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Electronic Supplementary Information (ESI):

Promotion of Photocatalytic Hydrogen Production by Utilization of Triplet Excited States of Organic Dyes and Adjustment of π-π Interactions

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Content

Additional data and spectra

Materials

Tetrahydrofuran (THF) was dried over and distilled from a K–Na alloy under an atmosphere of dry argon. All solvents were of analytical grade and used without further purification. Urea, bis(di-tert-butyl(4-dimethylaminophenyl)phosphine)dichloro palladium(II)(Pd(amphos)Cl_2), tri-*n*-butyltinchloride, 4,7-dibromo-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole, *N*-bromosuccinimide (NBS), *N*,*N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, 2-(tributylstannyl)thiophene, 3-ethylthiophene, 3-butylthiophene, 3-hexylthiophene, 3-octylthiophene, 3-(2-ethylhexyl)thiophene, 3-(2-butyloctyl)thiophene, 3-(2-hexyldecyl)thiophene, 3-(2-octyldodecyl)thiophene, 3-(2-decyltetradecyl)thiophene and 4,7-dibromo-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole, were purchased and used directly as received.

Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 MHz using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. Elemental analyses were performed by a Perkin-Elmer microanalyzer. MALDI-TOF spectra were measured on an AB SCIEX MALDI-TOF/TOF 5800. UV-vis spectra were conducted on a Shimadzu UV-2550 spectrometer. Photoluminescence and phosphorescence spectra in solution at 77 K were performed on a Hitachi F-4700 fluorescence spectrophotometer. Photoluminescence spectra and fluorescence lifetimes, and phosphorescence spectra at solid state were determined by a FLS980 spectrometer. Phosphorescence lifetimes were determined with PicoQuant FluoTime 300. The Fourier transform infrared (FTIR) spectra were obtained on Thermo Nicolet IS 10 FT-IR spectrometer with KBr as the diluents in the frequency range of 4000-400 cm^{-1}. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were performed on UV-3600 Ultraviolet-Visible-Near Infrared Spectrophotometer with MPC-3100 Multi-Purpose Large-Sample Compartment. UPS spectra were obtained by ThermoFisher ESCALAB XI+. RTP photographs of organic luminogens at solid state were captured with a Tanon 5200 multi-chemiluminescence imager (cooling temperature of Charge-coupled Device lens is -40 ^{o}C)

DFT calculations

DFT calculations were performed on Gaussian 09 program (Revision D09). The ground state (S_0) geometries were optimized with the Becke's three-parameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6–31 G(d) basis sets. To simulate the isolation effect of alkyl chains, the lengths of alkyl chains perpendicular to thiophene planes in the default state were measured by CHEM 3D as efficient lengths.

Synthesis of polymeric carbon nitride (PCN) and preparation of PCN/Pt, dye/PCN and dye/PCN/Pt

In a typical synthesis, 10 g of urea was calcined at 550 ^{o}C in air for 2 h at the heating rate of 10 ^{o}C min^{-1}. The obtained solid (PCN) was grounded into powder with an agate mortar. Then, PCN powder (500 mg) and $H_2PtCl_6\cdot 6H_2O$ (40 mg) was added into a mixture methanol aqueous solution (120 mL, v/v = 5:1) in a beaker, and the solution was irradiated by a Xe lamp (300 W) for 3h, 3.0 wt.% PCN/Pt was obtained by filtration and washed 3 times by water. PCN/Pt (100 mg) and dyes (2 mg) were immersed in a $CHCl_3$ solution (10 mL) and kept stirring at room-temperature in the dark for 3 hours, then the solvent was removed by rotary evaporation to give dyes/PCN/Pt.

Characterization of PCN, PCN/Pt, dye/PCN and dye/PCN/Pt

The powder X-ray diffraction patterns were recorded by Rigaku MiniFlex 600 using Cu-Kα radiation from 5^{o} to 80^{o}. Transmission electron microscopy (TEM) were obtained in JEM-F200 transmission electron microscope. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo Fisher Nexsa instrument with a monochromatized Al Kα line source. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were performed on Perkinelmer LAMBDA 850 UV/Vis Spectrophotometer. The Fourier transform infrared (FTIR) spectra Thermo Nicolet IS 50 FT-IR spectrometer with KBr as the diluents in the frequency range of 4000-400 cm^{-1}. Fluorescence spectra and lifetimes were determined with FLS980 spectrometer. Water contact angle were performed at POWERREACH JC2000D contact angle measuring instrument.

Photoelectrochemical Measurements

Photocurrent density curves and Electrochemical Impedance Spectroscopy (EIS) were obtained in a conventional three electrode cell by ModuLab XM ECS, using a Pt plate as the counter electrode and a Ag/AgCl (3 M KCl) electrode as the reference electrode. The working electrode was prepared on indium-tin oxide (ITO) glass, that was cleaned by sonication in ethanol and acetone for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 5 mg of sample (PCN, PCN/Pt, dye/PCN/Pt) was dispersed in a 0.5 mL solution (480 μL of absolute ethanol and 20 μL of Nafion solution) by sonication to get a slurry. The slurry was spread onto pretreated ITO glass. After air-drying, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin to get a 1 cm × 1 cm film electrode. A Na_2SO_4 solution (0.5 M) was used as the electrolyte. Before testing, the electrolyte was purged with N_2 to remove dissolved oxygen. EIS was determined over the frequency range of 10^{-2} - 10^{6} Hz with an ac amplitude of 10 mV at the open circuit voltage and -1.2 V (vs. RHE), respectively.

Photocatalytic test

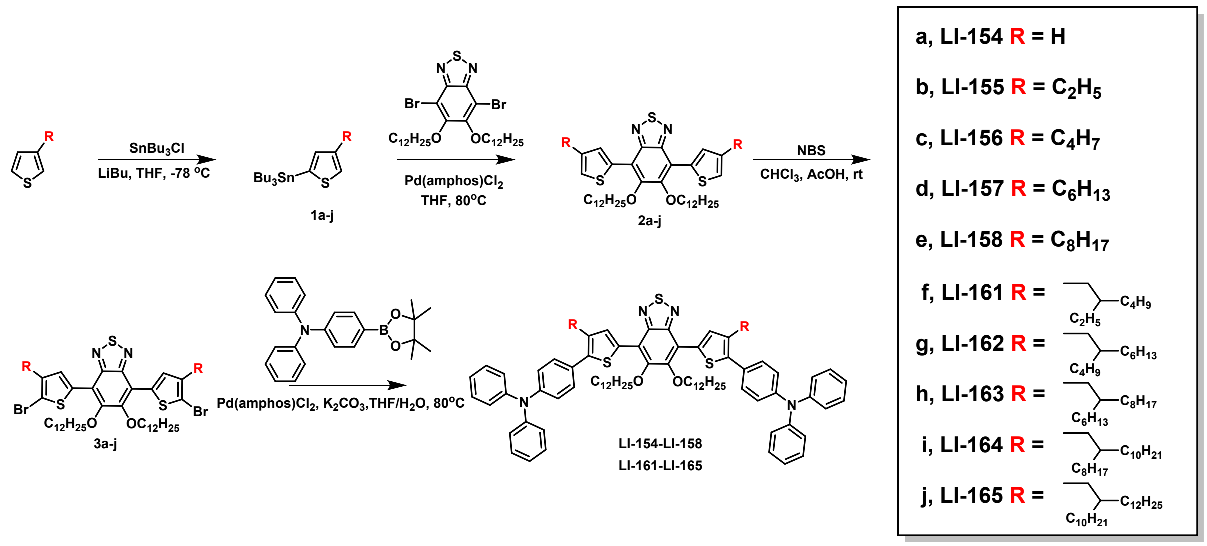
Photocatalytic hydrogen evolution arrays were performed in a Pyrex top-irradiation reaction vessel linked to a glass closed gas system. H_2 production was carried out by dispersing 50 mg of photocatalyst powder in an aqueous solution (100 mL) containing triethanolamine (10 vol.%) as sacrificial electron donor. The mixture was evacuated several times to remove air completely before irradiation under a 300 W Xe-lamp and a water-cooling filter. The mixture was kept at room temperature by a flow of cooling water. The generated gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) with Argon as the carrier gas.

The apparent quantum yield (AQY) for H_2 evolution was acquired with monochromatic LED lamps with a band-pass filter of 420, 450, 490 and 520 nm. The intensities were 17.1, 13.2, 13.0 and 8.5 mW cm^{-2}, respectively (Newport 2936-R optical power meter). The irradiation area was 9 cm^2 for the monochromatic light. Depending on the amount of hydrogen produced by the photocatalytic reaction in 1 h, the AQY value was calculated by the following Equation:

$$AQY\% = \frac{2 \times Number\ of\ H_2}{Number\ of\ incident\ photons} \times 100\% = \frac{2 \times R_{H_2} \times N_A}{S \times P \times t \times \frac{\lambda}{hc}} \times 100\%$$

Where R_{H_2} denotes the evolved hydrogen amount (μmol), N_A is the Avogadro constant, S is the illumination area, P and λ are the intensity (W cm^{-2}) and wavelength (nm) of the monochromatic light, respectively. t is the irradiation time, h is the Plank constant, and c is the speed of light.

Structural characterization of organic dyes



Scheme S1. Synthetic routes of organic dyes **LI-154** ~ **LI-158** and **LI-161** ~ **LI-165**

The general synthesis of compound 1b-j:

Under nitrogen atmosphere, thiophene derivatives (1.0 equiv.) in THF (40 mL) was placed in Schlenk tube and stirred at -78 °C. *n*-Butyllithium (1.0 equiv.) was added dropwise, and the solution was stirred for 1 h under the same temperature. Then tributyltin chloride (1.0 equiv.) was added, and the reaction mixture was recovered to room temperature and stirred for overnight. The mixture was poured into water and extracted with dichloromethane for three times. The organic layer was combined and dried with anhydrous sodium sulfate. After the solvent was evaporated, the desired product was used directly in the next step without further purification.

The general synthesis of compound 2a-j:

Under nitrogen atmosphere, a mixture of 2-(Tributylstannyl)thiophene or compound **1b-j** (2.2 equiv.), 4,7-dibromo-5,6-bis(dodecyloxy) benzo [*c*][1,2,5] thiadiazole (1.0 equiv.) and Pd(amphos)Cl_2 (0.05 equiv.) in THF (40 mL) was placed in Schlenk tube and stirred at 80 °C for 12 h. After being cooled to room temperature, the mixture was poured into water and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous sodium sulfate. After the solvent was evaporated, the crude products were purified by column chromatography.

2a: 2-(Tributylstannyl)thiophene (1.05 g, 3.32 mmol) and orange solid (0.83 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.47 (dd, *J* = 3.8, 1.2 Hz, 2H, ArH), 7.50 (dd, *J* = 5.2, 1.2 Hz, 2H, ArH), 7.23 (dd, *J* = 5.2, 3.8 Hz, 2H, ArH), 4.11 (t, *J* = 7.1 Hz, 4H, OCH_2), 1.92 (p, *J* = 7.2 Hz, 4H, CH_2), 1.50-1.38 (m, 4H, CH_2), 1.35-1.25 (m, 32H, CH_2), 0.96 – 0.84 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.94, 150.98, 134.10, 130.54, 127.31, 126.77, 117.61, 74.36, 31.95, 30.35, 29.72, 29.69, 29.65, 29.57, 29.40, 25.96, 22.72, 14.15.

2b: 3-Ethylthiophene (0.37 g, 3.32 mmol) and orange solid (0.78 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (d, *J* = 1.4 Hz, 2H, ArH), 7.08 (d, *J* = 1.4 Hz, 2H, ArH), 4.09 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.71 (t, *J* = 7.7 Hz, 4H, CH_2), 1.92 (p, *J* = 7.2 Hz, 4H, CH_2), 1.77-1.65 (m, 4H, CH_2), 1.48-1.41 (m, 4H, CH_2), 1.35-1.27 (m, 32H, CH_2), 0.95-0.85 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.97, 151.01, 142.93, 133.81, 131.96, 122.30, 117.61, 74.27, 31.97, 31.95, 30.67, 30.64, 30.41, 29.76, 29.72, 29.70, 29.65, 29.53, 29.49, 29.42, 29.36, 27.87, 26.87, 26.80, 26.04, 22.73, 22.72, 17.54, 17.30, 14.15, 13.63.

2c: 3-Butylthiophene (0.47 g, 3.32 mmol) and orange solid (0.80 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 2H, ArH), 7.09 (s, 2H, ArH), 4.09 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.72 (t, *J* = 7.7 Hz, 4H, CH_2), 1.92 (p, *J* = 7.2 Hz, 4H, CH_2), 1.71 (p, *J* = 7.7 Hz, 4H, CH_2), 1.48 –1.40 (m, 8H, CH_2), 1.31-1.27 (m, 32H, CH_2), 0.97 (t, *J* = 7.4 Hz, 6H, CH_3), 0.90-0.87 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.97, 151.00, 142.88, 133.80, 131.95, 122.30, 117.60, 74.28, 32.76, 31.95, 30.39, 30.34, 29.73, 29.69, 29.67, 29.63, 29.40, 26.02, 22.72, 22.50, 14.14, 13.99.

2d: 3-Hexylthiophene (0.56 g, 3.32 mmol) and orange solid (1.05 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (d, *J* = 1.4 Hz, 2H, ArH), 7.09 (q, *J* = 0.9 Hz, 2H, ArH), 4.09 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.71 (t, *J* = 7.6 Hz, 4H, CH_2), 1.92 (p, *J* = 7.1 Hz, 4H, CH_2), 1.77-1.65 (m, 4H, CH_2), 1.46-1.39 (m, 8H, CH_2), 1.35-1.25 (m, 36H, CH_2), 0.95-0.84 (m, 12H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.95, 150.99, 142.94, 133.79, 131.95, 122.30, 117.59, 77.36, 77.04, 76.73, 74.27, 31.98, 31.79, 31.63, 30.67, 30.60, 30.42, 29.76, 29.72, 29.70, 29.65, 29.46, 29.43, 29.16, 29.09, 27.87, 26.89, 26.04, 22.83, 22.74, 22.70, 22.66, 17.54, 14.17, 13.66.

2e: 3-Octylthiophene (0.65 g, 3.32 mmol) and orange solid (0.94 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (s, 2H, ArH), 7.09 (s, 2H, ArH), 4.10 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.72 (t, *J* = 7.7 Hz, 4H, CH_2), 1.92 (p, *J* = 7.2 Hz, 4H, CH_2), 1.77-1.65 (m, 4H, CH_2), 1.47-1.28 (m, 56H, CH_2), 0.93-0.87 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.94, 150.98, 142.91, 133.78, 131.94, 122.28, 117.58, 77.34, 77.03, 76.71, 74.25, 31.96, 31.93, 30.65, 30.63, 30.40, 29.74, 29.70, 29.68, 29.63, 29.52, 29.47, 29.41, 29.34, 28.28, 27.86, 26.79, 26.03, 22.72, 17.52, 17.29, 14.14, 13.61.

2f: 3-(2-Ethylhexyl)thiophene (0.65 g, 3.32 mmol) and orange solid (0.97 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (d, *J* = 1.4 Hz, 2H, ArH), 7.06 (d, *J* = 1.3 Hz, 2H, ArH), 4.09 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.65 (d, *J* = 6.8 Hz, 4H, CH_2), 1.92 (p, *J* = 7.2 Hz, 4H, CH_2), 1.68-1.60 (m, 2H, CH), 1.48-1.41 (m, 4H, CH_2), 1.37-1.25 (m, 48H, CH_2), 0.96 -0.90 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.94, 151.02, 141.60, 133.62, 132.48, 123.22, 117.59, 74.23, 40.40, 34.67, 32.56, 31.96, 29.68, 29.40, 28.94, 27.86, 26.87, 26.02, 25.69, 23.13, 22.72, 17.54, 14.14, 13.62.

2g: 3-(2-Butyloctyl)thiophene (0.84 g, 3.32 mmol) and orange solid (0.95 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 7.06 (s, 2H, ArH), 4.10 (t, *J* = 7.2 Hz, 4H, OCH_2), 2.66 (d, *J* = 6.9 Hz, 4H, CH_2), 1.96-1.88 (m, 4H, CH_2), 1.72-1.68 (m, 2H, CH), 1.47-1.43 (m, 4H, CH_2), 1.37-1.27 (m, 64H, CH_2), 0.95-0.86 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.93, 151.03, 141.58, 133.59, 132.56, 123.23, 117.60, 74.22, 39.00, 35.04, 33.40, 31.97, 31.96, 30.42, 30.12, 29.69, 29.66, 29.41, 28.42, 26.55, 26.01, 23.13, 22.72, 14.14.

2h: 3-(2-Hexyldecyl)thiophene (0.93 g, 3.32 mmol) and orange solid (0.97 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 7.05 (s, 2H, ArH), 4.09 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.65 (d, *J* = 6.7 Hz, 4H, CH_2), 1.92 (p, *J* = 7.2 Hz, 4H, CH_2), 1.74-1.67 (m, 2H, CH), 1.46-1.41 (m, 4H, CH_2), 1.37-1.27 (m, 80H, CH_2), 0.91-0.82 (m, 18H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.91, 151.03, 141.58, 133.59, 132.54, 123.23, 117.59, 74.22, 39.00, 35.03, 33.42, 33.40, 31.97, 31.95, 30.41, 30.12, 29.79, 29.75, 29.71, 29.66, 29.41, 28.40, 28.29, 27.10, 26.79, 26.68, 26.66, 26.04, 22.73, 22.71, 17.30, 14.14, 13.61.

2i: 3-(2-Octyldodecyl)thiophene (1.21 g, 3.32 mmol) and orange solid (0.94 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (s, 2H, ArH), 7.05 (s, 2H, ArH), 4.09 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.65 (d, *J* = 6.8 Hz, 4H, CH_2), 1.92 (p, *J* = 7.2 Hz, 4H, CH_2), 1.70 (t, *J* = 5.9 Hz, 2H, CH), 1.46-1.42 (m, 4H, CH_2), 1.35-1.25 (m, 96H, CH_2), 0.90-0.85 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.91, 151.03, 141.58, 133.59, 132.55, 123.23, 117.60, 74.22, 38.99, 35.04, 33.40, 31.97, 31.95, 30.41, 30.12, 29.76, 29.71, 29.69, 29.67, 29.41, 29.39, 26.69, 26.05, 22.73, 22.71, 14.14.

2j: 3-(2-Decyltetradecyl)thiophene (1.40 g, 3.32 mmol) and orange oil (1.07 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 7.05 (s, 2H, ArH), 4.09 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.65 (d, *J* = 6.8 Hz, 4H, CH_2), 1.92 (p, *J* = 7.3 Hz, 4H, CH_2), 1.73-1.67 (m, 2H, CH), 1.46-1.43 (m, 4H, CH_2), 1.34-1.23 (m, 112H, CH_2), 0.90-0.85 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): δ 151.91, 151.03, 141.58, 133.60, 132.55, 123.23, 117.60, 74.22, 39.00, 35.05, 33.41, 31.98, 31.96, 30.42, 30.13, 29.77, 29.75, 29.73, 29.70, 29.68, 29.43, 29.40, 26.70, 26.06, 22.74, 22.72, 14.15, 13.72.

The general synthesis of compound 3a-j:

Compound **2a-j** (1.0 equiv.) was dissolved in 60 mL mixture solvent ($CHCl_3/AcOH$ = 1/1). Then NBS (2.2 equiv.) was added in batch and reacted at room temperature in dark for 3 h. After that, the mixture was poured into water and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous sodium sulfate. After the solvent was evaporated, the crude products were purified by column chromatography.

3a: Compound **2a** (0.67 g, 1.0 mmol) and orange solid (0.55 g, 67%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.37 (d, J = 4.1 Hz, 2H, ArH), 7.17 (d, J = 4.1 Hz, 2H, ArH), 4.12 (t, J = 7.2 Hz, OCH_2), 1.94 (p, J = 7.2 Hz, CH_2), 1.48-1.42(m, 4H, CH_2), 1.38-1.25(m, 32H, CH_2), 0.92-0.84 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): δ 151.91, 151.02, 141.58, 133.59, 132.54, 123.24, 117.59, 74.23, 38.97, 35.03, 33.41, 33.09, 31.98, 30.41, 29.80, 29.76, 29.71, 29.67, 29.42, 28.93, 26.66, 26.04, 23.14, 22.73, 14.22, 14.16.

3b: Compound **2b** (0.72 g, 1.0 mmol) and orange solid (0.55 g, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.33 (s, 2H, ArH), 4.11 (t, J = 7.2 Hz, 4H, OCH_2) 2.69 (t, J = 7.7 Hz, 4H, CH_2), 1.95 (p, J = 7.2 Hz, 4H, CH_2), 1.55-1.24 (m, 42H, CH_2, CH_3), 0.91-0.85 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.54, 150.45, 142.96, 133.90, 131.18, 116.94, 112.21, 74.50, 31.98, 30.37, 29.76, 29.72, 29.69, 29.60, 29.42, 26.01, 23.10, 22.74, 14.32, 14.16.

3c: Compound **2c** (0.78 g, 1.0 mmol) and orange solid (0.59 g, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 2H, ArH), 4.11 (t, J = 7.2 Hz, 4H, OCH_2), 2.67 (t, J = 7.7 Hz, 4H, CH_2), 1.94 (p, J = 7.2 Hz, 4H, CH_2), 1.71-1.63 (m, 4H, CH_2), 1.48-1.41 (m, 8H, CH_2), 1.38-1.25 (m, 32H, CH_2), 0.98 (t, J = 7.3 Hz, 6H, CH_2), 0.90-0.87 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.56, 150.48, 141.73, 133.76, 131.61, 116.94, 112.59, 74.49, 32.04, 31.95, 30.34, 29.73, 29.69, 29.67, 29.58, 29.40, 25.98, 22.72, 22.44, 14.14.

3d: Compound **2d** (0.84 g, 1.0 mmol) and orange solid (0.71 g, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 2H, ArH), 4.11 (t, J = 7.2 Hz, 4H, OCH_2), 2.66 (t, J = 7.6 Hz, 4H, CH_2), 1.94 (p, J = 7.2 Hz, 4H, CH_2), 1.72-1.64 (m, 4H, CH_2), 1.49-1.27 (m, 48H, CH_2), 0.92-0.87 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.52, 150.46, 141.78, 133.75, 131.60, 116.93, 112.60, 74.48, 31.98, 31.72, 30.37, 29.89, 29.77, 29.73, 29.71, 29.62, 29.44, 29.07, 26.01, 22.75, 22.69, 14.18.

3e: Compound **2e** (0.89 g, 1.0 mmol) and orange solid (0.64 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (s, 2H, ArH), 4.12 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.67 (t, *J* = 7.6 Hz, 4H, CH_2), 1.96 (p, *J* = 7.2 Hz, 4H, CH_2), 1.70 (p, *J* = 7.3 Hz, 4H, CH_2), 1.51-1.25 (m, 56H, CH_2), 0.92-0.87 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.52, 150.44, 141.75, 133.77, 131.61, 116.92, 112.62, 74.46, 31.99, 31.96, 30.38, 29.92, 29.78, 29.74, 29.72, 29.69, 29.63, 29.49, 29.44, 29.41, 29.36, 26.03, 22.75, 22.74, 14.16.

3f: Compound **2f** (0.89 g, 1.0 mmol) and orange solid (0.77 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 2H, ArH), 4.13 (t, *J* = 7.2 Hz, 4H, OCH_2), 2.61 (d, *J* = 7.2 Hz, 4H, CH_2), 1.96 (p, *J* = 7.3 Hz, 4H, CH_2), 1.81-1.69 (m, 2H, CH), 1.51-1.44 (m, 4H, CH_2), 1.42-1.26 (m, 48H, CH_2), 0.98-0.85 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.54, 150.49, 140.91, 133.59, 132.18, 116.94, 113.27, 74.45, 40.04, 33.87, 32.55, 31.98, 30.36, 29.76, 29.72, 29.70, 29.62, 29.43, 28.83, 26.00, 25.77, 23.15, 22.74, 14.20, 14.16.

3g: Compound **2g** (1.00 g, 1.0 mmol) and orange solid (0.70 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 4.11 (t, *J* = 7.2 Hz, 4H, OCH_2), 2.60 (d, *J* = 7.1 Hz, 4H, CH_2), 1.94 (p, *J* = 7.3 Hz, 4H, CH_2), 1.77 (s, 2H, CH), 1.49 -1.42 (m, 4H, CH_2), 1.36-1.23 (m, 64H, CH_2), 0.91-0.85 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.53, 150.52, 140.93, 133.53, 132.24, 116.95, 113.23, 74.47, 38.60, 34.19, 33.40, 33.12, 31.96, 30.33, 29.77, 29.75, 29.69, 29.60, 29.41, 28.82, 26.55, 25.99, 23.13, 22.72, 14.19, 14.14.

3h: Compound **2h** (1.09 g, 1.0 mmol) and orange solid (0.73 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 4.12 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.60 (d, *J* = 7.0 Hz, 4H, CH_2), 1.94 (p, *J* = 7.2 Hz, 4H, CH_2), 1.77 (s, 2H, CH), 1.48-1.42 (m, 4H, CH_2), 1.39-1.24 (m, 80H, CH_2), 0.90-0.84 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.53, 150.52, 140.93, 133.53, 132.25, 116.95, 113.24, 74.46, 38.60, 34.19, 33.44, 33.41, 31.96, 31.94, 31.61, 30.34, 30.09, 29.76, 29.69, 29.61, 29.41, 29.40, 26.59, 26.56, 26.00, 22.73, 22.70, 22.67, 14.14.

