

Electronic Supplementary Information (ESI)

Improving photovoltaic performance by installing alkyl chains perpendicular to π -conjugated plane of organic dye for dye-sensitized solar cells

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General

All chemicals and reagents were used as received from chemical companies without further purification. Column chromatography was performed using with silicagel as a stationary phase. Cyclic voltammetry (CV) was performed on a CH Instruments 624D potentiostat/galvanostat system. All CV measurements were carried out in anhydrous CH₂Cl₂ containing 0.1 M TBAHFP as a supporting electrolyte, purging with argon prior to conduct the experiment. Platinum electrode was used as a working electrode, Ag/AgNO₃ in saturated KNO₃(aq.) as a reference electrode, and a platinum wire as a counter electrode. UV-Vis spectra were measured in CH₂Cl₂ solution or TiO₂ film using UV-3600 Spectrophotometer (SHIMADZU). Mass spectra were measured on a Shimadzu Biotech matrix-assisted laser desorption ionization (MALDI) mass spectrometer. The ¹H- and ¹³C-NMR measurements were performed by a DRX-400 or DRX-600 spectrometer (Bruker BioSpin). Geometry optimization and Molecular orbital distributions of three dyes were performed using B3LYP functional and 6-31G (d,p) basis set implemented in the Gaussian 09 program package.¹

Cell Fabrication and characterization

The device fabrication was performed as follows. A double-layered TiO₂ film as photoanode containing 11 μm main transparent layer with ca. 20 nm sized titania particles and a 5 μm scattering layer with ca. 400 nm sized titania particles were screen printed on the fluorine-doped tin oxide (FTO) conducting glass substrate. The double-layered film were heated to 520 °C and sintered for 1 hour and then cooled to 80 °C, following additional treatment with 0.1 M HCl aqueous solution. The resulted TiO₂ films were washed, dried and then dipped into a 3 × 10⁻⁴ M acetonitrile/n-BuOH (1/1, v/v) solution of the corresponding sensitizer, or a mixture of sensitizer (0.3 mM) and DCA (20 mM) in CH₃CN/n-BuOH (1/1, v/v) for 40 h. Afterwards, the dye-loaded TiO₂ film and a platinum coated conducting glass were assembled into a DSSC of a sandwich type and sealed by heating the Surlyn spacer (40 mm thick). An electrolyte consisting of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I₂, 0.1 M LiI and 0.5 M TBP in acetonitrile was injected into the spacer from the counterelectrode side through a pre-drilled hole, and then the hole was sealed with a Bynel sheet and a thin-glass-slide cover by heating.

The *I-V* characteristics were carried out by using a black metal mask with an aperture area of 0.2304 cm⁻² under standard AM 1.5 sunlight, 100 mW·cm⁻² (WXS-155S-10: Wacom Denso Co. Japan). Monochromatic IPCE spectra were determined with monochromatic incident light of 1 × 10¹⁶ photons per cm² under 100 mW·cm⁻² in director current mode (CEP-2000BX, Bunko-Keiki). The IMVS were characterized with a potentiostat (Solartron1287) equipped with a frequency response analyzer (Solartron1255B) at an open-circuit condition based on a monochromatic illumination (420 nm) controlled by a Labview system to obtain the photovoltaic response induced by the modulated light.

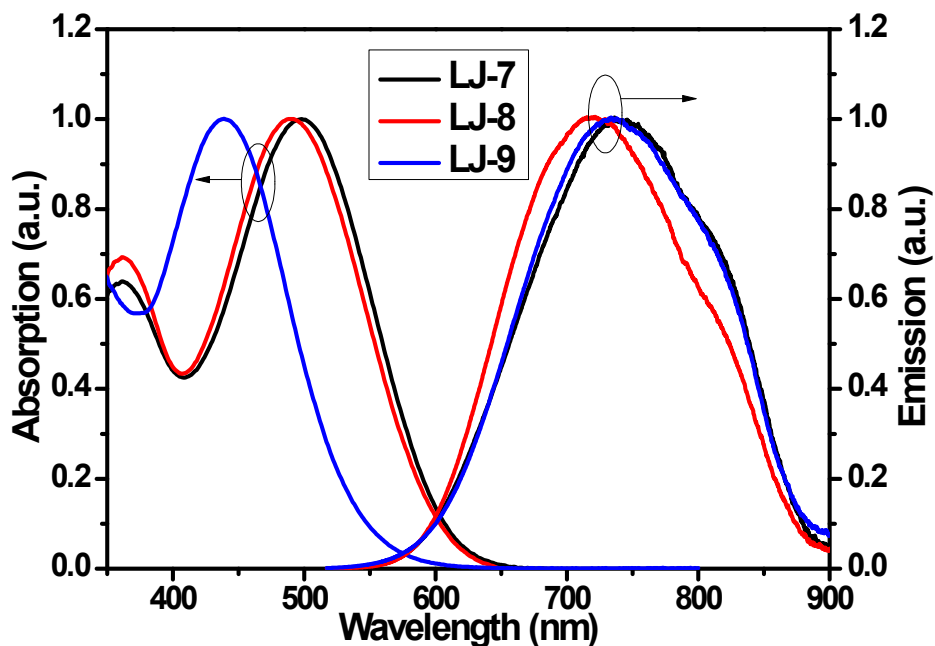


Fig. S1 Normalized UV-vis and emission spectra of dyes LJ-7, LJ-8 and LJ-9 in CH_2Cl_2 .

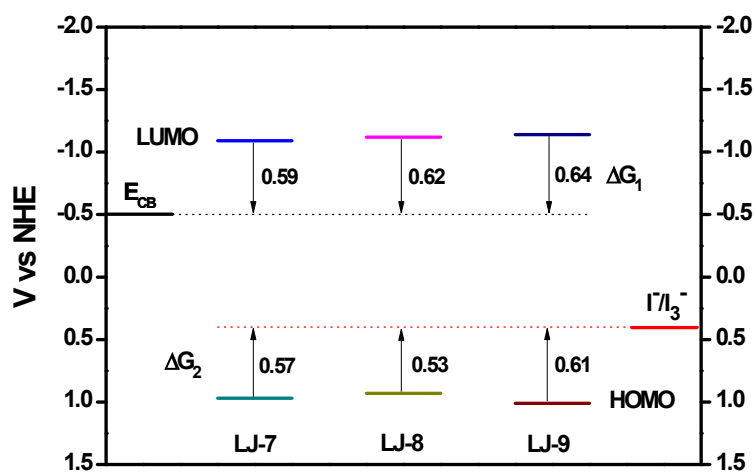


Fig. S2 Energy-level diagram of dyes LJ-7, LJ-8, and LJ-9, the electrolyte and TiO_2 , E_{CB} : energy level of conduction band of TiO_2 ; ΔG_1 : driving force for electron injection; ΔG_2 : driving force for regeneration of the oxidized dyes.

