

Supporting information

Tetraarylethenes fluorescent dyes with aggregation-induced emission for LED-driven photocuring and 3D printing

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1. Experimental Section

1.1 Detail information of the raw materials, initiators and monomers

The reagents and solvents required for the synthesis of tetrastylene-based derivatives were of reagent grade and do not require purification. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) and diaryliodonium salt (ONI) were synthesized according to literature as photoinitiator. Tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), polyethylene Glycol acrylate (PEG) were chosen as the monomers for free radical photopolymerization (FRP) and E51 epoxy was chosen as the monomer for cationic photopolymerization (CP). These monomers were all from Guangzhou Lihou Trading Co. Ltd, China. N-ethyl-carbazole (Cz-bi) and N-hexyl-carbazole (Cz-hex) were prepared according to literature procedures.

1.2 Photopolymerization experiment

A Fourier transform infrared spectrometer (Nicolet 5700, 4000-7000 cm^{-1} wavelength range) was used to record the infrared spectrum of the uncured resin, and the infrared spectrum was recorded at different exposure time intervals. The double bond conversion rate is calculated by the change of absorption intensity at 6165 cm^{-1} , and the double bond conversion rate is calculated by the formula (1):

$$Conversion\% = \left[1 - \frac{S_t}{S_0} \right] \times 100\% \quad (1)$$

In this formula, S_0, S_t are the peak areas of the carbon-carbon double bond absorption peak before and after curing, respectively.

The characteristic absorption peak of the epoxy group is at 6075 cm^{-1} , and the peak at 4680 cm^{-1} is used as a reference. The conversion rate of the epoxy group is calculated by comparing the changes in the peak areas of the two peaks. The conversion rate is calculated by the formula (2) Calculated:

$$Conversion\% = \left[1 - \left(\frac{S_t}{R_t} / \frac{S_0}{R_0} \right) \right] \times 100\% \quad (2)$$

In this formula, S_0, S_t are the peak areas of the epoxy group absorption peak before and after curing, R_0, R_t are the peak areas of the reference peak before and after curing, respectively.

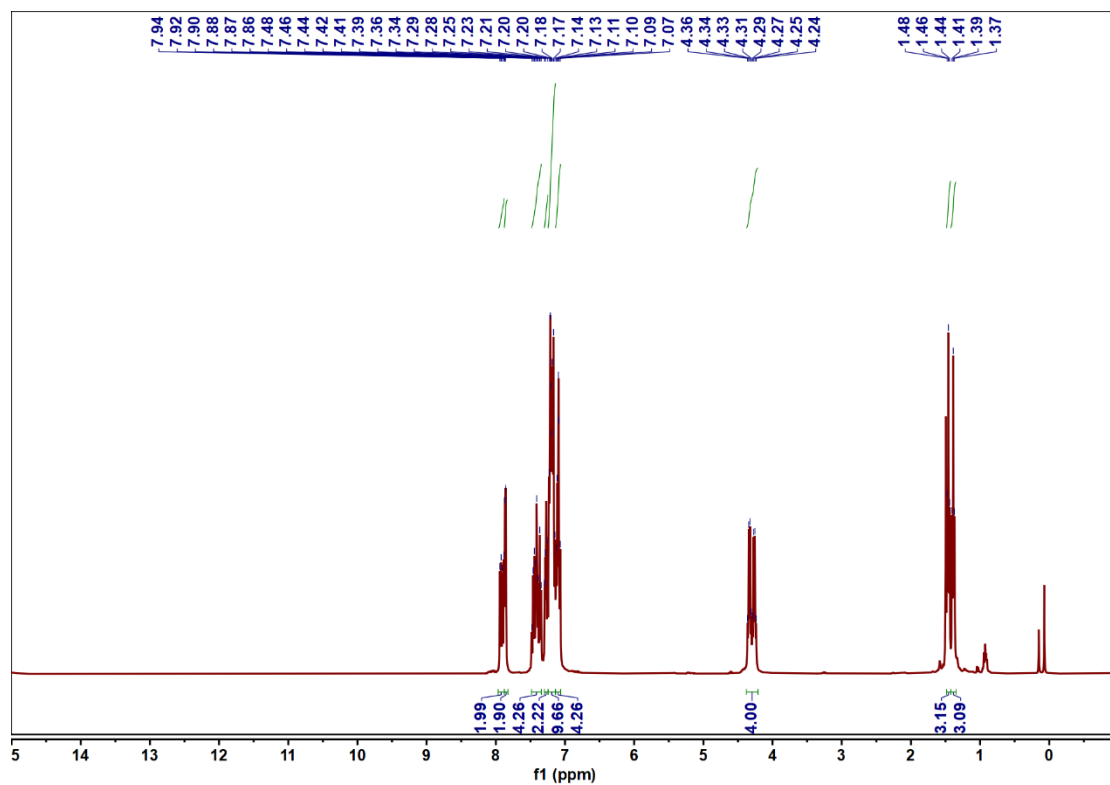
The photopolymerization experiment is the same as above. The equipment used to monitor the photopolymerization reaction is an F-4500 (Hitachi High-Technologies Corporation) fluorescence spectrophotometer. Calculate the fluorescence intensity by formula (3):

