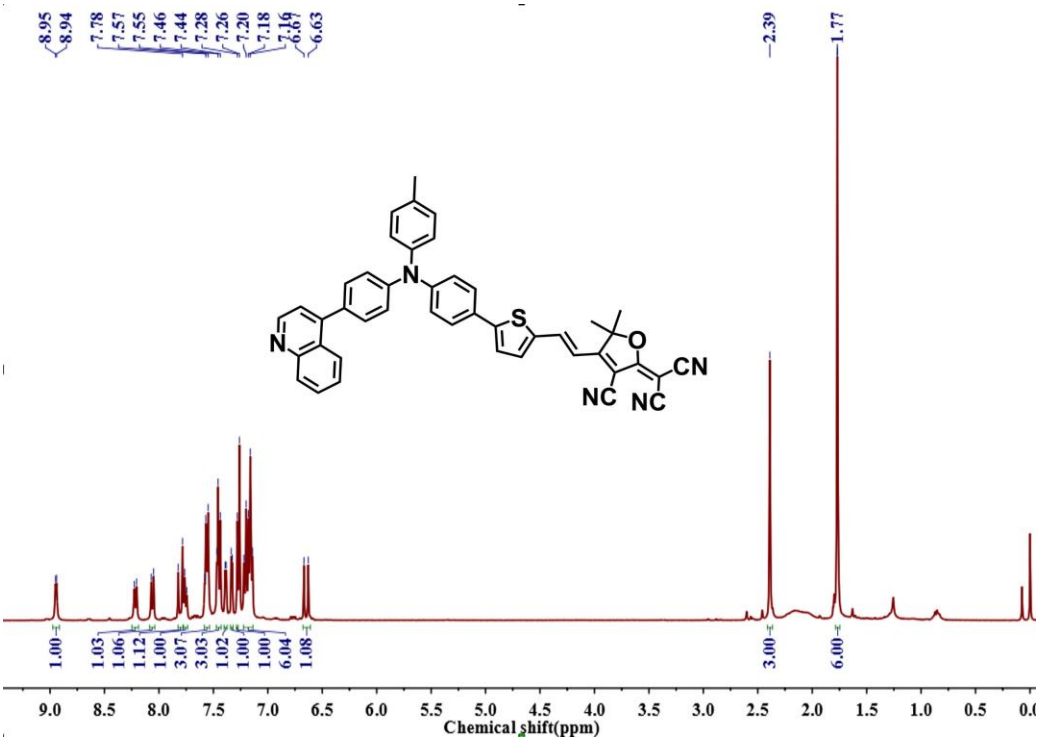



**Fig. S6** $^{1}$H NMR spectrum of FCN-TPAQ in $CDCl_3$.

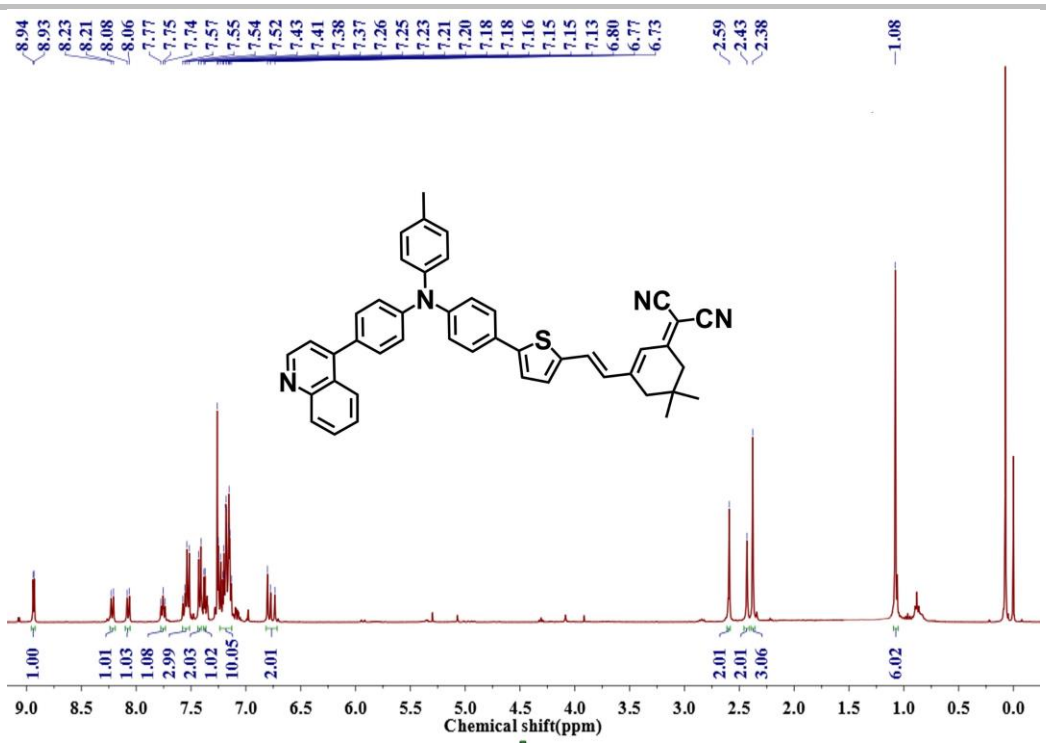



**Fig. S7** $^{1}H$ NMR spectrum of ACN-TPAQ in $CDCl_3$.

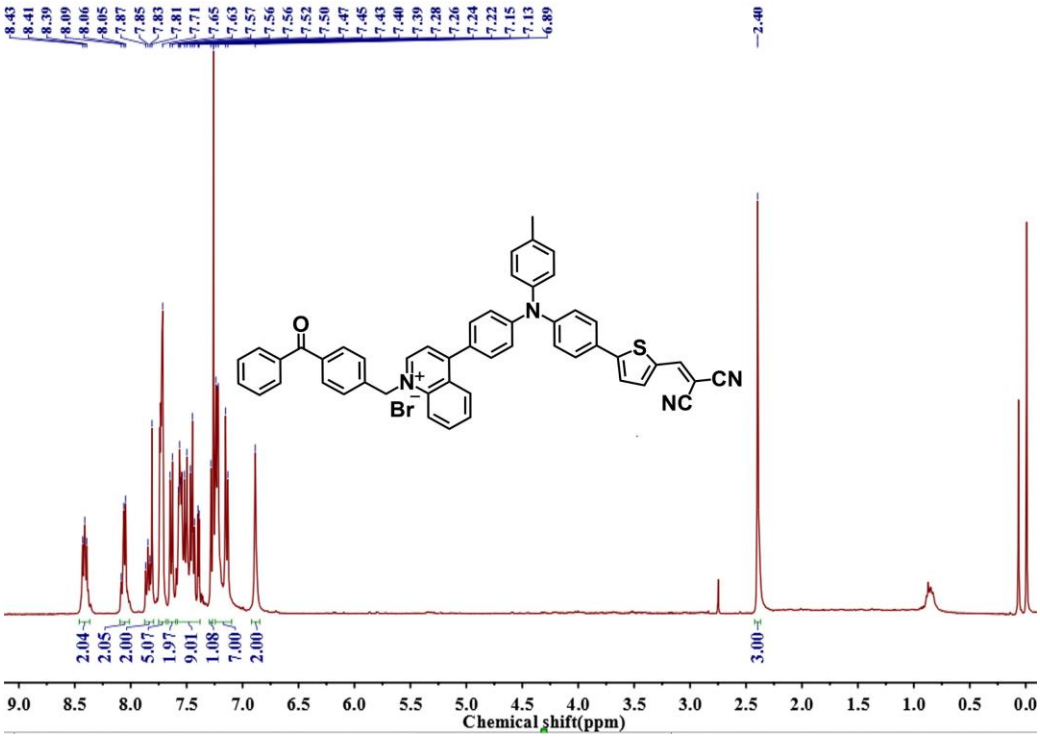



**Fig. S8** $^{1}H$ NMR spectrum of CN-TPAQ-BP in $CDCl_3$.

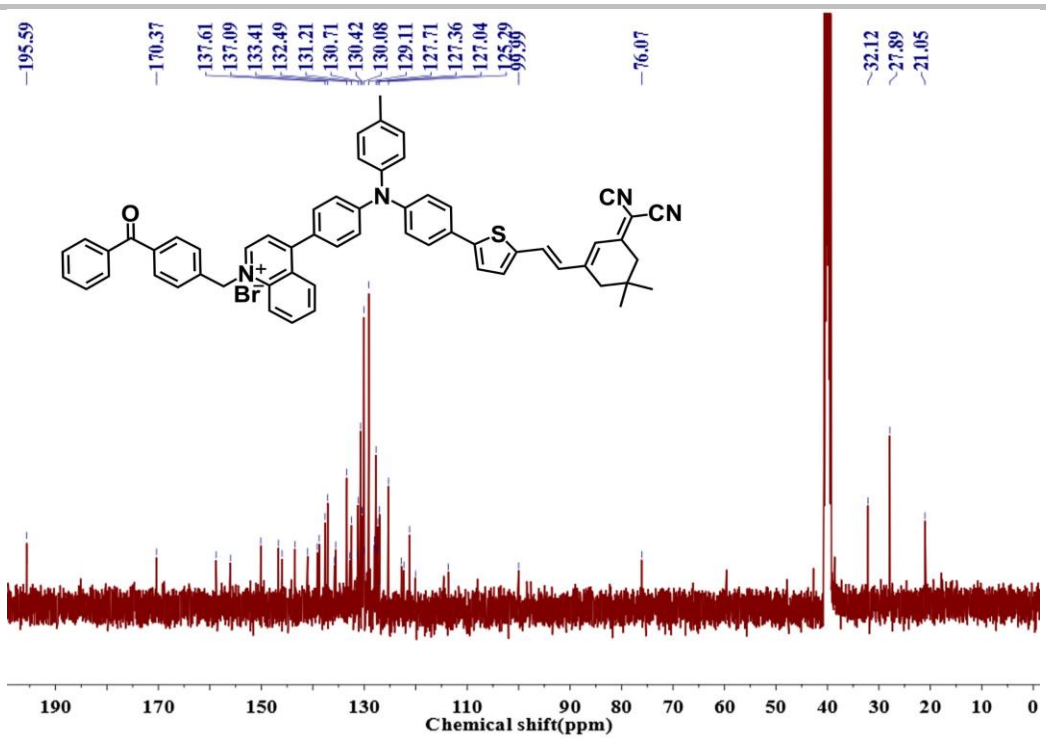



**Fig. S9** $^{13}C$ NMR spectrum of CN-TPAQ-BP in $CDCl_3$.

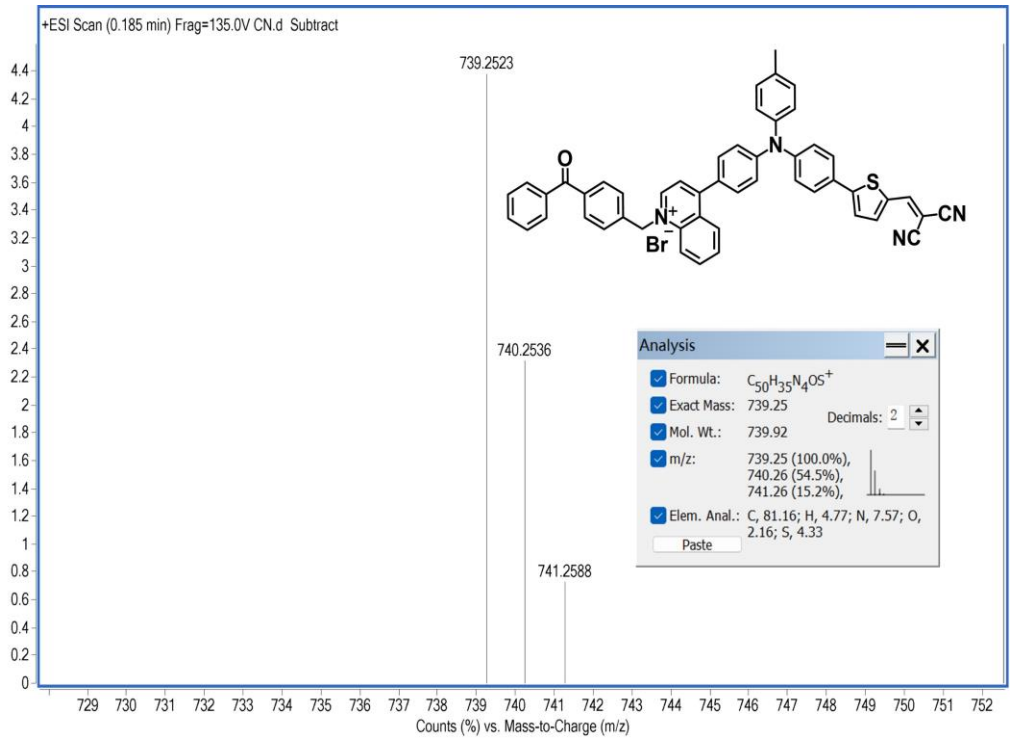



**Fig. S10** ESI-MS spectrum of CN-TPAQ-BP.

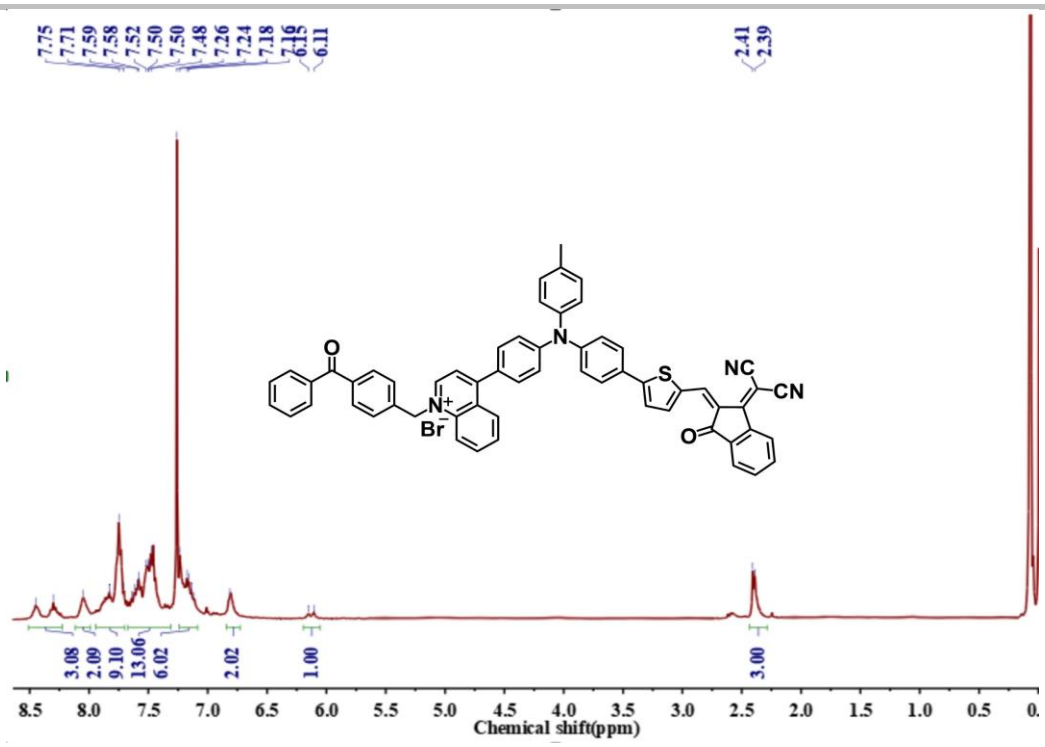



**Fig. S11** $^{1}$H NMR spectrum of ICN-TPAQ-BP in $CDCl_3$

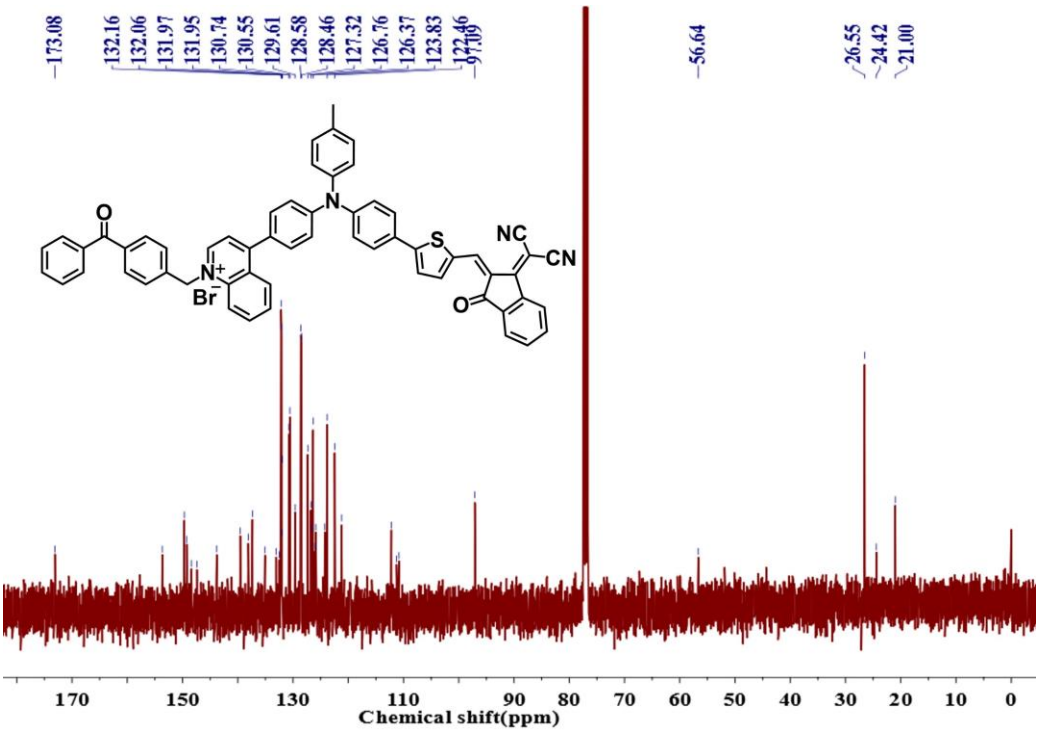