DFT Calculation

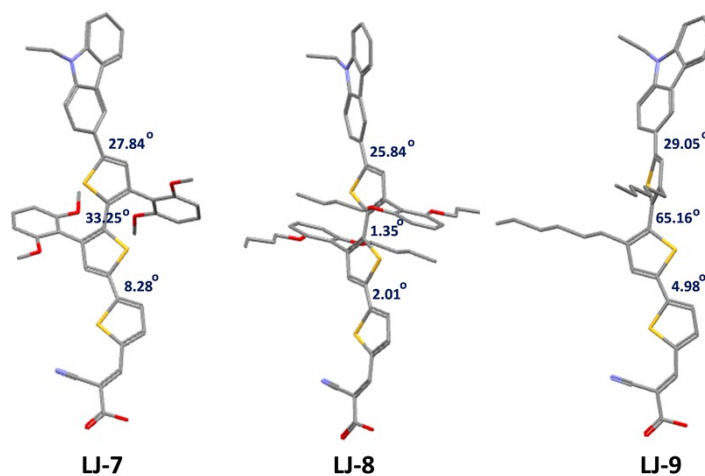


Fig. S3 Optimized ground-state geometries and dihedral angles between the π -planes of LJ-7, LJ-8 and LJ-9.

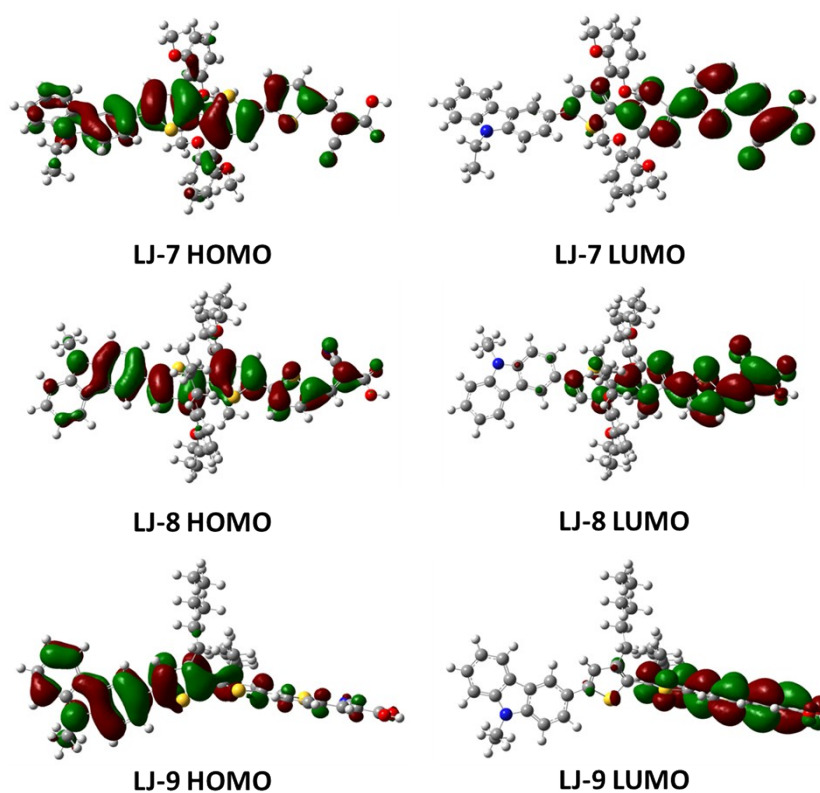


Fig. S4 The HOMO and LUMO of dyes LJ-7, LJ-8 and LJ-9 optimized at B3LYP/6-31G** level.

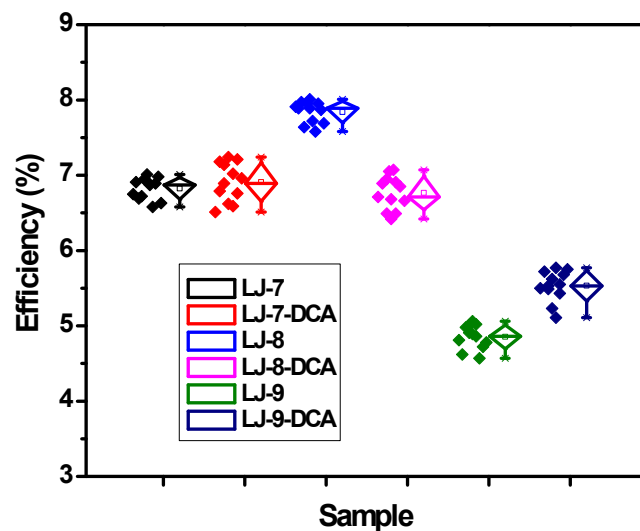


Fig. S5 The power conversion efficiency statistics of DSSCs based on dyes LJ-7, LJ-8 and LJ-9 with/without DCA coadsorption. (12 devices for each sample).