$$I = I_t / I_0 \quad (3)$$

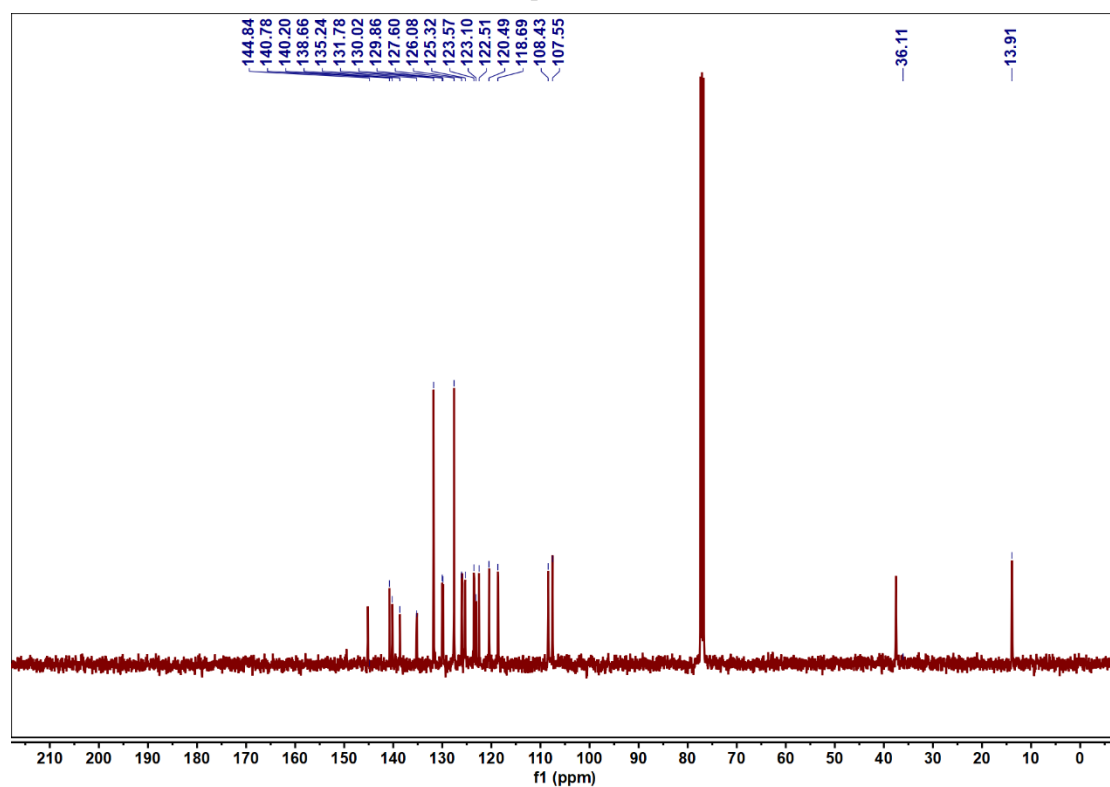
In this formula, I_0, I_t are the areas of the largest emission peaks before and after curing, respectively.