**Fig. S12** $^{13}$C NMR spectrum of ICN-TPAQ-BP in $CDCl_3$.

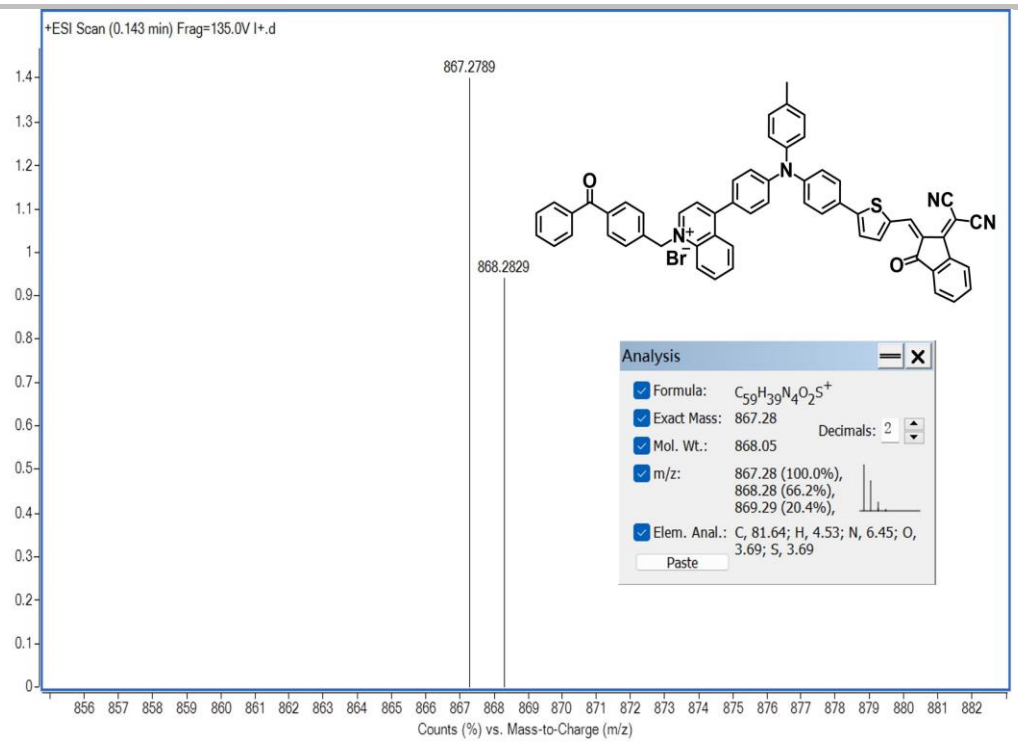



**Fig. S13** ESI-MS spectrum of ICN-TPAQ-BP.

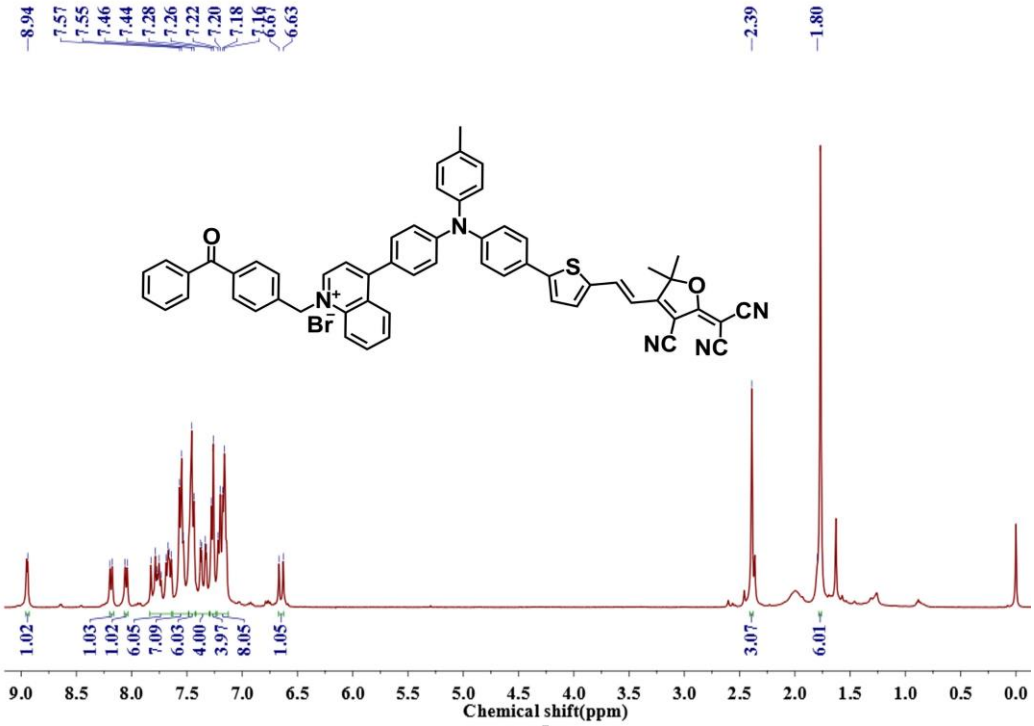



**Fig. S14** $^{1}$H NMR spectrum of FCN-TPAQ-BP in $CDCl_3$

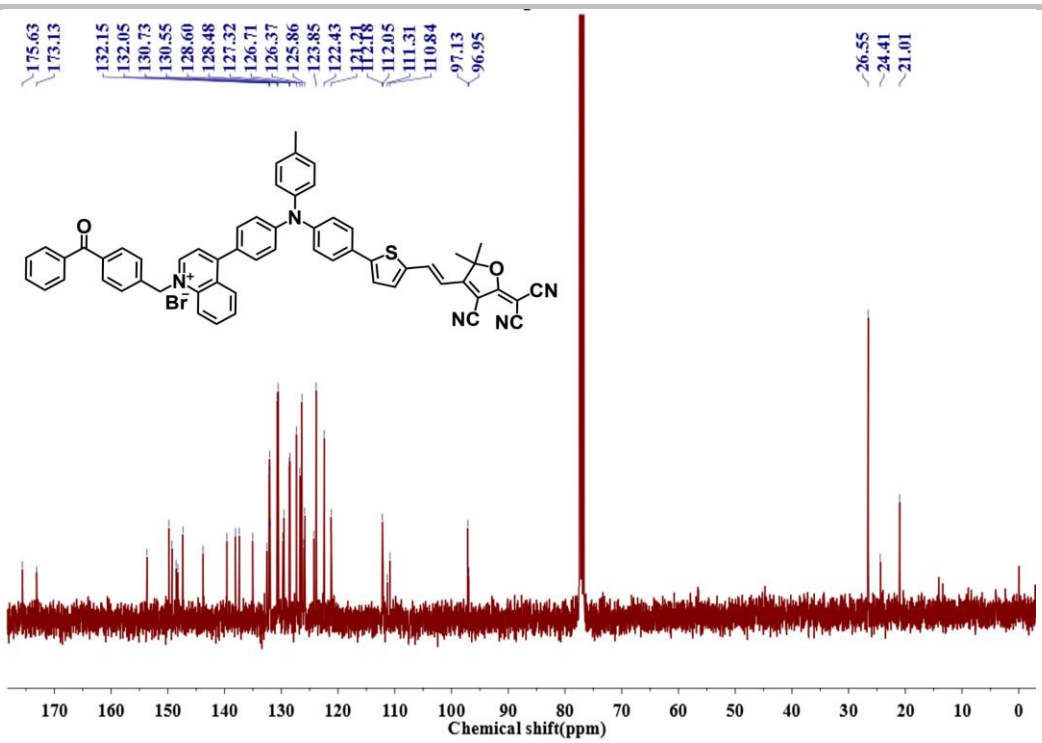



**Fig. S15** $^{13}C$ NMR spectrum of FCN-TPAQ-BP in $CDCl_3$.

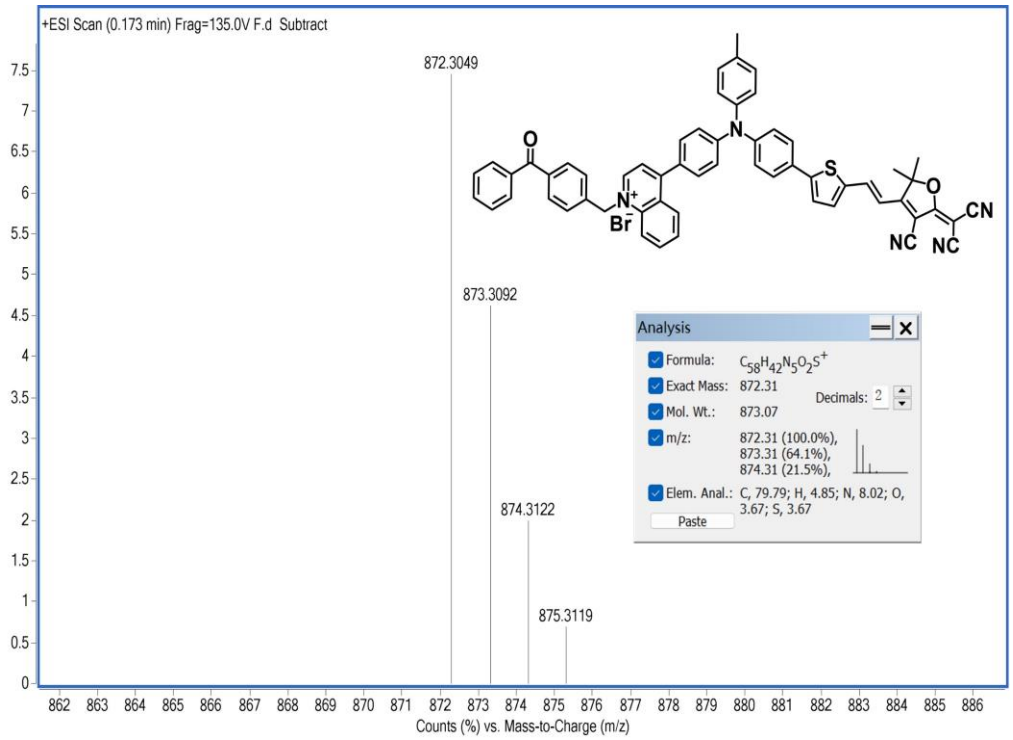



**Fig. S16** ESI-MS spectrum of FCN-TPAQ-BP.

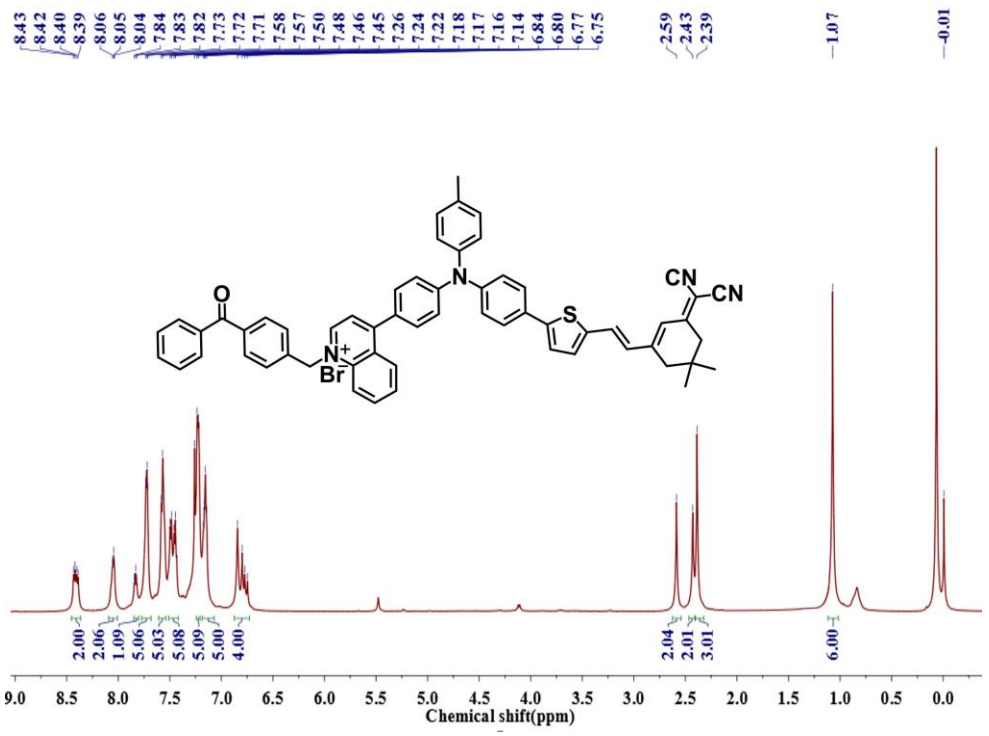



**Fig. S17** $^{1}$H NMR spectrum of ACN-TPAQ-BP in $CDCl_3$.

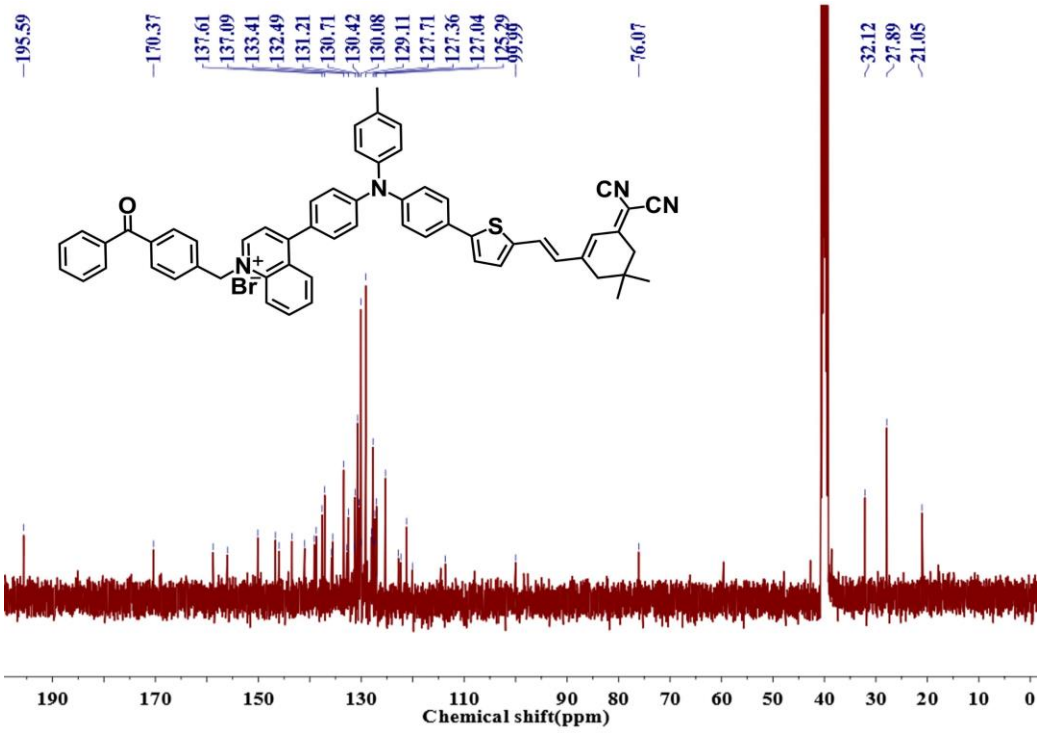



**Fig. S18** $^{13}$C NMR spectrum of ACN-TPAQ-BP in DMSO-$d_6$.

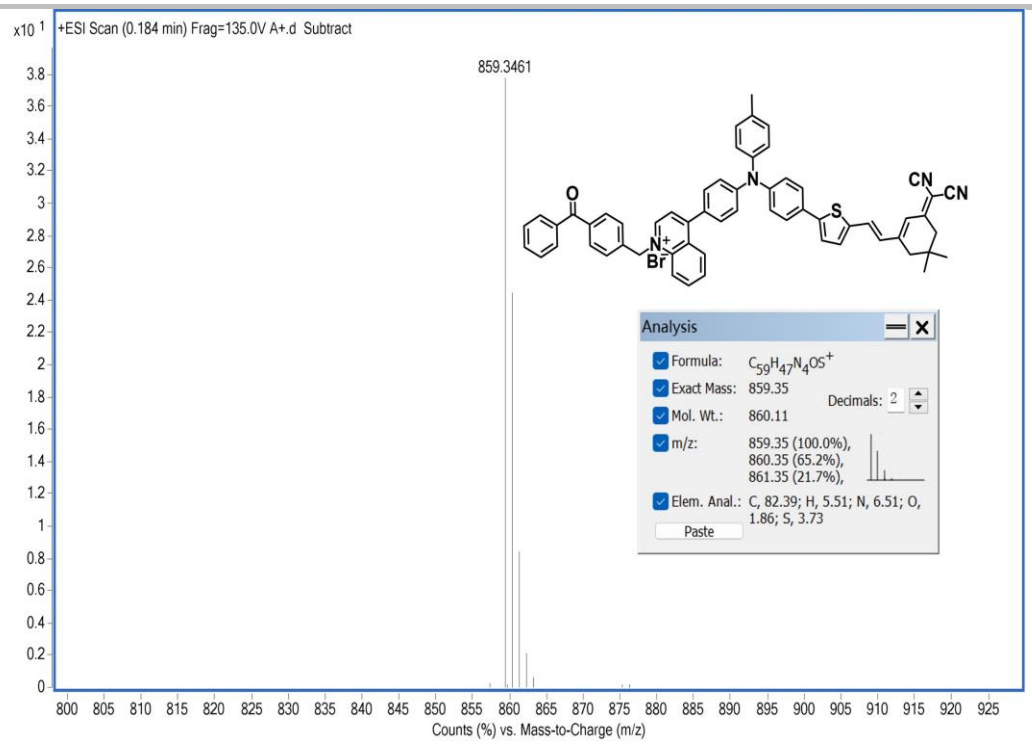