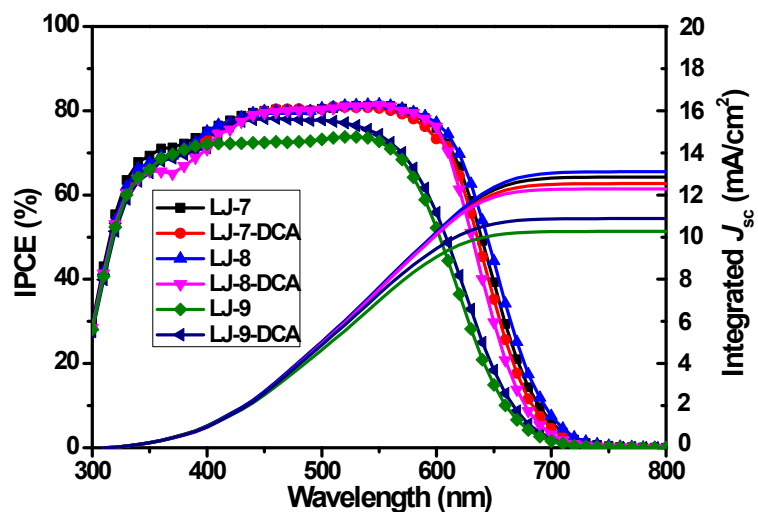


Fig. S6 IPCE spectra and the integrated J_{sc} of DSSCs based on dyes LJ-7, LJ-8 and LJ-9 with/without DCA coadsorption.

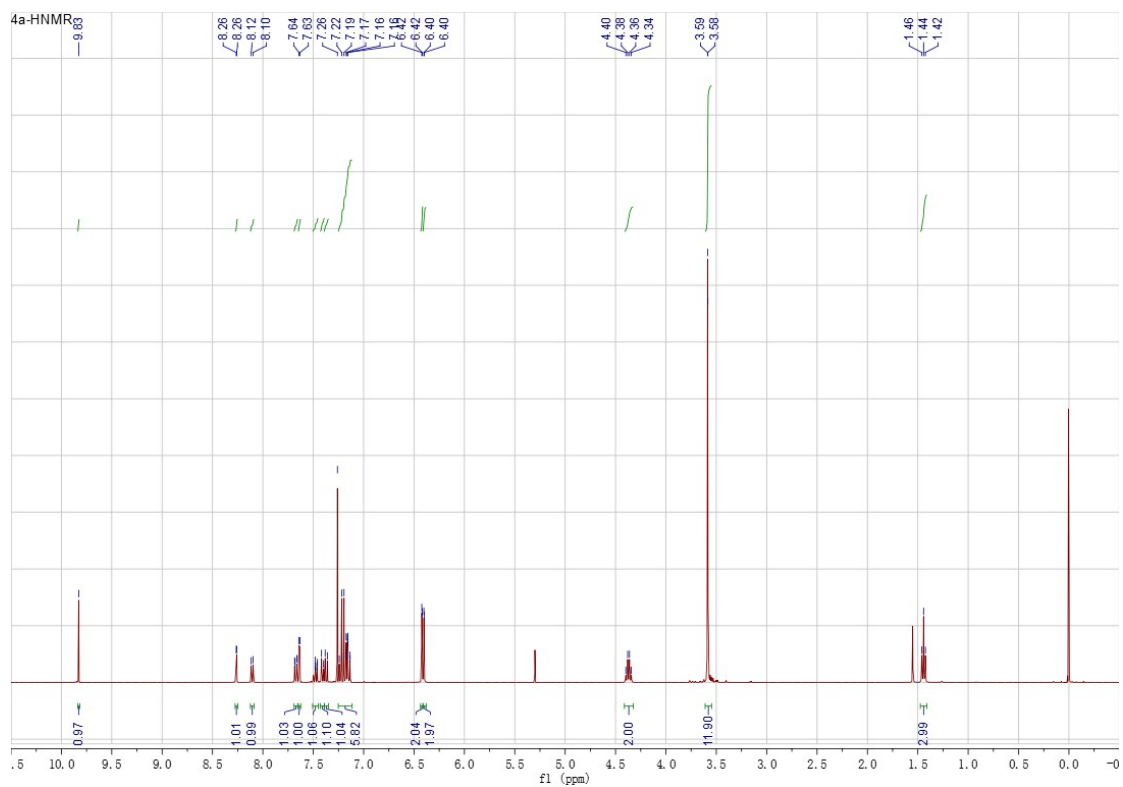


Fig. S7 ¹H NMR spectra of compound 4a.

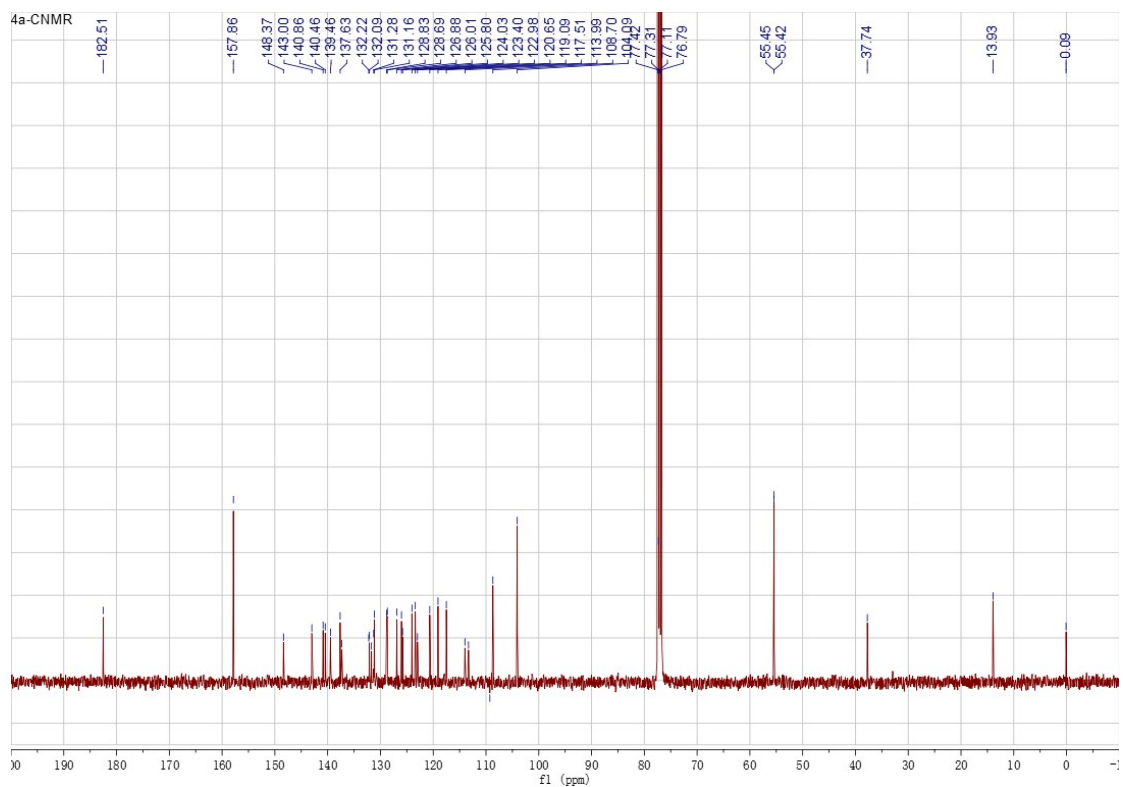


Fig. S8 ¹³C NMR spectra of compound 4a.