2. Characterization

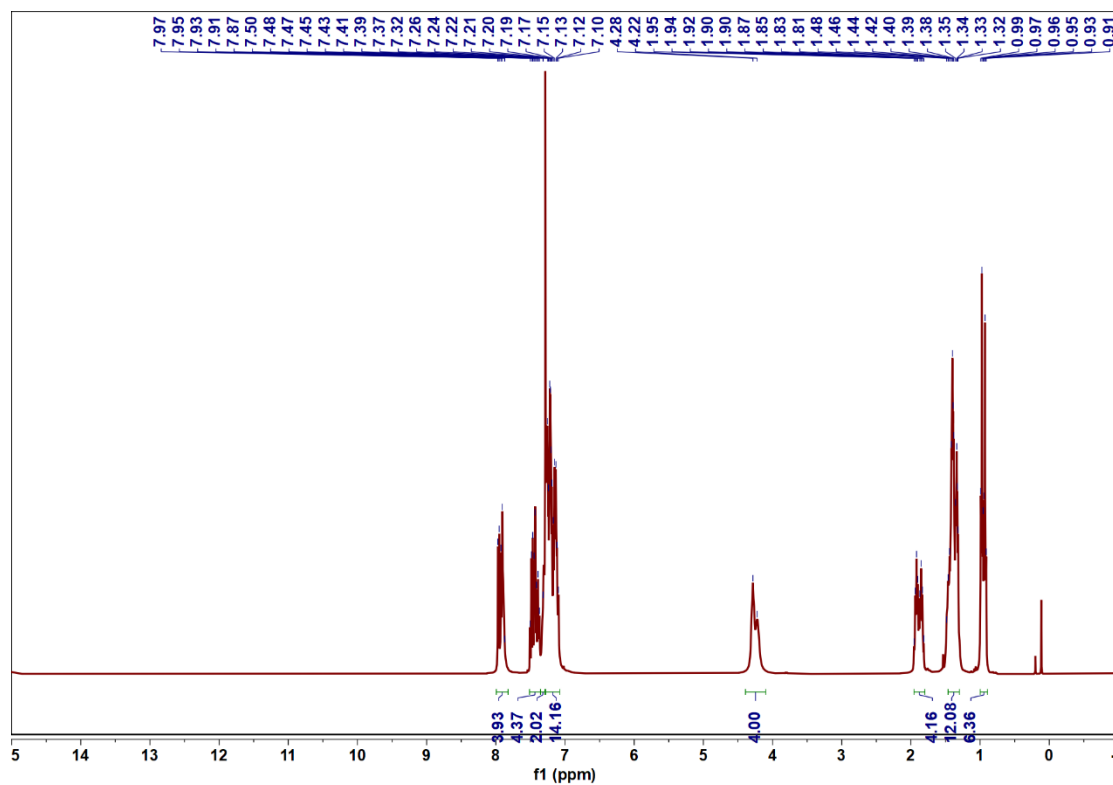
2.1 NMR spectra of dyes



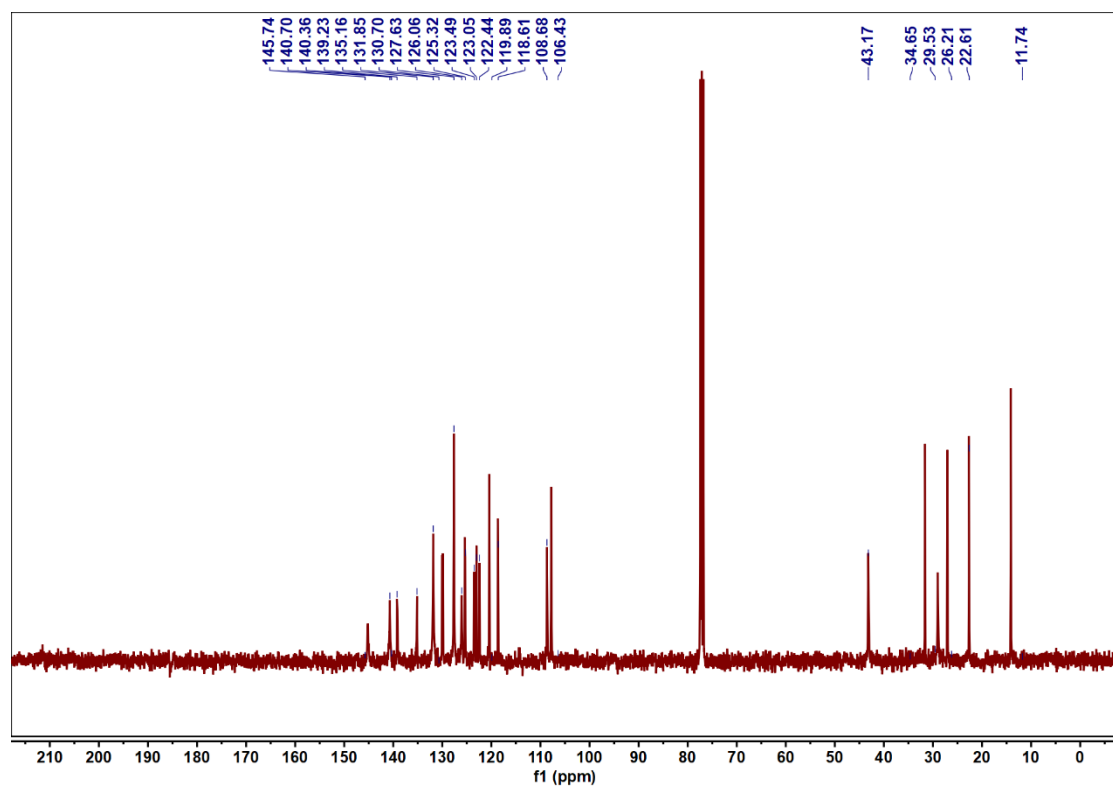
The ^1H NMR spectrum of Cz-bi-Ph



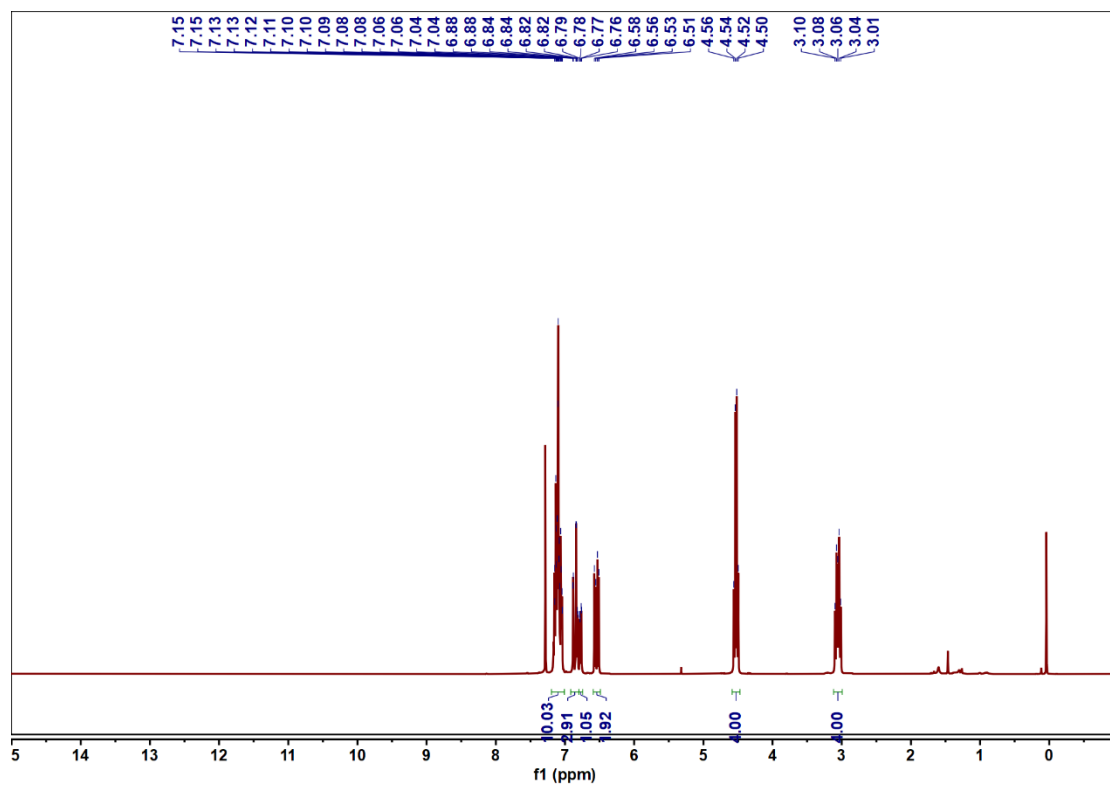
The ^{13}C NMR spectrum of Cz-bi-Ph



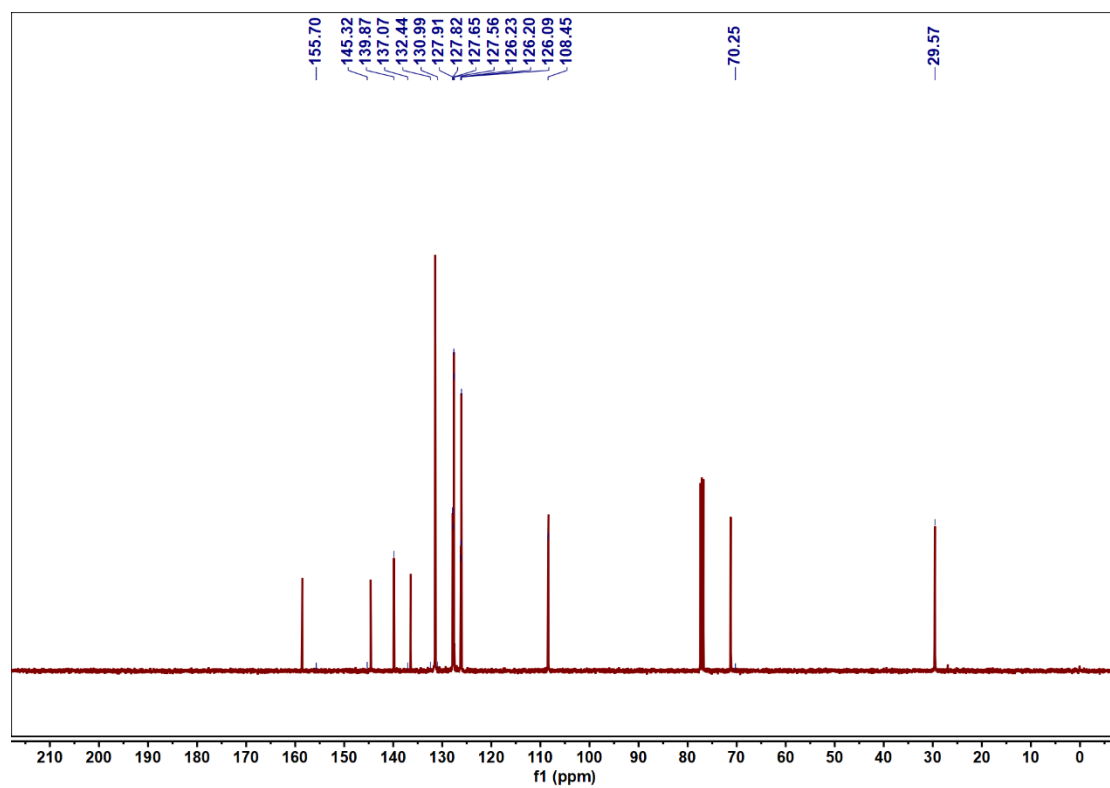
The ^1H NMR spectrum of Cz-hex-Ph