3i: Compound **2i** (1.20 g, 1.0 mmol) and orange oil (0.97 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 4.11 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.59 (d, *J* = 7.1 Hz, 4H, CH_2), 1.94 (p, *J* = 7.2 Hz, 4H, CH_2), 1.79-1.75 (m, 2H, CH), 1.48-1.43 (m, 4H, CH_2), 1.38-1.21 (m, 96H, CH_2), 0.90-0.84 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.53, 150.52, 140.94, 133.53, 132.25, 116.95, 113.24, 74.46, 38.59, 34.21, 33.42, 31.97, 31.94, 30.34, 30.09, 29.76, 29.74, 29.71, 29.69, 29.62, 29.51, 29.42, 29.40, 29.38, 26.59, 26.00, 22.73, 22.70, 14.13.

3j: Compound **2j** (1.31 g, 1.0 mmol) and orange oil (0.96 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (s, 2H, ArH), 4.11 (t, *J* = 7.2 Hz, 4H, OCH_2), 2.59 (d, *J* = 7.1 Hz, 4H, CH_2), 1.94 (p, *J* = 7.2 Hz, 4H,

CH_2), 1.77 (m, 2H, CH), 1.48-1.43 (m, 4H, CH_2), 1.36-1.21 (m, 112H, CH_2), 0.91-0.84 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.53, 150.52, 140.94, 133.53, 132.25, 116.95, 113.24, 74.46, 38.59, 34.21, 33.41, 31.97, 31.94, 30.35, 30.09, 29.76, 29.73, 29.71, 29.68, 29.62, 29.42, 29.38, 26.59, 26.00, 22.73, 22.71, 14.14.

The general synthesis of LI-154-158 and LI-161-LI-165

Under atmosphere of nitrogen, a mixture of the compound 3**a-j** (1.0 equiv.), *N*,*N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline(2.2 equiv.), Pd(amphos)Cl_2 (0.1 equiv.) and potassium carbonate (10.0 equiv.) in 10 mL mixed solvent (THF/H_2O = 10/1) was placed in a 100 mL dry Schlenk tube and stirred at 80 °C for 24 hours. The mixture was poured into water and extracted with chloroform three times. The combined organic layers were dried with anhydrous sodium sulfate. After the solvent was evaporated, the crude products were purified by column chromatography.

LI-154: Compound **3a** (165 mg, 0.2 mmol) and red solid (200 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.43 (d, *J* = 4.0 Hz, 2H, ArH), 7.56-7.47 (m, 4H, ArH), 7.28 (d, *J* = 4.0 Hz, 2H, ArH), 7.26-7.17 (m, 8H, ArH), 7.11-6.94 (m, 16H, ArH), 4.09 (t, *J* = 7.0 Hz, 4H, OCH_2), 1.90 (p, *J* = 7.2 Hz, 4H, CH_2), 1.48-1.25 (m, 36H, CH_2), 0.79 (t, *J* = 6.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.59, 150.96, 147.53, 147.43, 145.49, 132.97, 131.97, 129.39, 128.53, 126.66, 124.63, 123.68, 123.19, 122.27, 117.43, 74.46, 32.00, 30.55, 29.79, 29.74, 29.43, 26.20, 22.77, 14.22. MS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{74}H_{82}N_4O_2S_3$: 1154.560, found 1154.566; Elemental Analysis Calcd for $C_{74}H_{82}N_4O_2S_3$: C, 76.91; H, 7.15; N, 4.85; S, 8.32. Found: C, 76.72; H, 7.32; N, 4.50 S, 8.53.

LI-155: Compound **3b** (177 mg, 0.2 mmol) and red solid (202 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.34 (s, 2H, ArH), 7.35-7.32 (m, 4H, ArH), 7.24 -7.19 (m, 8H, ArH), 7.11-7.03 (m, 12H, ArH), 7.00-6.96 (m, 4H, ArH), 4.08 (t, 4H, *J* = 7.2 Hz, OCH_2), 2.75 (dd, 4H, *J* = 5.6 Hz, CH_2), 1.88 (p, 4H, *J* = 7.2 Hz, CH_2), 1.42-1.36 (m, 4H, CH_2), 1.28 (t, 6H, *J* = 7.6 Hz, CH_3), 1.22-1.17 (m, 32H, CH_2), 0.79 (t, 6H, *J* = 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.78, 151.02, 147.59, 147.08, 139.52, 139.33, 133.10, 131.86, 129.83, 129.34, 128.50, 124.68, 123.14, 117.31, 74.37, 31.94, 30.45, 29.71, 29.67, 29.37, 26.14, 22.71, 22.26, 15.60, 14.14. MS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{78}H_{90}N_4O_2S_3$: 1210.623, found 1210.636; Elemental Analysis Calcd for $C_{78}H_{90}N_4O_2S_3$: C, 77.31; H, 7.49; N, 4.62; S, 7.94. Found: C, 77.40; H, 7.25; N, 4.34; S, 7.51.

LI-156: Compound **3c** (188 mg, 0.2 mmol) and A red solid (188 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 2H, ArH), 7.36-7.30 (d, *J* = 8.2 Hz, 4H, ArH), 7.26-7.17 (m, 8H, ArH), 7.11-6.94 (m, 16H, ArH), 4.07 (t, *J* = 7.2 Hz, 4H, OCH_2), 2.71 (t, *J* = 7.8 Hz, 4H, CH_2), 1.88 (p, *J* = 7.0 Hz, 4H, CH_2), 1.69-1.61 (m, 4H, CH_2), 1.42 -1.17 (m, 40H, CH_2), 0.86 (t, *J* = 7.4 Hz, 6H, CH_3), 0.79 (t, *J* = 6.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.78, 151.03, 147.61, 147.06, 139.82, 138.07, 133.49, 131.74, 129.90, 129.35, 128.59, 124.68, 123.13, 117.31, 74.36, 33.36, 31.95, 30.46, 29.72, 29.69, 29.38, 28.74, 26.15, 22.76, 22.72, 14.15. MS (MALDI-TOF, m/z): [M]$^+$ calcd for $C_{82}H_{98}N_4O_2S_3$: 1266.685, found 1266.711; Elemental Analysis Calcd for $C_{82}H_{98}N_4O_2S_3$: C, 77.68; H, 7.79; N, 4.42; S, 7.59. Found: C, 78.01; H, 7.47; N, 4.17. S, 7.34

LI-157: Compound **3d** (200 mg, 0.2 mmol) and red solid (225 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 2H, ArH), 7.36- 7.30 (m, 4H, ArH), 7.26-7.16 (m, 8H, ArH), 7.13-6.94 (m, 16H, ArH), 4.08 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.70 (t, *J* = 7.9 Hz, 4H, CH_2), 1.88 (p, *J* = 7.2 Hz, 4H, CH_2), 1.72-1.60 (m, 4H, CH_2), 1.46-1.17 (m, 48H, CH_2), 0.83-0.86 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.77, 151.02, 147.60, 147.04, 139.80, 138.11, 133.48, 131.72, 129.88, 129.33, 128.57, 124.68, 123.12, 117.30, 77.34, 77.03, 76.71, 74.34, 31.94, 31.16, 30.45, 29.72, 29.68, 29.49, 29.38, 29.35, 28.98, 26.15, 22.71, 14.14. MS (MALDI-TOF, m/z): [M]$^+$ calcd for $C_{86}H_{106}N_4O_2S_3$: 1322.748, found 1322.794; Elemental Analysis Calcd for $C_{86}H_{106}N_4O_2S_3$: C, 78.02; H, 8.07; N, 4.23; S, 7.26. Found: C, 78.15; H, 7.94; N, 4.16; S, 7.28.

LI-158: Compound **3e** (210 mg, 0.2 mmol) and red solid (184 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.38 (s, 2H, ArH), 7.44- 7.36 (m, 4H, ArH), 7.33-7.26 (m, 4H, ArH), 7.20-7.09 (m, 12H, ArH), 7.08-7.03 (m, 4H, ArH), 4.15 (t, *J* = 7.0 Hz, 4H, OCH_2), 2.78 (t, *J* = 7.7 Hz, 4H, CH_2), 1.95 (p, *J* = 7.2 Hz, 4H, CH_2), 1.78-1.66 (m, 4H, CH_2), 1.51-1.24 (m, 56H, CH_2), 0.94 (t, *J* = 7.4 Hz, 6H, CH_3), 0.89-0.85 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.77, 151.03, 147.60, 147.05, 139.80, 138.11, 133.49, 131.73, 129.89, 129.34, 128.58, 124.68, 123.13, 123.11, 117.31, 74.35, 31.95, 31.17, 30.46, 29.73, 29.69, 29.67, 29.50, 29.38, 29.35, 28.99, 26.16, 22.71, 14.15. MS (MALDI-TOF, m/z): [M]$^+$ calcd for $C_{90}H_{114}N_4O_2S_3$: 1378.810, found 1378.788; Elemental Analysis Calcd for $C_{90}H_{114}N_4O_2S_3$: C, 78.33; H, 8.33; N, 4.06; S, 6.97. Found: C, 78.26; H, 8.16; N, 3.97; S, 6.94.

LI-161: Compound **3f** (210 mg, 0.2 mmol) and red solid (198 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.34 (s, 2H, ArH), 7.44- 7.37 (m, 4H, ArH), 7.32-7.25 (m, 8H, ArH), 7.18-7.10 (m, 12H, ArH), 7.07-7.02 (m, 4H, ArH), 4.15 (t, *J* = 7.1 Hz, 4H, OCH_2), 2.72 (d, *J* = 7.1 Hz, 4H, CH_2), 1.95 (p, *J* = 7.2 Hz, 4H, CH_2), 1.67 (h, *J* = 6.3 Hz, 2H, CH), 1.53-1.41 (m, 4H, CH_2), 1.37-1.21 (m, 48H, CH_2), 0.91-0.78 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.75, 151.06, 147.64, 147.05, 140.53, 137.31, 133.91, 131.57, 130.23, 129.32, 128.80, 124.60, 123.20, 123.07, 117.33, 74.32, 40.61, 32.79, 32.62, 31.95, 30.43, 29.73, 29.69, 29.38, 28.73, 26.13, 25.80, 23.12, 22.71, 14.20, 14.15, 10.83. MS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{90}H_{114}N_4O_2S_3$: 1378.810, found 1378.815; Elemental Analysis Calcd for $C_{90}H_{114}N_4O_2S_3$: C, 78.33; H, 8.33; N, 4.06; S, 6.97. Found: C, 77.94; H, 8.17; N, 3.82; S, 6.77.

LI-162: Compound **3g** (232mg, 0.2 mmol) and red solid (152 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (s, 2H, ArH), 7.43-7.36 (m, 4H, ArH), 7.31-7.26 (m, 8H, ArH), 7.19-7.14 (m, 8H, ArH), 7.13-7.09 (m, 4H, ArH), 7.07- 7.03 (m, 4H, ArH), 4.15 (t, J = 7.1 Hz, 4H, OCH_2), 2.72 (d, J = 7.0 Hz, 4H, CH_2), 1.95 (p, J = 7.2 Hz, 4H, CH_2), 1.77-1.69 (m, 2H, CH), 1.51-1.43 (m, 4H, CH_2), 1.39-1.23 (m, 64H, CH_2), 0.89-0.82 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.73, 151.07, 147.63, 147.03, 140.50, 137.28, 133.98, 131.55, 130.19, 129.32, 128.78, 124.63, 123.11, 123.08, 117.33, 74.32, 39.16, 33.47, 33.18, 31.97, 31.95, 30.44, 29.80, 29.74, 29.69, 29.38, 28.74, 26.48, 26.15, 23.13, 22.75, 22.71, 14.20, 14.16, 14.14. MS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{98}H_{130}N_4O_2S_3$: 1492.324, found 1492.948; Elemental Analysis Calcd for $C_{98}H_{130}N_4O_2S_3$: C, 78.88; H, 8.78; N, 3.75; S, 6.44. Found: C, 78.87; H, 8.70; N, 3.68; S, 6.36.

LI-163: Compound **3h** (255 mg, 0.2 mmol) and red solid (156 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (s, 2H, ArH), 7.40-7.38 (m, 4H, ArH), 7.30-7.26 (m, 8H, ArH), 7.18-7.13 (m, 8H, ArH), 7.12-7.10 (m, 4H, ArH), 7.07-7.03 (m, 4H, ArH), 4.15 (t, J = 7.1 Hz, 4H, OCH_2), 2.72 (d, J = 7.0 Hz, 4H, CH_2), 1.95 (p, J = 7.2 Hz, 4H, CH_2), 1.75-1.71 (m, 2H, CH), 1.49-1.43 (m, 4H, CH_2), 1.39-1.22 (m, 80H, CH_2), 0.88-0.81 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.72, 151.07, 147.63, 147.03, 140.51, 137.28, 133.97, 131.54, 130.18, 129.32, 128.76, 124.65, 123.09, 123.07, 117.32, 74.32, 39.19, 33.50, 33.16, 31.97, 31.95, 30.45, 30.14, 29.80, 29.75, 29.71, 29.43, 29.39, 26.54, 26.48, 26.16, 22.75, 22.71, 14.16, 14.14. MS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{106}H_{146}N_4O_2S_3$: 1603.061, found 1603.075; Elemental Analysis Calcd for $C_{106}H_{146}N_4O_2S_3$: C, 79.35; H, 9.17; N, 3.49; S, 5.99. Found: C, 79.26; H, 8.96; N, 3.37; S, 5.77.

LI-164: Compound **3i** (276 mg, 0.2 mmol) and red oil (180 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (s, 2H, ArH), 7.41-7.37 (m, 4H, ArH), 7.30-7.26 (m, 8H, ArH), 7.16-7.14 (m, 8H, ArH), 7.13-7.09 (m, 4H, ArH), 7.07-7.03 (m, 4H, ArH), 4.15 (t, J = 7.1 Hz, 4H, OCH_2), 2.72 (d, J = 7.1 Hz, 4H, CH_2), 1.95 (p, J = 7.2 Hz, 4H, CH), 1.77-1.71 (m, 2H, CH_2), 1.51-1.43 (m, 4H, CH_2), 1.39-1.22 (m, 96H, CH_2), 0.88-0.83 (m, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.71, 151.06, 147.61, 147.01, 140.48, 137.27, 133.94, 131.53, 130.17, 129.30, 128.75, 124.63, 123.07, 117.31, 74.29, 39.17, 33.48, 33.16, 31.93, 30.44, 30.13, 29.77, 29.74, 29.69, 29.42, 29.38, 26.52, 26.15, 22.69, 14.13. MS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{114}H_{162}N_4O_2S_3$: 1715.186, found 1715.167; Elemental Analysis Calcd for $C_{114}H_{162}N_4O_2S_3$: C, 79.76; H, 9.51; N, 3.26; S, 5.60. Found: C, 79.45; H, 9.17; N, 3.03; S, 5.42.

LI-165: Compound **3j** (300 mg, 0.2 mmol) and red oil (189 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.34 (s, 2H, ArH), 7.40-7.38 (m, 4H, ArH), 7.30-7.26 (m, 8H, ArH), 7.16-7.14 (m, 8H, ArH), 7.12-7.10 (m, 4H, ArH), 7.07-7.03 (m, 4H, ArH), 4.15 (t, J = 7.1 Hz, 4H, OCH_2), 2.77-2.65 (m, 4H, CH_2), 1.98-1.92 (m, 4H, CH_2), 1.75-1.71 (m, 2H, CH), 1.50-1.44 (m, 4H, CH_2), 1.39-1.22 (m, 112H, CH_2), 0.88-0.84 (m, 18H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):151.71, 151.06, 147.01, 137.27, 133.94, 130.17, 129.30, 128.76, 124.63, 123.08, 77.33, 77.02, 76.70, 74.29, 39.17, 33.47, 33.15, 31.93, 30.44, 30.13, 29.77, 29.74, 29.69, 29.38, 26.52, 26.14, 22.70, 14.13. MS (MALDI-TOF, m/z): $[M]^+$ calcd for $C_{122}H_{178}N_4O_2S_3$: 1827.311, found 1827.291; Elemental Analysis Calcd for $C_{122}H_{178}N_4O_2S_3$: C, 80.12; H, 9.81; N, 3.06; S, 5.26. Found: C, 79.88; H, 9.59; N, 2.83; S, 4.95.