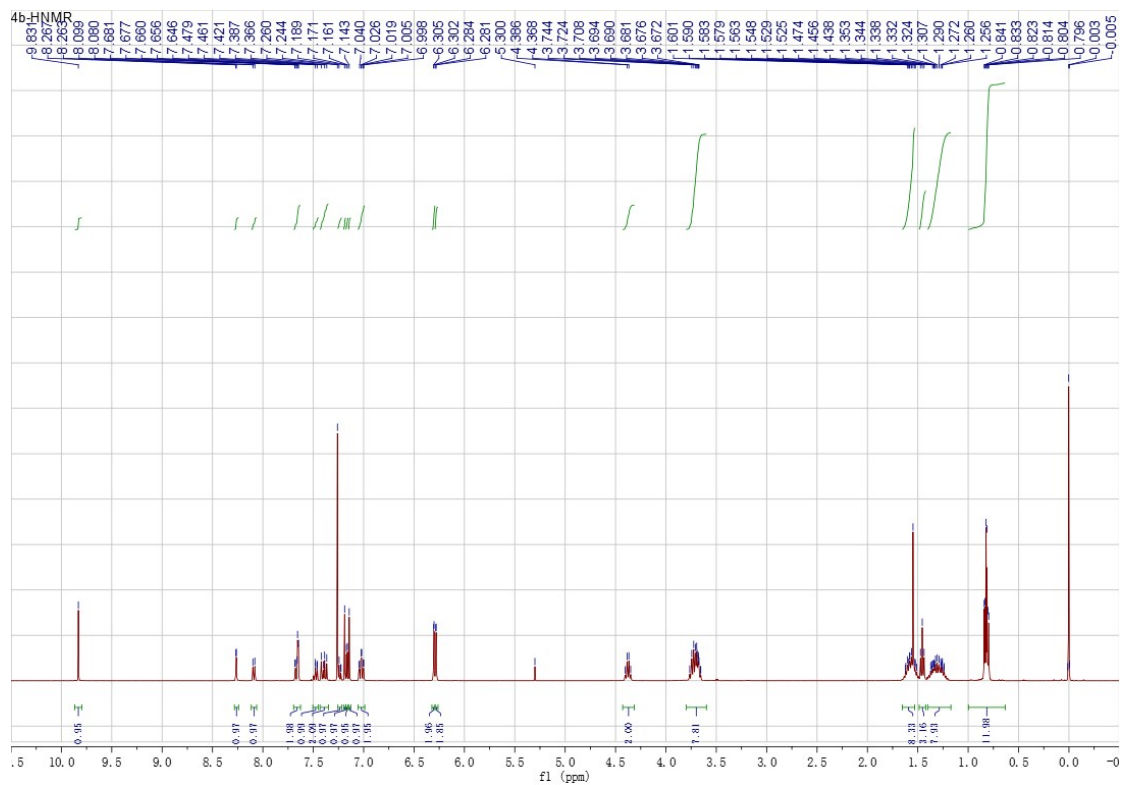


Fig. S9 ¹H NMR spectra of compound 4b.

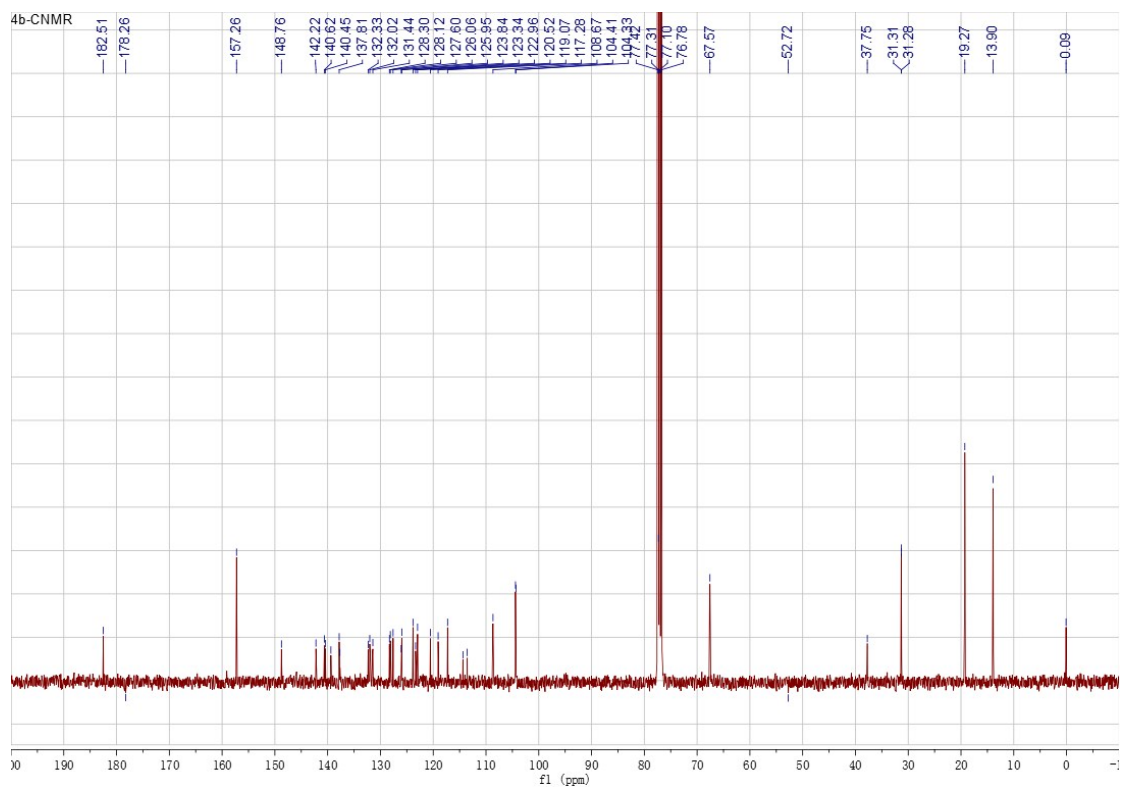


Fig. S10 ¹³C NMR spectra of compound 4b.

