

Adjusting and Visualizing the Stability of Acyl Chloride through Delocalization Effect and Introducing AIEgens

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Materials and measurements

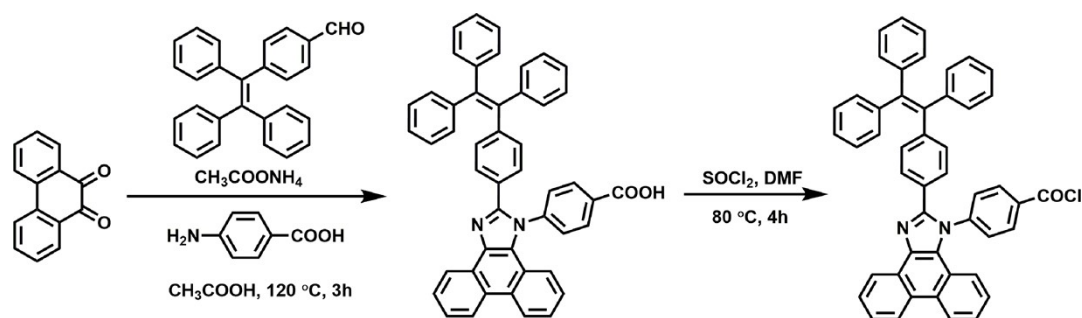
All the reagents and solvents were purchased from commercial sources and used as received. Tetrahydrofuran (THF) for optical properties test was distilled from sodium benzophenone ketyl under nitrogen and solvents for solvation effect are of spectral level. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 500 spectrometer in appropriated deuterated solution. High resolution mass spectra (HRMS) were measured on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. UV-vis absorption spectra were recorded with a Shimadzu UV-2600 spectro-photometer. Measurements of Photoluminescence spectra were carried out on Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields in solutions and solid states were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaaurus_QY. PBS (phosphate buffer solution) were purchased from Thermo Fisher Scientific (Shanghai, China).

Synthesis of TPEPOH

A mixture of phenanthrenequinone (416 mg, 2.0 mmol), 4-aminobenzoic acid (1.37 g, 10.0 mmol), 4-(1,2,2-triphenylvinyl)benzaldehyde (720 mg, 2.0 mmol), ammonium acetate (616 mg, 8.0 mmol), and acetic acid (30 mL) was refluxed for 4 h under nitrogen. After that, the solid products were cooled to room temperature and then was filtered. Washed with water and CH₃OH for three times, thus-obtained flavescent powder was dispersed in ethyl acetate solvent and refluxing for 2 h. The White powder was dried under vacuum and used directly for the next step. (yield: 89%). ¹H NMR (500 MHz, *d*-DMSO) δ 13.46 (s, 1H), 8.94–8.87 (m, 2H), 8.66–8.63 (d, 1H), 8.18–8.16 (d, 2H), 7.78–7.74 (m, 3H), 7.71–7.66 (m, 1H), 7.58–7.54 (t, 1H), 7.39–7.35 (t, 1H), 7.29–7.27 (d, 2H), 7.16–7.08 (m, 10H), 6.98–6.94 (m, 4H), 6.92–6.88 (m, 4H).

Synthesis of TPEPCI

The elaborated synthetic information and NMR data of **TPEPCI** were given in the supporting information (Figure S4 and S10). **TPEPOH** (300 mg, 0.44 mmol) was put into dry two-neck round-bottom flask in nitrogen atmosphere. After then, sulfur dichloride (8 mL) and dry DMF (2 drops) was slowly injected into flask and stirred at 80 °C for 4 h. After the reaction, excess sulfur dichloride was removed by rotary evaporator, the yellow solid was put into distilled water (20 mL) and extraction with DCM for three times, drying with anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to obtain yellow powder. (Yield: 65%). ¹H NMR (500 MHz, *d*-DMSO) δ 9.02-8.96 (m, 2H), 8.81-8.79 (d, 1H), 8.22-8.20 (d, 2H), 7.86-7.79 (m, 3H), 7.69-7.65 (m, 1H), 7.40-7.37 (6, 2H), 7.29-7.27 (d, 2H), 7.24-7.07 (m, 10H), 7.01-6.87 (m, 4H), 6.92-6.88 (m, 4H).