**Fig. S19** ESI-MS spectrum of ACN-TPAQ-BP.

# 3 Results and Discussion

## 3.1 Photophysical Properties

**Table S1.** Calculated energy of the singlet (S) and triplet (T) excited states

| Compounds | CN-TPAQ-BP | ICN-TPAQ-BP | FCN-TPAQ-BP | ACN-TPAQ-BP |
|---|---|---|---|---|
| $S_1$ | 2.6030 | 2.6318 | 2.5962 | 2.5189 |
| $S_2$ | 3.5918 | 3.1041 | 3.1506 | 3.0053 |
| $S_3$ | 3.6477 | 3.5519 | 3.3335 | 3.2529 |
| $T_1$ | 1.7949 | 1.7048 | 1.3726 | 1.3023 |
| $T_2$ | 1.9217 | 1.9405 | 1.9202 | 1.8553 |
| $T_3$ | 2.8313 | 2.3326 | 2.4052 | 2.3979 |
| $T_4$ | 3.0127 | 2.8672 | 2.8189 | 2.7856 |
| $T_5$ | 3.0754 | 3.0049 | 3.0125 | 2.9626 |
| $T_6$ | 3.3421 | 3.0113 | 3.0299 | 3.0098 |
| $T_7$ | 3.4155 | 3.1686 | 3.2828 | 3.1731 |

**Table S2.** Photophysical properties of the compounds

| Compounds | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\varepsilon$ ($M^{-1}$ $cm^{-1}$) | τ (ns) | | ROS yield (RB=1) | $\Delta E_{L\text{-}H}$ (eV) | SOC constant ($S_1$-$T_1$) |
|---|---|---|---|---|---|---|---|---|
| | | | | $\tau_1$ | $\tau_2$ | | | |
| CN-TPAQ-BP | 496 | 806 | 18600 | 2.01 | 13.41 | 3.208 | 3.921 | 0.5630 |
| ICN-TPAQ-BP | 491 | 822 | 10400 | 1.87 | 14.32 | 3.493 | 4.128 | 0.450 |
| FCN-TPAQ-BP | 500 | 873 | 14800 | 2.10 | 13.49 | 4.760 | 3.928 | 0.6795 |
| ACN-TPAQ-BP | 500 | 815 | 21800 | 2.00 | 14.32 | 4.480 | 3.934 | 0.6363 |