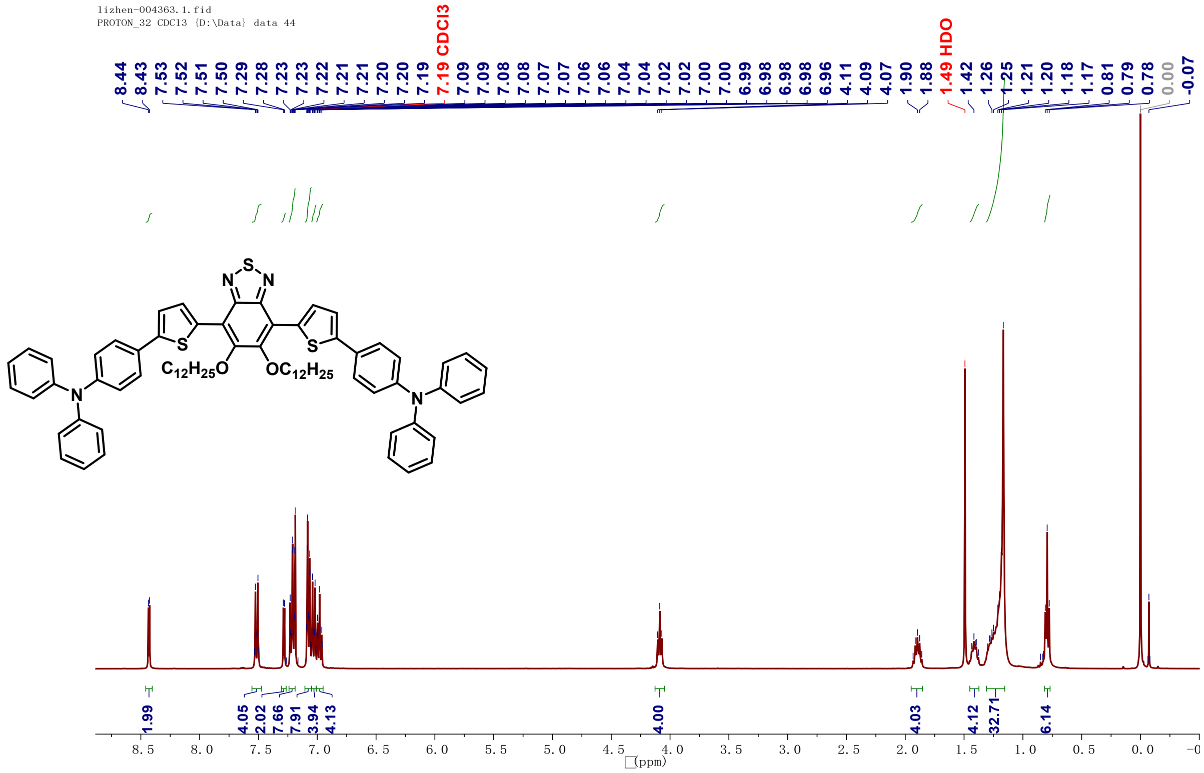


Figure S1. ^{1}H NMR spectrum of **LI-154.**

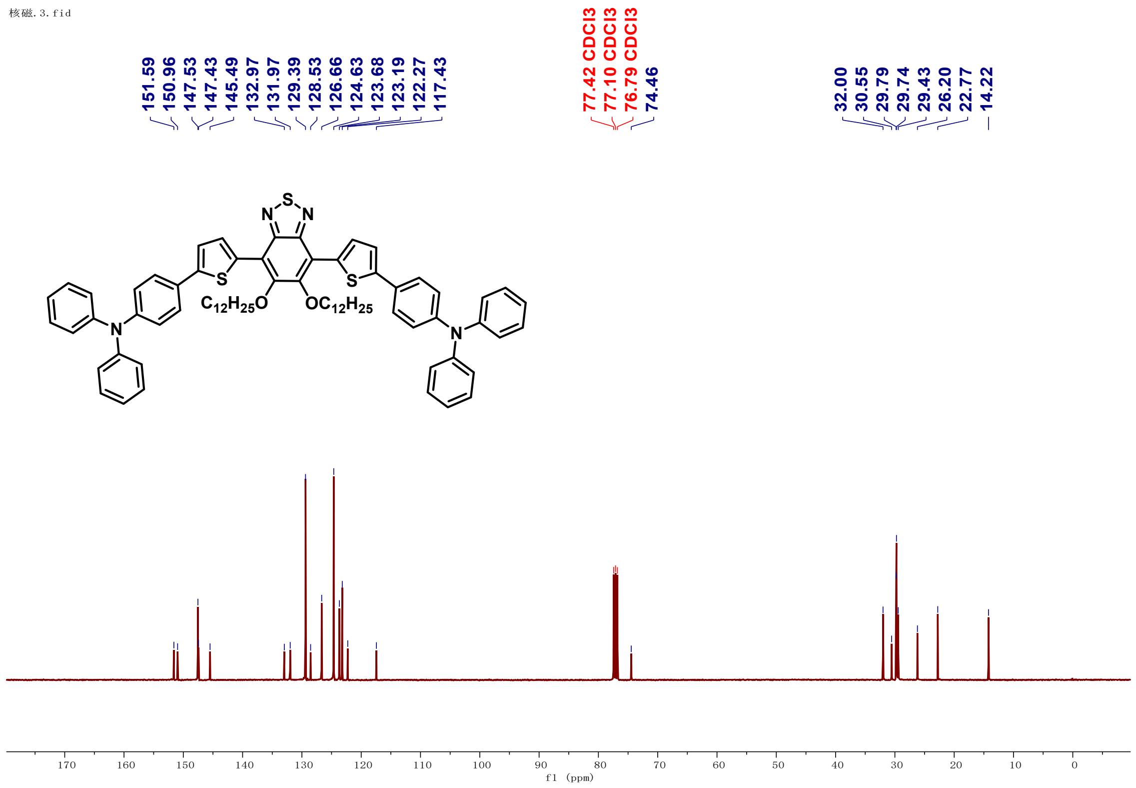


Figure S2. ^{13}C NMR spectrum of **LI-154.**

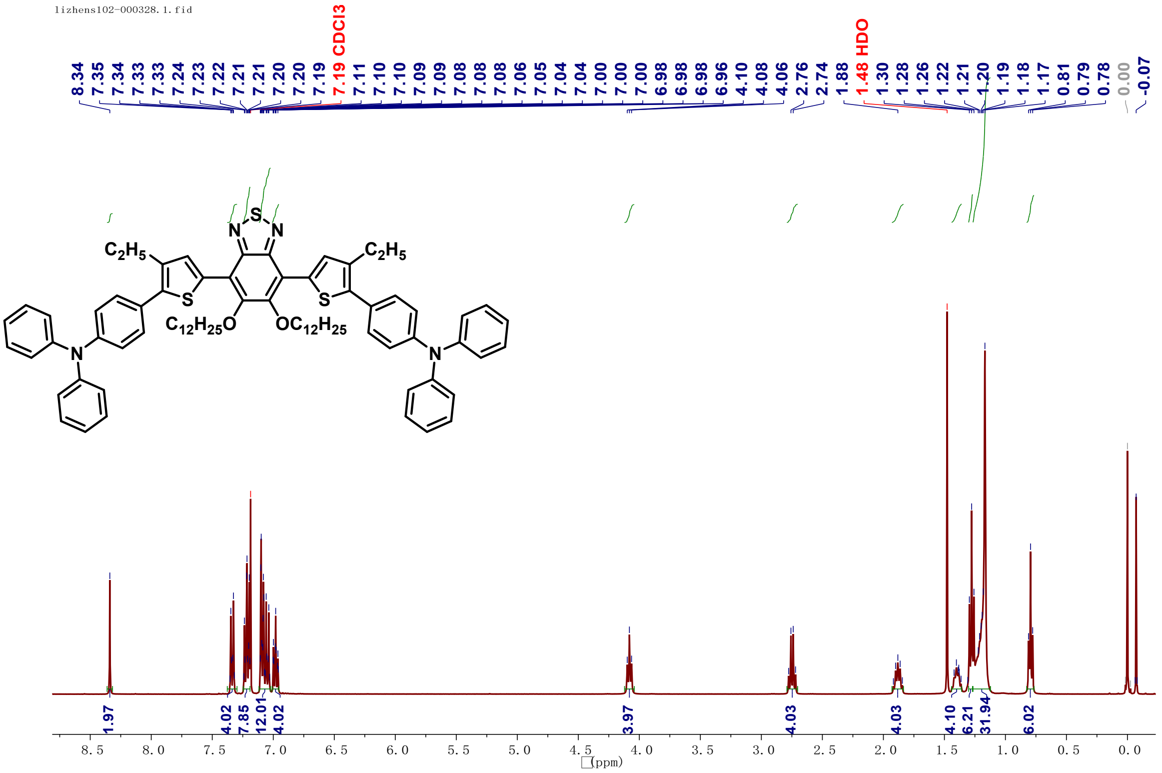


Figure S3. ^{1}H NMR spectrum of **LI-155.**

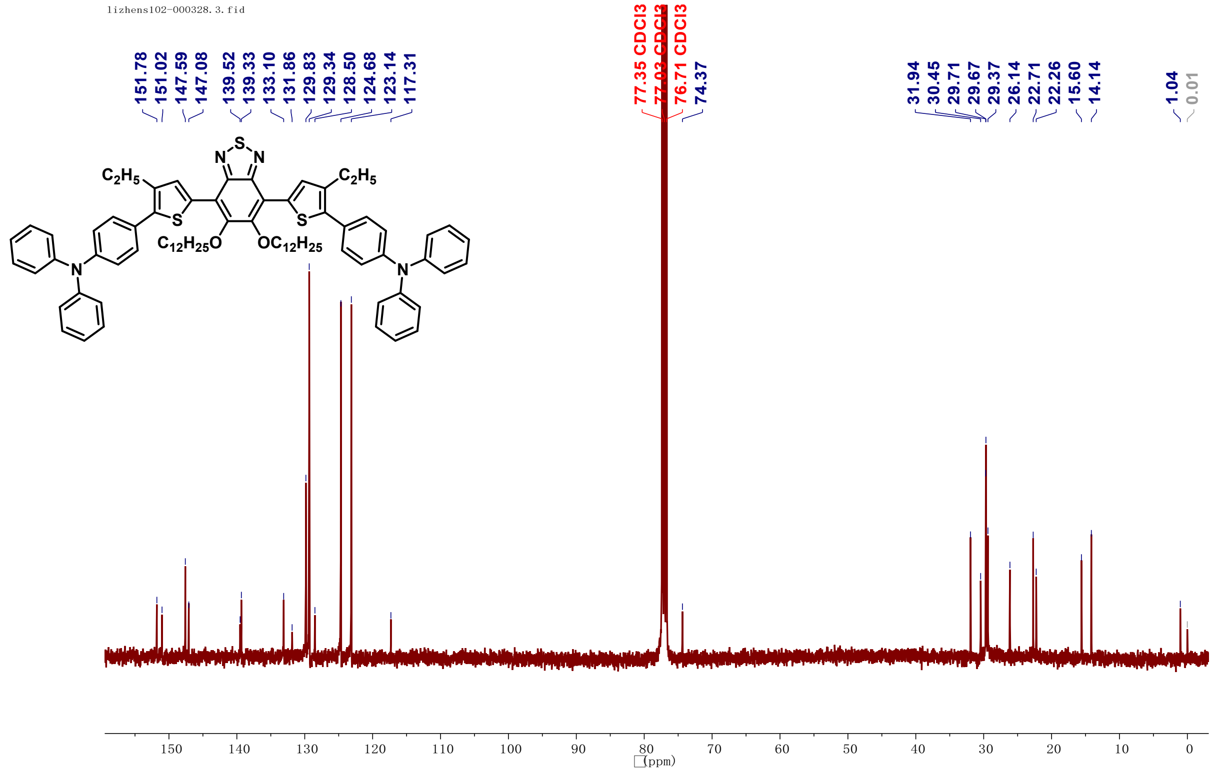


Figure S4. ^{13}C NMR spectrum of **LI-155.**

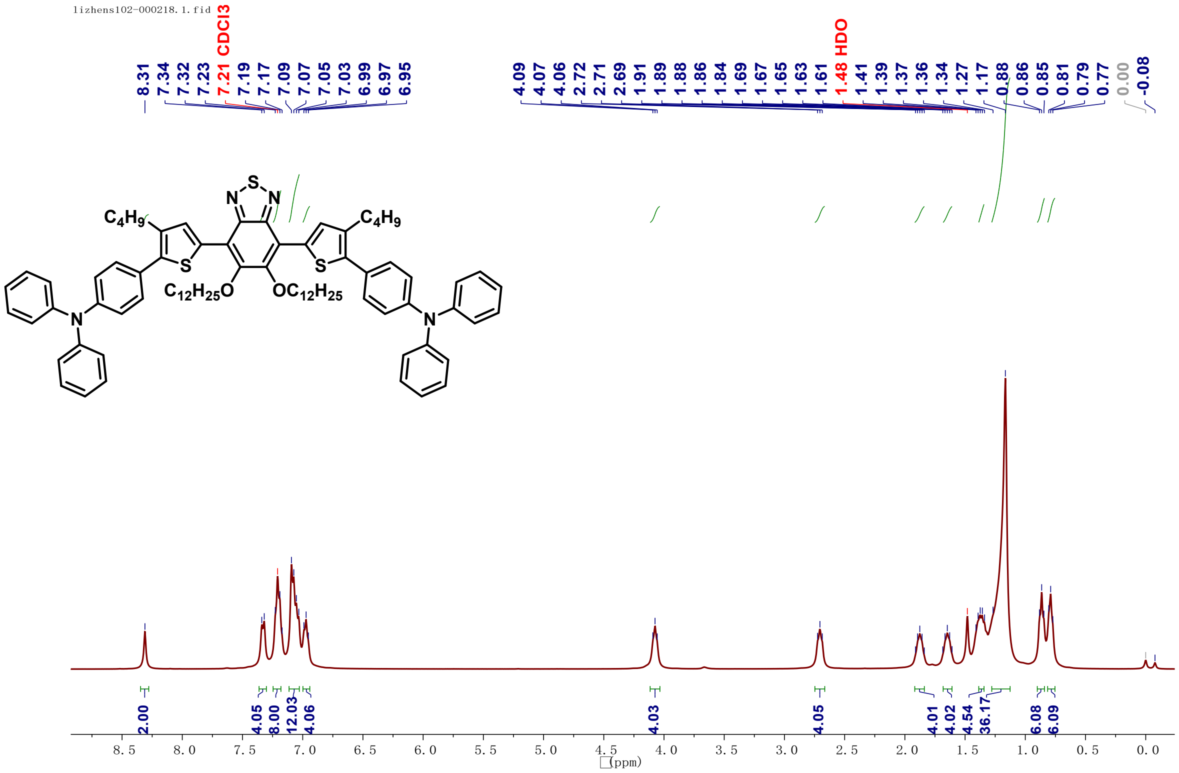


Figure S5. ^{1}H NMR spectrum of **LI-156.**

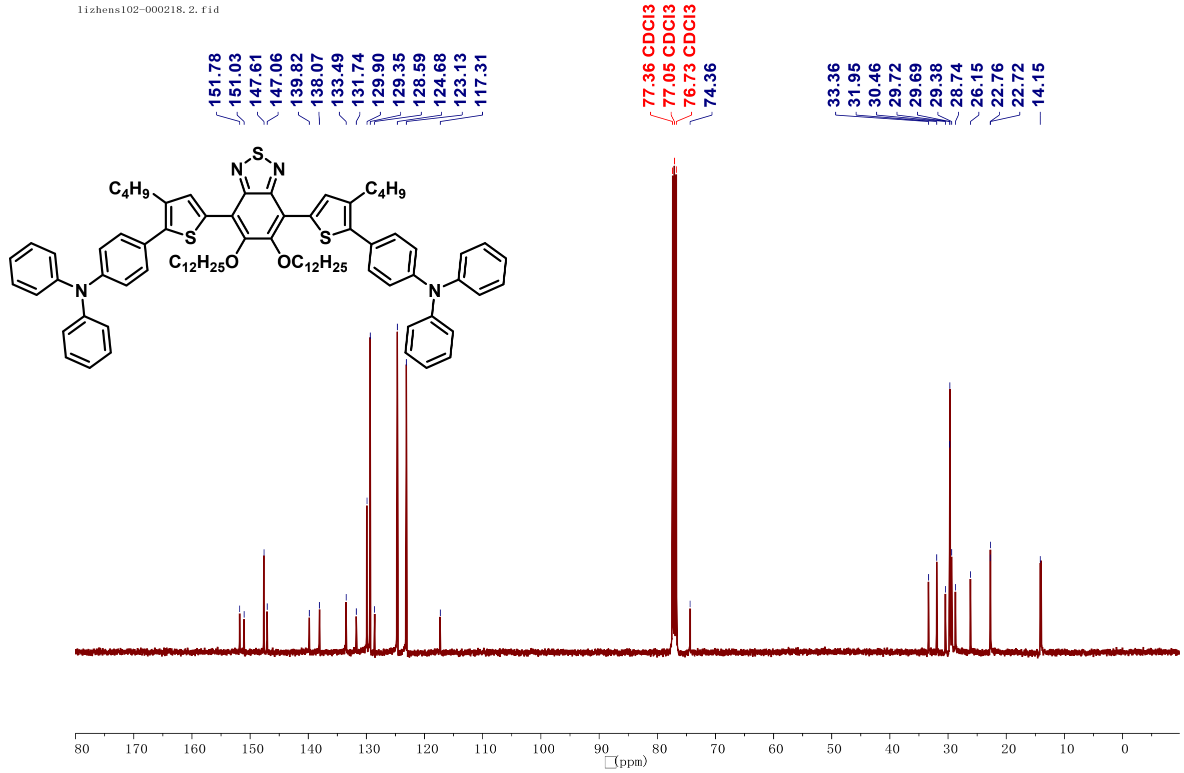


Figure S6. ^{13}C NMR spectrum of **LI-156.**

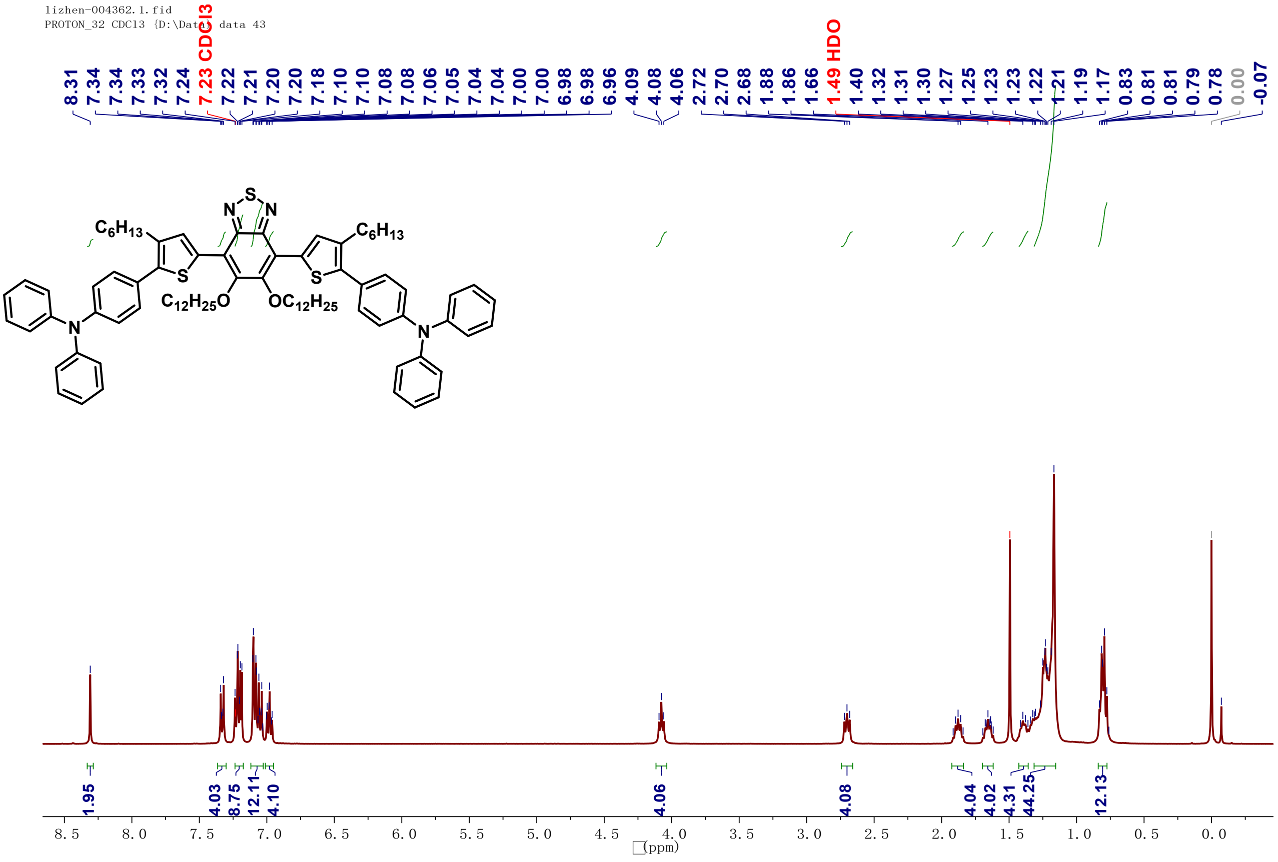


Figure S7. ^{1}H NMR spectrum of **LI-157.**

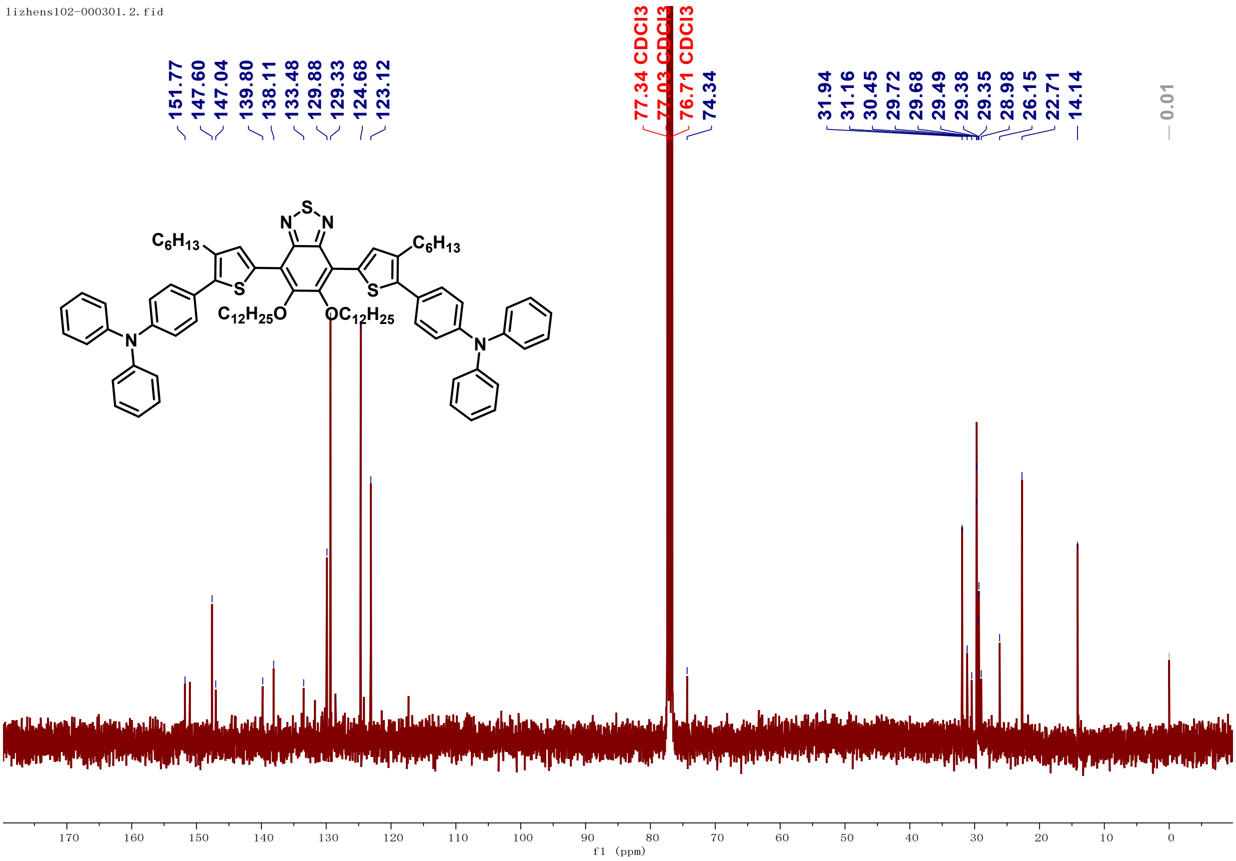


Figure S8. ^{13}C NMR spectrum of **LI-157.**

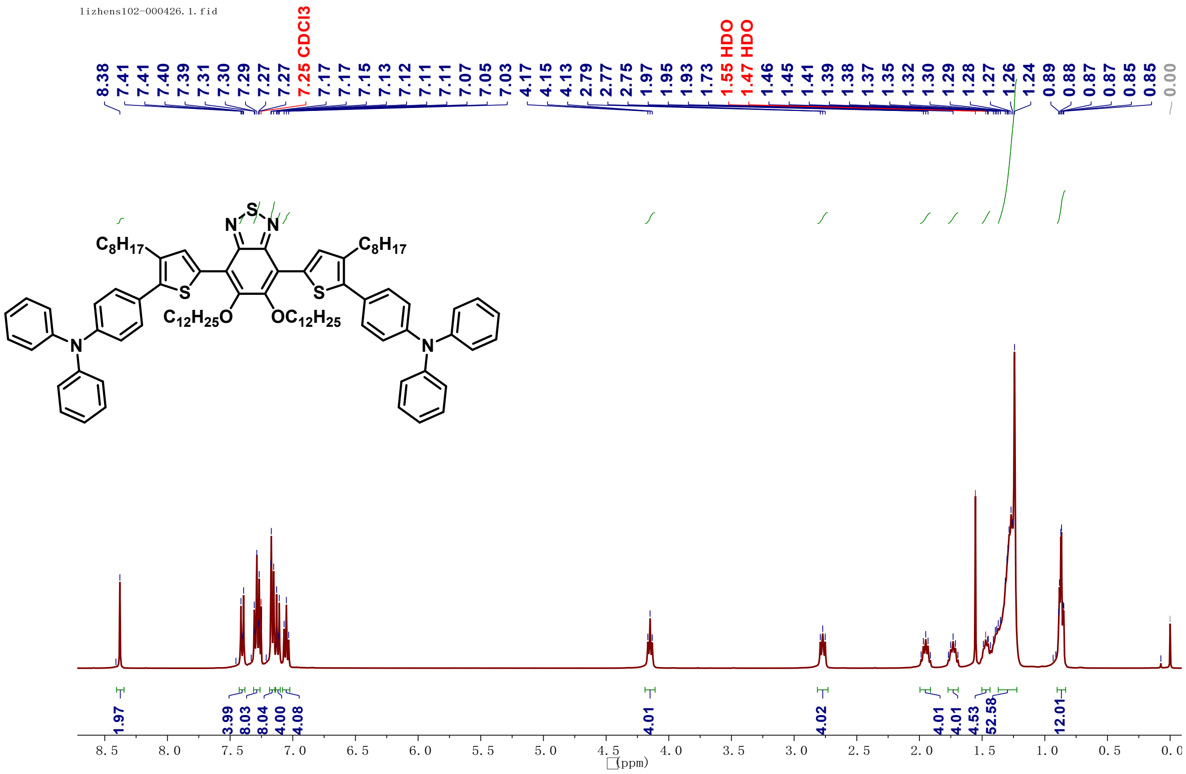


Figure S9. ^{1}HNMR spectrum of **LI-158.**

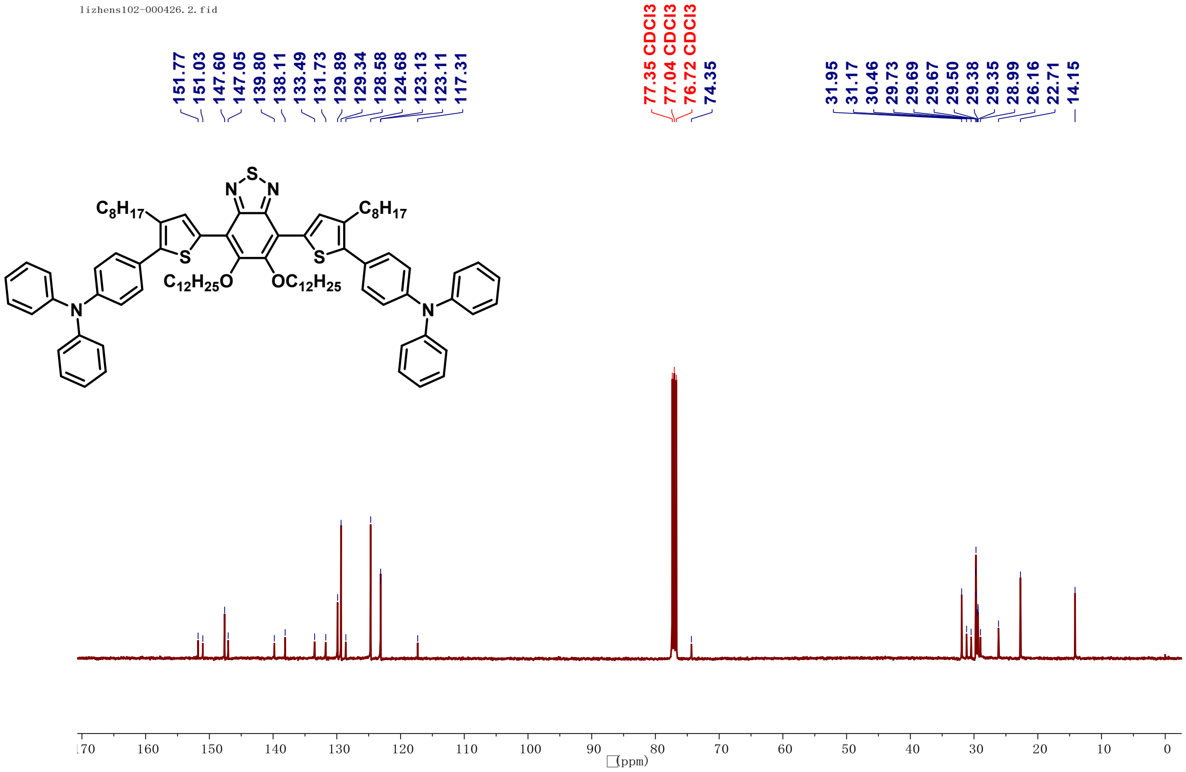


Figure S10. ^{13}C NMR spectrum of **LI-158.**

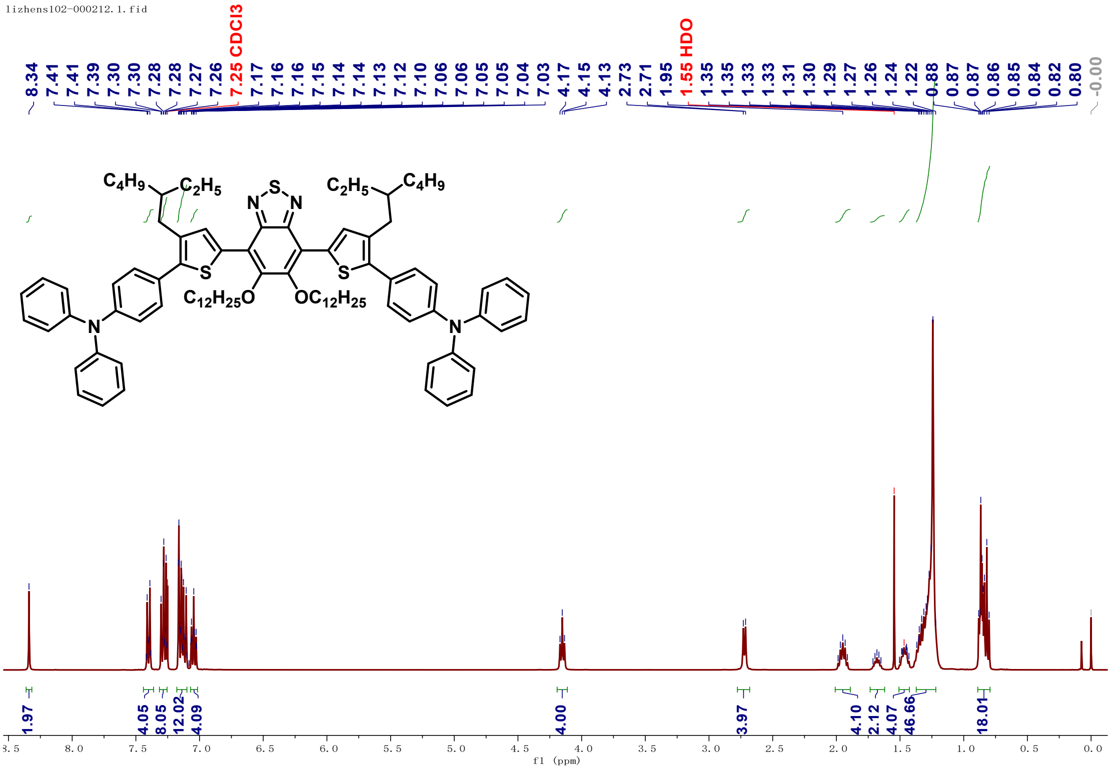


Figure S11. ^{1}HNMR spectrum of **LI-161.**

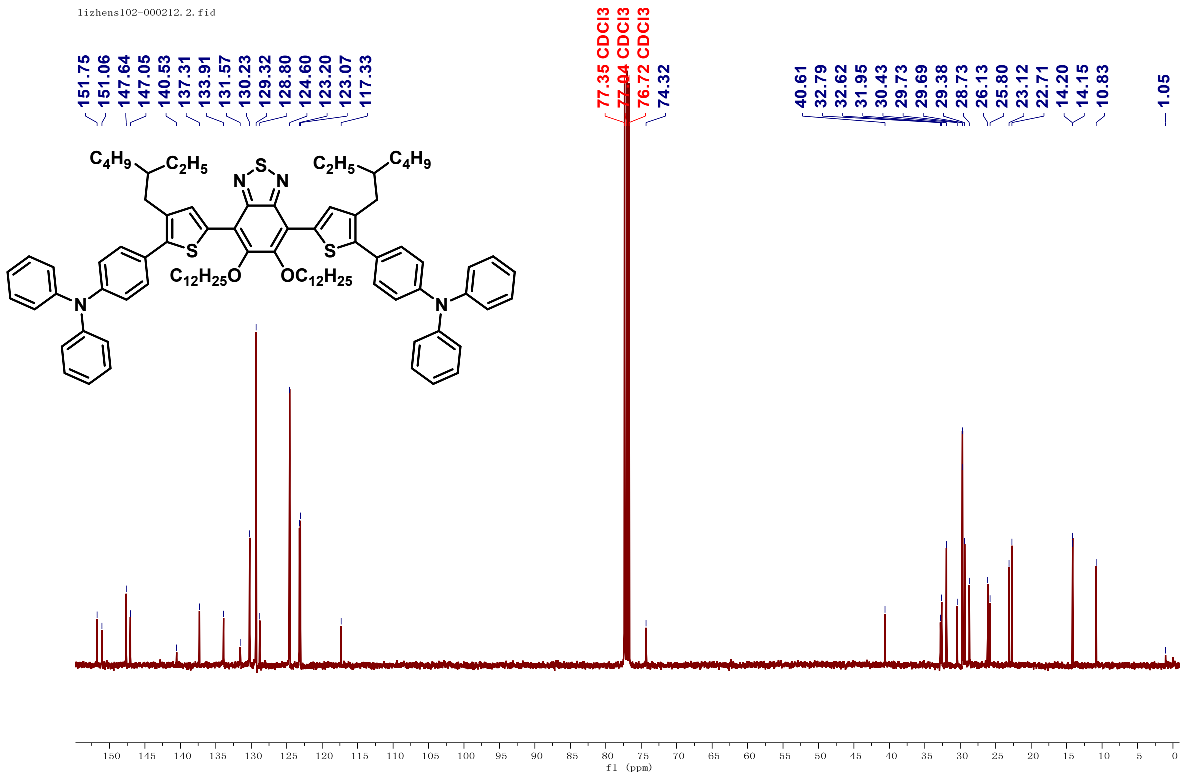