Scheme S1. Synthetic route and structures of **TPEPOH** and **TPEPCI**

Configuration of pH buffer

The pH buffers from pH = 3–13 were fabricated by mixing Britton-Robison buffer solution (0.04 mol/L H_3PO_4 , H_3BO_3 , CH_4COOH aqueous solution) and 0.2 mol/L NaOH aqueous solution. While the pH buffers of pH=1 and 2 were obtained KCl–HCl aqueous solution.

Table S1. The basic photophysical data of **TPEPCI** and **TPEPOH**.

	$\lambda_{\text{em-max}}$ (nm) / FWHM (nm) / Φ_{PL} (%)			
	THF	Mixture	Powder	Crystal
TPEPCI	432 / 114 / 0.7	502 / 98 / 26.2	495 / 80 / 36.6	500 / 75 / 42.6
TPEPOH	484 / 116 / 0.1	485 / 94 / 40.2	461 / 70 / 74.1	--

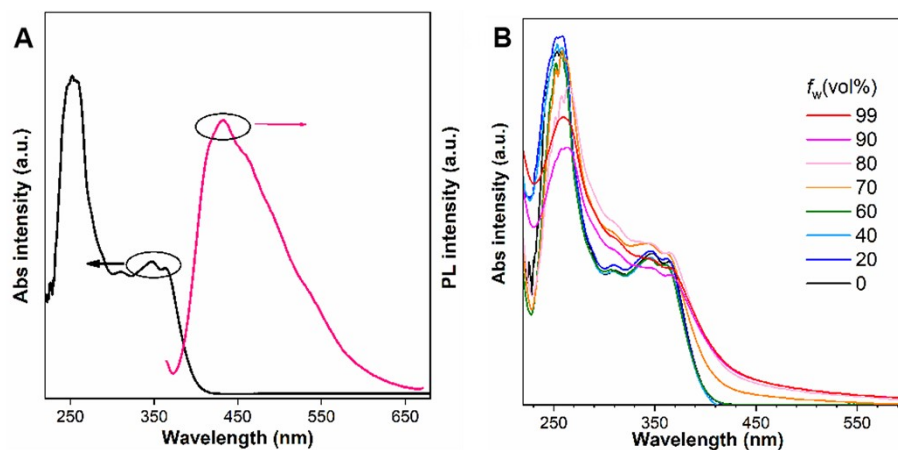


Figure S1. (A) Absorption and emission spectra of **TPEPCI** in THF solvent (concentration: 10^{-5} mol/L). (B) UV-Vis absorption spectra of **TPEPCI** in THF-water mixture solvents with different water fractions (0–99%).