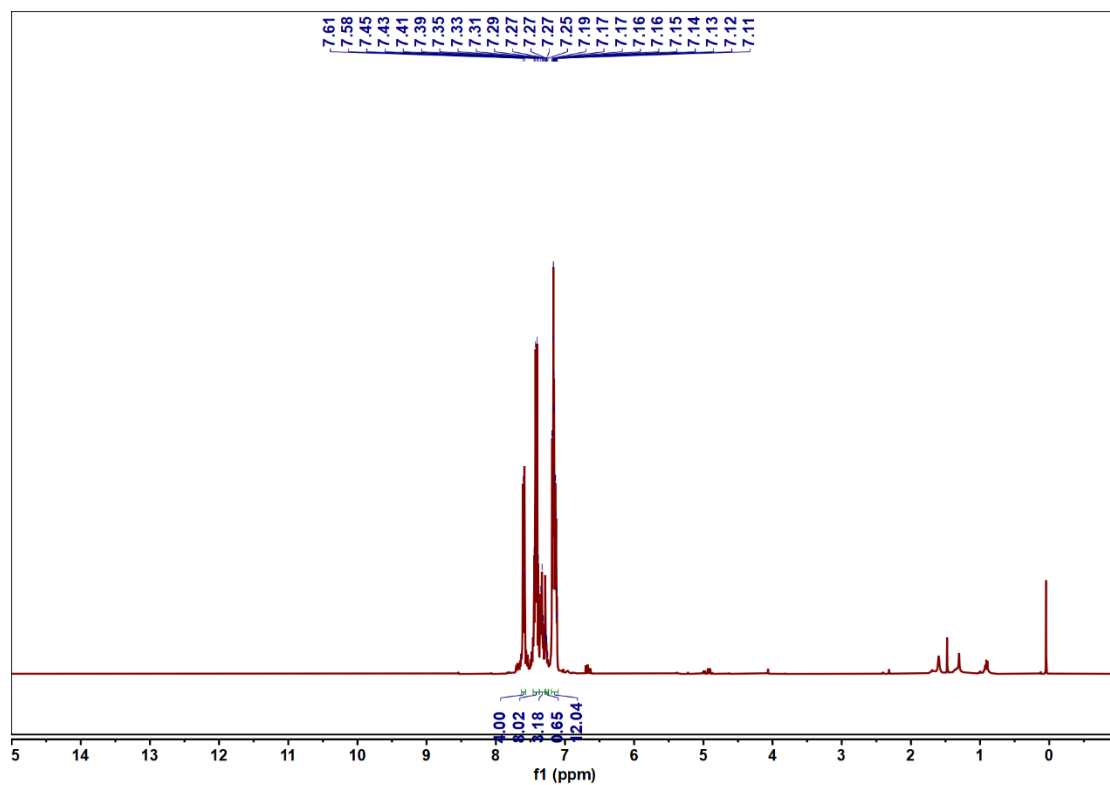
The ^{13}C NMR spectrum of Cz-hex-Ph



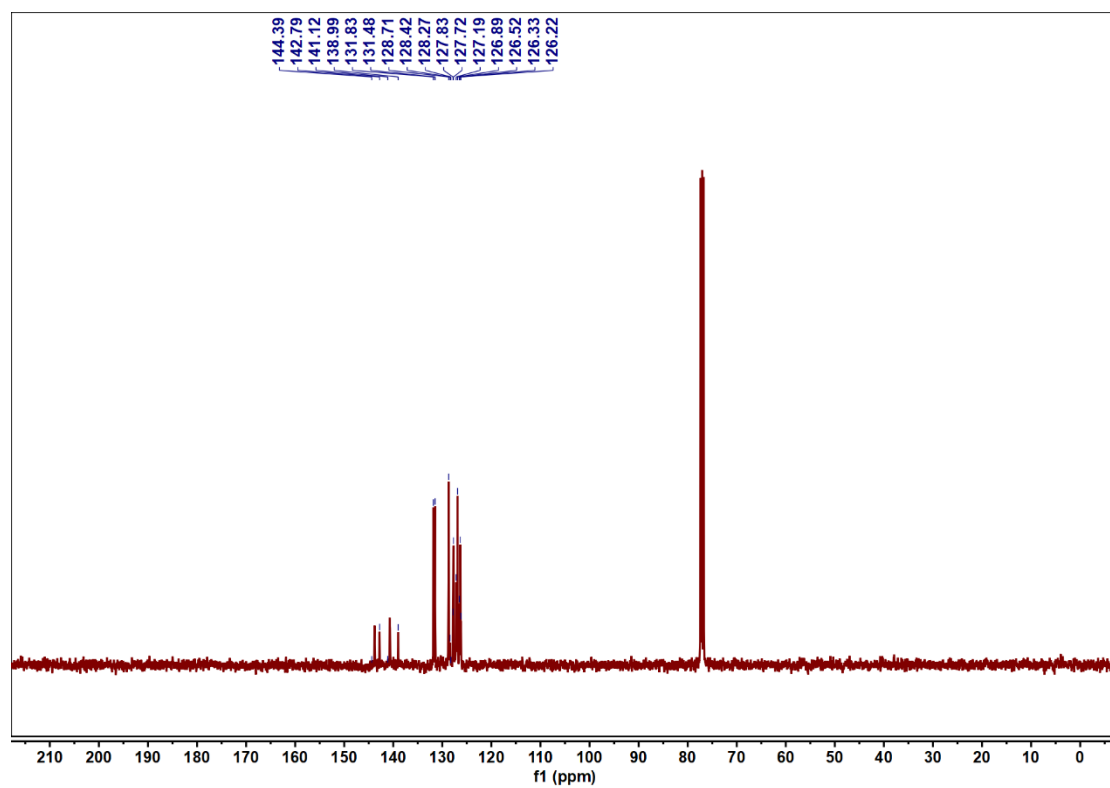
The ^1H NMR spectrum of **DHBF-Ph**



The ^{13}C NMR spectrum of **DHBF-Ph**

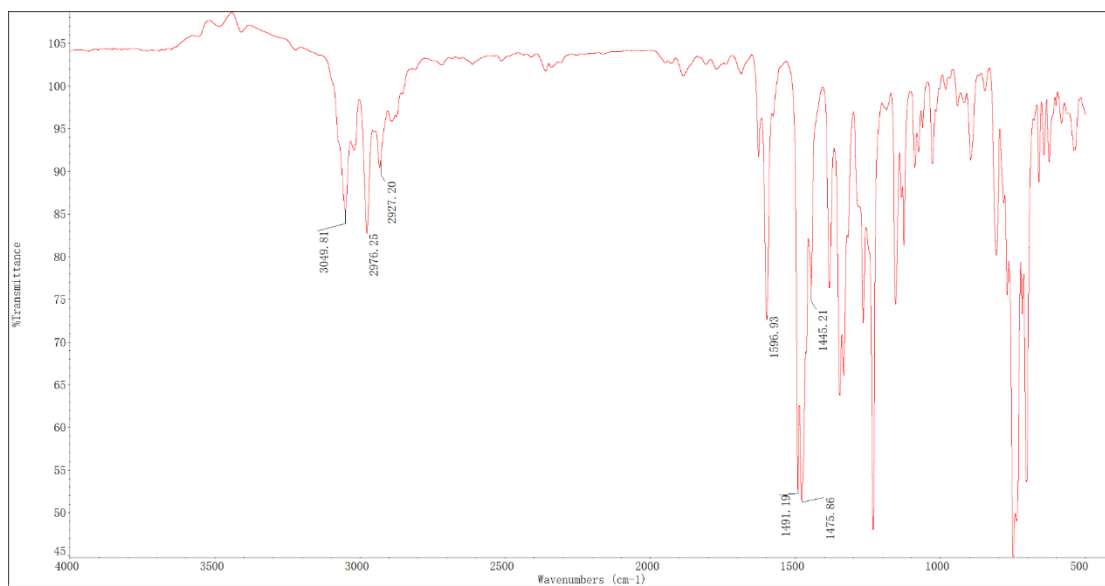


The ^1H NMR spectrum of **BP-Ph**

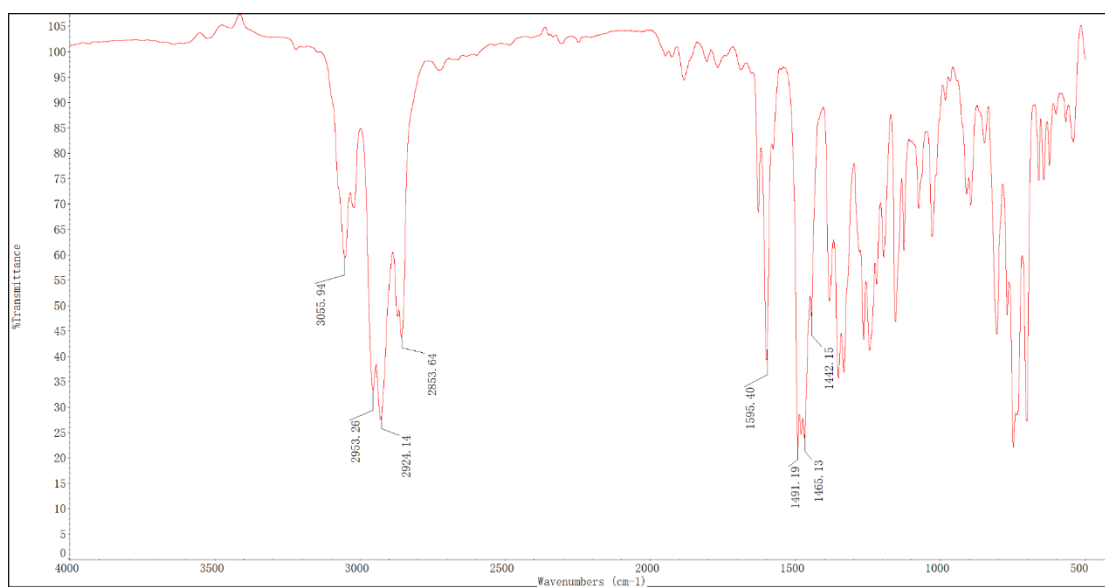


The ^{13}C NMR spectrum of **BP-Ph**