Figure S12. ^{13}C NMR spectrum of **LI-161.**

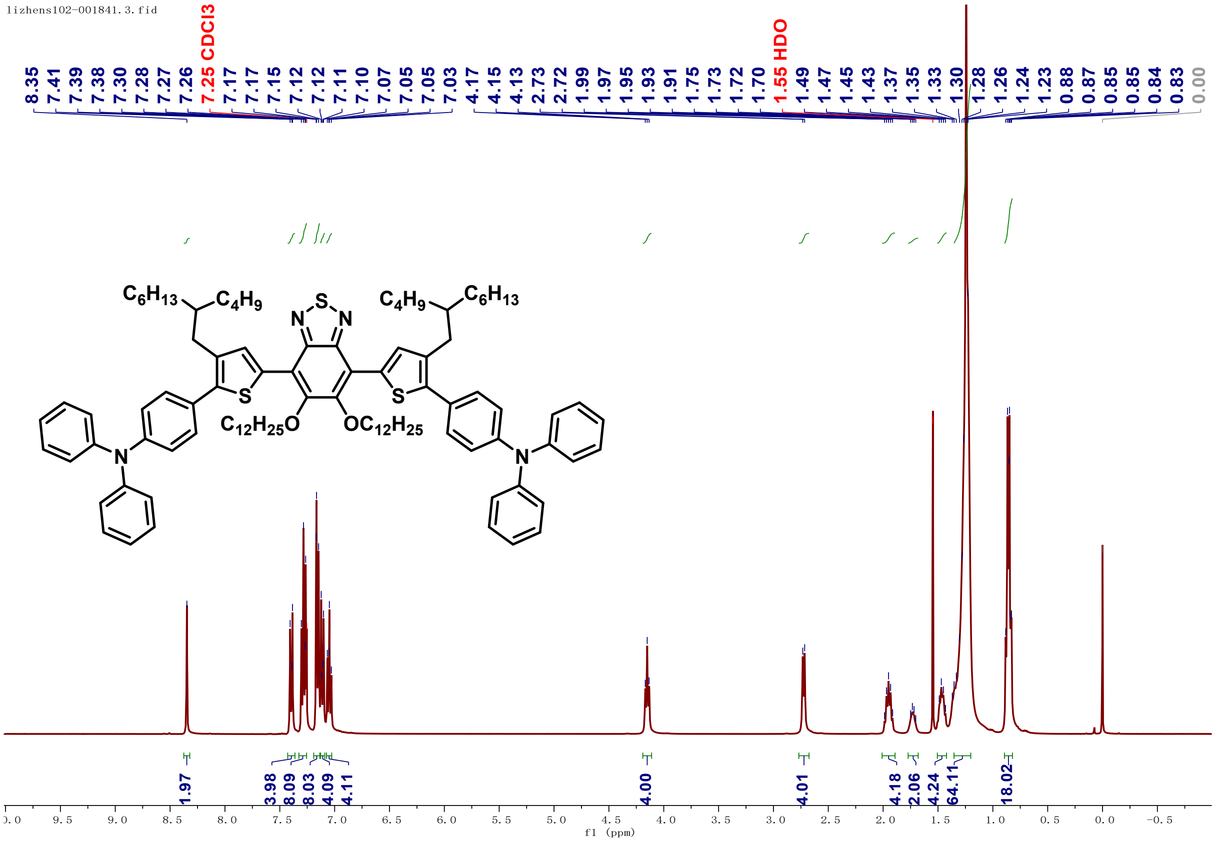


Figure S13. ^{1}HNMR spectrum of **LI-162.**

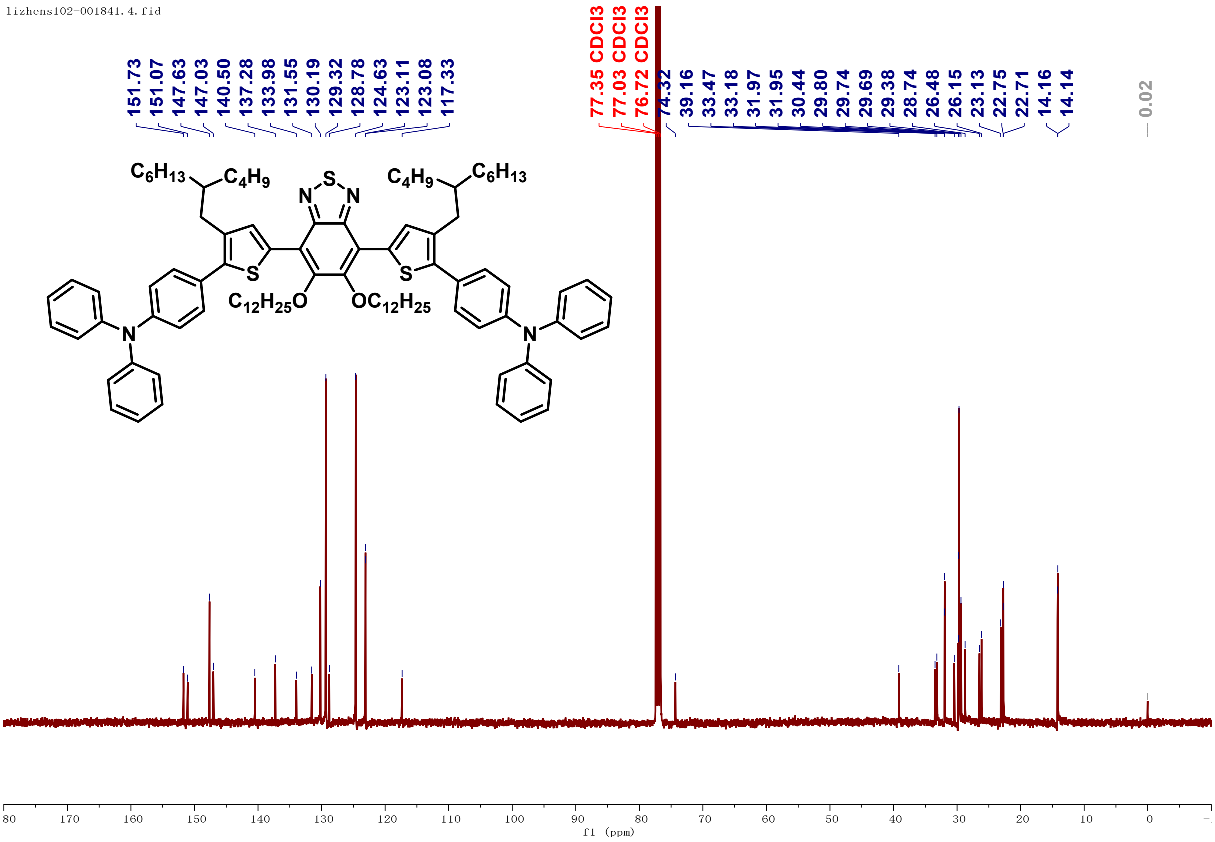


Figure S14. ^{13}C NMR spectrum of **LI-162.**

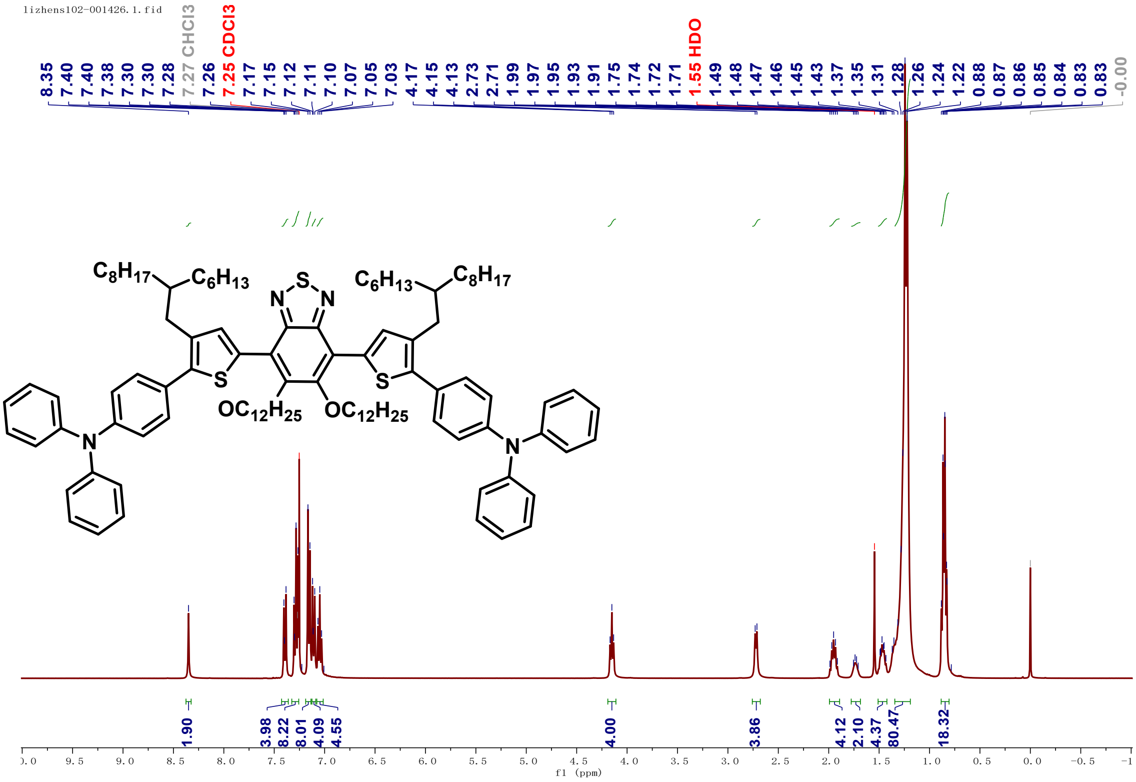


Figure S15. ^{1}HNMR spectrum of **LI-163.**

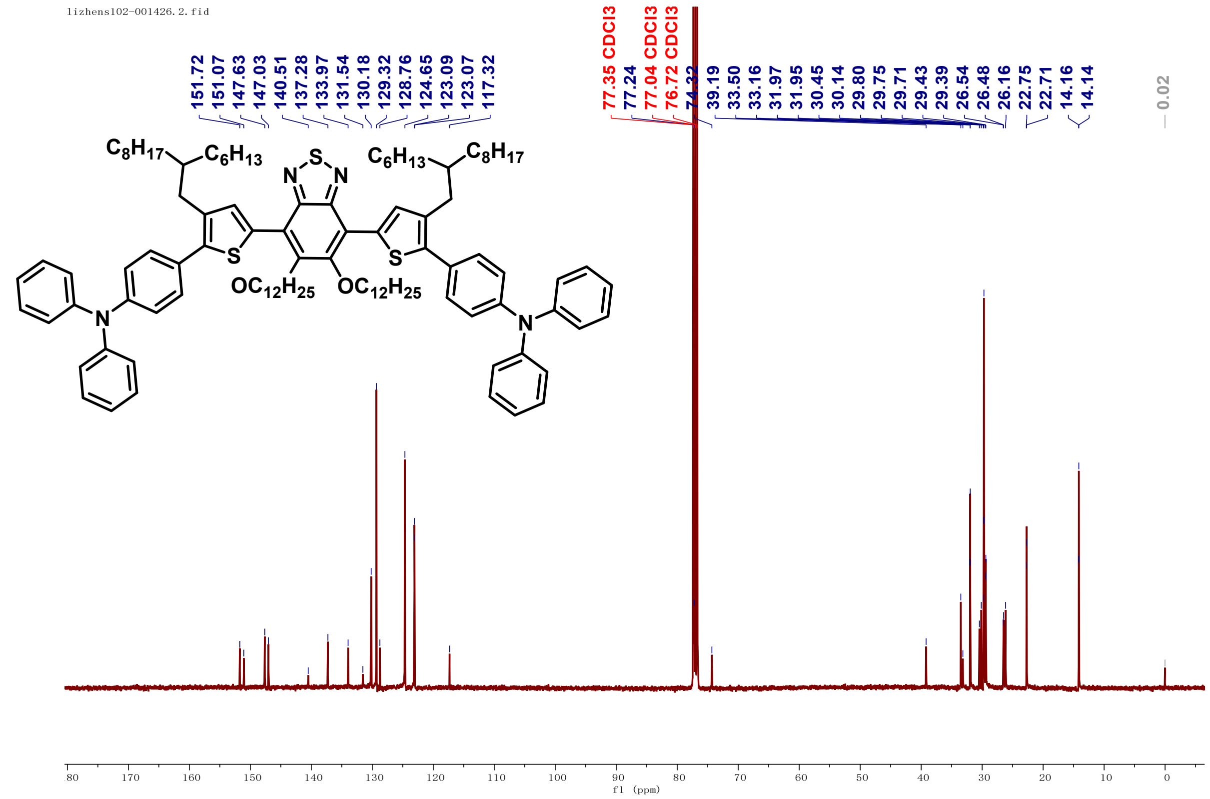


Figure S16. ^{13}C NMR spectrum of **LI-163.**

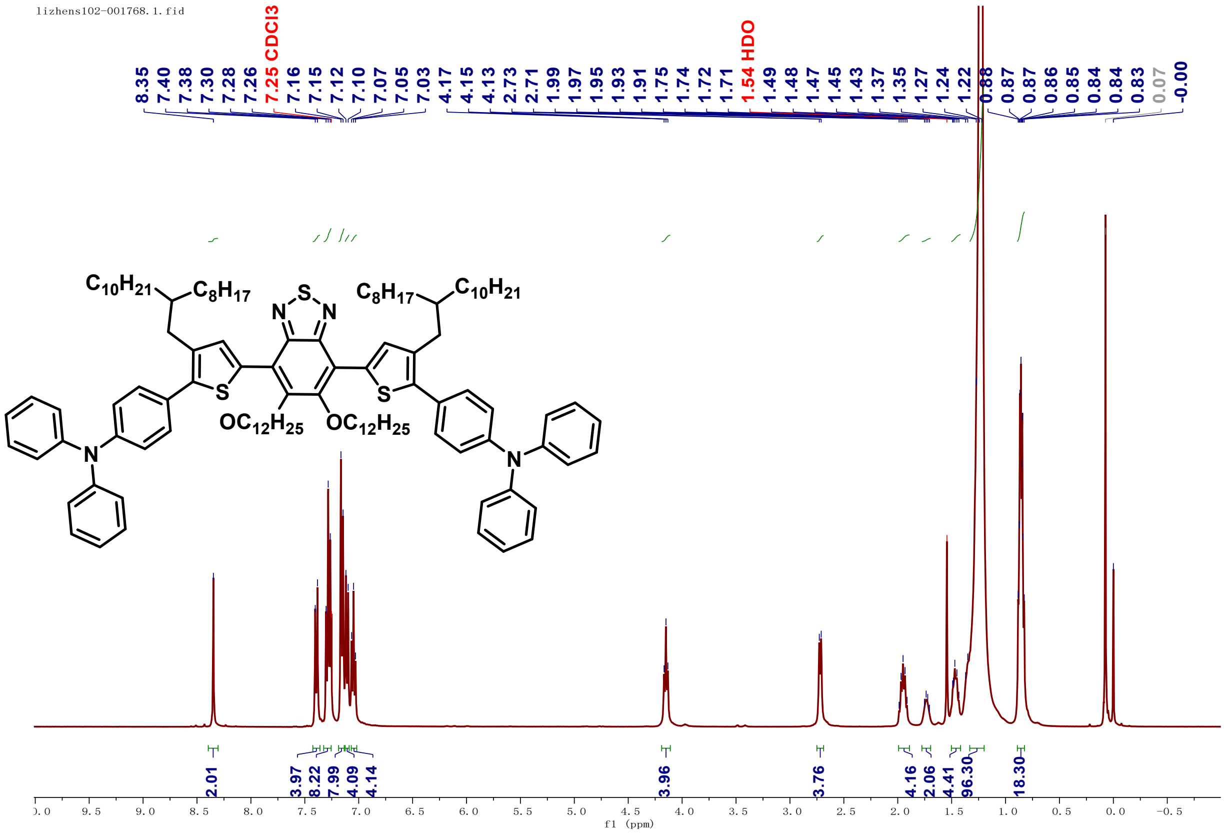


Figure S17. ^{1}HNMR spectrum of **LI-164.**

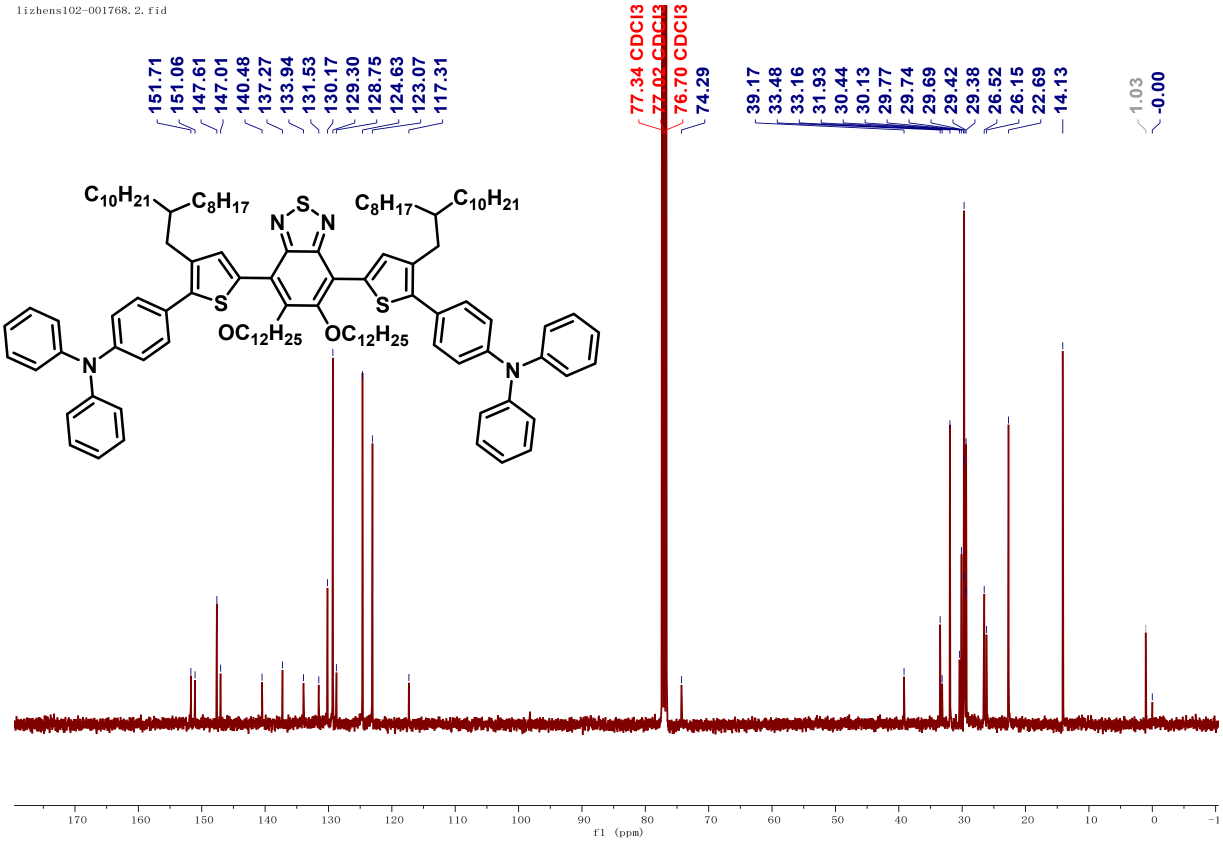


Figure S18. ^{13}C NMR spectrum of **LI-164.**

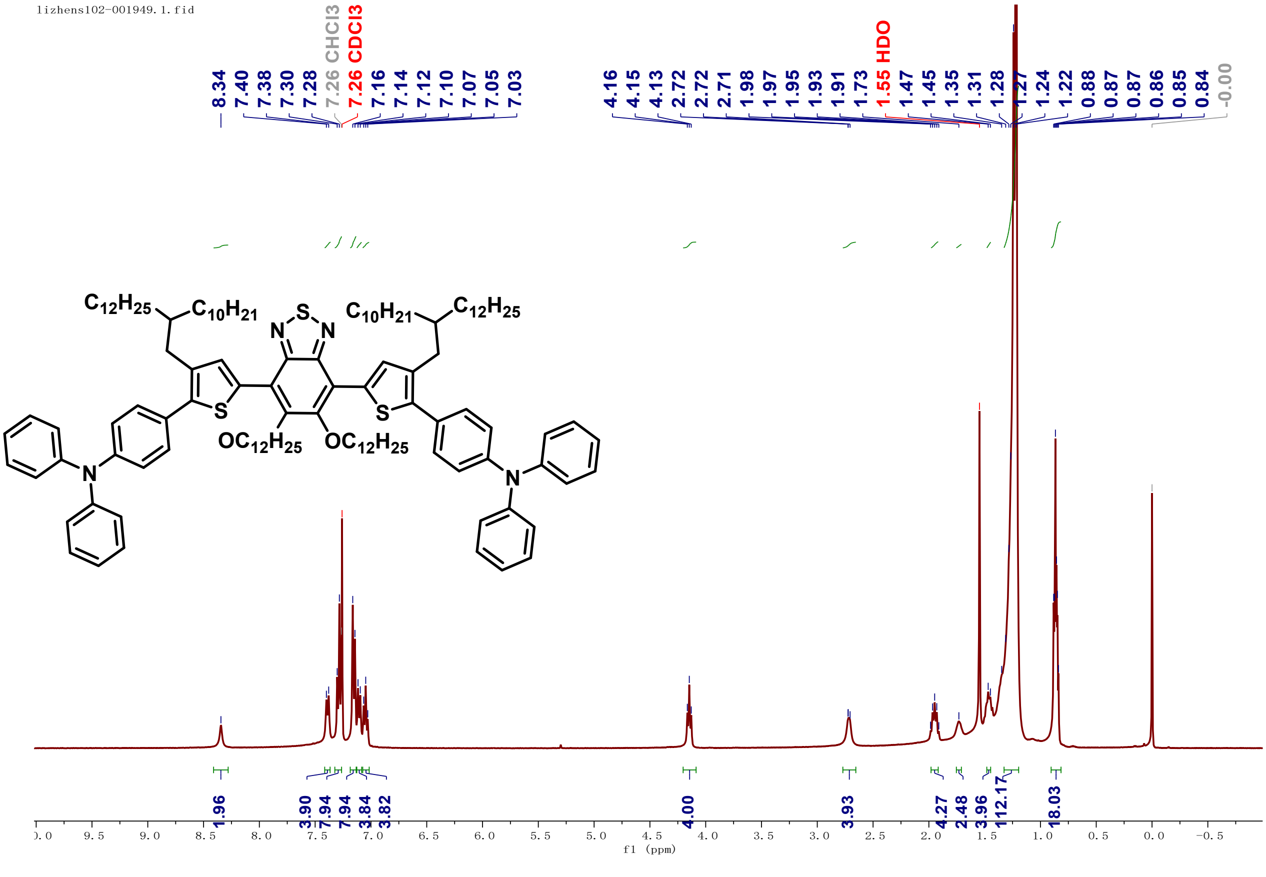


Figure S19. ^{1}HNMR spectrum of **LI-165.**

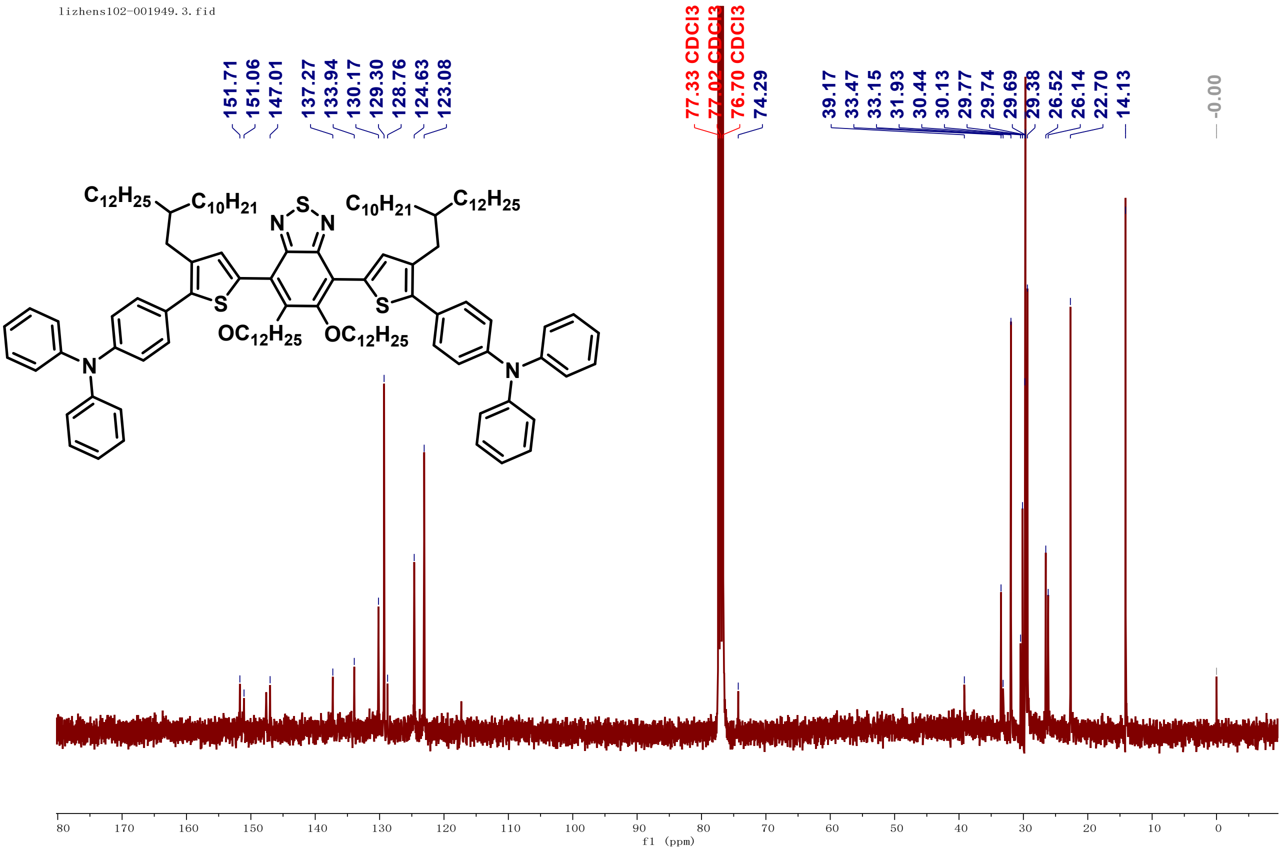
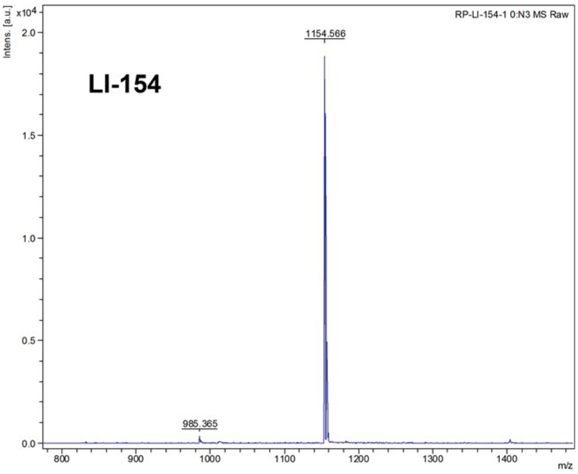
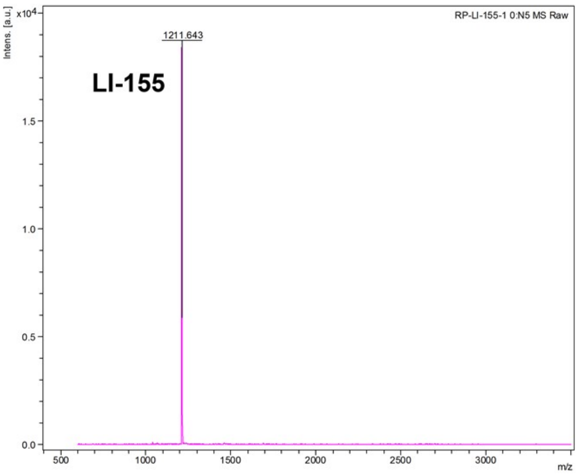


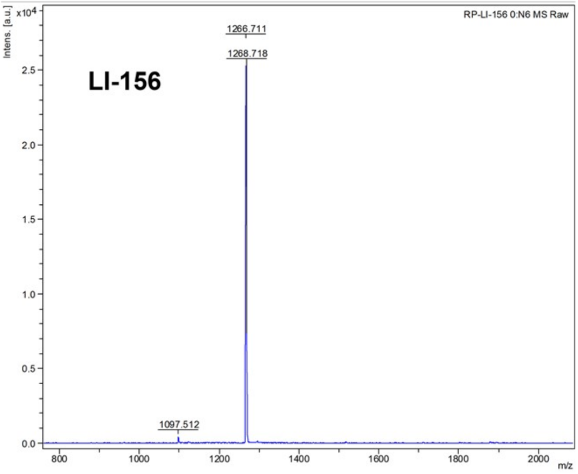
Figure S20. ^{13}C NMR spectrum of **LI-165.**



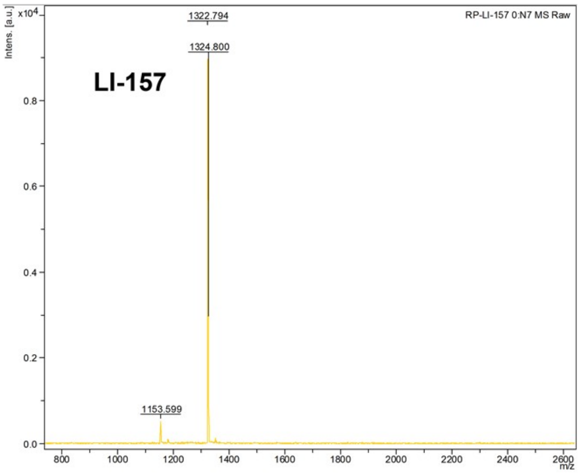
LI-154



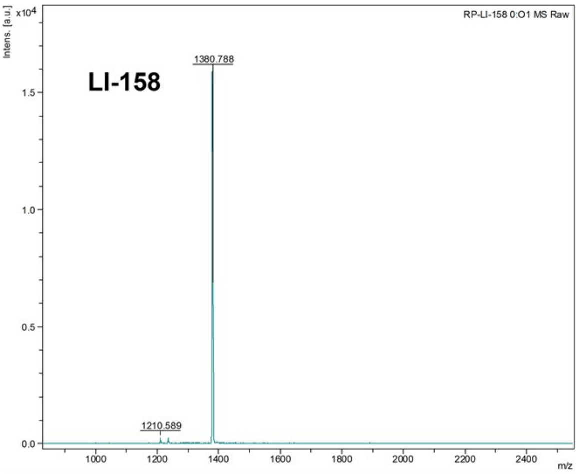
LI-155



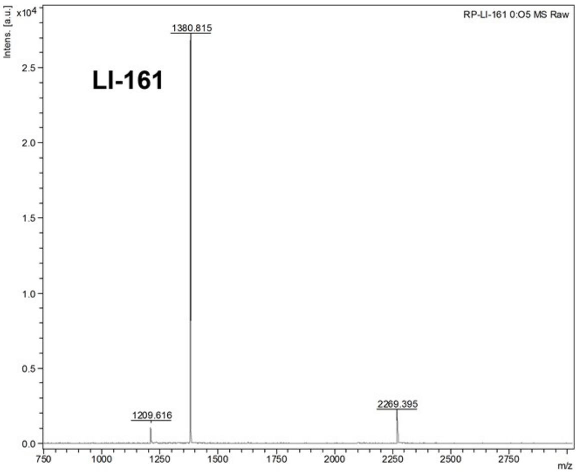
LI-156



LI-157