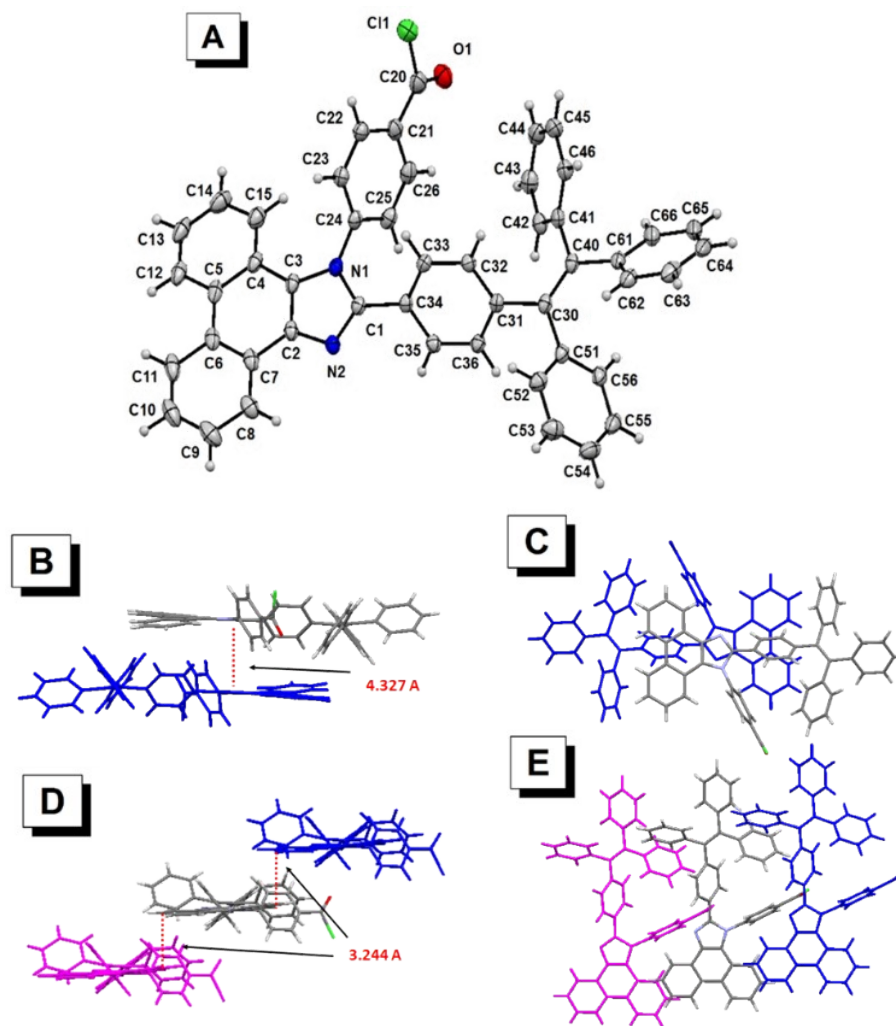


Figure S2. Crystal structure of TPEPCI (A); The interaction packing mode of TPEPCI between two symmetrical conformations from side view (B) and top view (C); The interaction packing mode (D) and (E).

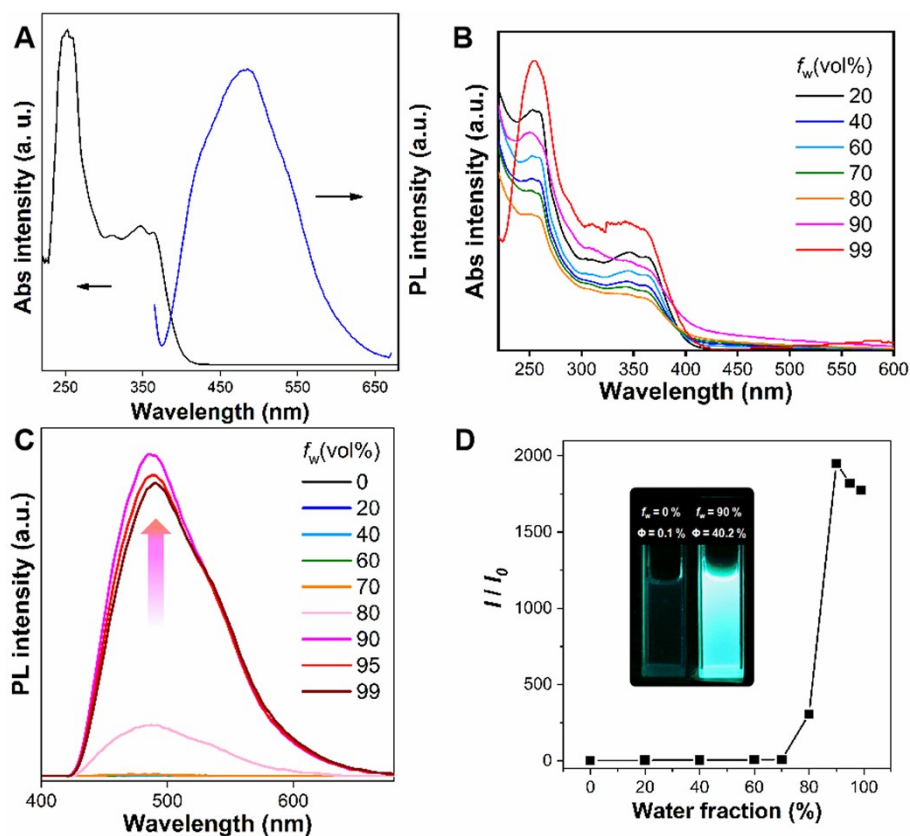


Figure S3. (A) Absorption and emission spectra of **TPEPOH** in THF solvent (concentration: 10^{-5} mol/L); (B) UV-Vis absorption spectra of **TPEPOH** in THF-water mixture solvents with different water fractions (0–99%); (C) Fluorescence emission spectra of **TPEPOH** in THF-water mixture solvents with different water fractions (0–99%); (D) Plots of I/I_0 versus water fractions in THF-water mixtures, where I_0 is the PL intensity in pure THF solution (Inset: fluorescent images of f_w 0 % and 90 %).