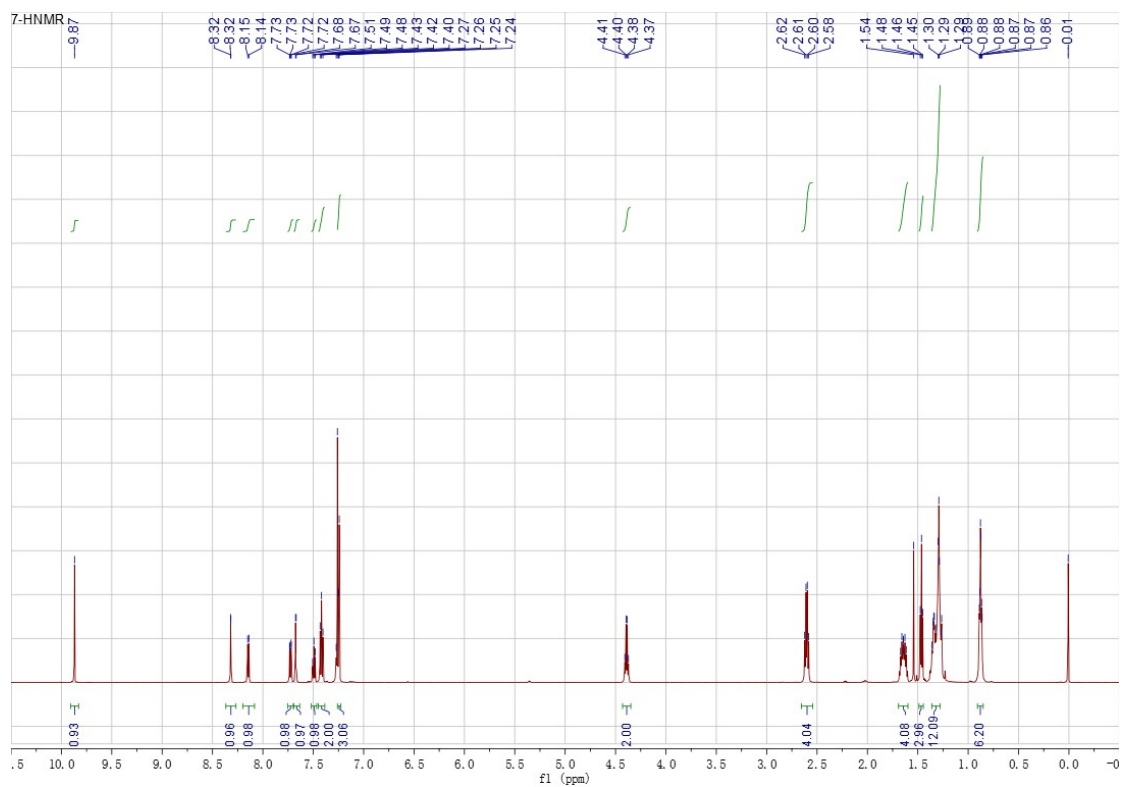


Fig. S11 ¹H NMR spectra of compound 7.

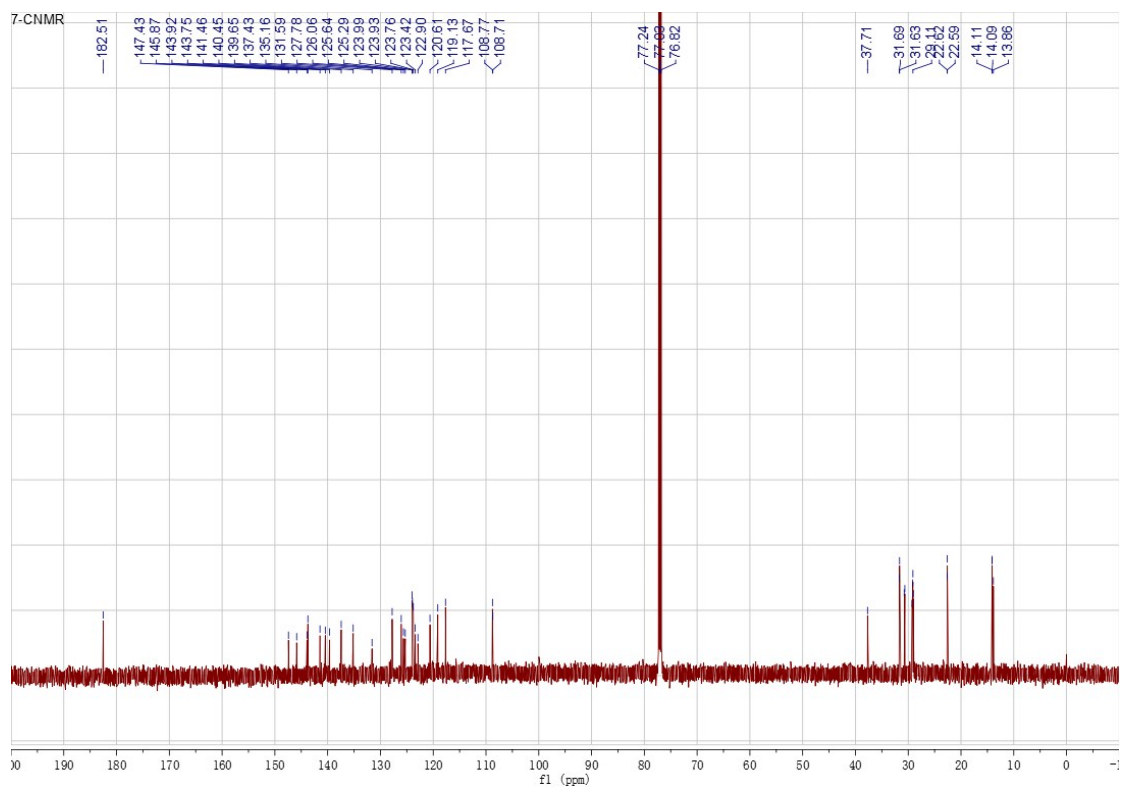


Fig. S12 ¹³C NMR spectra of compound 7.

