Supporting Information

Pyrazino-[2,3-f][1,10]phenanthroline as a new anchoring group of organic dyes for dye-sensitized solar cells

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Measurement and characterization

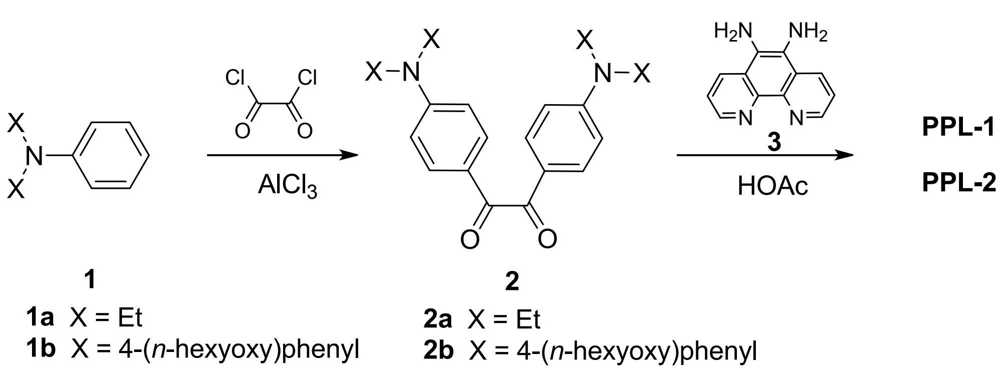
NMR spectra were recorded on a BRUKER AVANCE 400 MHz instrument. The residual solvent protons (^{1}H) or the solvent carbons (^{13}C) are used as internal standards. ^{1}H NMR data are presented as follows: the chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant (Hz), integration). The following abbreviations are used in the reported NMR data: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Fluorescence spectra were determined on a Jasco FP-6600. Cyclic voltammetry spectra were recorded on a Shanghai Chenhua CHI660C electrochemical workstation. Mass spectra were taken on a Bruker Daltonics Inc. spectrometer. The photocurrent–voltage (I–V) characteristics were recorded at room temperature using a computer-controlled Keithley 2400 source meter under air mass (AM) 1.5 simulated illumination (100 mW cm^{-2}, Oriel, 67005). The action spectra of the monochromatic incident photo-to-current conversion efficiency (IPCE) for solar cells were collected using a commercial setup (PV-25 DYE, JASCO). A 300-W Xenon lamp was employed as the light source for generation of a monochromatic beam. Calibrations were performed with a standard silicon photodiode. IPCE is defined as IPCE (λ) = $hcJ_{sc}/e\varphi\lambda$, where h is Planck's constant, c the speed of light in a vacuum, e the electronic charge, λ the wavelength in meters (m), J_{sc} the short-circuit photocurrent density (A m^{-2}), and φ the incident radiation flux (W m^{-2}).

Materials

All of solvents were purified according to standard methods. All reagents were commercially obtained from Alfa Aesar Chemical Co. and J&K Chemical Co. and used without further purification unless otherwise specified. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. 5,6-Diamine -1,10-phenanthroline **3** was synthesized according to the reference procedure.[1]

Synthetic procedures and characterization data

Scheme S1. Synthetic route to **PPL-1** and **PPL-2** dyes



Synthesis of 2a. *N,N*-Diethylbenzenamine **1a** (1.49 g, 10.0 mmol) was dissolved in dichloromethane (40 mL), followed by adding $AlCl_3$ (1.60 g, 12.0 mmol) in several portions at 0 ^{0}C. After stirring at this temperature for 15 min, the mixture solution was added dropwise to a solution of oxalyl dichloride (0.64 g, 5.0 mmol) within 15 min. Then the mixture was warmed to room temperature and stirred for another 10 h. After quenched by adding aqueous 10% HCl (10 mL), the mixture was diluted with dichloromethane (50 mL) and washed with saturated $NaHCO_3$ solution (100 mL), water (100 mL), and brine (100 mL) sequentially. The organic phase was dried over anhydrous $MgSO_4$, concentrated in vacuum, and purified by silica-gel column chromatography (eluting with dichloromethane/petroleum ether, 50/50, v/v) to afford the product **2a** (1.14 g, 65%) as a yellow solid. Mp 83-85 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, *J* = 9.0 Hz, 4H), 6.62 (d, *J* = 9.3 Hz, 4H), 3.42 (q, *J* =6.9 Hz, 8H), 1.19 (t, *J* =6.9 Hz, 12H). ^{13}C NMR (CDCl3, 100 MHz): δ 193.74, 152.05, 132.56, 121.04, 110.44, 44.67, 12.49. MS (MALDI): m/z 375.20 ([M+Na]$^+$).