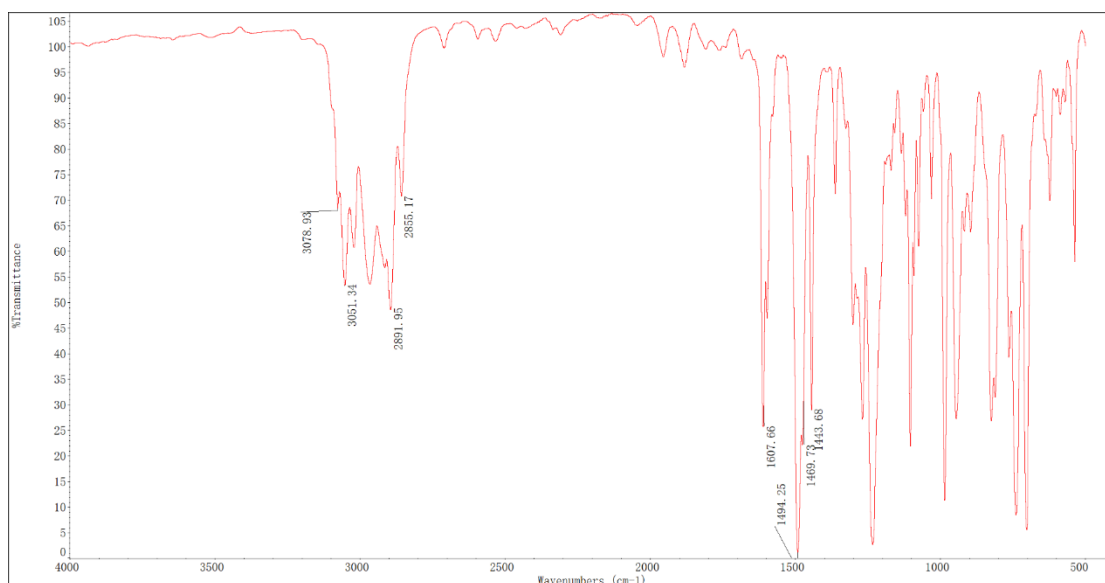
2.2 IR spectra of dyes



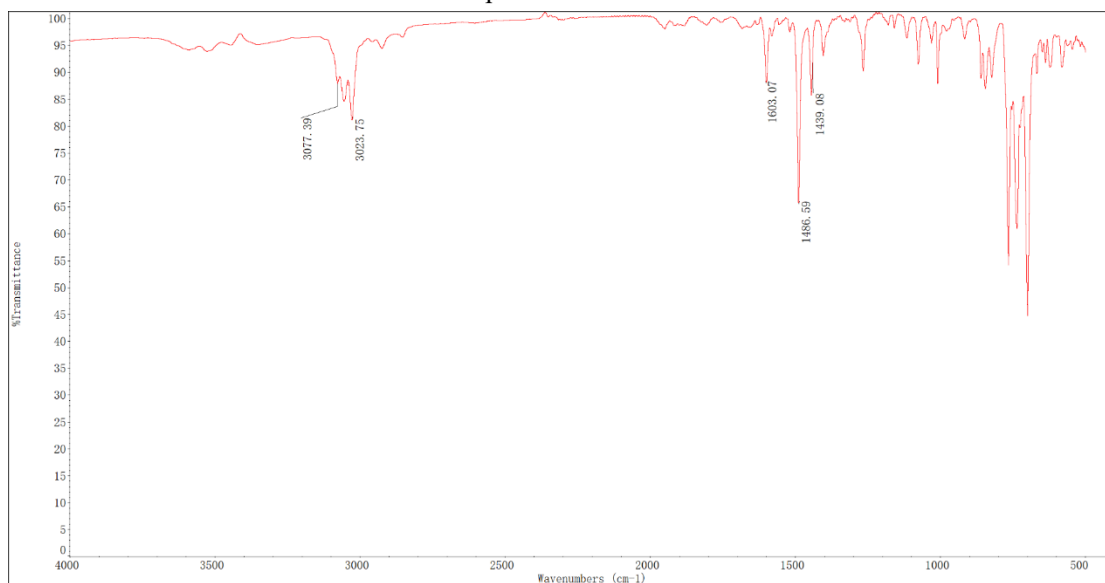
The IR spectrum of Cz-bi-Ph



The IR spectrum of Cz-hex-Ph

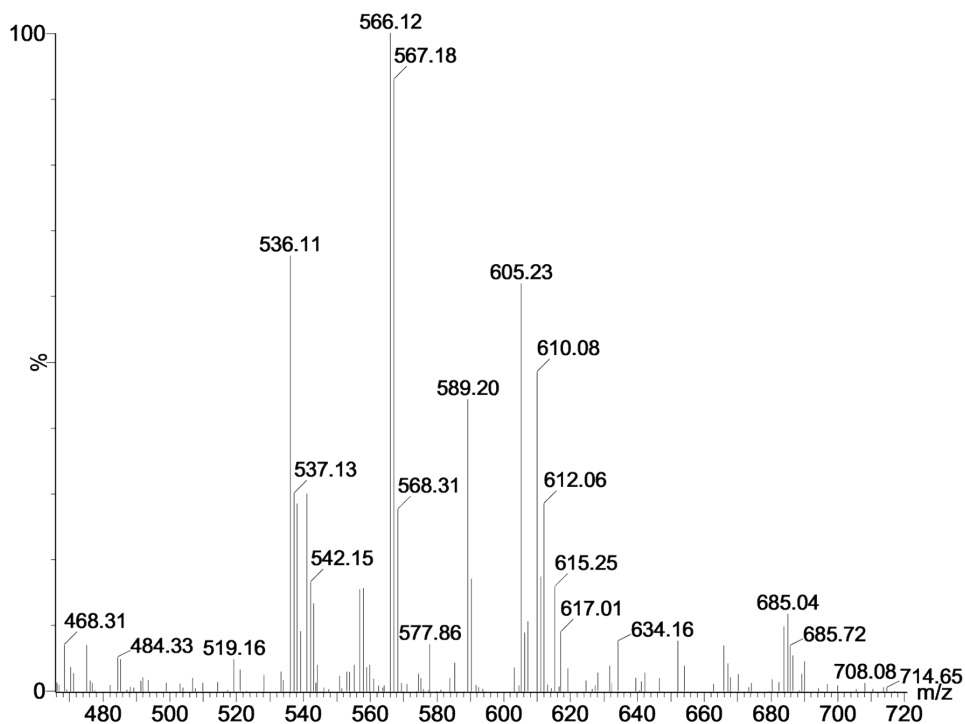


The IR spectrum of **DHBPh**

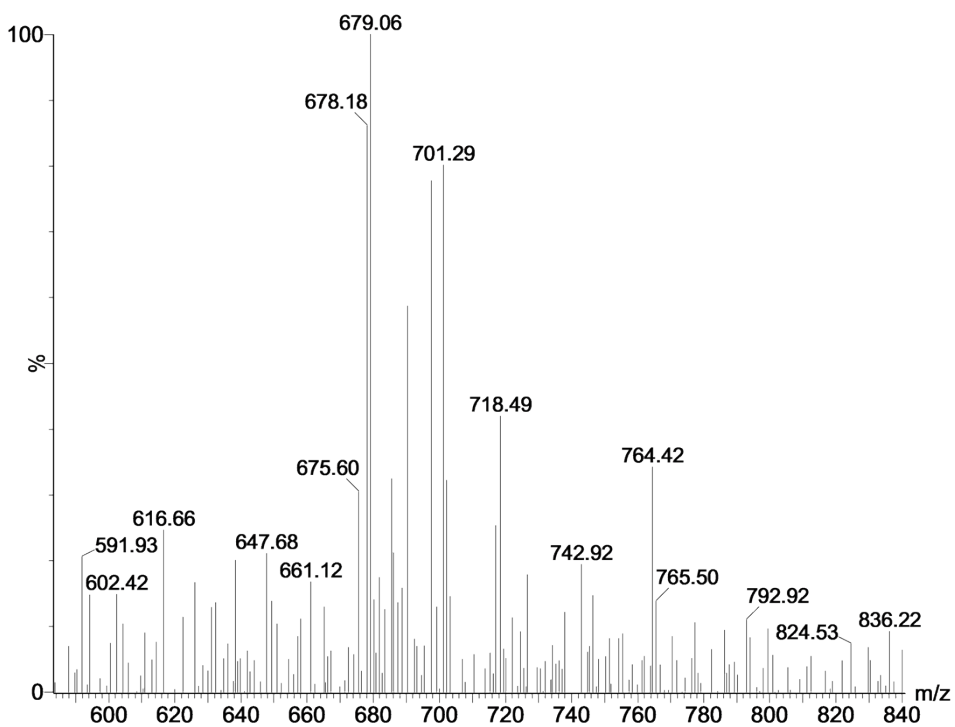


The IR spectrum of **BP-Ph**