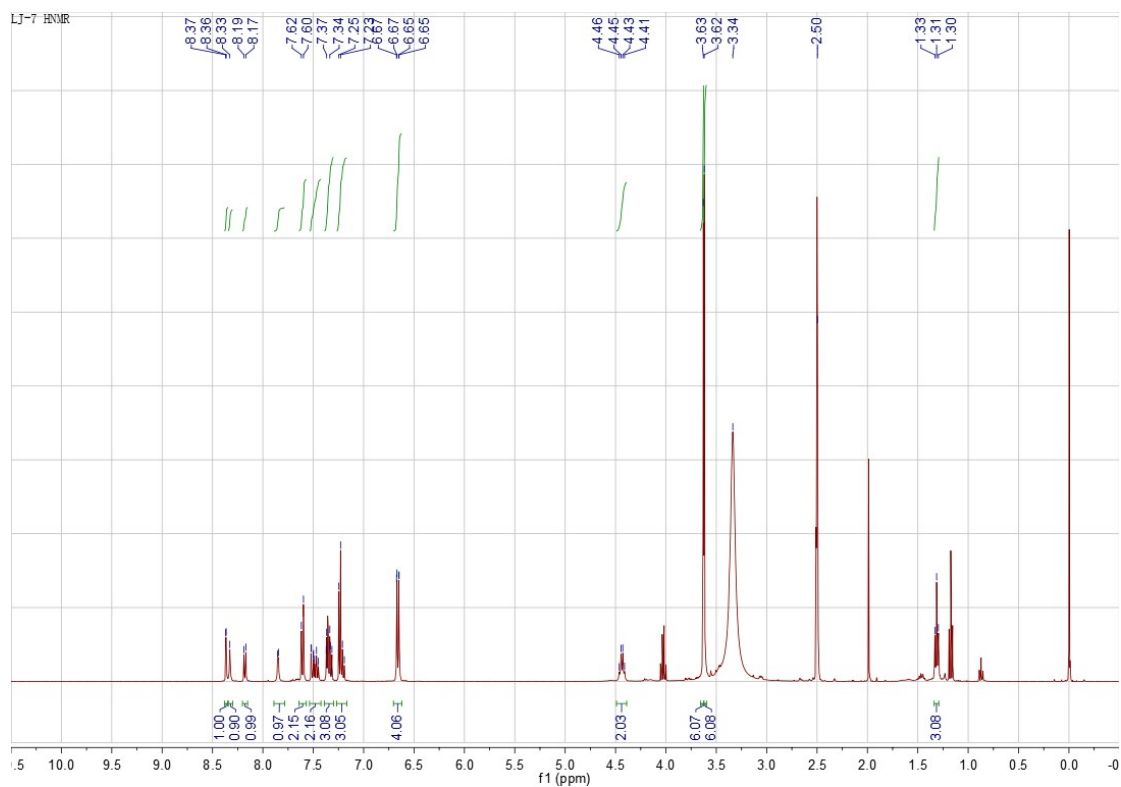


Fig. S13 ^1H NMR spectra of dye LJ-7.

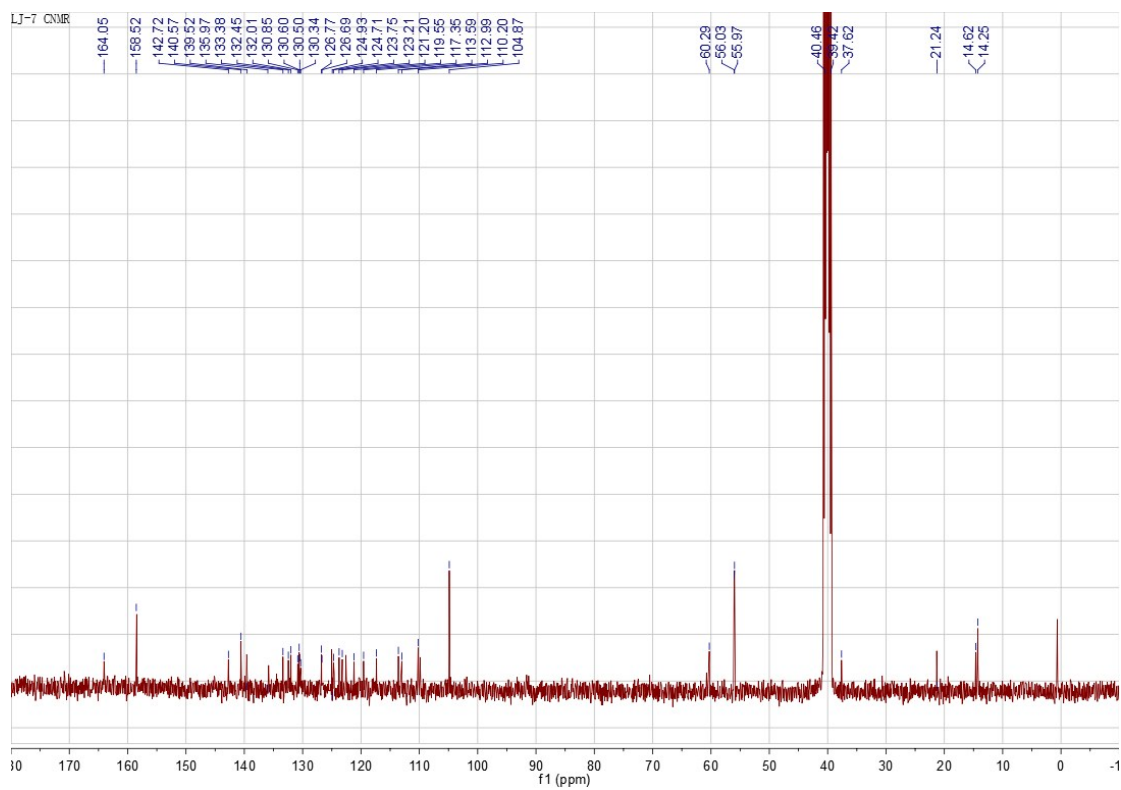


Fig. S14 ^{13}C NMR spectra of dye LJ-7.