LI-158



LI-161

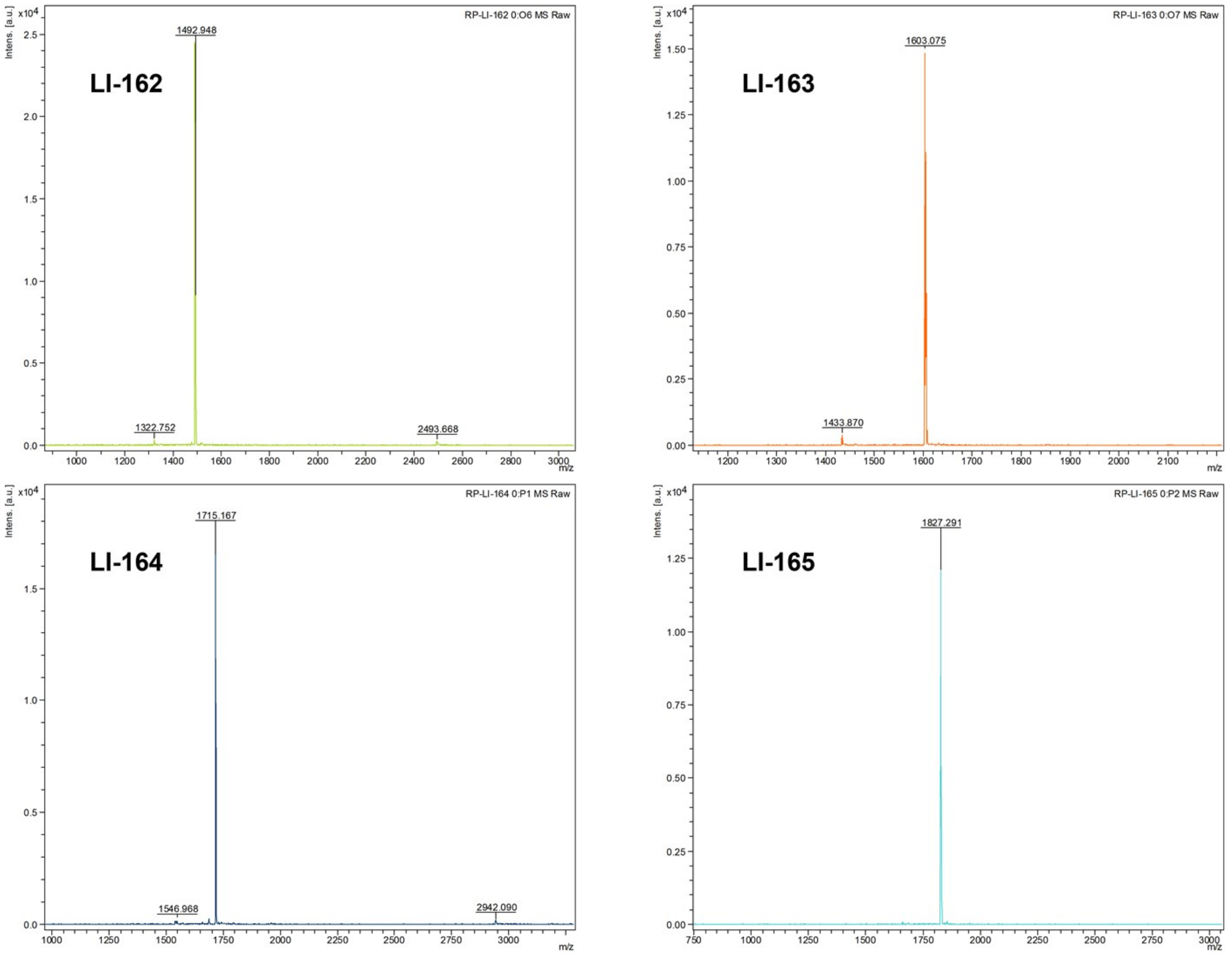


Figure S21. MALDI-TOF spectra of dyes.

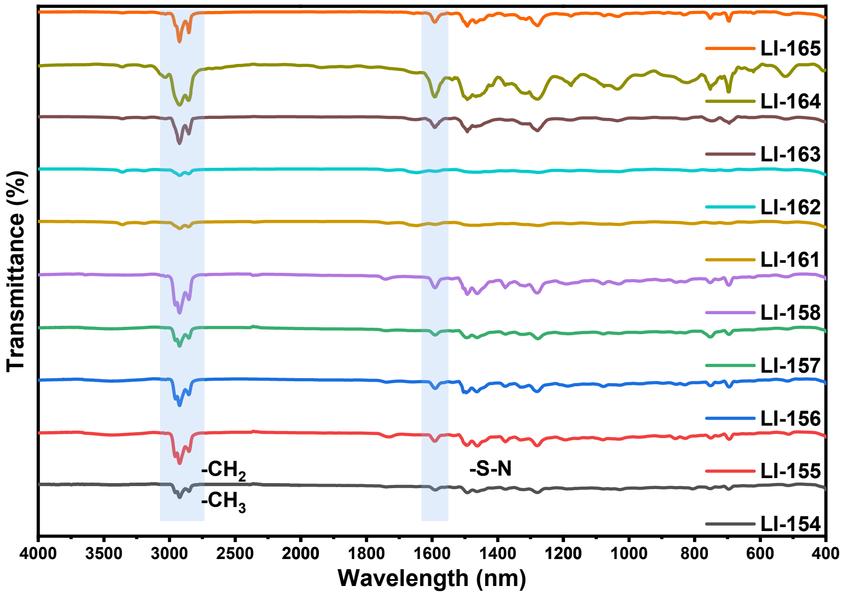


Figure S22. FTIR spectra of organic dyes in the range of 4000-400 cm^{-1}.

Photophysical property of organic dyes

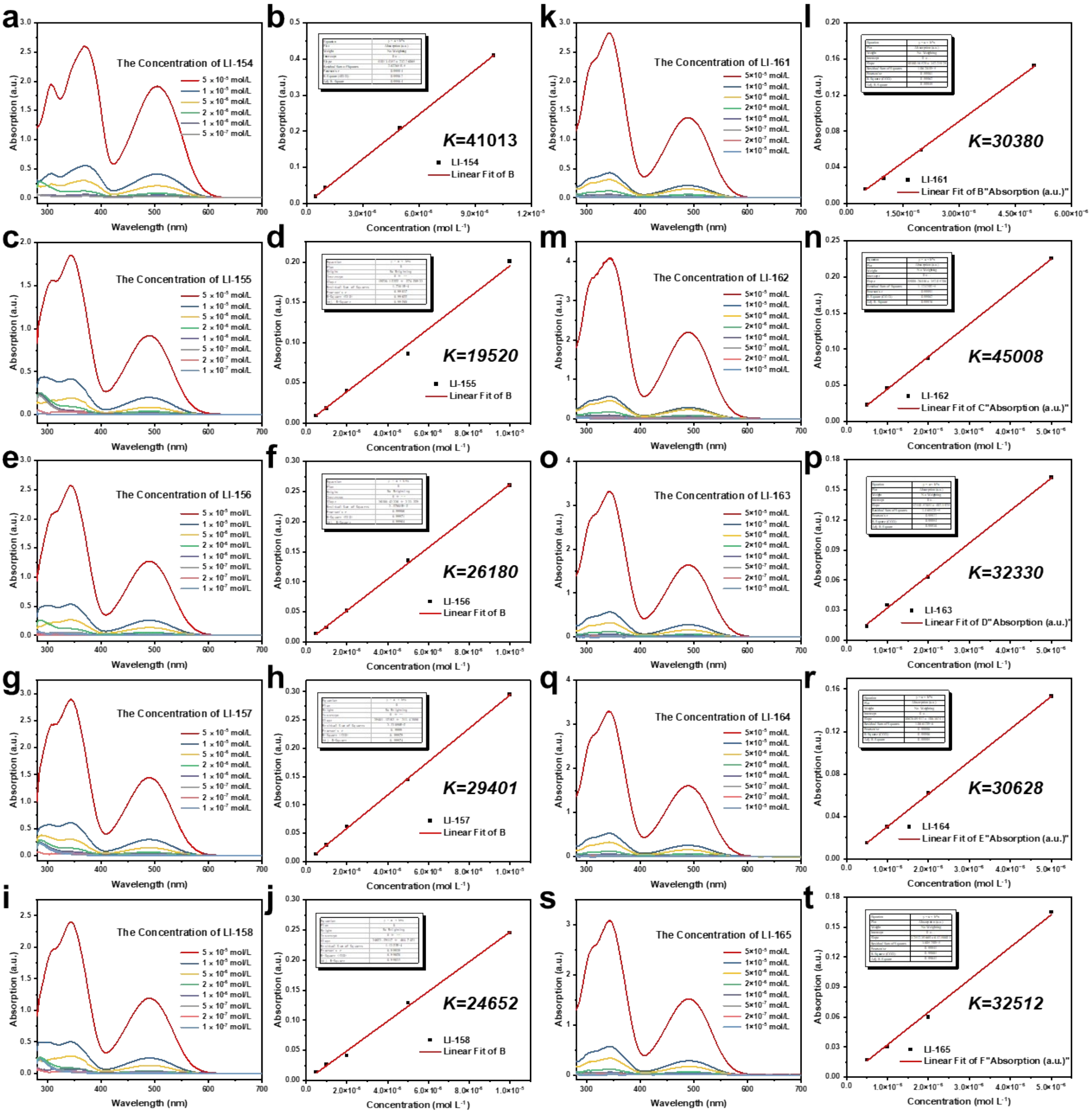


Figure S23. The UV absorption spectra of **LI-154** (a), **LI-155** (c), **LI-156** (e), **LI-157** (g), **LI-158** (i), **LI-161** (k), **LI-162** (m), **LI-163** (o), **LI-164** (q) and **LI-165** (s) with different concentrations in CH_2Cl_2 solution. The molar extinction coefficient (504 nm) fitting curve of **LI-154** (b), the molar extinction coefficient (490 nm) fitting curve of dyes (d, f, h, j. l, n, p, r, t).

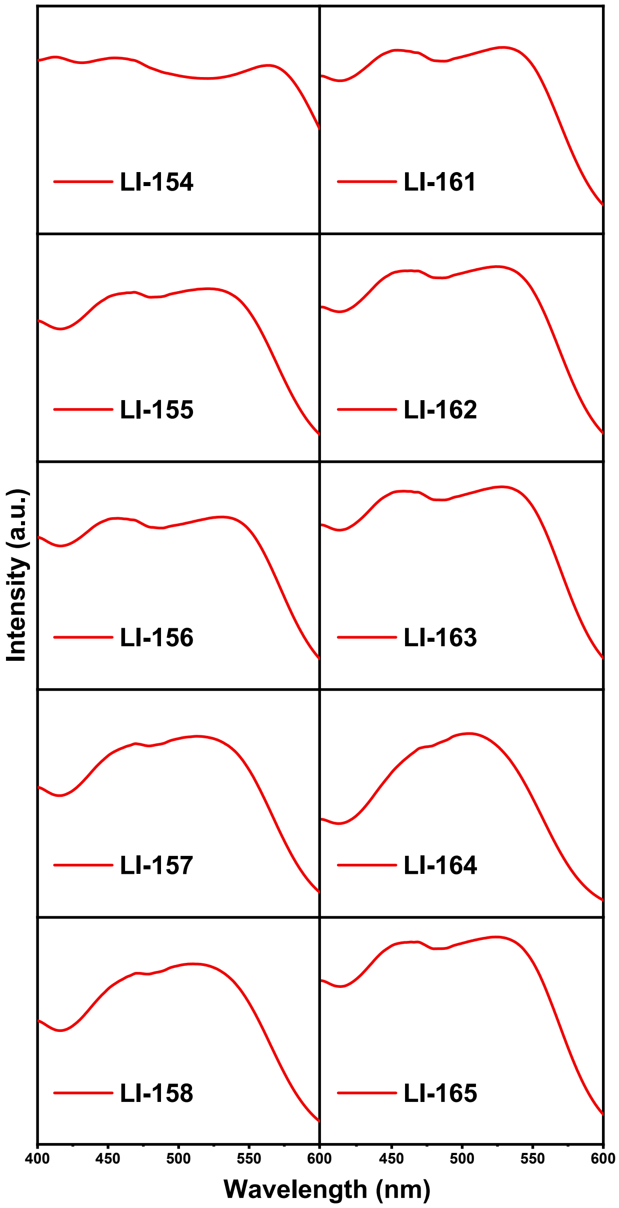


Figure S24. Excitation spectra of dyes in CH_2Cl_2 solution at the concentration of 5×10^{-5} mol L^{-1}.

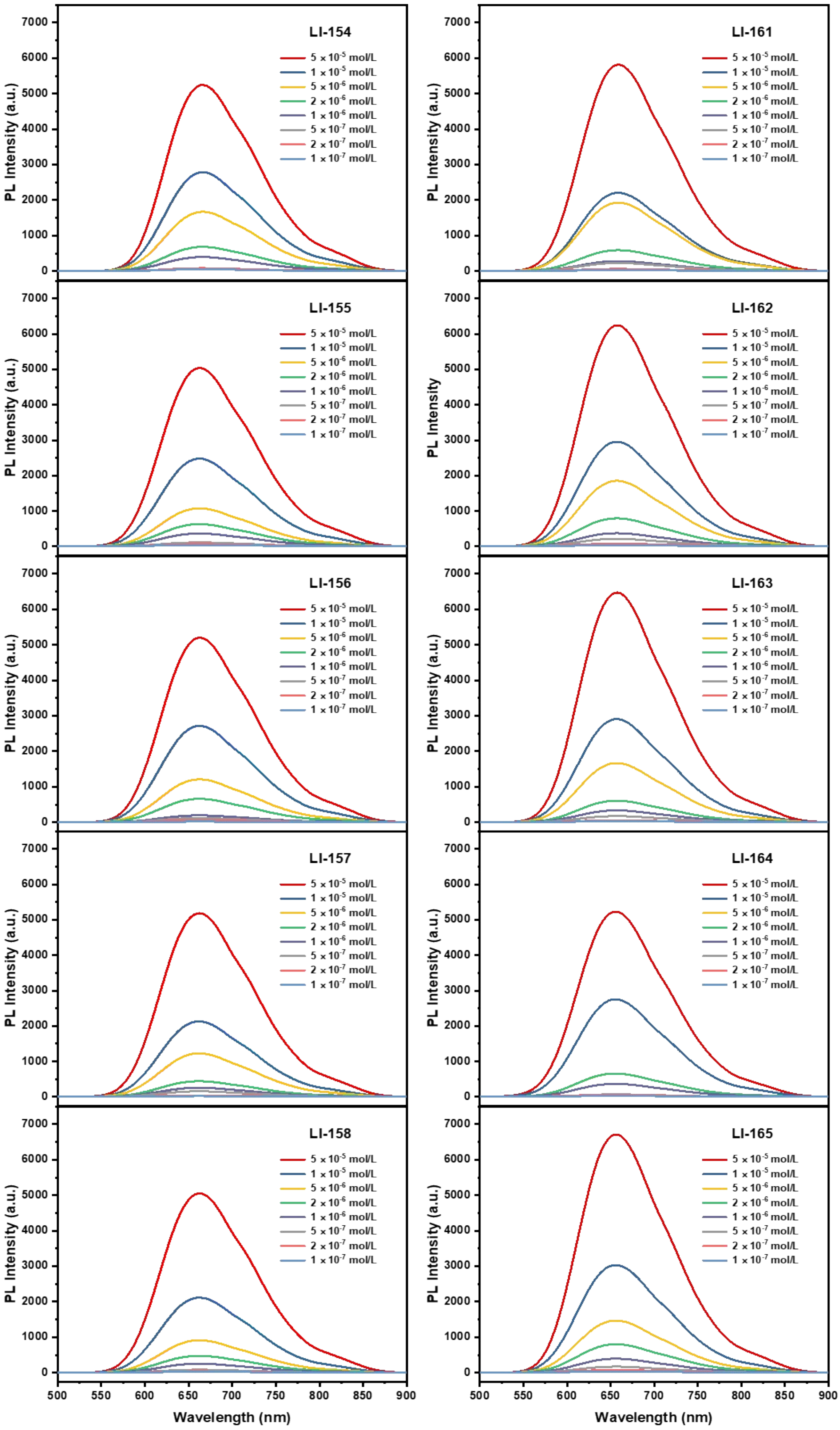


Figure S25. Photoluminescence spectra of dyes in CH_2Cl_2 solution with different concentrations (λ_{ex} = 560 nm).