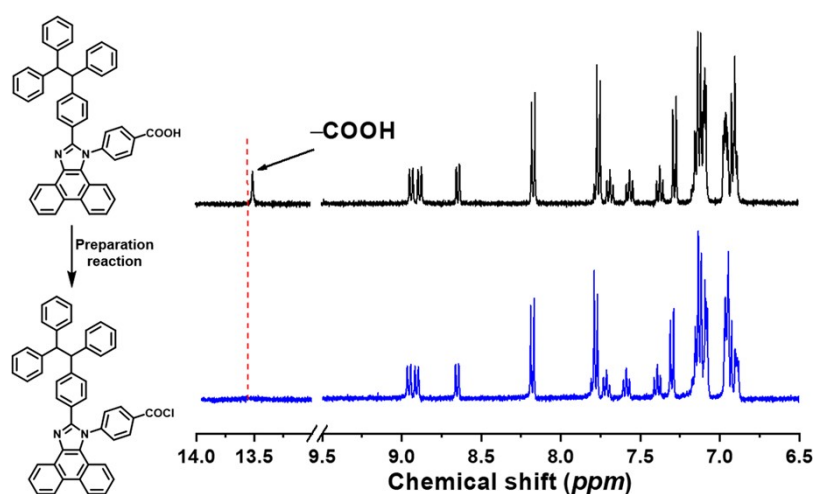


Figure S4. ^1H NMR spectra of **TPEPOH** and **TPEPCL**.

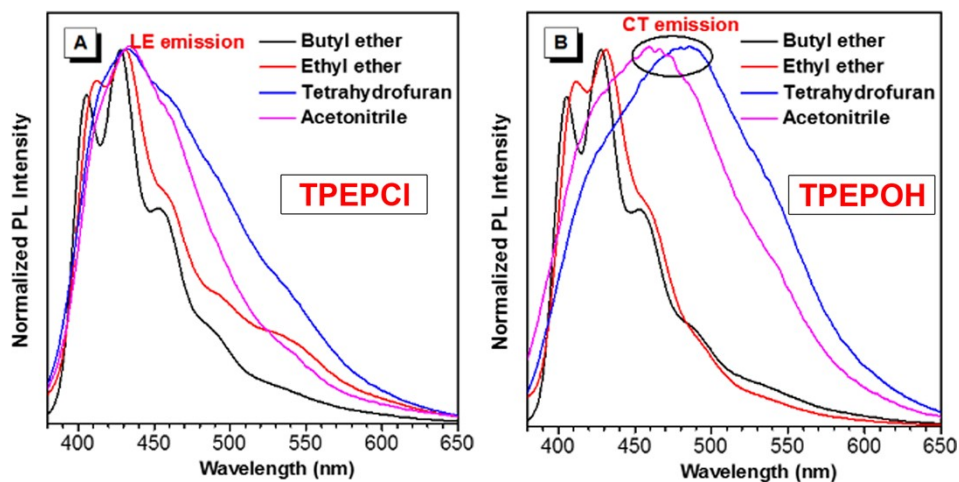


Figure S5. Normalized PL spectra of (A) TPEPOH and (B) TPEPCI in various solvents with different polarities.