Synthesis of 2b. The synthetic procedure was the same as synthesis of the compound **2a** except the compound **1b** in place of the compound **1a**. The product **2b** was obtained as a light yellow solid. Yield: 51%. ^{1}H NMR (CDCl3, 400 MHz): δ 7.71, (d, *J* = 9.0 Hz, 4H), 7.09 (d, *J* = 9.0 Hz, 8H), 6.86 (d, *J* = 9.0 Hz, 8H), 6.78 (d, *J* = 9.0 Hz, 4H), 3.94 (t, *J* =6.6 Hz, 8H), 1.73-1.82 (m, 8H), 1.41-1.50 (m, 8H), 1.26-1.36 (m, 16H), 0.91 (t, *J* =6.6 Hz, 12H). ^{13}C NMR (CDCl3, 100 MHz): δ 193.49, 156.95, 138.46, 131.71, 12.02, 124.04, 116.55, 115.52, 31.59, 29.25, 25.74, 22.61, 14.05.. MS (MALDI): m/z 967.56 ([M+Na]$^+$).

Synthesis of PPL-1 and PPL-2. A mixture solution of 5,6-diamine -1,10-phenanthroline **3** (0.42 g, 2.0 mol) and compounds **2a** or **2b** (3.0 mmol) in glacial acetic acid (20 mL) was refluxed for 24 h. After removal of the solvent in vacuum, the residue was dissolved in dichloromethane (100 mL) and washed with saturated $NaHCO_3$ solution (100 mL), water (100 mL), and brine (100 mL), sequentially. The organic phase was dried over anhydrous $MgSO_4$, concentrated in vacuum, and purified by silica-gel column chromatography (eluting with MeOH/dichloromethane, 5/95, v/v) to afford the desired product.

PPL-1 was obtained as a brown solid. Yield: 35%. Mp >180 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.54 (d, *J* = 8.1 Hz, 2H), 9.23 (d, *J* = 4.2 Hz, 2H), 7.72-7.7.77 (m, 6H), 6.69 (d, *J* = 7.2 Hz, 4H), 3.42 (q, *J* = 6.3 Hz, 8H), 1.22 (t, *J* =6.9 Hz, 12H). ^{13}C NMR (CDCl3, 100 MHz): δ 152.41, 151.26, 148.36, 147.18, 136.42, 133.01, 131.22, 127.47, 125.86, 123.62, 111.06, 44.43, 12.63. HR-MS (MALDI): cacld for $C_{34}H_{34}N_6$, 526.2845; found, m/z 527.2906 ([M+1]$^+$).