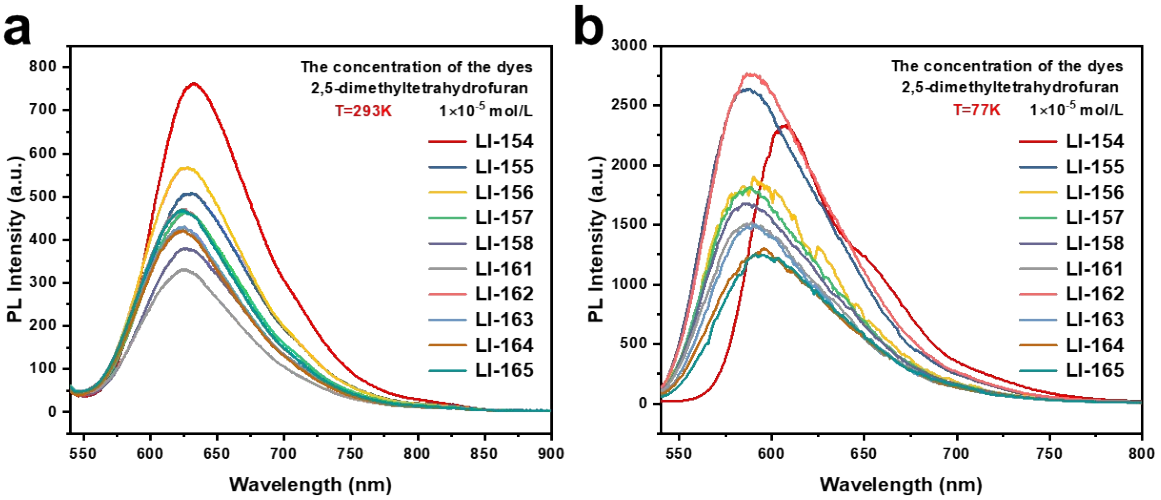


Figure S26. Photoluminescence spectra of dyes in 2,5-dimethyltetrahydrofuran solution at 293K (a) and 77 K (b) (1×10^{-5} mol L^{-1}, λ_{ex} = 520 nm).

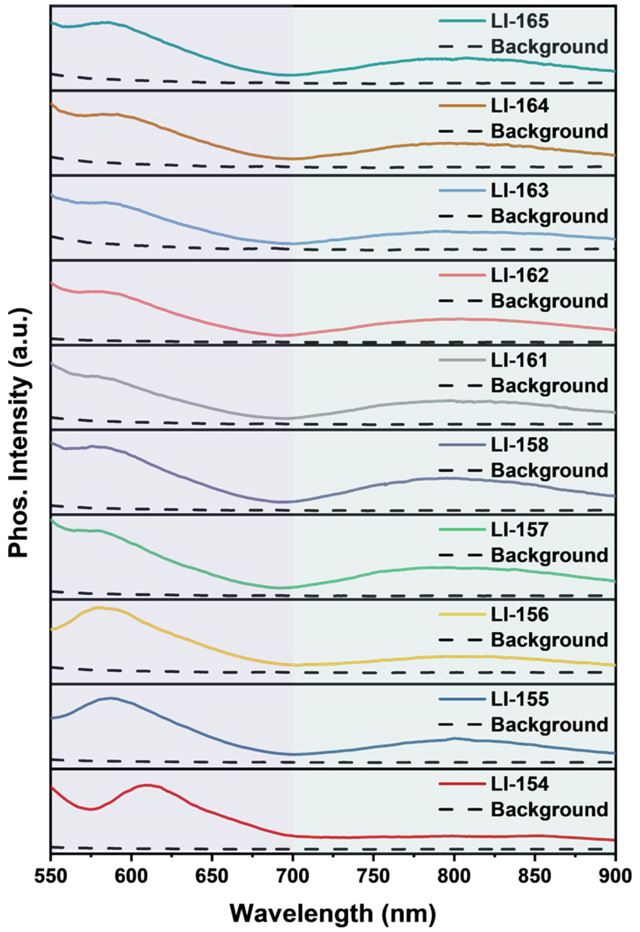


Figure S27. Phosphorescence spectra of dyes in 2,5-dimethyltetrahydrofuran solution at 77 K (1×10^{-5} mol L^{-1}, λ_{ex} = 520 nm).

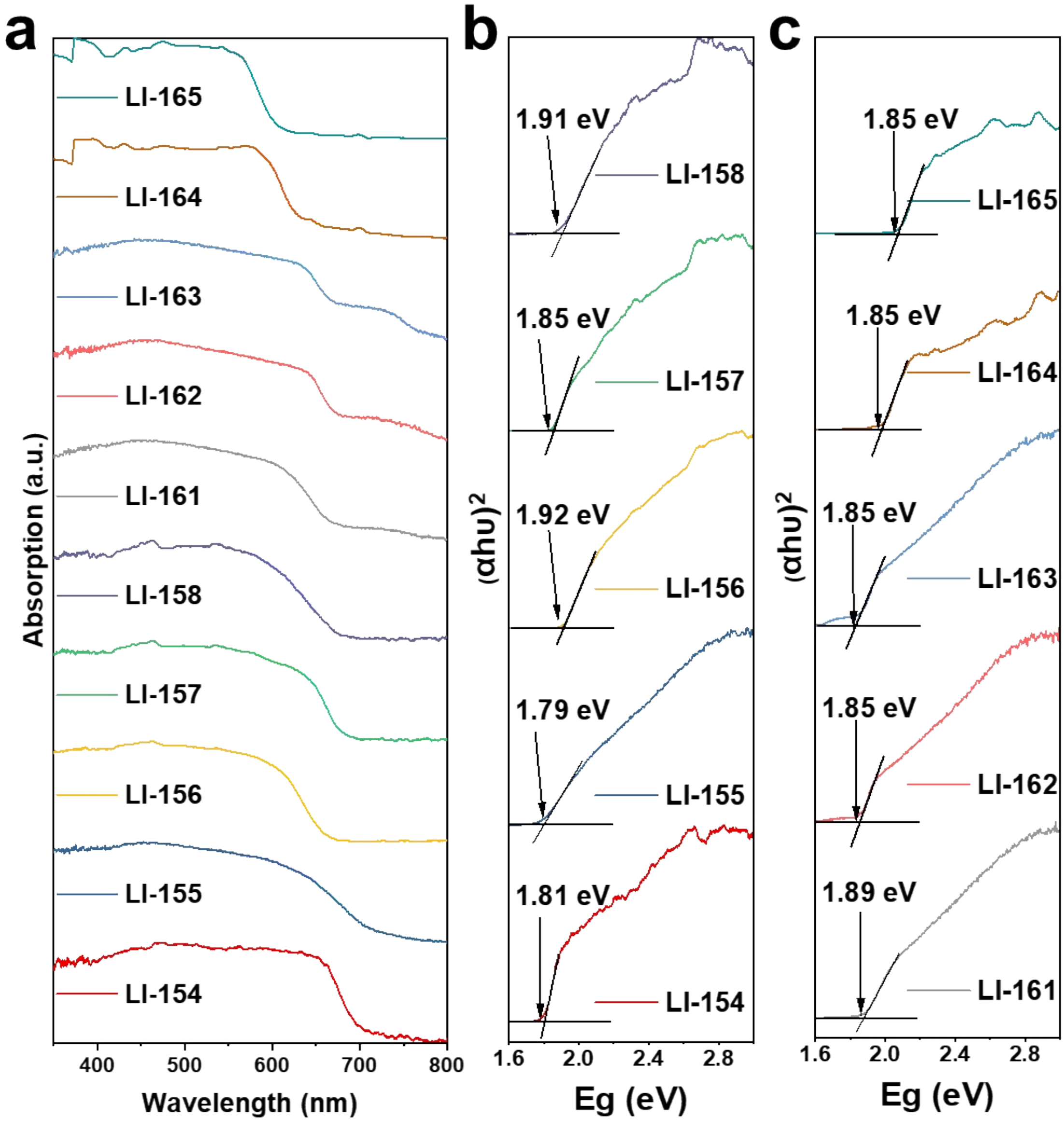
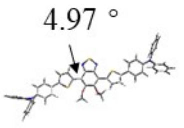
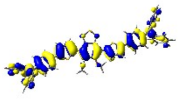
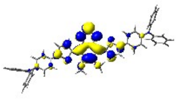
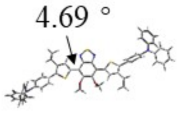
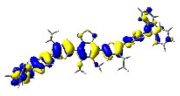
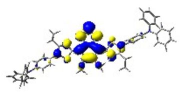
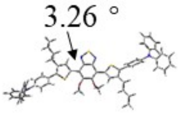
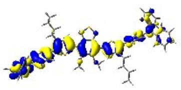
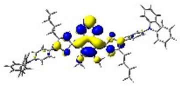
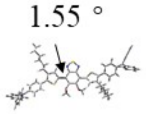
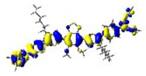
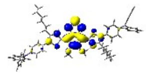
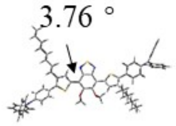
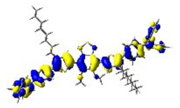
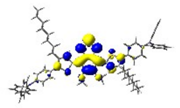
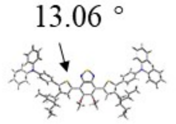
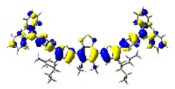
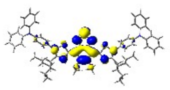
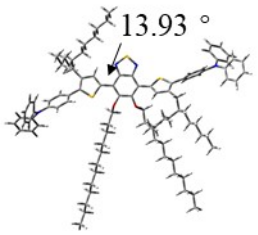
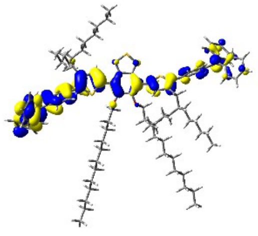
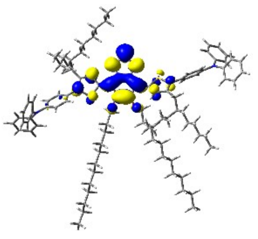


Figure S28. (a) UV–vis DRS absorption spectra of **LI-154**, **LI-155**, **LI-156**, **LI-157**, **LI-158**, **LI-161**, **LI-162**, **LI-163** at solid state, due to **LI-164** and **LI-165** oily nature, a thin film UV-vis is used instead. (b, c) The bandgaps of dyes calculated by Tauc-plot.

	OPT	HOMO	LUMO
LI-154			
LI-155			
LI-156			
LI-157			
LI-158			
LI-161			
LI-162			

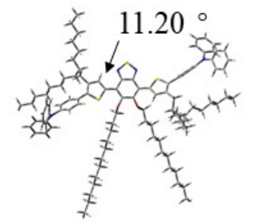
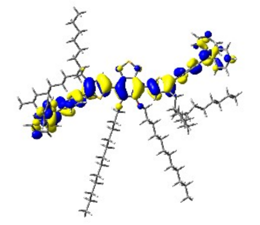
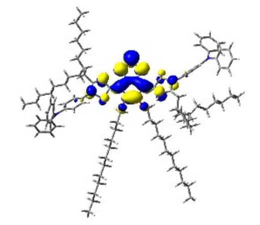
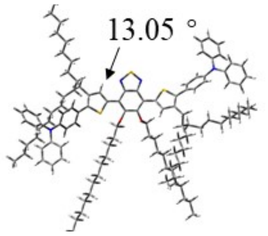
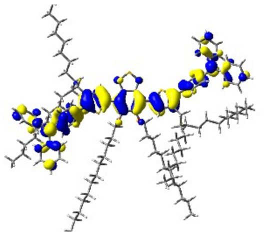
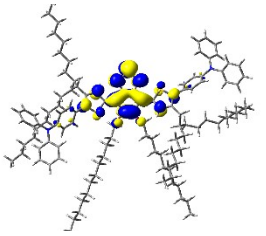
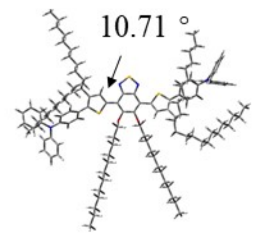
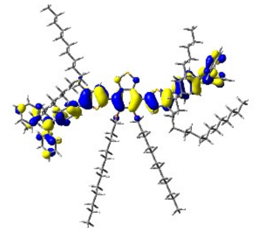
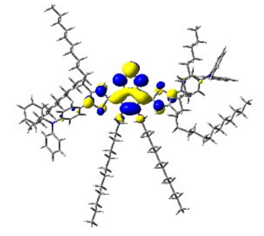
LI-163			
LI-164			
LI-165			

Figure S29. Optimized molecular configurations and frontier orbital distribution of organic dyes.

Table S1 Fluorescence lifetimes of organic dyes

Sample	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_{ave} (ns)
LI-154	1.30	0.35	4.74	0.65	3.53
LI-155	1.96	0.52	4.22	0.48	3.05
LI-156	1.44	0.52	4.62	0.48	2.97
LI-157	2.78	0.34	7.65	0.66	6.01
LI-158	2.67	0.33	6.85	0.67	5.48
LI-161	1.82	0.50	4.90	0.50	3.35
LI-162	3.10	0.44	8.85	0.56	6.33
LI-163	3.32	0.47	8.92	0.53	6.31
LI-164	1.55	0.43	4.13	0.57	3.02
LI-165	1.64	0.63	3.72	0.37	2.40

For organic dyes **LI-154-LI-158** and **LI-161-LI-163**, fluorescence lifetimes were measured at solid state, for **LI-164** and **LI-165** with oily nature, a thin film is used instead. (λ_{ex} = 375 nm, λ_{em} = 690 nm).

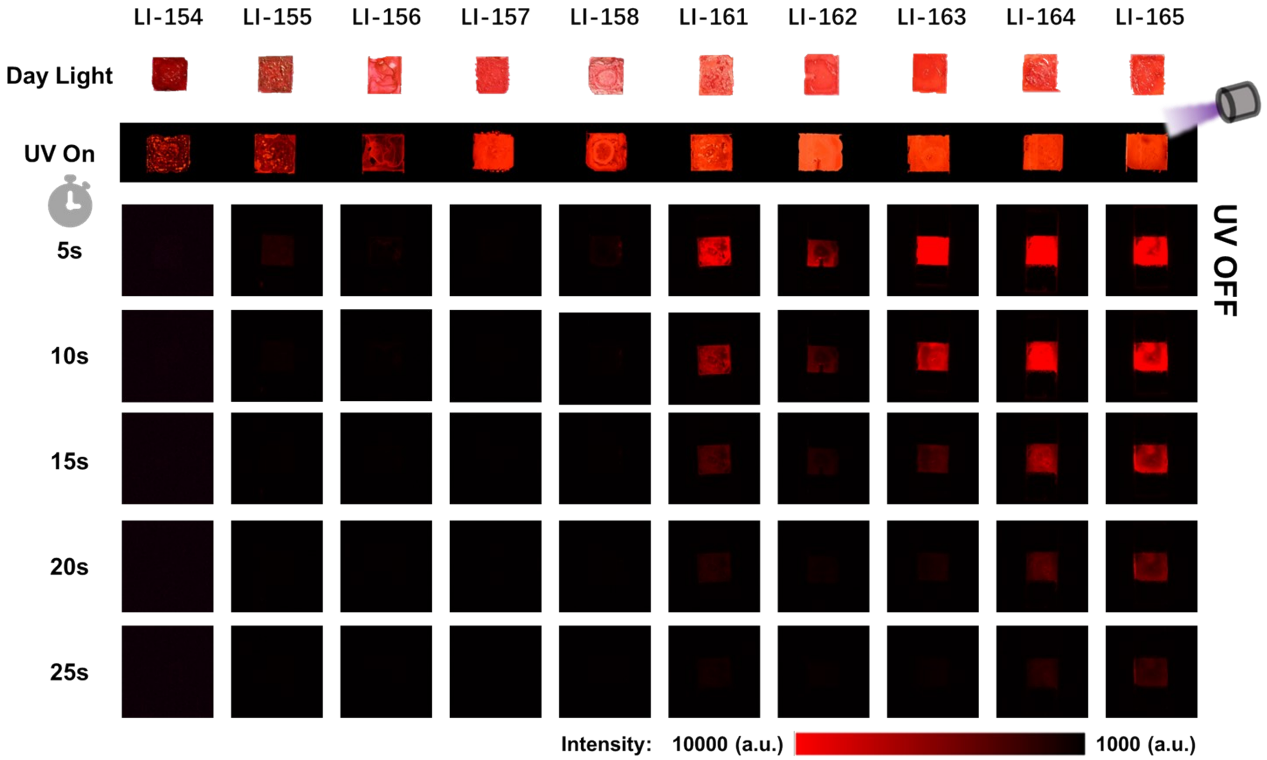


Figure S30. Photographs of organic dyes in thin film under different conditions captured by a camera, and afterglow imaging captured by a chemiluminescence imager (colors only represent phosphorescence intensity) at different time after UV off.

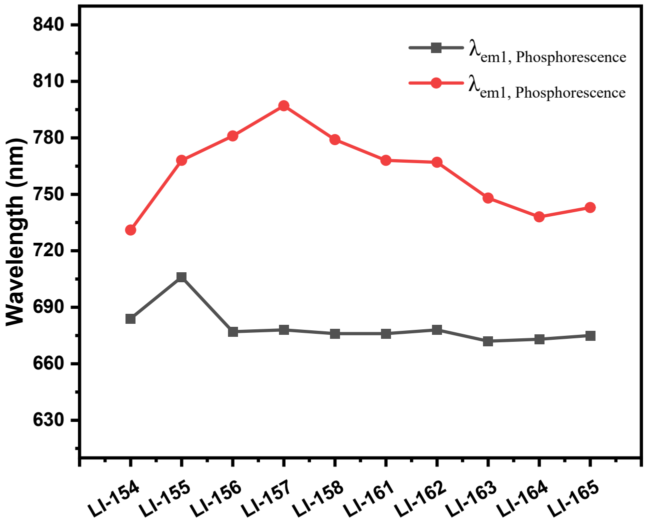


Figure S31. The phosphorescence emission wavelengths of organic dyes.

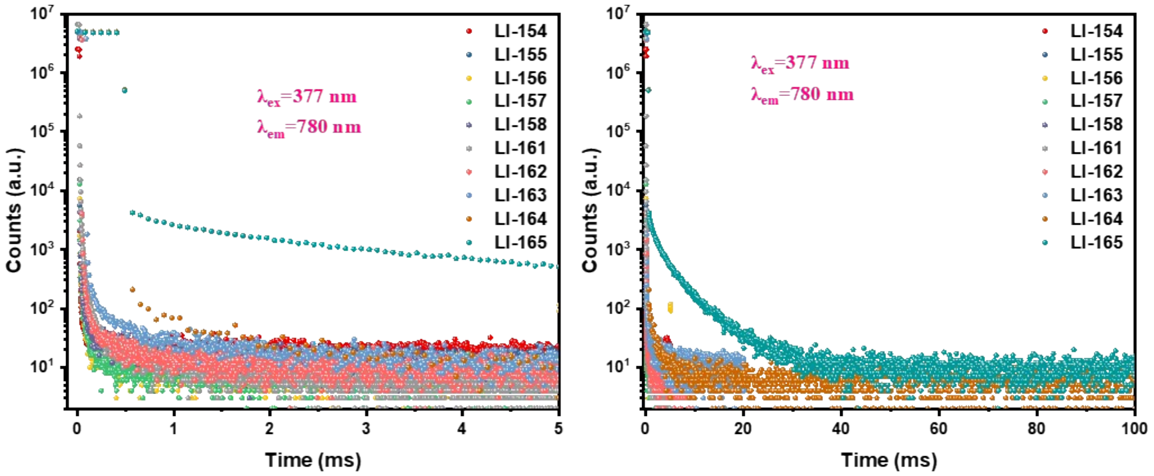


Figure S32. Phosphorescence decay of organic dyes in thin film. (λ_{ex} = 377 nm, λ_{em} = 780 nm).

Table S2 Phosphorescence lifetimes of organic dyes in thin film (λ_{ex} = 377 nm, λ_{em} = 780 nm)

Sample	τ_1 (ms)	A_1	τ_2 (ms)	A_2	τ_3 (ms)	A_3	τ_{ave} (ms)
LI-154	0.004	0.470	0.037	0.051	0.730	0.015	0.027
LI-155	0.006	0.590	0.046	0.139	0.460	0.017	0.024
LI-156	0.006	0.380	0.039	0.108	0.630	0.008	0.023
LI-157	0.004	2.754	0.050	0.152			0.006
LI-158	0.005	1.870	0.045	0.196	1.017	0.021	0.019
LI-161	0.007	2.32	0.044	0.227	0.730	0.027	0.018
LI-162	0.017	0.670	0.350	0.041			0.036
LI-163	0.057	0.380	1.190	0.046			0.179
LI-164	0.660	0.081	4.600	0.014			1.254
LI-165	1.254	2.339	5.256	0.949			2.409

Characterization of PCN, PCN/Pt and dye/PCN/Pt

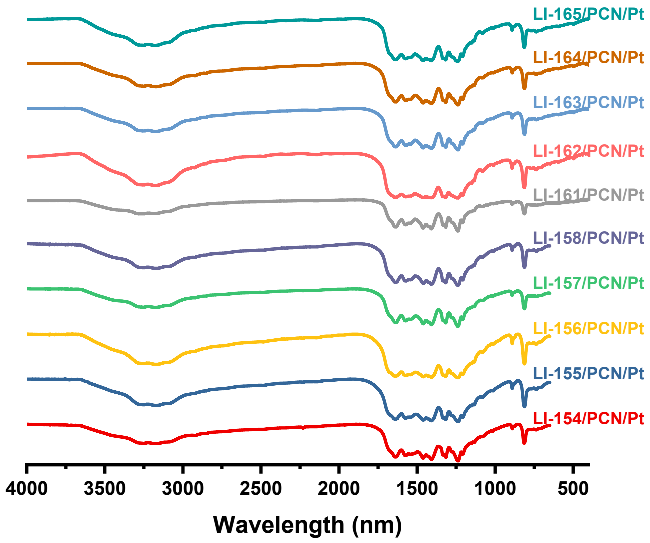


Figure S33. FTIR spectra of PCN, PCN/Pt and dye/PCN/Pt.

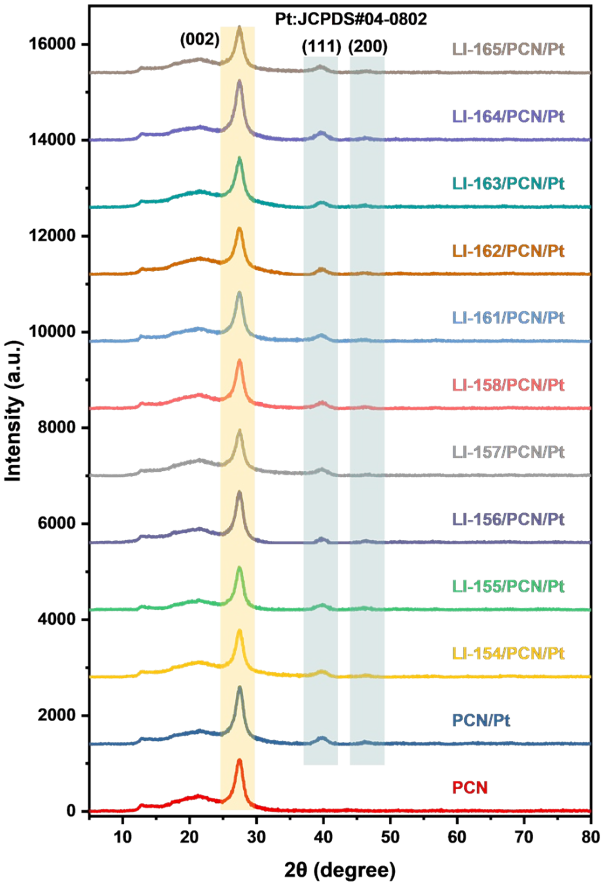


Figure S34. XRD patterns of PCN, PCN/Pt and dye/PCN/Pt.