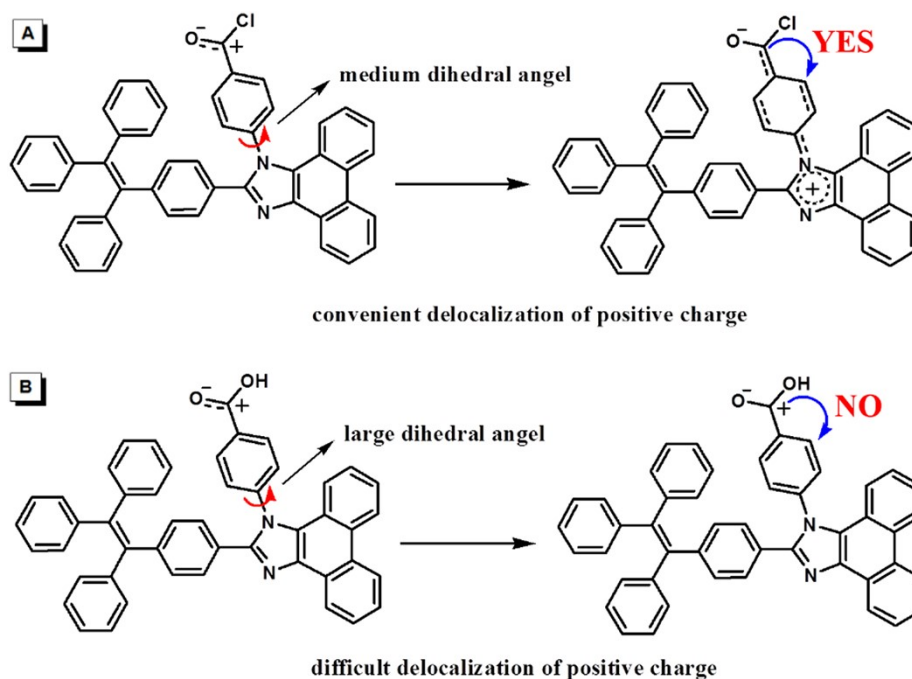


Figure S6. Possible delocalized process of TPEPCI and TPEPOH and their PL spectra in various solvents with different polarity.

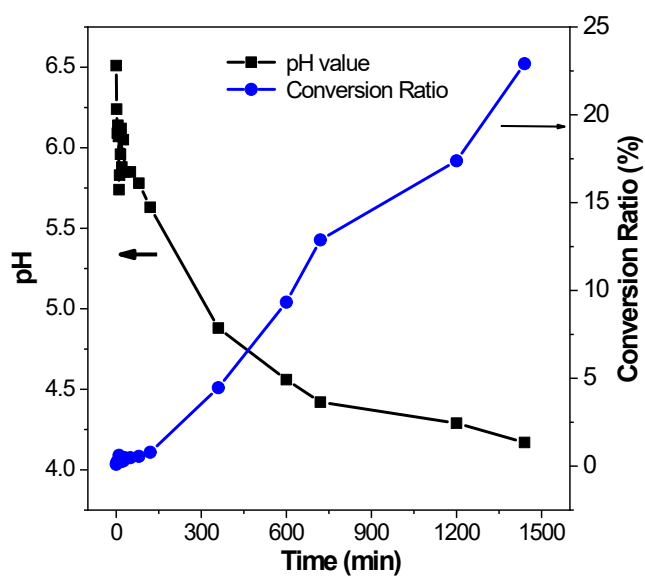


Figure S7. Plots of the pH value and conversion ratio versus time.

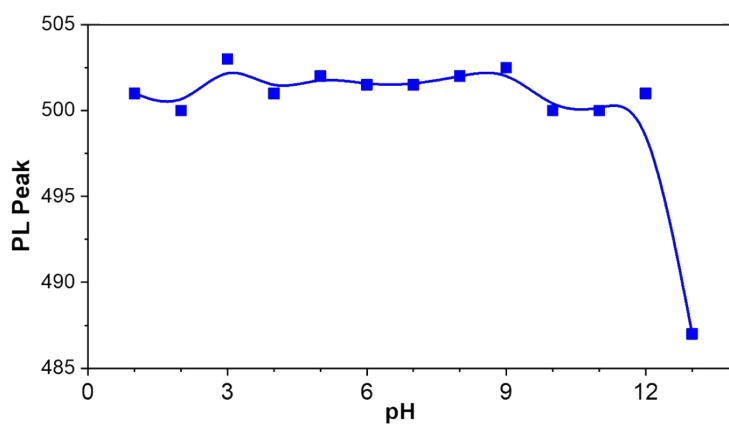


Figure S8. The emission intensity variation of TPEPCI in an aqueous solution with different pH values. (The fluorescence peak locations observed with different buffers ($f_w = 99\%$))