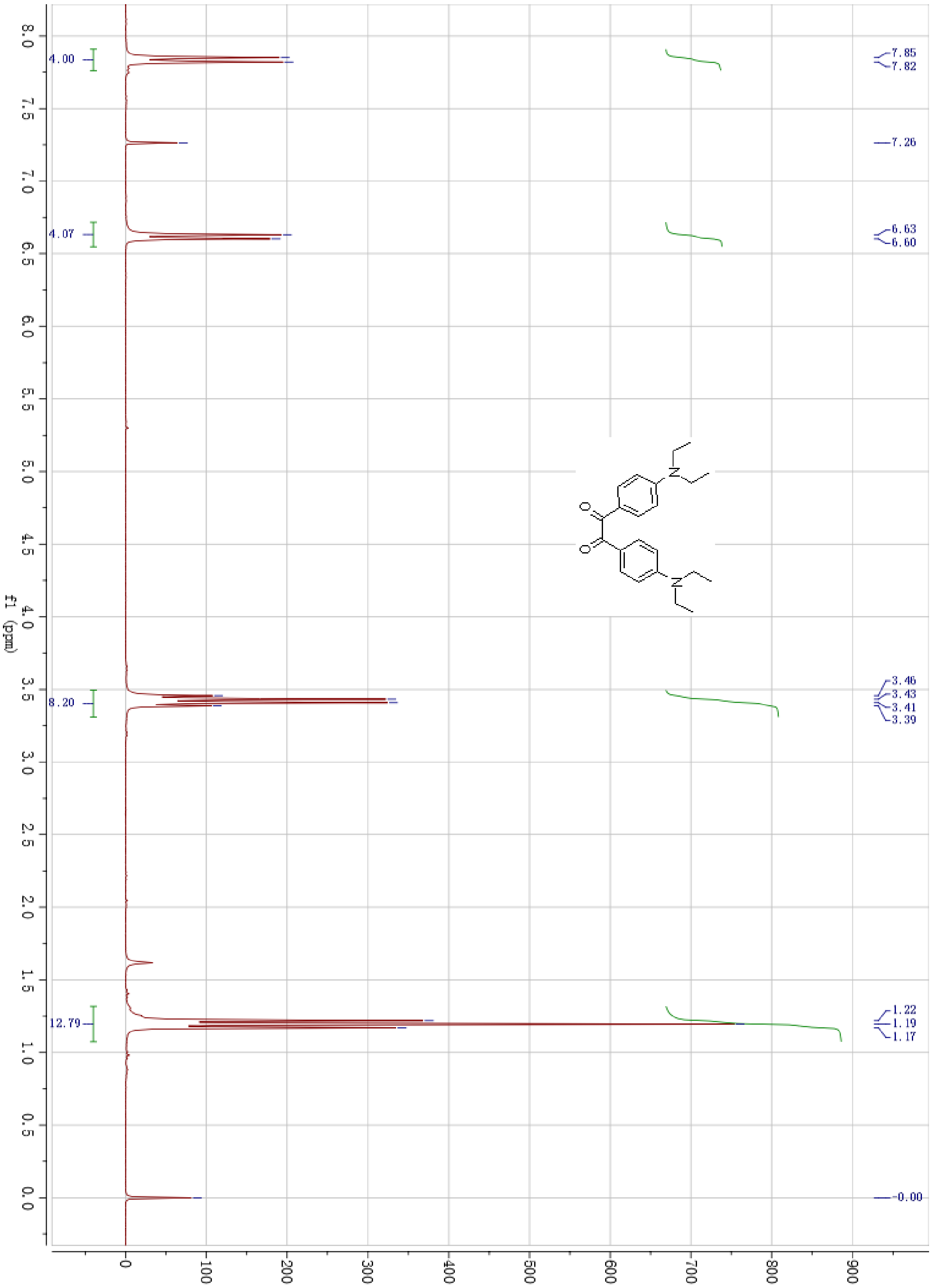
PPL-2 was obtained as a red brown solid. Yield: 30%. Mp >220 ^{0}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.68 (d, *J* = 7.8 Hz, 2H), 9.47 (d, *J* = 4.2 Hz, 2H), 7.92 (d, *J* = 4.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 4H), 7.13 (d, *J* = 9.0 Hz, 8H), 6.86-6.91 (m, 12H), 3.96 (t, *J* =6.6 Hz, 8H), 1.75-1.84 (m, 8H), 1.43-1.50 (m, 8H), 1.26-1.37 (m, 16H), 0.89 (t, *J* =6.9 Hz, 12H).. ^{13}C NMR (CDCl3, 100 MHz): δ