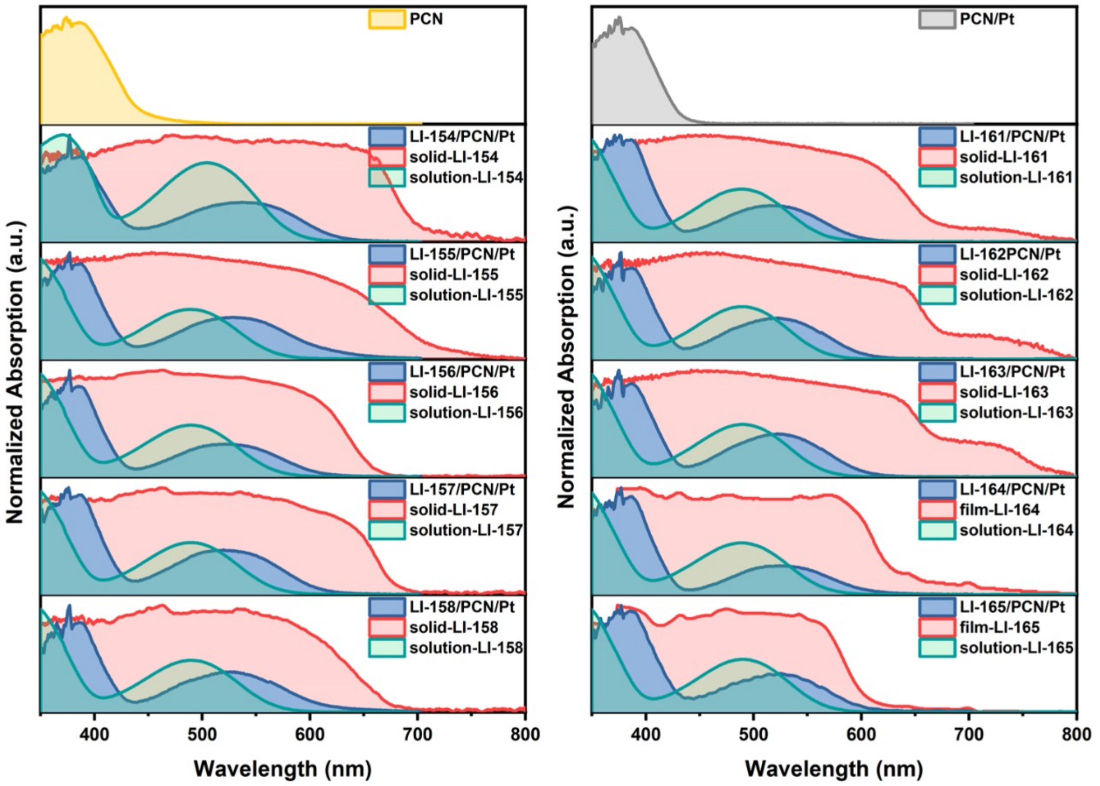


Figure S35. UV–vis DRS absorption spectra of dye/PCN/Pt (blue line), dye at solid or film state (red line), and UV–vis absorption spectra of dye in CH_2Cl_2 solution (1×10^{-5} mol L^{-1}, green line).

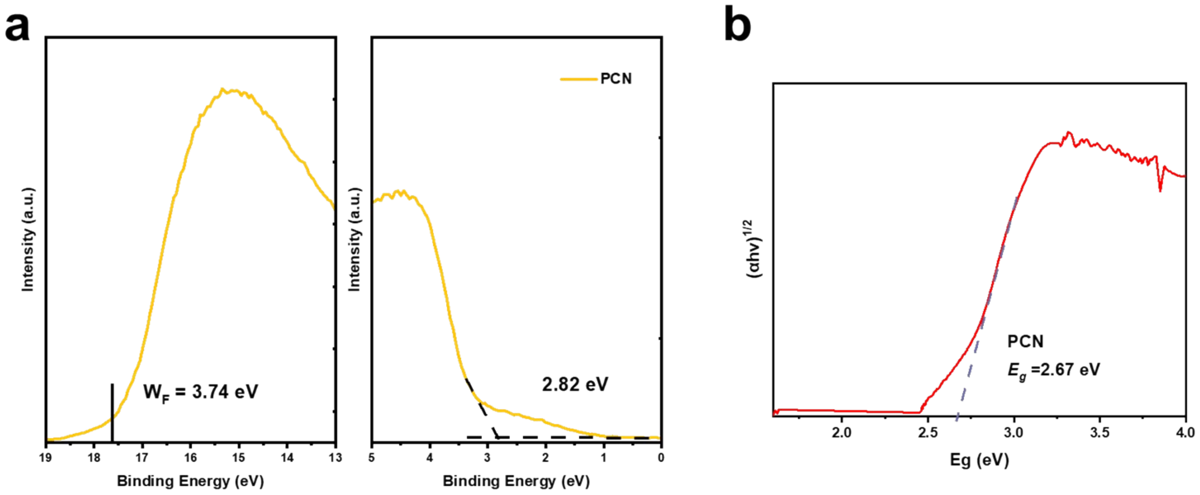


Figure S36. (a) UPS spectra of PCN, HOMO energy level is calculated according to the following equation: E_{HOMO} (*vs*. vacuum conditions) = – (E_{photon} – width of UPS spectra), where E_{photon} denotes the excitation energy of He Ⅰ (21.22 eV). b) The bandgaps of PCN calculated by Tauc-plot.

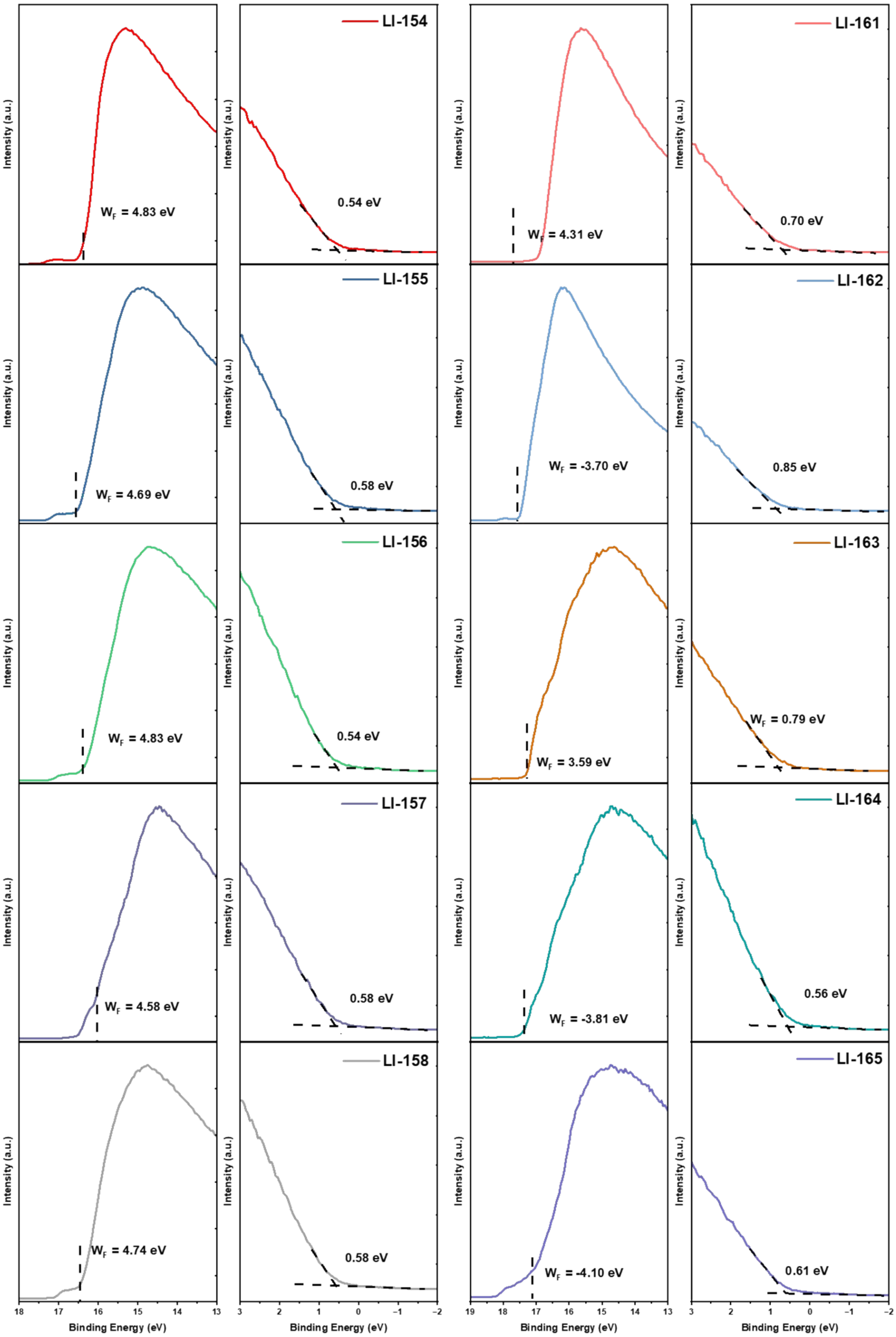


Figure S37. UPS spectra of dyes, HOMO energy levels are calculated according to the following equation: E_{HOMO} (*vs*. vacuum conditions) = – (E_{photon} – width of UPS spectra), where E_{photon} denotes the excitation energy of He Ⅰ (21.22 eV).

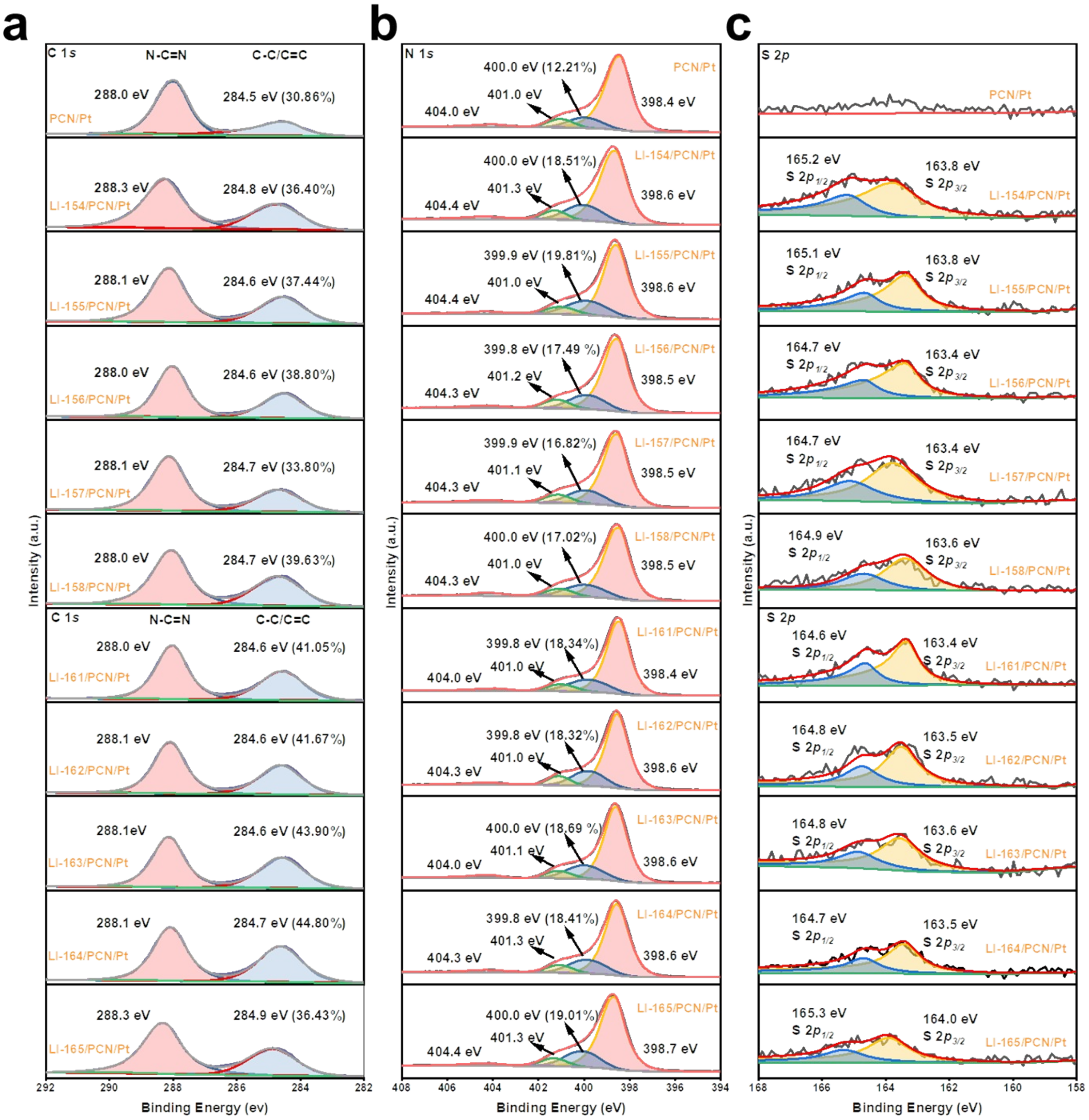


Figure S38. High-resolution XPS spectra of PCN/Pt and dye/PCN/Pt: (a) C 1 s, (b) N 1 s, and (c) S 2p.

Table S3. Relative ratios of two carbon species determined by C 1*s* spectra

Sample	N-C=N			C=C/C-C		
	Binding Energy (eV)	Area	%	Binding Energy (eV)	Area	%
PCN/Pt	288.0	106668	69.1%	284.5	47726	30.9%
LI-154/PCN/Pt	288.3	137729	63.6%	284.8	79048	36.4%
LI-155/PCN/Pt	288.1	118849	62.6%	284.6	71286	37.4%
LI-156/PCN/Pt	288.0	121050	61.2%	284.6	76909	38.8%
LI-157/PCN/Pt	288.1	118045	66.2%	284.7	60352	33.8%
LI-158/PCN/Pt	288.0	110030	60.4%	284.7	72394	39.6%
LI-161/PCN/Pt	288.0	143876	59.0%	284.6	100421	41.0%
LI-162/PCN/Pt	288.1	114146	58.3%	284.6	81732	41.7%
LI-163/PCN/Pt	288.1	124327	56.1%	284.6	97583	43.9%
LI-164/PCN/Pt	288.1	95069	55.2%	284.7	77438	44.8%
LI-165/PCN/Pt	288.3	115427	63.6%	284.9	66298	36.4%

Table S4. Relative ratios of four nitrogen species determined by N 1*s* spectra

Sample	π-π excitations			Quaternary N			Tertiary N			sp^2 N		
	Binding Energy (eV)	Area	%	Binding Energy (eV)	Area	%	Binding energy (eV)	Area	%	Binding Energy (eV)	Area	%
PCN/Pt	404.0	15227	5.8%	401.0	20305	7.7%	400.0	32216	12.2%	398.4	196293	74.3%
LI-154/PCN/Pt	404.4	17591	5.8%	401.3	22110	7.2%	400.0	56829	18.5%	398.6	210537	68.5%
LI-155/PCN/Pt	404.4	14501	5.4%	401.0	20759	7.7%	399.9	53299	19.8%	398.6	180606	67.1%
LI-156/PCN/Pt	404.3	14470	5.3%	401.2	21232	7.8%	399.8	47533	17.5%	398.5	188662	69.4%
LI-157/PCN/Pt	404.3	16344	6.1%	401.1	21312	7.9%	399.9	45321	16.8%	398.5	186621	69.2%
LI-158/PCN/Pt	404.3	13870	5.9%	401.0	16870	7.1%	400.0	40242	17.0%	398.5	165580	70.0%
LI-161/PCN/Pt	404.0	17078	5.5%	401.0	22741	7.3%	399.8	57535	18.3%	398.4	219459	69.0%
LI-162/PCN/Pt	404.3	13627	5.4%	401.0	19426	7.7%	399.8	46197	18.3%	398.6	173019	68.6%
LI-163/PCN/Pt	404.0	13988	5.2%	401.1	19306	7.2%	400.0	50446	18.7%	398.6	186308	69.0%
LI-164/PCN/Pt	404.3	12336	6.0%	401.3	15432	7.4%	399.8	38255	18.4%	398.6	141879	68.2%
LI-165/PCN/Pt	404.4	13344	5.2%	401.3	18303	7.0%	400.0	49347	19.0%	398.7	178751	68.8%

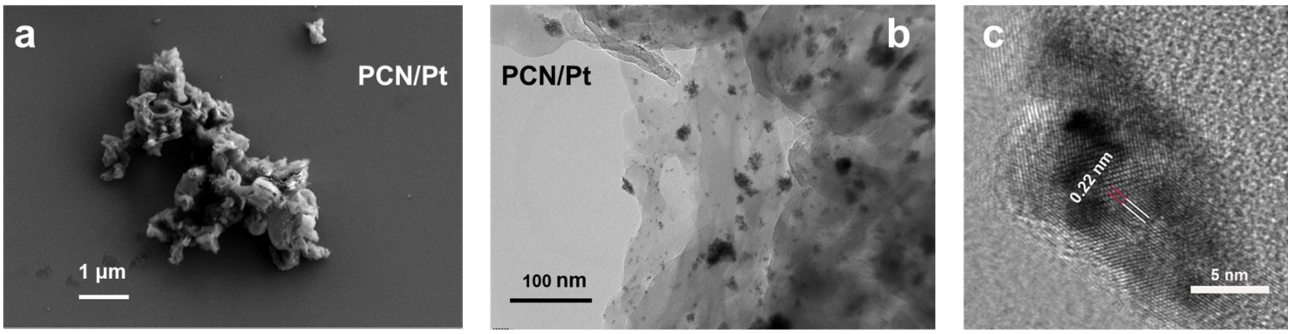


Figure S39. SEM and TEM images of PCN (a) and PCN/Pt (b). The Pt morphology on the surface of PCN (c).

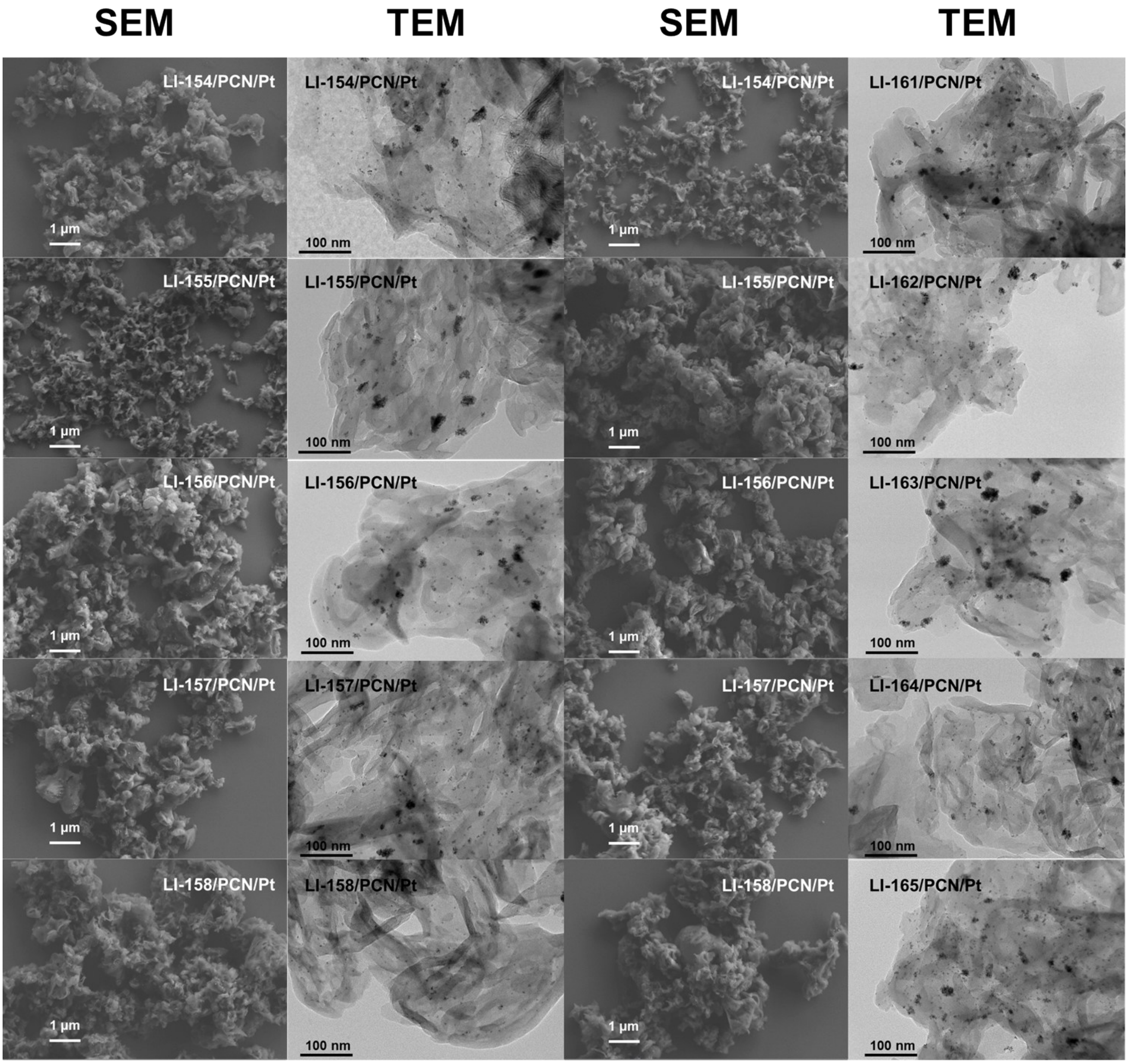


Figure S40. SEM and TEM images of dye/PCN/Pt.

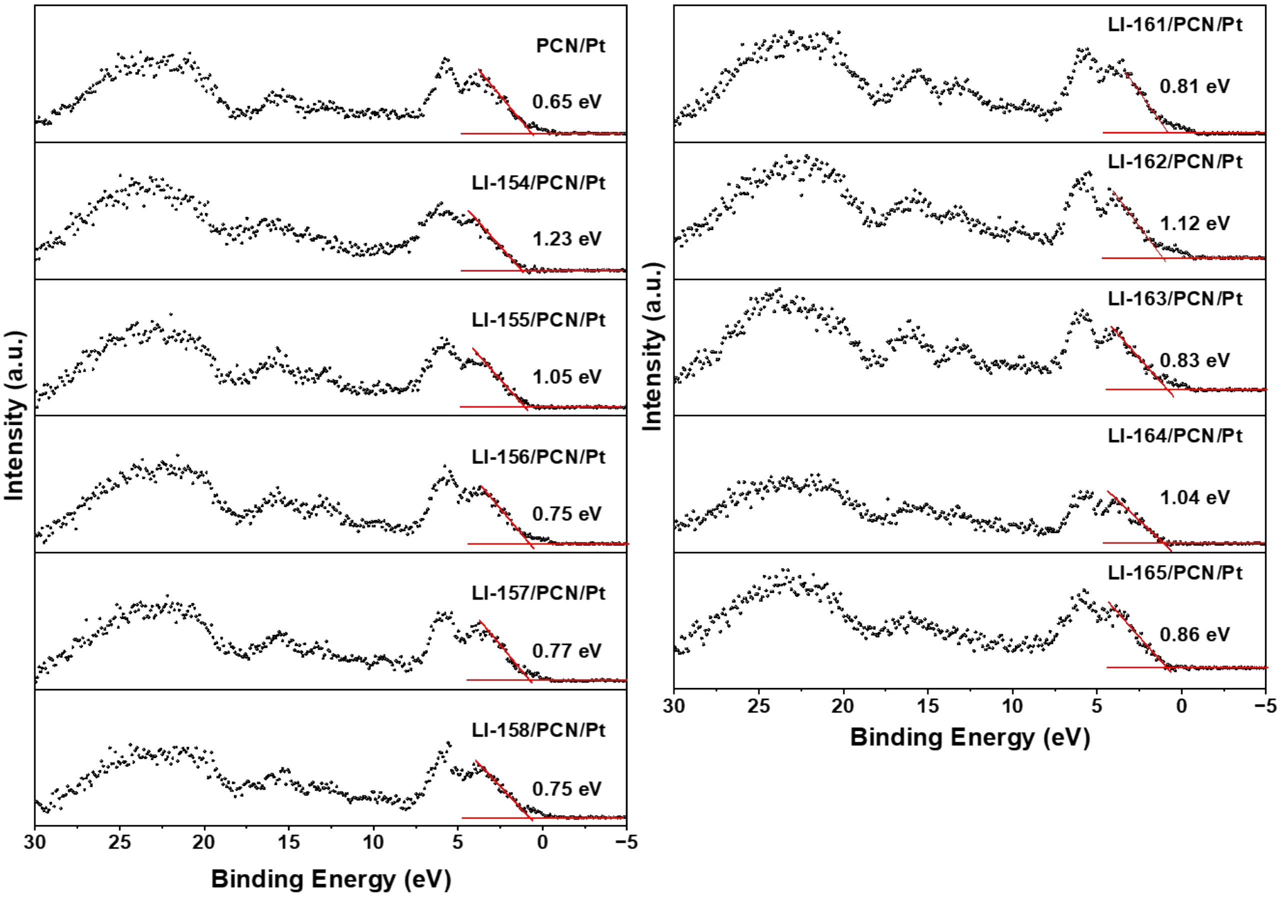


Figure S41. VB XPS spectra of PCN/Pt and dye/PCN/Pt.