## 3.2 AIE properties

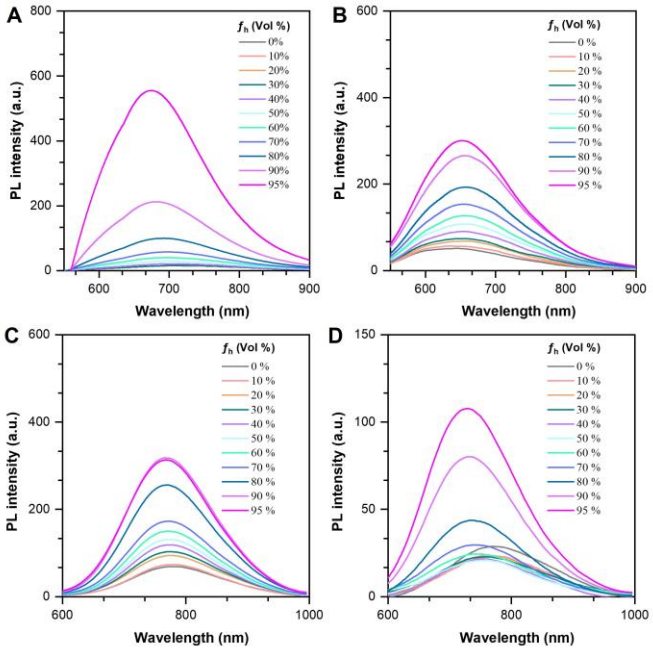



**Fig. S20** PL spectra of (A) CN-TPAQ-BP, (B) ICN-TPAQ-BP, (C) FCN-TPAQ-BP, (D) ACN-TPAQ-BP, in acetonitrile/diethyl ether mixture with different diethyl ether fractions (0-95%).

## 3.3 Photostability and solvation effect

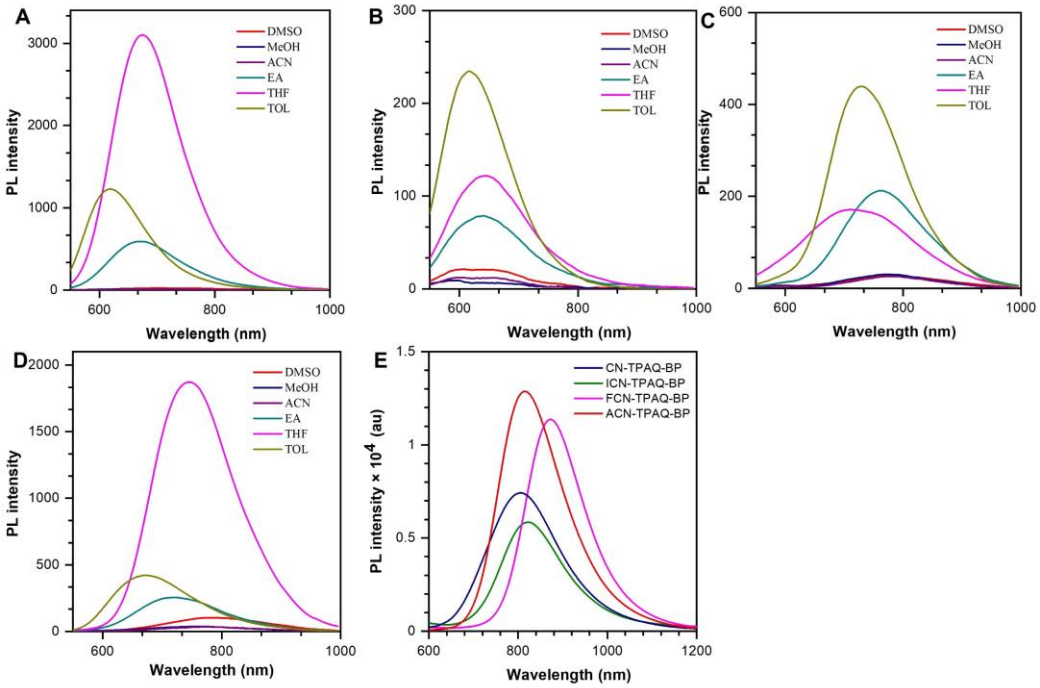



**Fig. S21** PL spectra of(A) CN-TPAQ-BP, (B) ICN-TPAQ-BP, (C) FCN-TPAQ-BP, (D) ACN-TPAQ-BP in different solvents (10 μM). (E) PL spectra of compounds in the solid state.

### 3.4 ROS generation

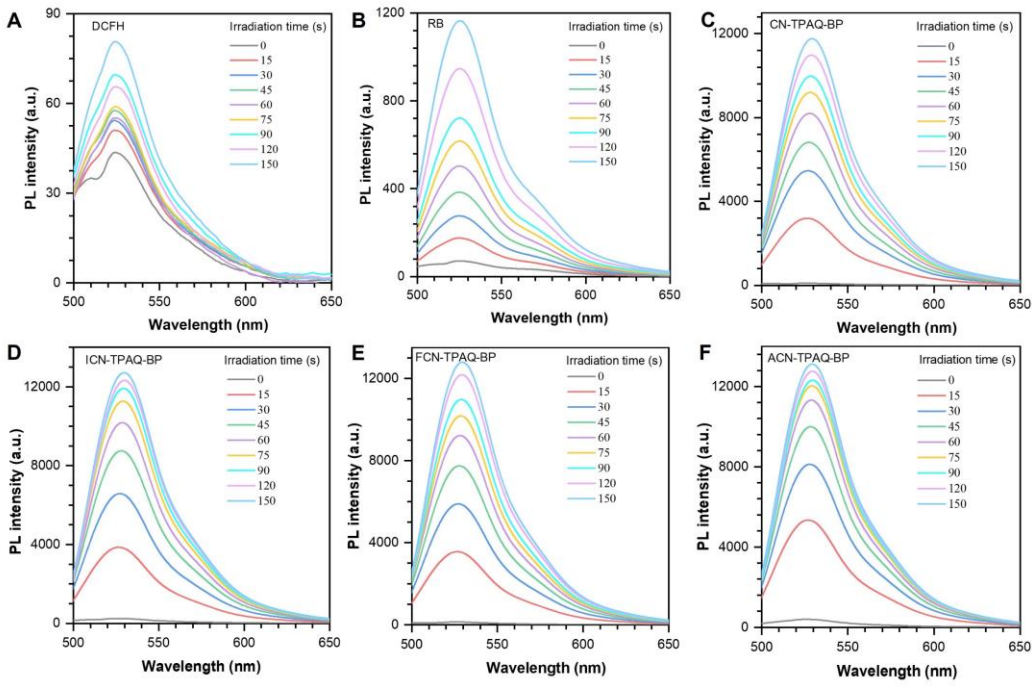



**Fig. S22** ROS generation of (A) DCFH, (B) RB, (C) CN-TPAQ-BP, (D) ICN-TPAQ-BP, (E) FCN-TPAQ-BP, and (F) ACN-TPAQ-BP (1 μM) upon exposure to white light using DCFH (10 μM) as an indicator.

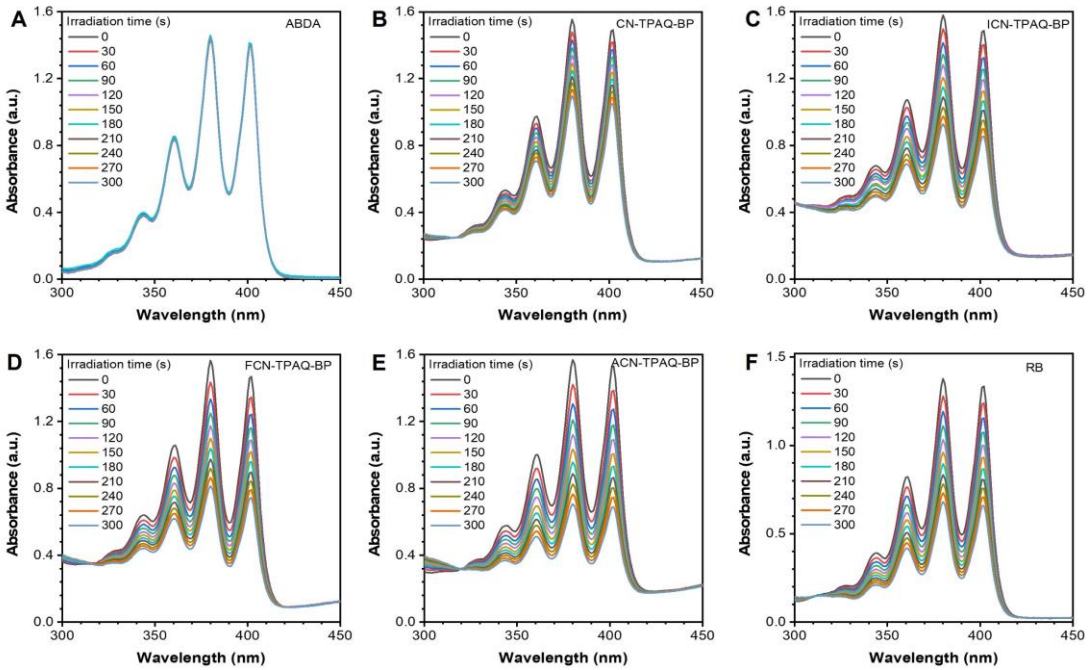



**Fig. S23** Absorption of ABDA (50 μM, $^1O_2$ probe) in water in the absence (blank, A) and presence of (B) CN-TPAQ-BP, (C) ICN-TPAQ-BP, (D) FCN-TPAQ-BP, (E) ACN-TPAQ-BP and (F) RB (10 μM) under white light irradiation for different time.