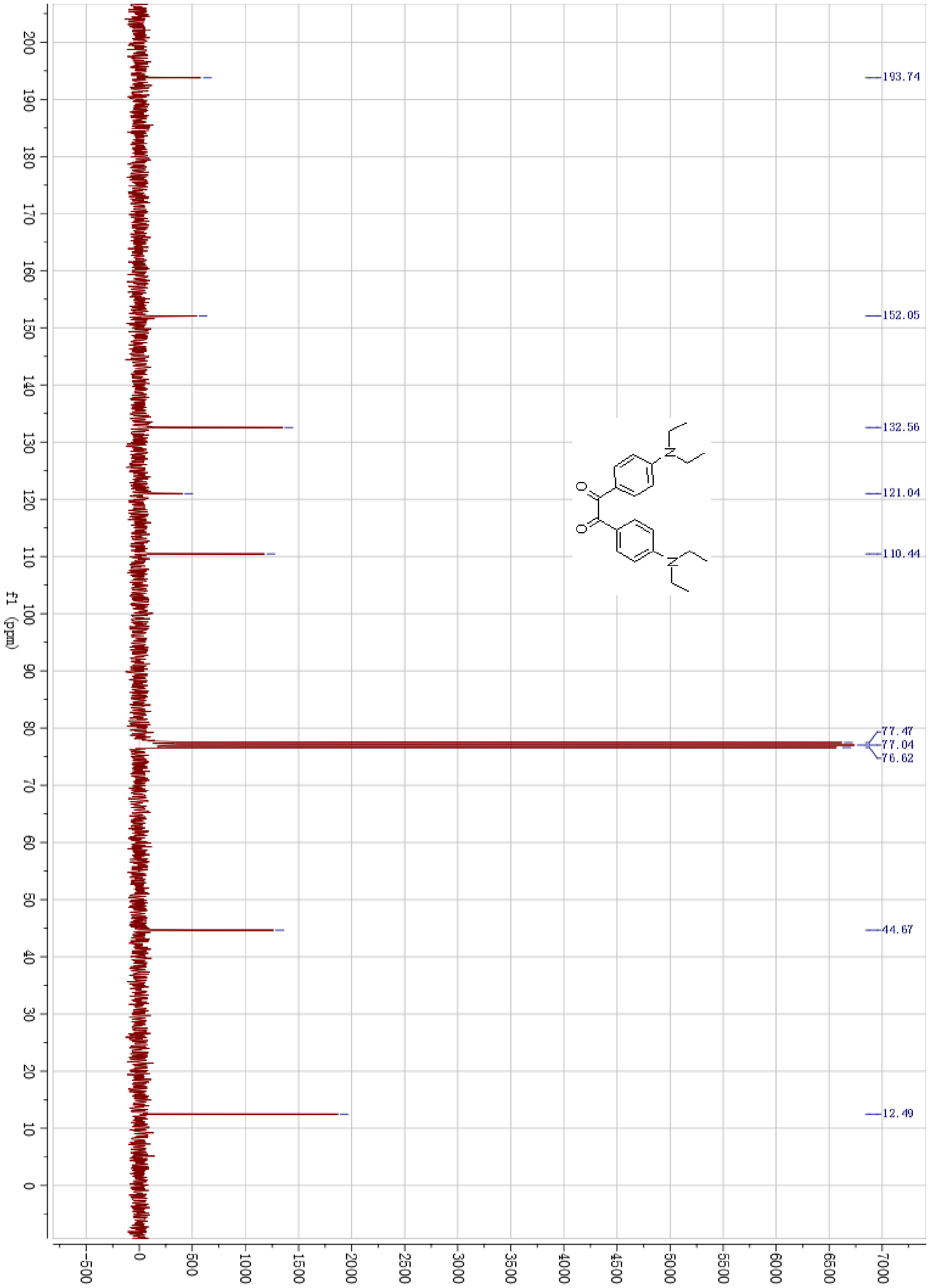
152.41, 151.26, 148.36, 147.18, 136.42, 133.01, 131.22, 127.47, 125.86, 123.62, 111.06, 44.43, 12.63. HR-MS (MALDI): cacld for $C_{74}H_{82}N_6O_4$, 1118.6398; found, m/z 1118.6383 (M^+).

DSC fabrication

The nanocrystalline TiO_2 pastes (particle size, 20 nm) were prepared using a previously reported procedure.[2] Fluorine doped thin oxide (FTO, 4 mm thickness, 10 ohms/sq, Nippon Sheet Glass, Japan) conducting electrodes were washed with soap and water, followed by sonication for 10 min in acetone and isopropanol, respectively. Following a drying period, the electrodes were then submerged in a 40 mM aqueous solution of $TiCl_4$ for 30 min at 75 ^{0}C, and then washed by water and ethanol, respectively. On the electrodes, an 11 μm thick nanocrystalline TiO_2 layer and 6 μm thick TiO_2 light scattering layer (particle size, 400 nm, PST-400C) were prepared by the screen-printing method. The TiO_2 electrodes were heated at 500 °C for 30 min, followed by treating with a 40 mM aqueous solution of $TiCl_4$ for 30 min at 75 ^{0}C and subsequent sintering at 500 ^{0}C for 30 min. The thickness of TiO_2 films was measured by a profiler, Sloan, Dektak3. The electrodes were immersed in a dye bath containing 0.2 mM **PPL-1** or **PPL-2** and 20 mM 3α,7*α*-dihydroxy-5*β*-cholic acid (chenodeoxycholic acid) in a 4-*tert*-butanol/acetonitrile/tetrahydrofuran solvent mixture (1:1:0.2, v/v) and kept for 24 h at room temperature. The dyed electrodes were then rinsed with the mixed solvent to remove excess dye. A platinum-coated counter electrode was prepared according to the previous report, [3] and two holes were drilled on its opposite sides. The two electrodes were sealed together with a 25 μm thick thermoplastic Surlyn frame. An electrolyte solution was then introduced through one of the two holes in the counter electrode, and the holes were sealed with the thermoplastic Surlyn. The electrolyte contains 0.68 M dimethyl imidiazolium iodide, 0.05 M iodine, 0.10 M LiI, 0.05 M guanidinium thiocyanate, and 0.40 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (85:15, v/v). All the devices were prepared with a photoactive area of about 0.3 cm^2, and a metal mask of 0.165 cm^2 was covered on the device for photovoltaic property measurements.