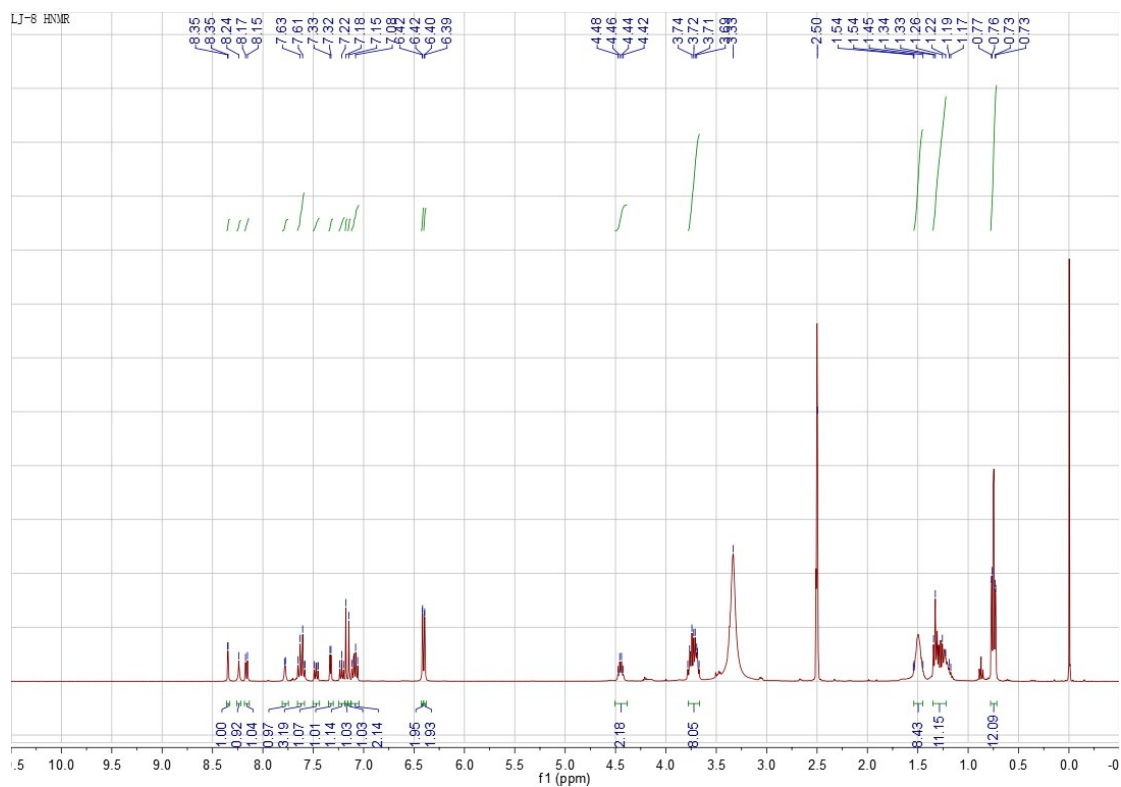


Fig. S15 ¹H NMR spectra of dye LJ-8.

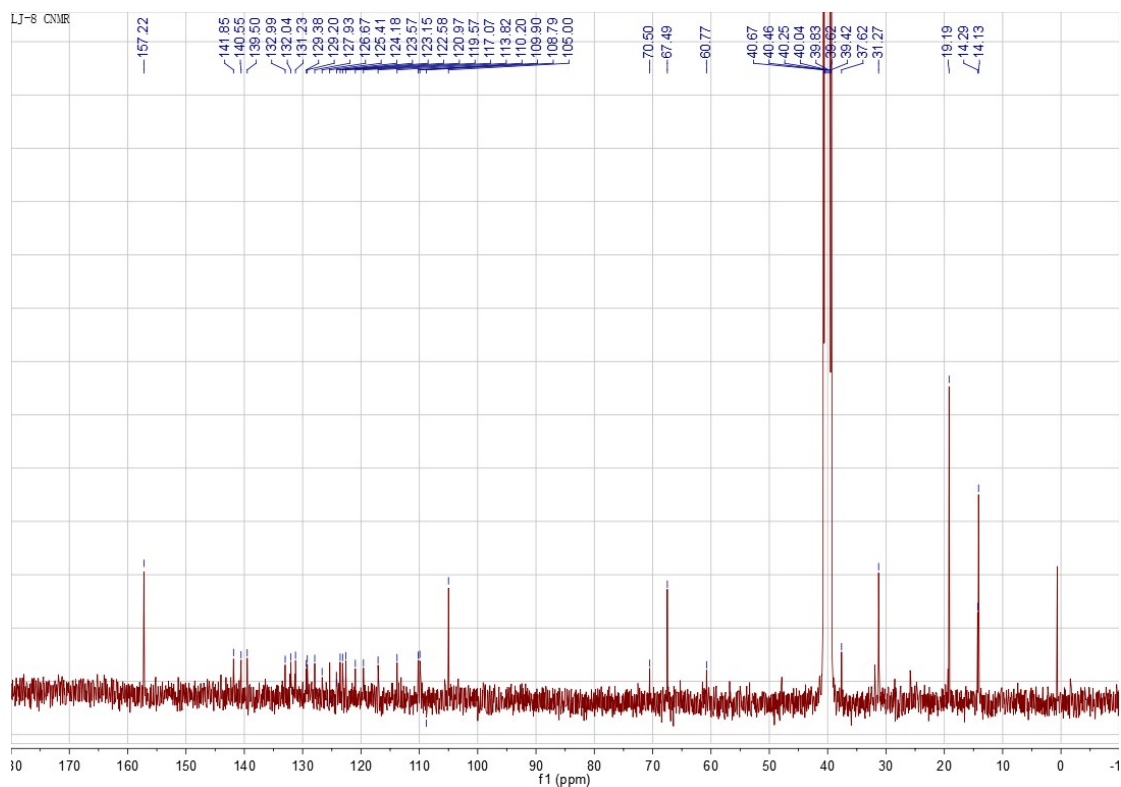


Fig. S16 ¹³C NMR spectra of dye LJ-8.