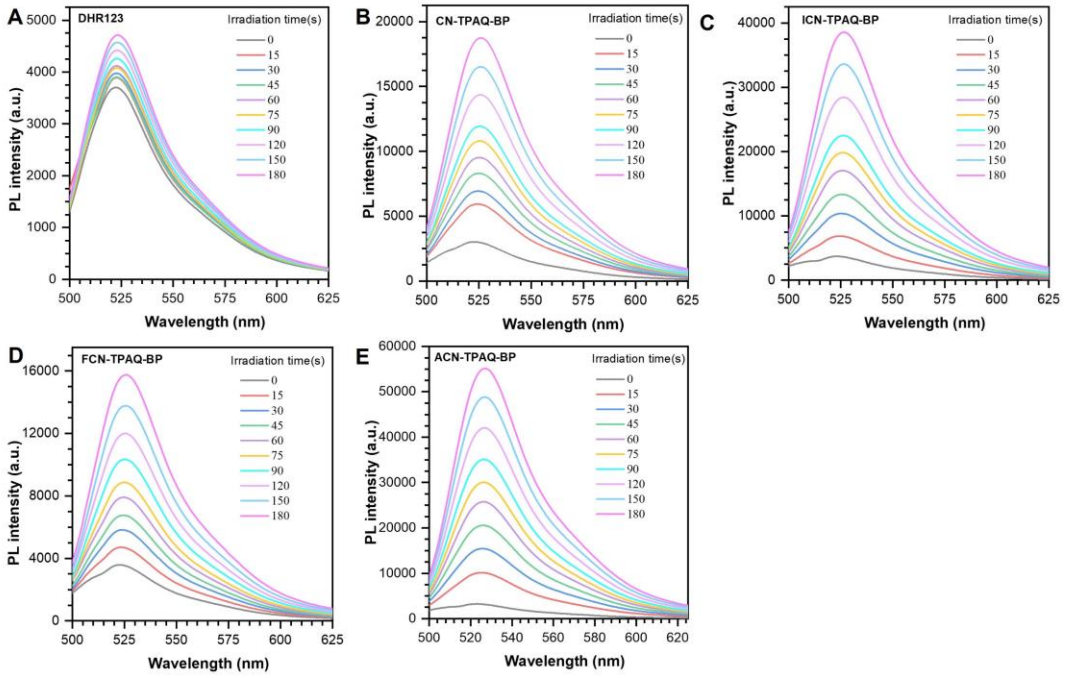



**Fig. S24** PL spectra of DHR 123 (5 μM) in PBS in the presence of (A) blank, (B) CN-TPAQ-BP, (C) ICN-TPAQ-BP, (D) FCN-TPAQ-BP and (E) ACN-TPAQ-BP (1 μM) after exposure to white light irradiation (10 mW $cm^{-2}$) with different time.

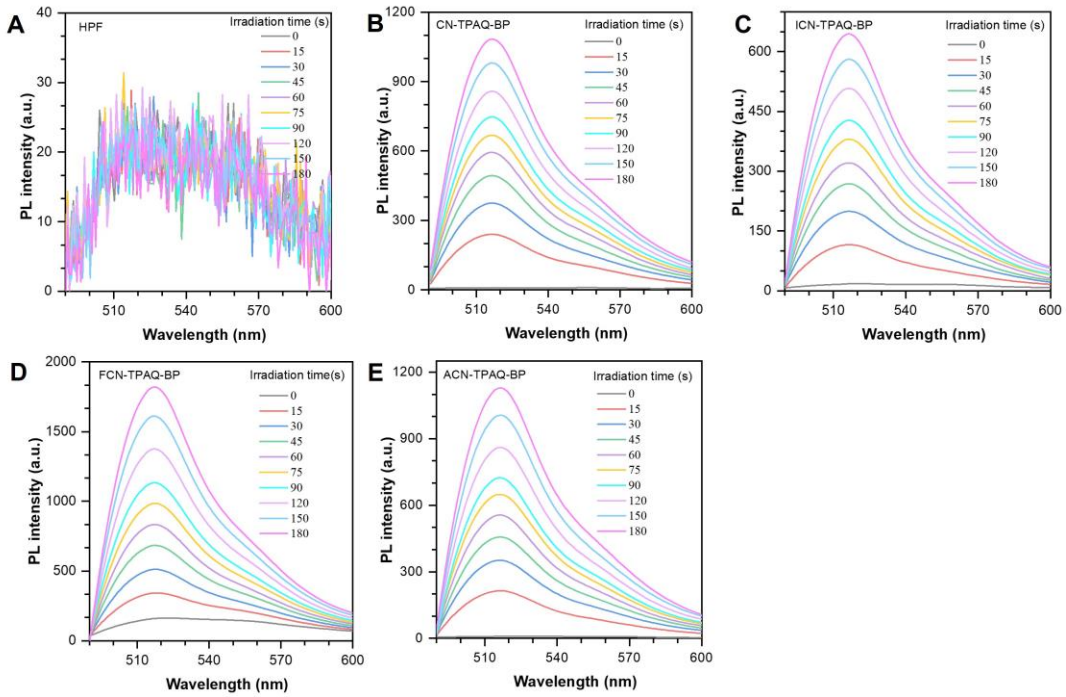



**Fig. S25** PL spectra of HPF (5 μM, •OH probe) in the absence (blank, A) and presence of (B) CN-TPAQ-BP, (C) ICN-TPAQ-BP, (D) FCN-TPAQ-BP and (E) ACN-TPAQ-BP (1 μM) in PBS upon white light irradiation with 10 mW $cm^{-2}$ for different time.

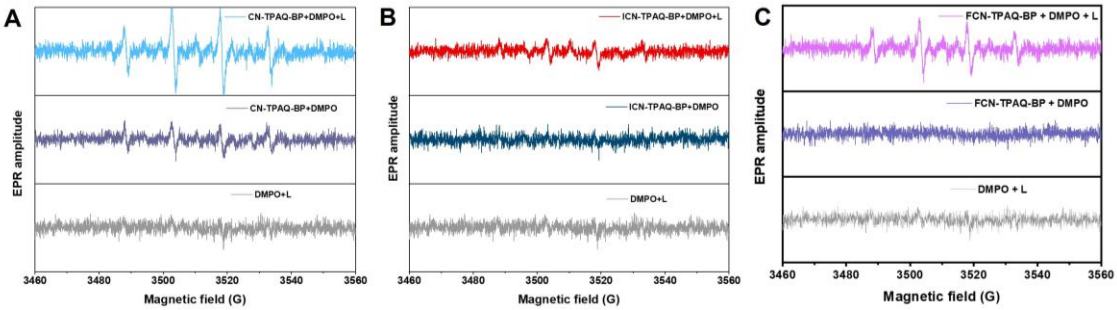



**Fig. S26** EPR signals of DMPO (10 μL) in the presence (A) CN-TPAQ-BP and (B) ICN-TPAQ-BP (C) FCN-TPAQ-BP in $H_2O$ with/without white light irradiation (10 mW $cm^{-2}$) for 5 min.

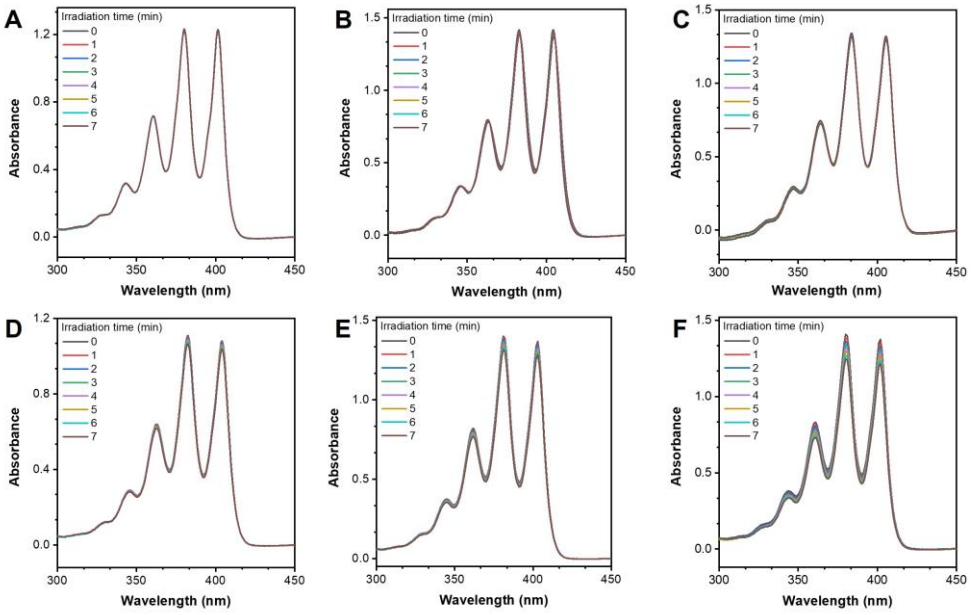


**Fig. S27** (A-F) The absorbance spectra of ABDA (100 μM, $^1O_2$ probe) in the presence of CN-TPAQ-BP (10 μM) in mixtures of DMSO and PBS with different PBS fractions (0%, 20%, 40%, 60%, 80% and 95%) upon white-light irradiation (10 mW $cm^{-2}$).