^{1}H and ^{13}C NMR spectra of the compounds





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121.04
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44.67
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180
170
160
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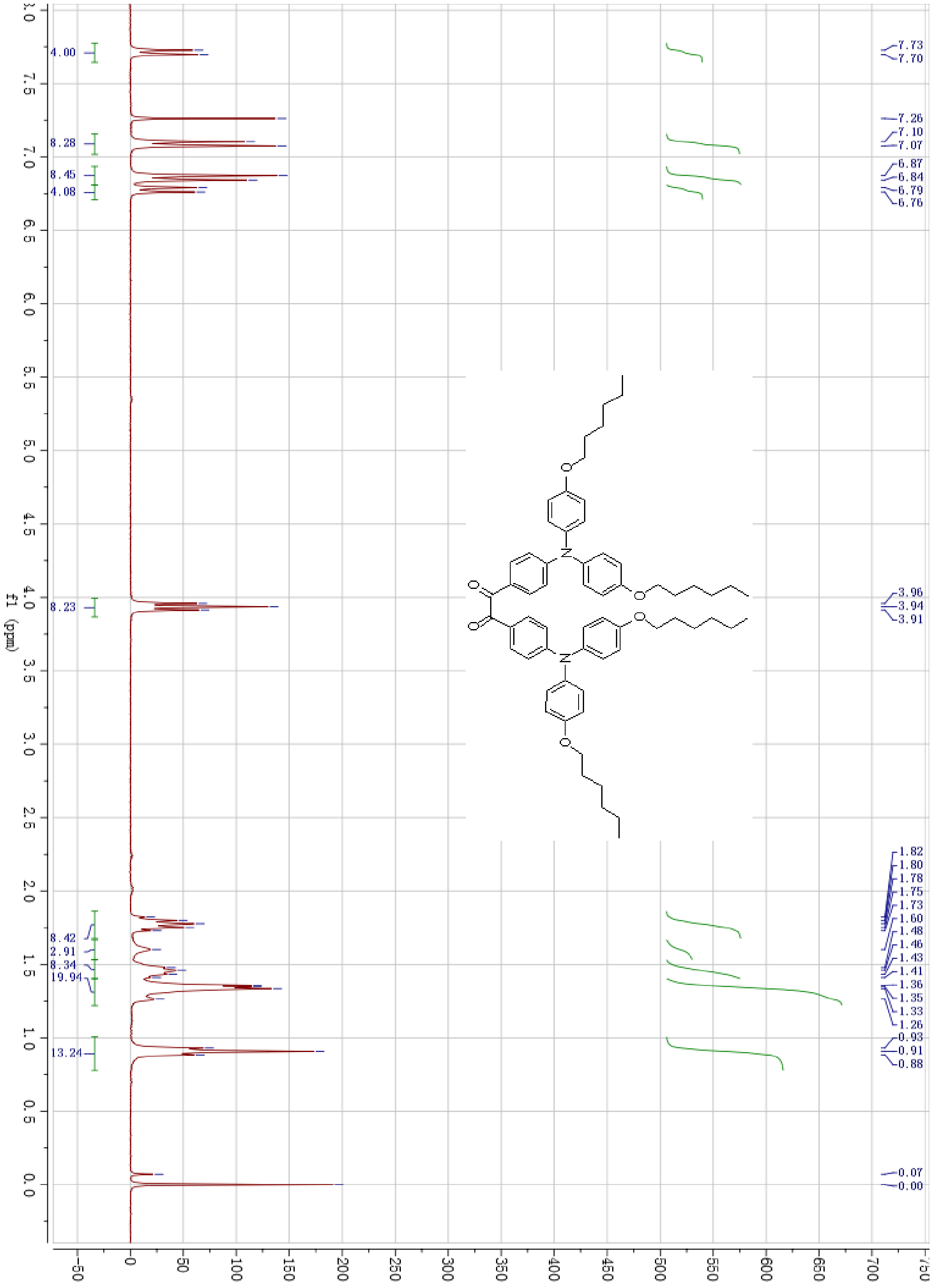