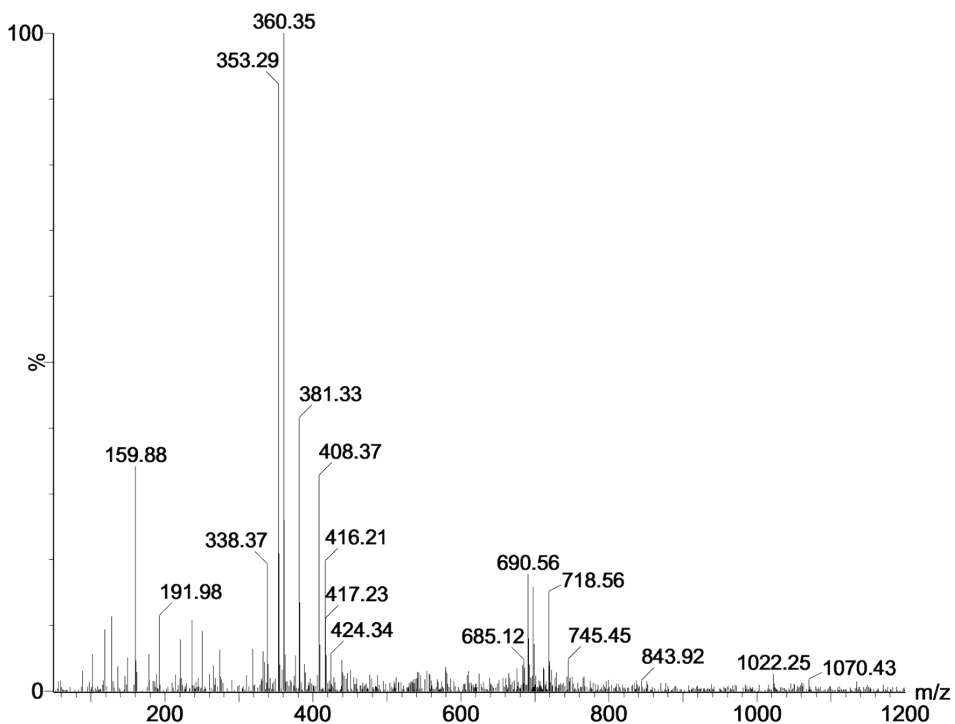
3. HRMS spectra of dyes



The HRMS spectrum of Cz-bi-Ph



The HRMS spectrum of Cz-hex-Ph



The HRMS spectrum of DHBF-Ph

4. Photochemical property of dyes

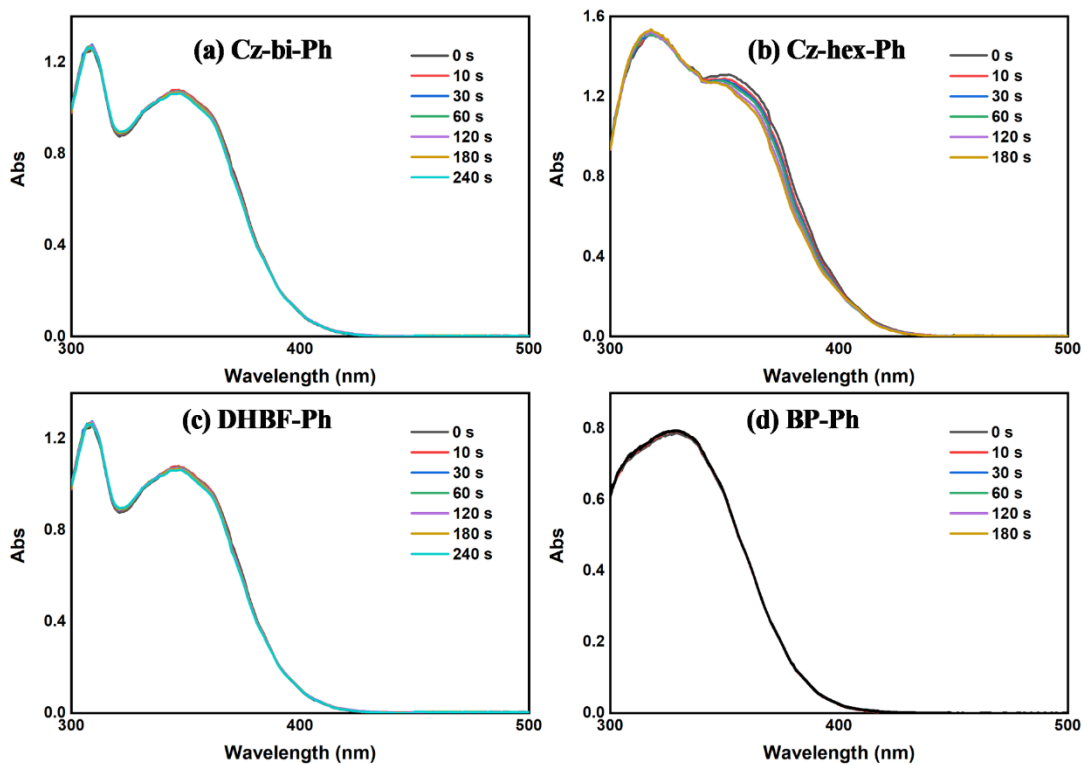


Fig. S1. UV absorption spectrum of (a) Cz-bi-Ph, (b) Cz-hex-Ph, (c) DHBF-Ph, and (d) BP-Ph under 405 nm LED at different time