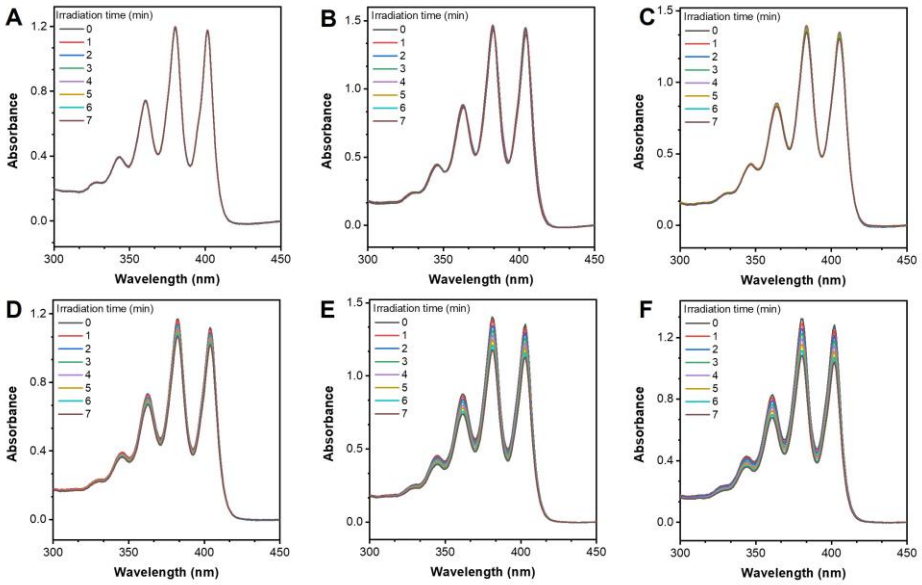



**Fig. S28** (A-F) The absorbance spectra of ABDA (100 μM, $^1O_2$ probe) in the presence of ICN-TPAQ-BP (10 μM) in mixtures of DMSO and PBS with different PBS fractions (0%, 20%, 40%, 60%, 80% and 95%) upon white-light irradiation (10 mW $cm^2$).

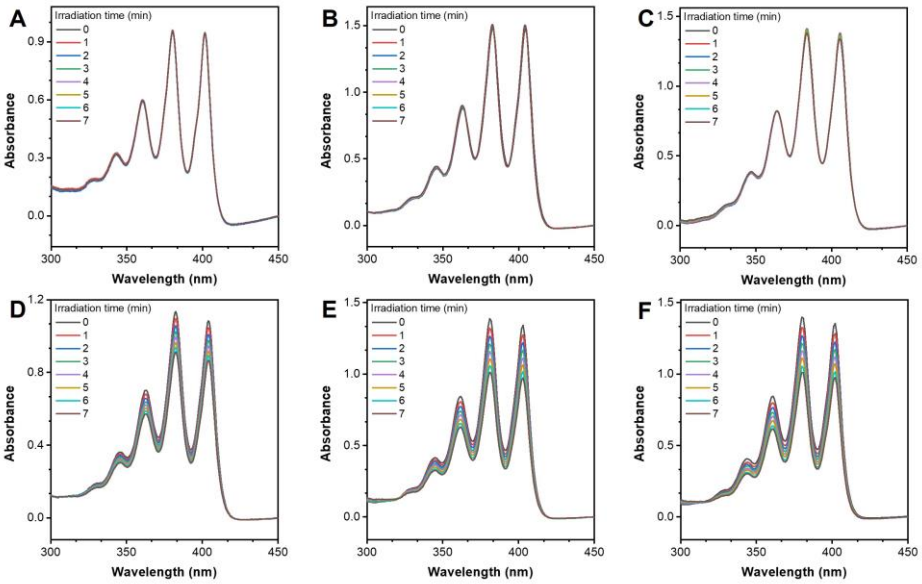



**Fig. S29** (A-F) The absorbance spectra of ABDA (100 μM, $^1O_2$ probe) in the presence of FCN-TPAQ-BP (10 μM) in mixtures of DMSO and PBS with different PBS fractions (0%, 20%, 40%, 60%, 80% and 95%) upon white-light irradiation (10 mW $cm^{-2}$).

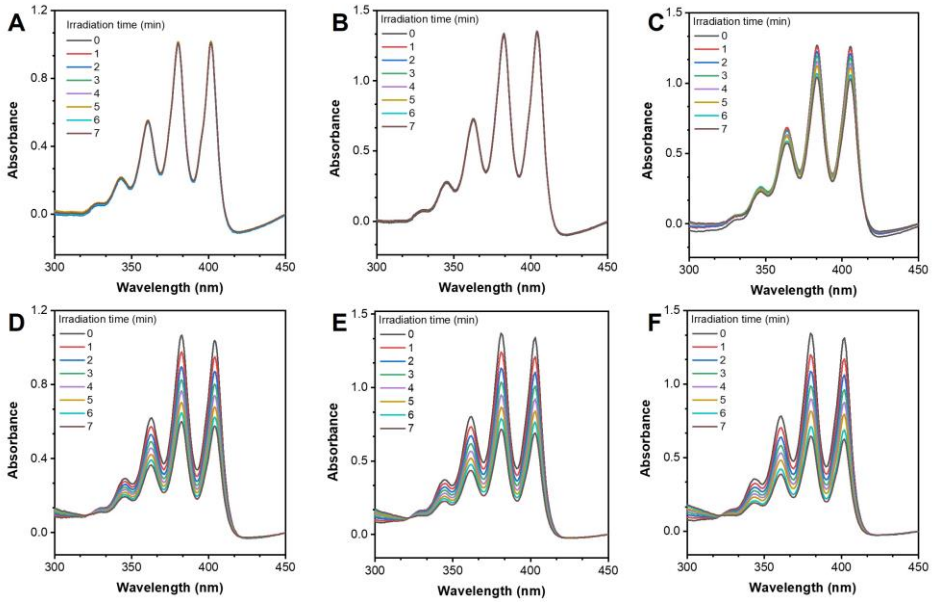



**Fig. S30** (A-F) The absorbance spectra of ABDA (100 μM, $^1O_2$ probe) in the presence of ACN-TPAQ-BP (10 μM) in mixtures of DMSO and PBS with different PBS fractions (0%, 20%, 40%, 60%, 80% and 95%) upon white-light irradiation (10 mW $cm^{-2}$).

### 3.5 Cell Imaging and cell viability

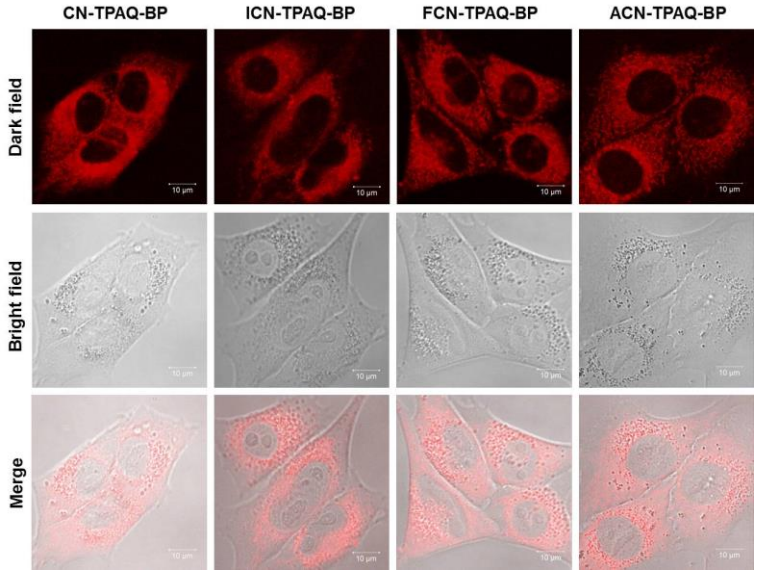



**Fig. S31** Fluorescence images of 4T1 cells stained with 10 μM CN-TPAQ-BP, ICN-TPAQ-BP, FCN-TPAQ-BP and ACN-TPAQ-BP for 6 h, respectively.

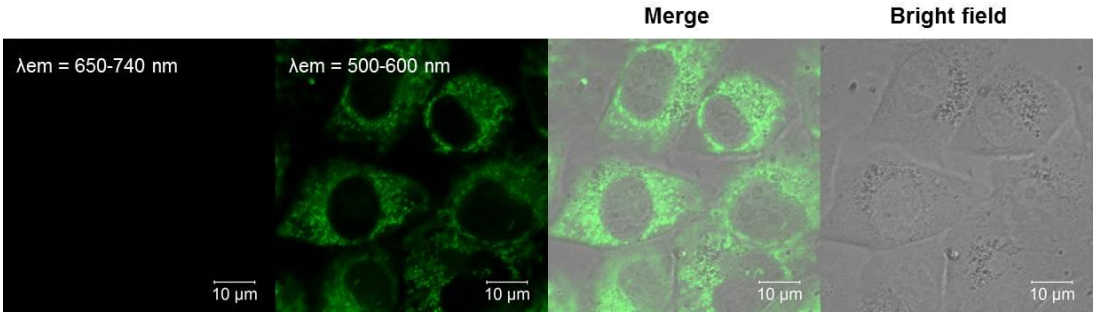



**Fig. S32** CLSM images of 4T1 cells co-stained with MitoTracker Green (conc.:1 μM), incubation time: 0.5 h, $\lambda_{ex}$ = 488 nm).