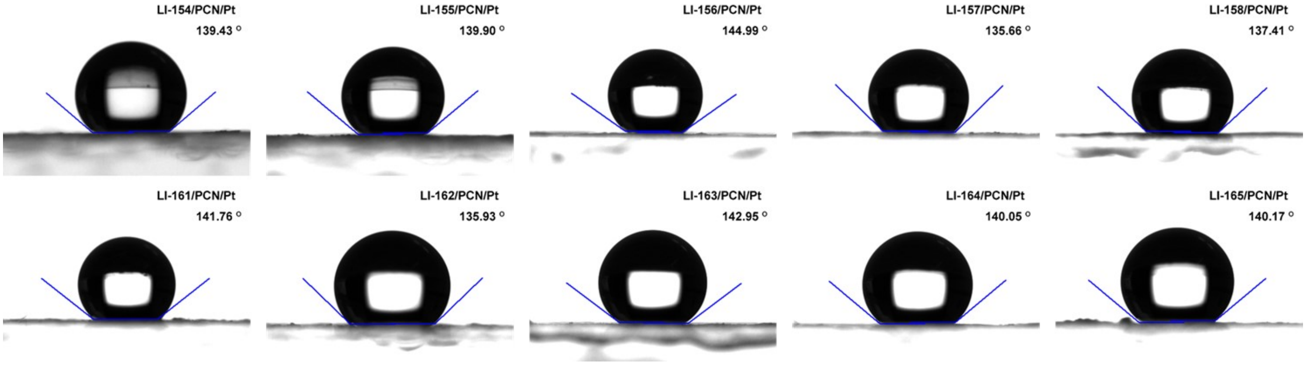
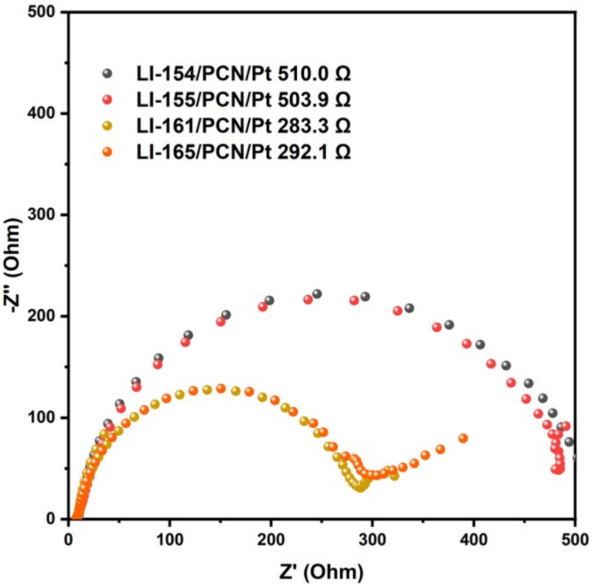


Figure S42. The water contact angles of dye/PCN/Pt electrodes.



Figrue S43. Electrochemical impedance spectra (EIS) Nyquist plots of dye/PCN/Pt (-1.2 V vs. RHE).

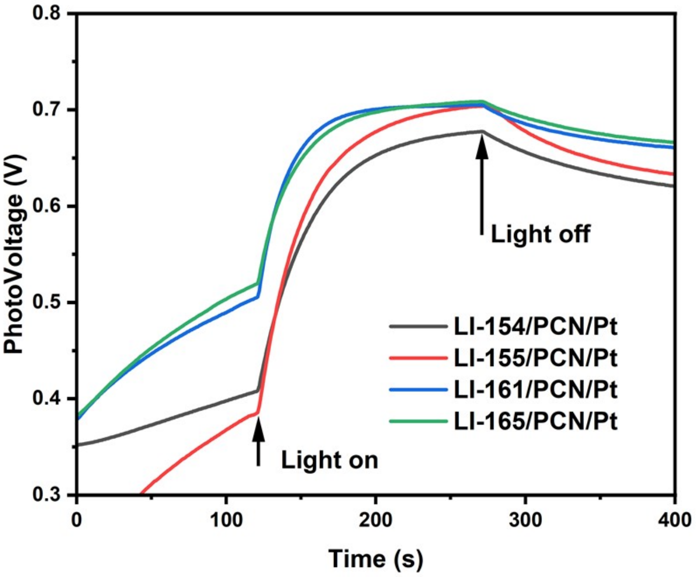


Figure S44. The transient open-circuit voltage decay (OCVD) of dye/PCN/Pt.

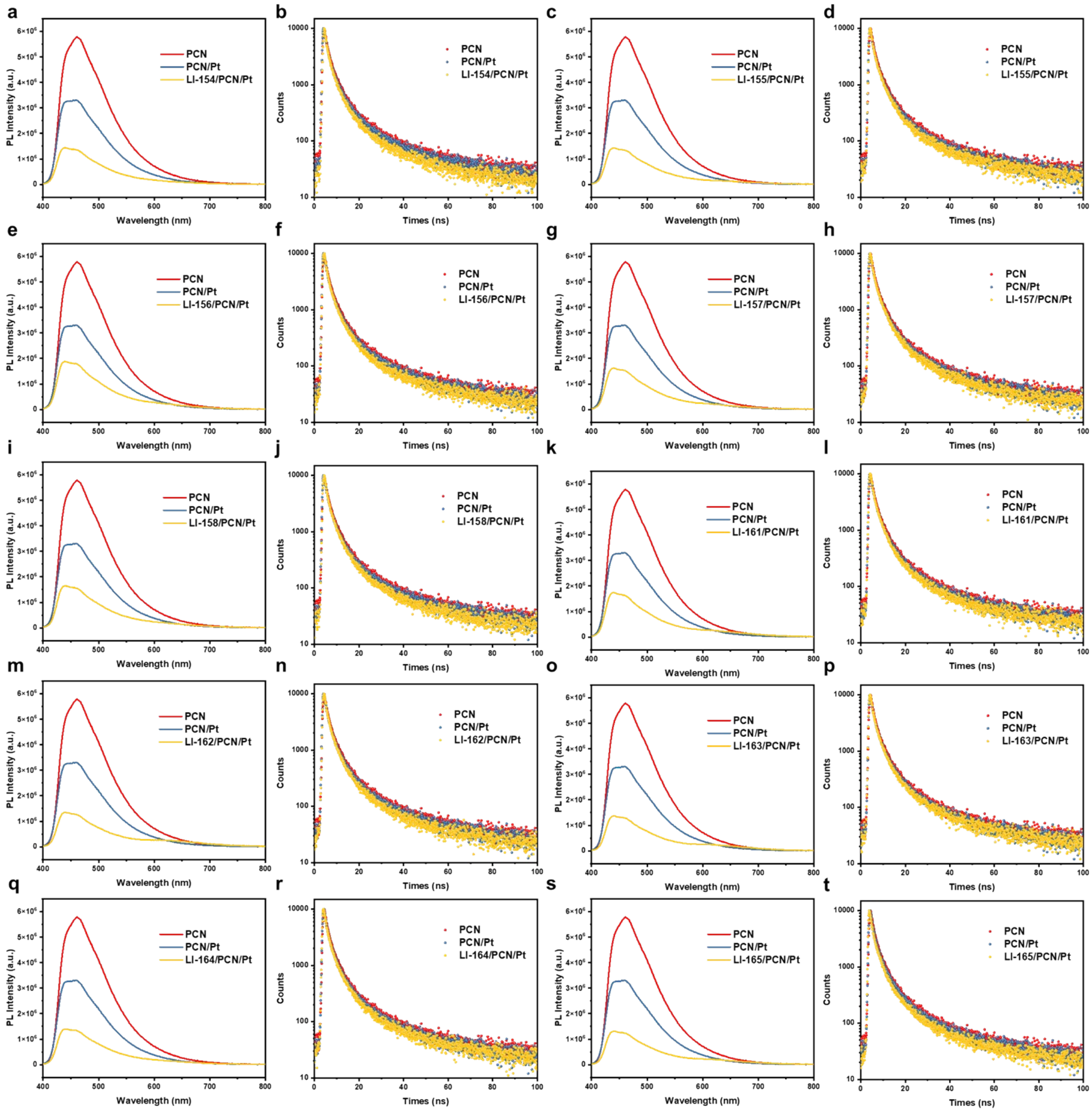


Figure S45. PL spectra of PCN, PCN/Pt and dye/PCN/Pt (λ_{ex} = 350 nm) (a, c, e, g, i, k, m, o, q, s). TRPL spectra of PCN, PCN/Pt, dye/PCN and dye/PCN/Pt (λ_{ex} = 375 nm, λ_{em} = 450 nm) (b, d, f, h, j. l, n, p, r, t)

Table S5. Fluorescence lifetimes of PCN, PCN/Pt and dye/PCN/Pt (λ_{ex} = 375 nm, λ_{em} = 450 nm)

Sample	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_3 (ns)	A_3	τ_{ave} (ns)
PCN	1.17	0.27	4.21	0.50	18.89	0.23	7.74
PCN/Pt	1.17	0.25	4.11	0.50	17.49	0.25	6.97
LI-154/PCN/Pt	1.01	0.28	3.79	0.51	17.01	0.21	5.85
LI-155/PCN/Pt	1.10	0.27	4.02	0.52	18.30	0.21	6.22
LI-156/PCN/Pt	1.08	0.22	3.98	0.52	17.75	0.22	6.14
LI-157/PCN/Pt	1.12	0.28	3.91	0.50	17.23	0.22	6.06
LI-158/PCN/Pt	1.07	0.28	3.90	0.51	17.20	0.21	5.95
LI-161/PCN/Pt	1.08	0.27	3.71	0.50	16.07	0.23	5.87
LI-162/PCN/Pt	1.14	0.30	3.94	0.49	17.16	0.21	5.90
LI-163/PCN/Pt	1.18	0.30	3.99	0.48	17.49	0.22	6.11
LI-164/PCN/Pt	1.28	0.34	4.42	0.47	19.62	0.19	6.28
LI-165/PCN/Pt	1.13	0.30	3.92	0.49	17.35	0.21	5.95

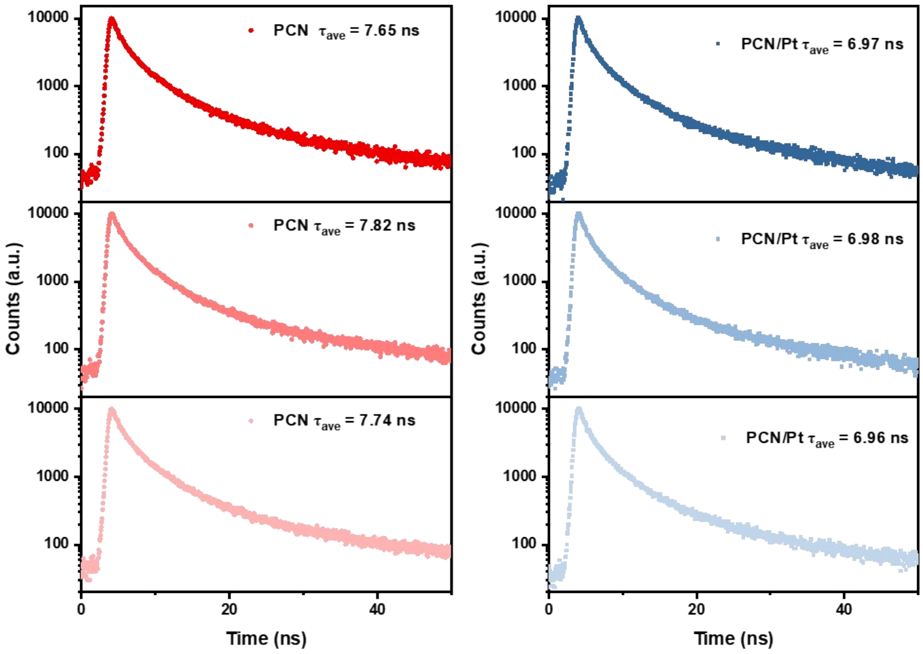


Figure S46. PL decay of PCN and PCN/Pt with three parallel experiments.

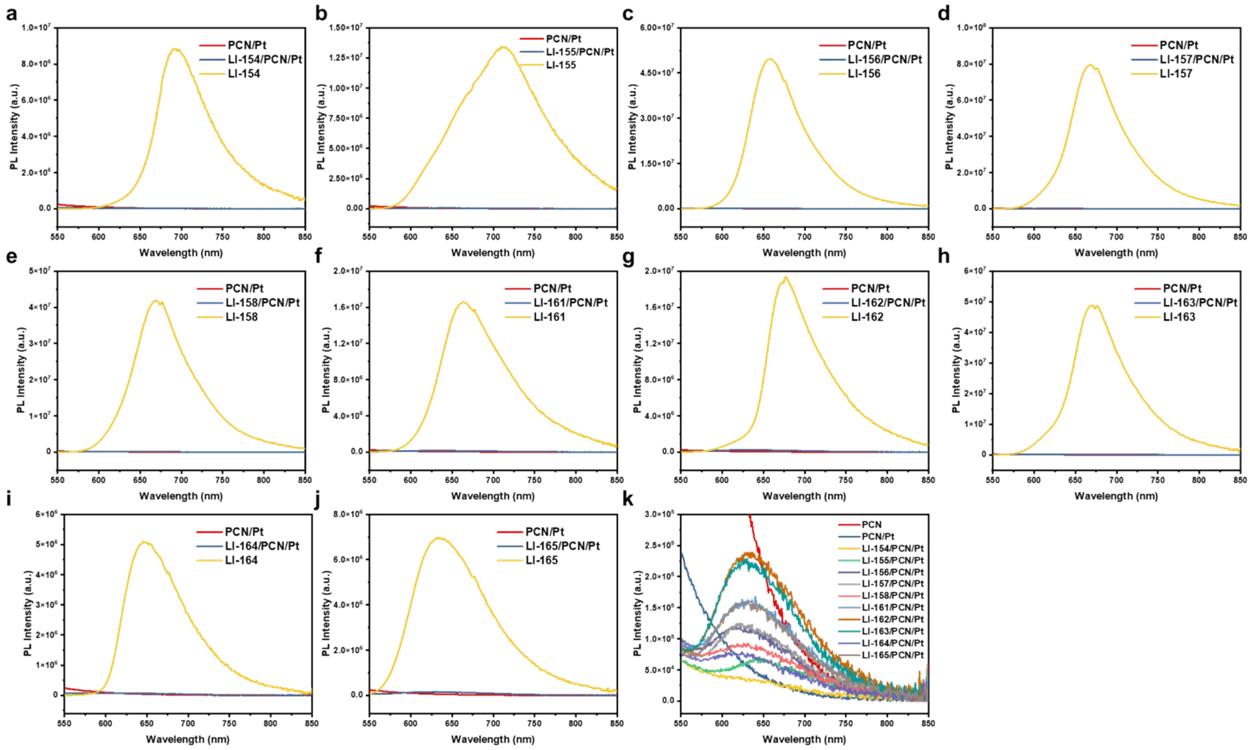


Figure S47. PL spectra of dye, PCN/Pt and dye/PCN/Pt ($\lambda_{ex} = 430$ nm).

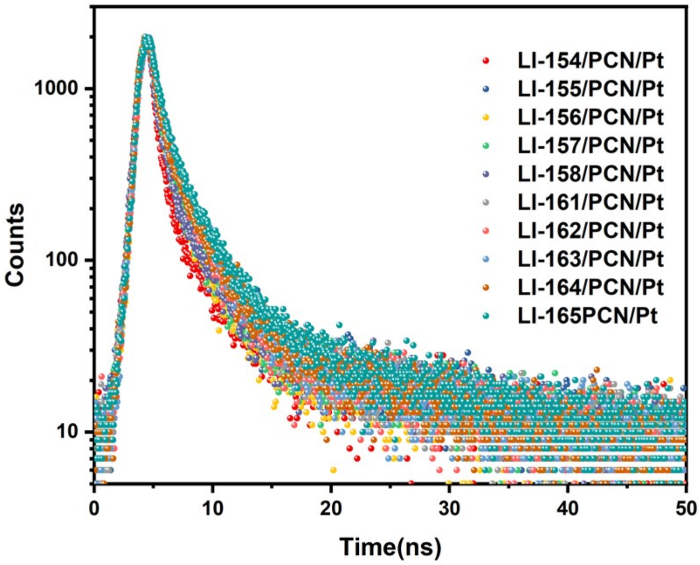


Figure S48. PL decay of dye/PCN/Pt ($\lambda_{ex} = 450$ nm, $\lambda_{em} = 660$ nm)

Table S6. Fluorescence lifetimes of dye/PCN/Pt (λ_{ex} = 450 nm, λ_{em} = 660 nm)

Sample	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_{ave} (ns)
LI-154/PCN/Pt	0.72	0.66	5.24	0.34	2.24
LI-155/PCN/Pt	0.98	0.68	6.04	0.32	2.58
LI-156/PCN/Pt	0.98	0.72	5.22	0.28	2.15
LI-157/PCN/Pt	0.97	0.69	5.39	0.31	2.36
LI-158/PCN/Pt	0.88	0.63	5.31	0.37	2.50
LI-161/PCN/Pt	1.23	0.66	5.24	0.34	2.60
LI-162/PCN/Pt	1.16	0.66	5.10	0.34	2.51
LI-163/PCN/Pt	1.11	0.62	4.74	0.38	2.49
LI-164/PCN/Pt	1.03	0.60	5.03	0.40	2.62
LI-165/PCN/Pt	1.27	0.64	5.77	0.36	2.89

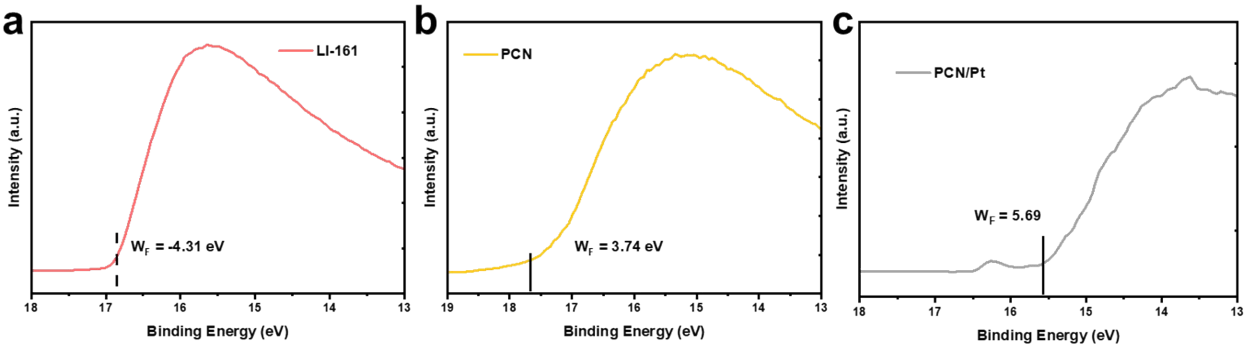


Figure S49. The calculated work function of **LI-161** (a), PCN (b) and PCN/Pt (c) by UPS.

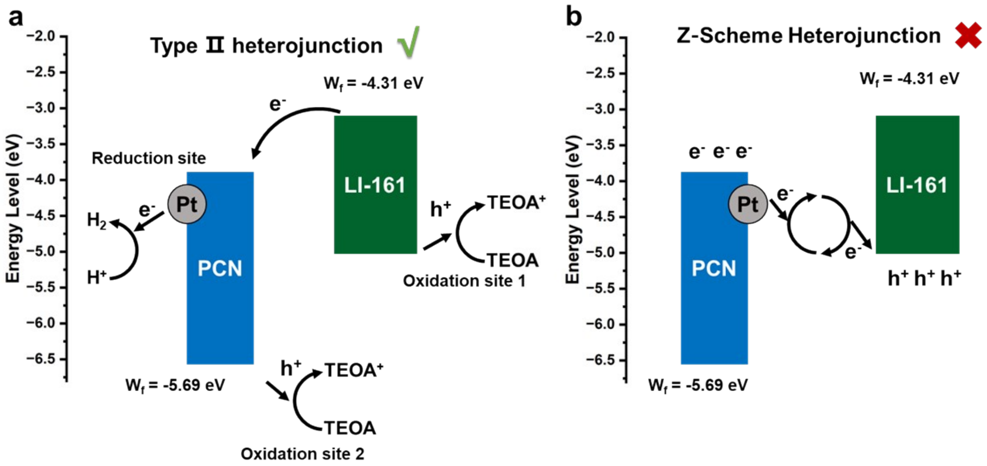


Figure S50. Proposed mechanism of LI-161/PCN/Pt system for photocatalytic hydrogen evolution.

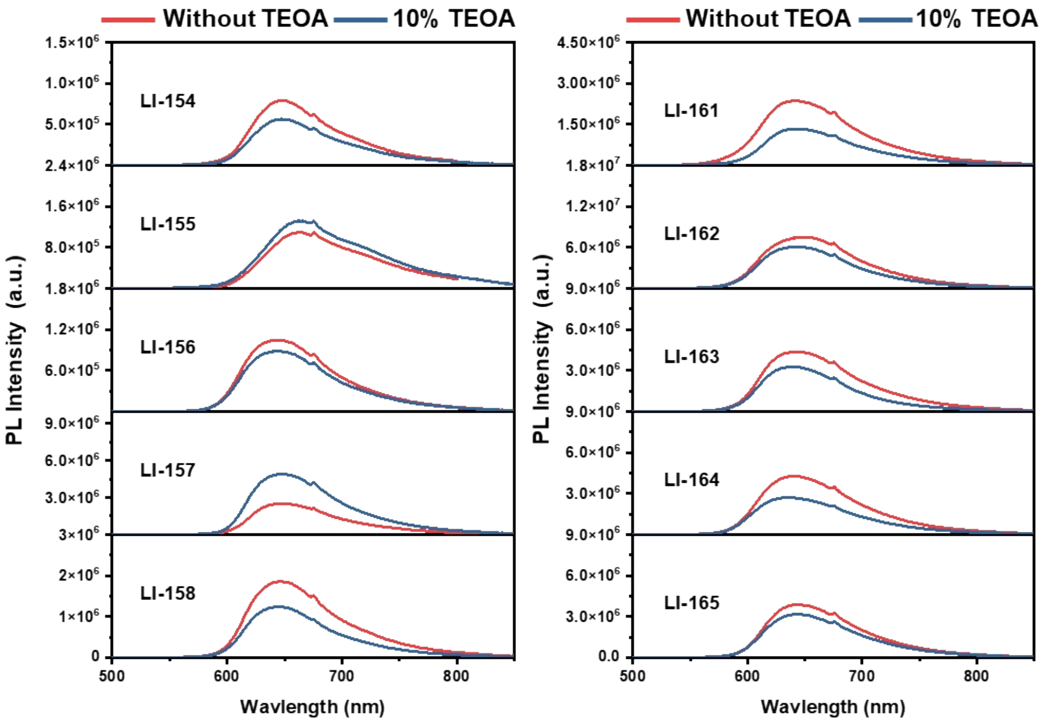


Figure S51. PL spectra of organic dyes (thin film) in water and 10% TEOA aqueous solution.

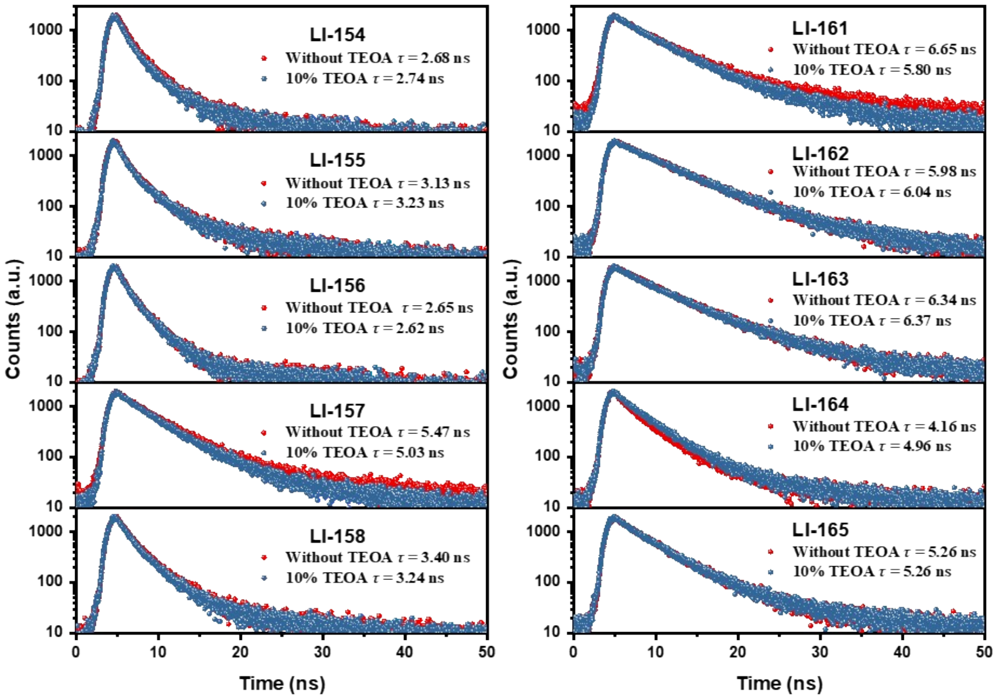


Figure S52. TRPL spectra of organic dyes (thin film) in water and 10% TEOA aqueous solution.

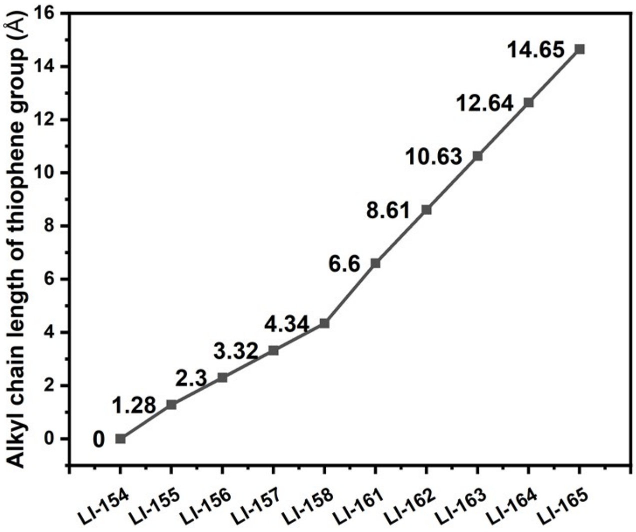


Figure S53. The effective lengths of alkyl chains substituted to thiophene moiety for isolation effect.