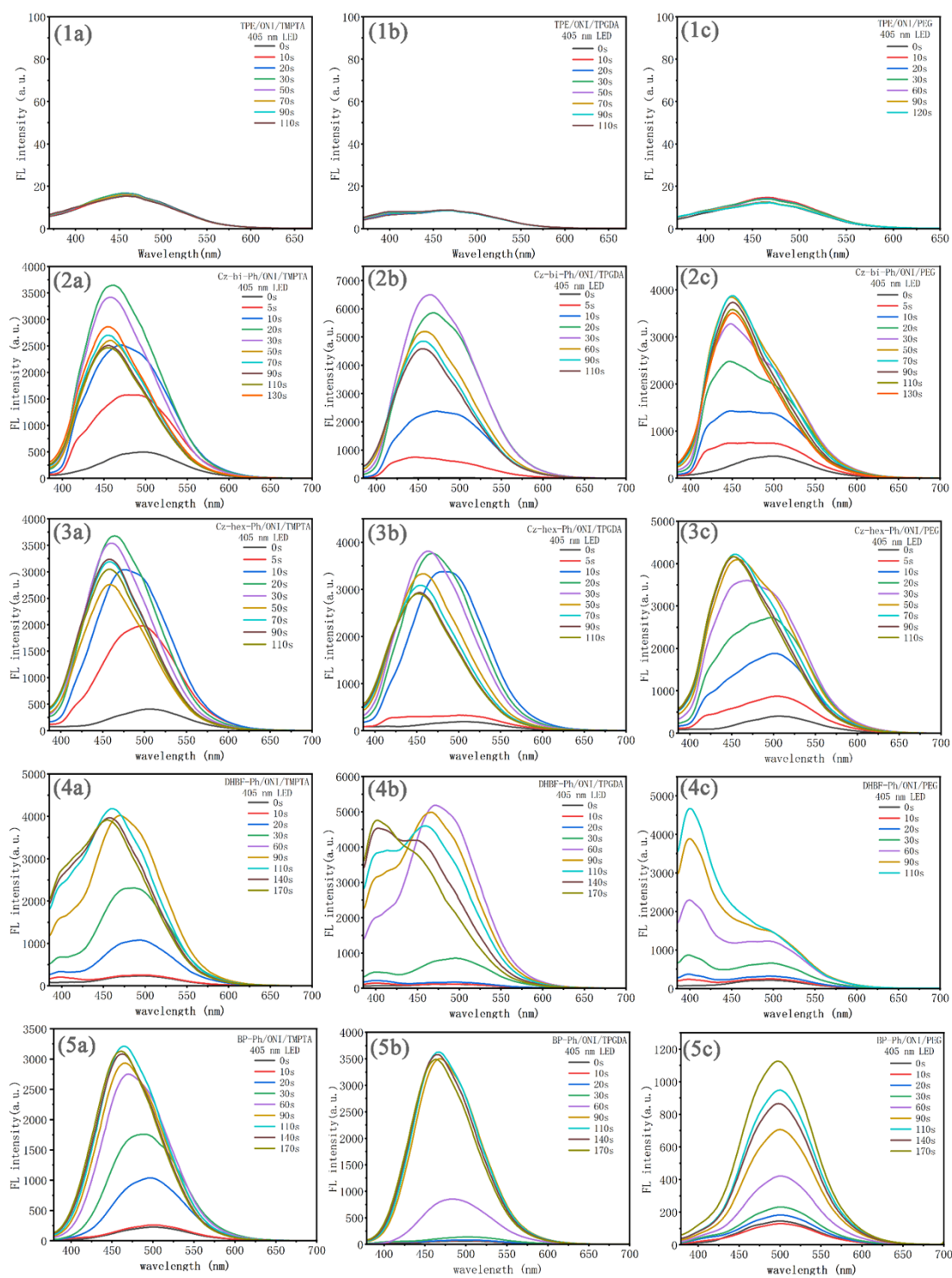


Fig. S2. (1a-c) Changes of fluorescence spectra in the photopolymerization of ETPTA initiated by TPE/ONI under 405 nm LED; (2a-c) Changes of fluorescence spectra in the photopolymerization of ETPTA initiated by Cz-bi-Ph/ONI under 405 nm LED; (3a-c) Changes of fluorescence spectra in the photopolymerization of ETPTA initiated by Cz-hex-Ph/ONI under 405 nm LED; (4a-c) Changes of fluorescence spectra in the photopolymerization of ETPTA initiated by DHBF-Ph/ONI under 405 nm LED; (5a-c) Changes of fluorescence spectra in the photopolymerization of ETPTA initiated by

BP-Ph/ONI under 405 nm LED.