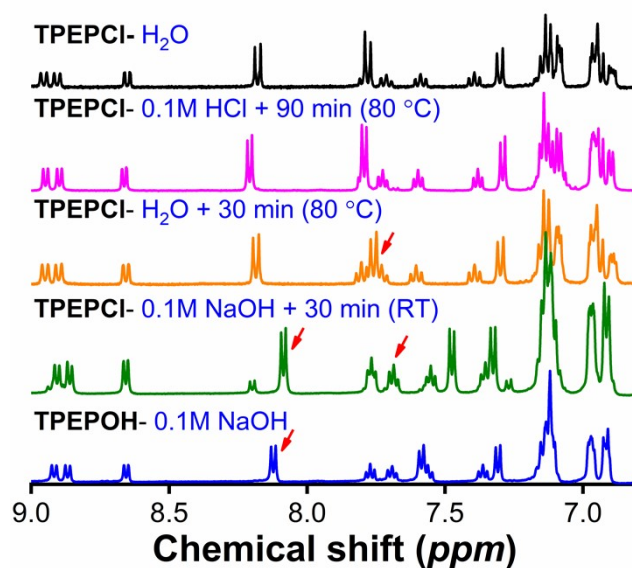


Figure S9. ^1H NMR spectra and dynamics investigation of **TPEPCI**, **TPEPOH** and their transformation: **TPEPCI** in *d*-DMSO/ H_2O ($\nu : \nu = 20 : 1$); **TPEPCI** in *d*-DMSO/0.1 M HCl aqueous solution ($\nu : \nu = 20 : 1$) 120 min (30 min at RT + 90 min at 80 °C); **TPEPCI** in *d*-DMSO/ 0.1M NaOH aqueous solution ($\nu : \nu = 20 : 1$) for 30 min at RT and **TPEPOH** in *d*-DMSO/ 0.1M NaOH aqueous solution ($\nu : \nu = 20 : 1$). (These peaks marked with red arrows are belonged to **TPEPOH** which confirms the appearance of hydrolysis process)

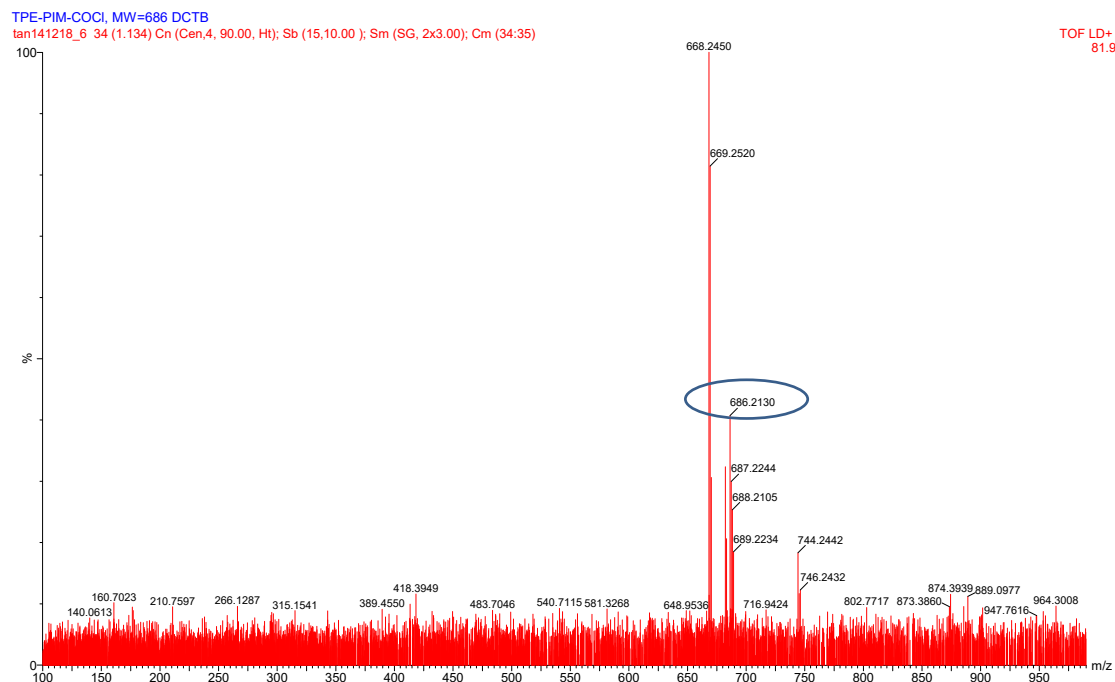


Figure S10. Mass spectrum of **TPEPCI**.