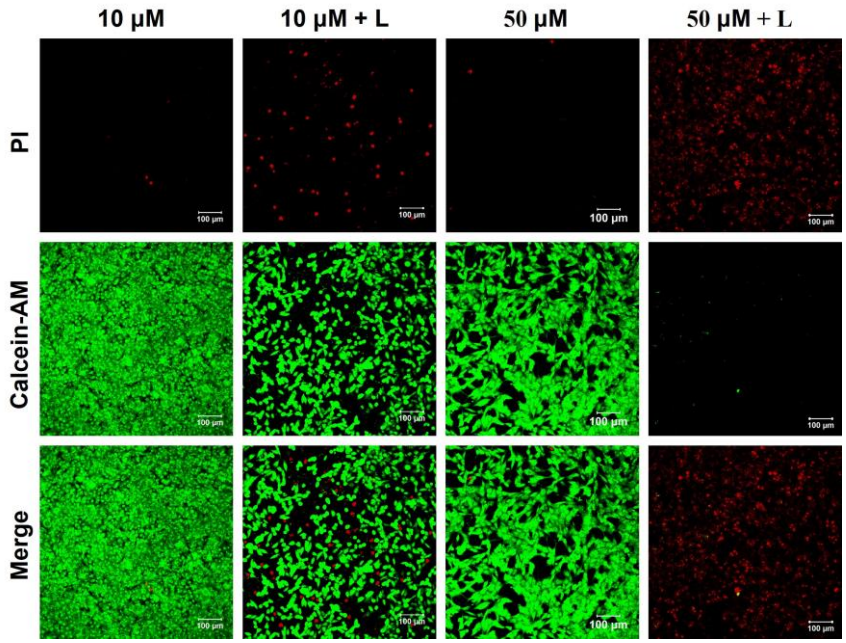



**Fig. S33** Live/dead staining assay of 4T1 cells after various treatments of CN-TPAQ-BP.

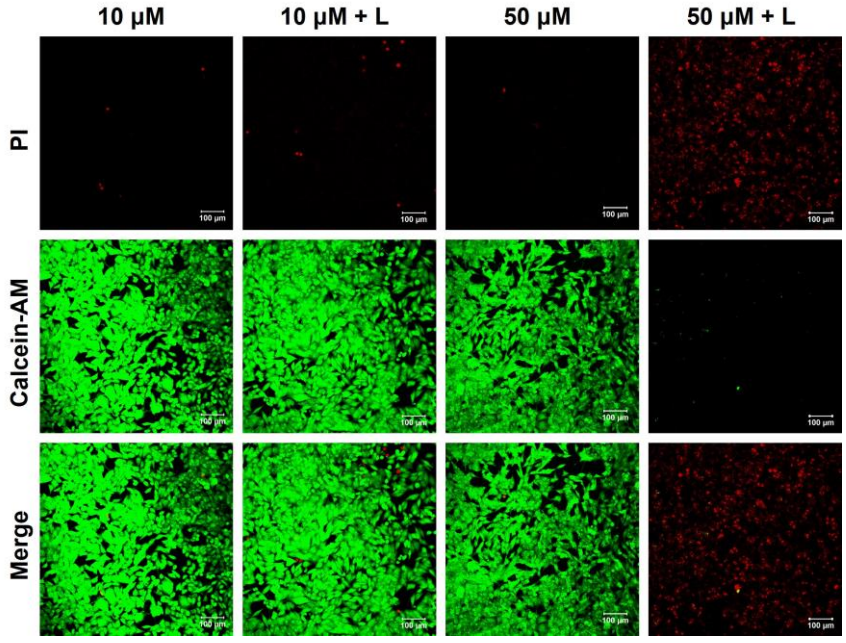



**Fig. S34** Live/dead staining assay of 4T1 cells after various treatments of ICN-TPAQ-BP.

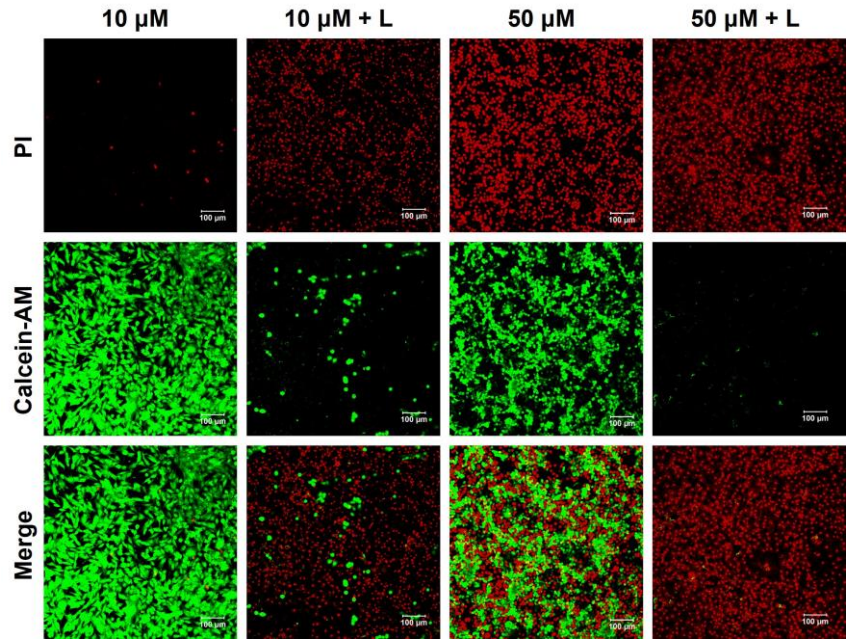



**Fig. S35** Live/dead staining assay of 4T1 cells after various treatments of ACN-TPAQ-BP.

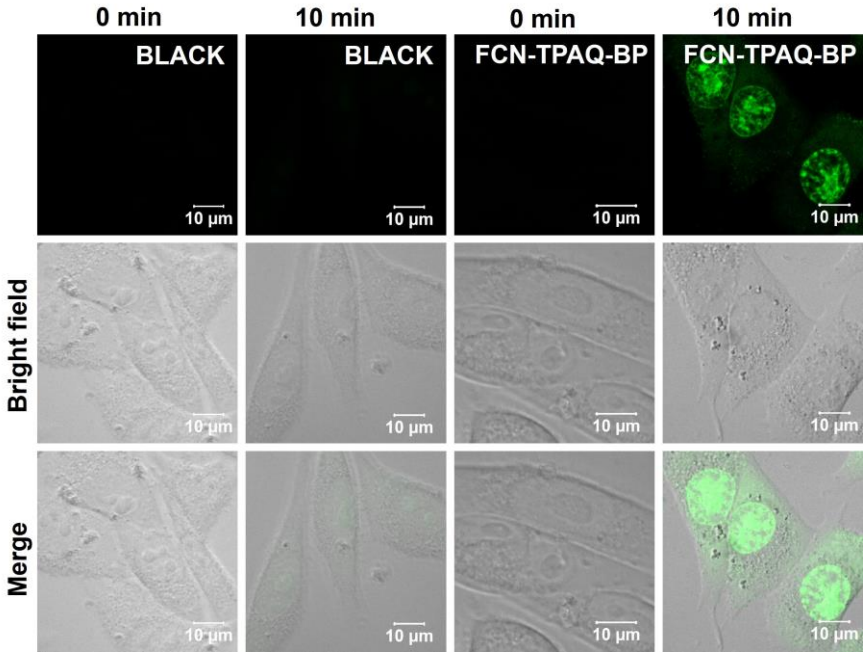



**Fig. S36** $O_2^{\cdot -}$ generation of FCN-TPAQ-BP (10 μM) in 4T1 cells by using DHE (5 μM) as indicators, before and after exposure to white light (0.4 mW $cm^{-2}$) irradiation.

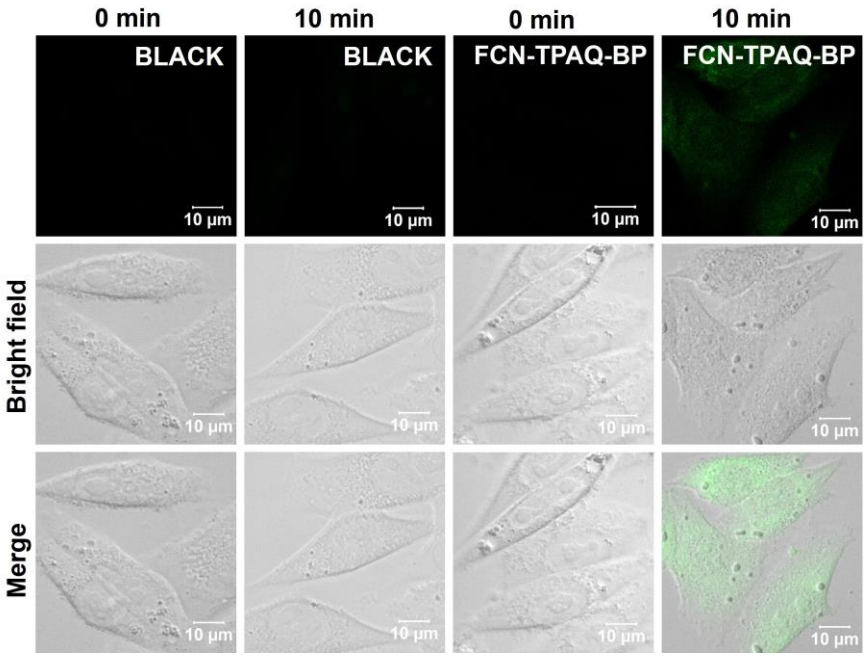



**Fig. S37** •OH generation of FCN-TPAQ-BP (10 μM) in 4T1 cells by using HPF (5 μM) as indicators, before and after exposure to white light (0.4 mW $cm^{-2}$) irradiation.