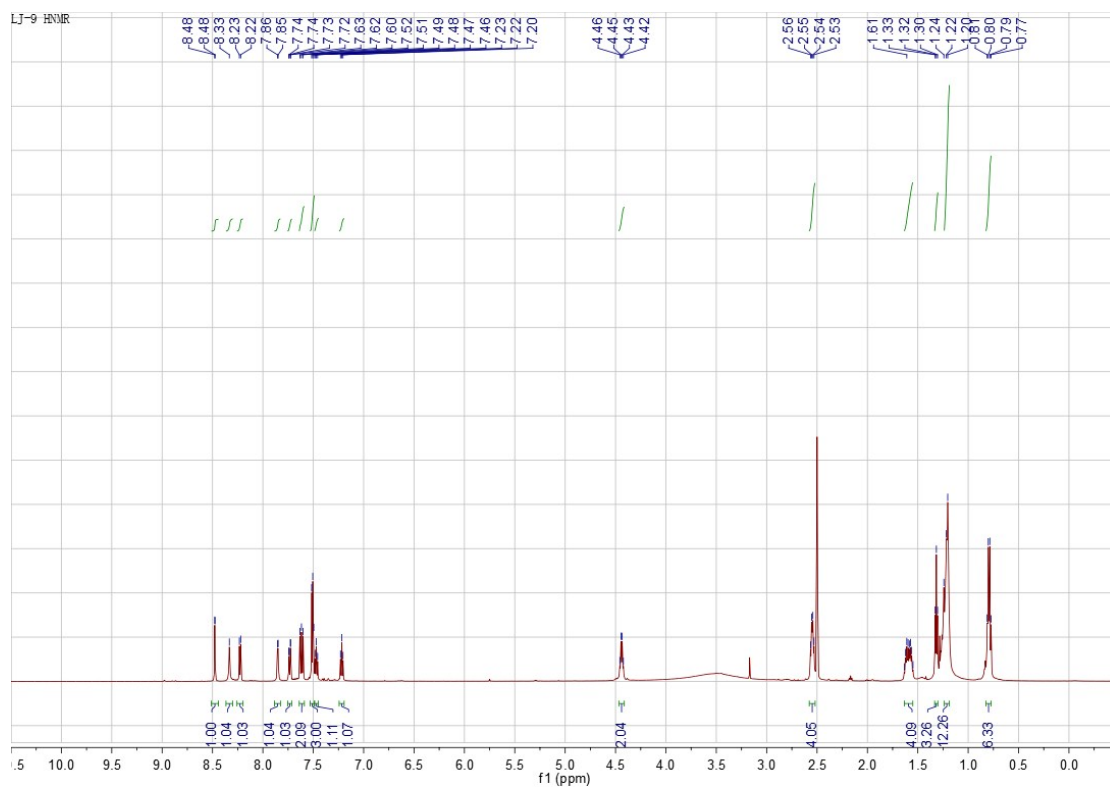


Fig. S17 ¹H NMR spectra of dye LJ-9.

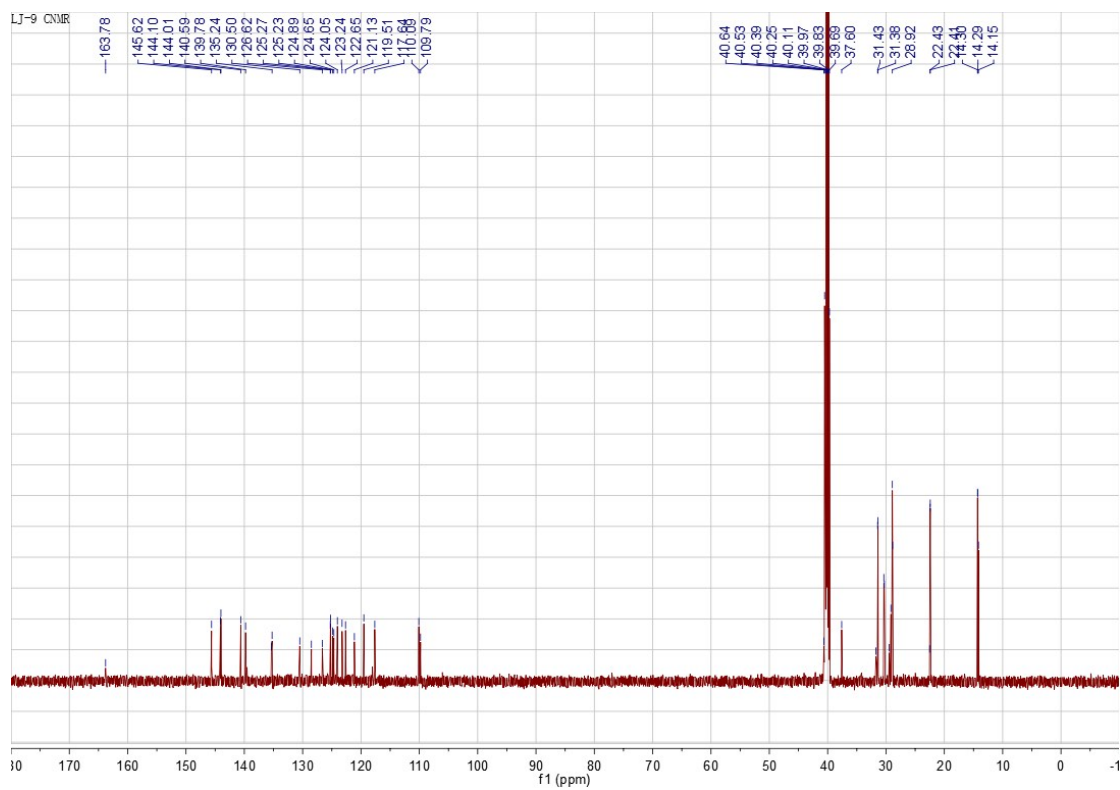


Fig. S18 ¹³C NMR spectra of dye LJ-9.

Reference

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