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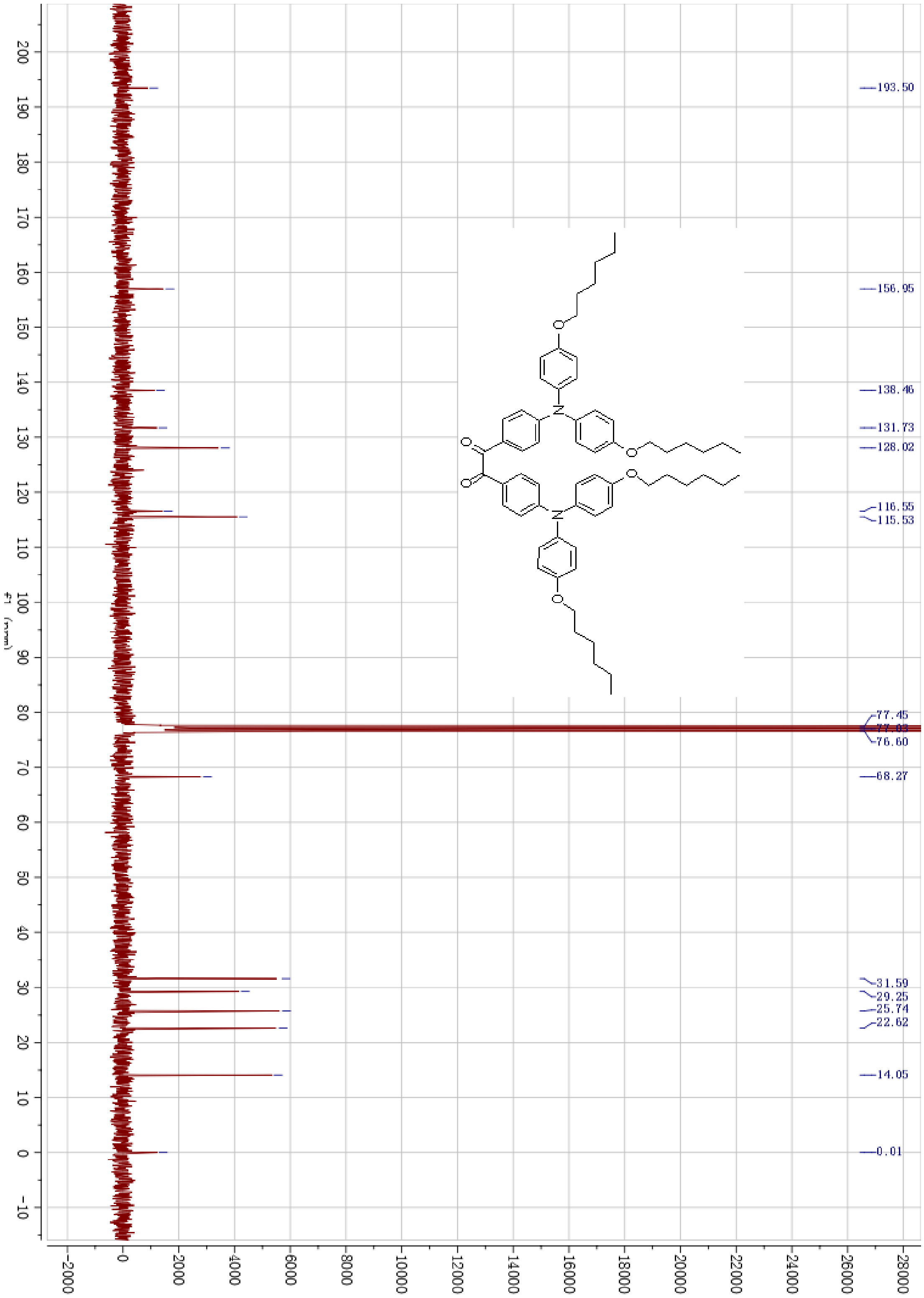
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14.05
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150
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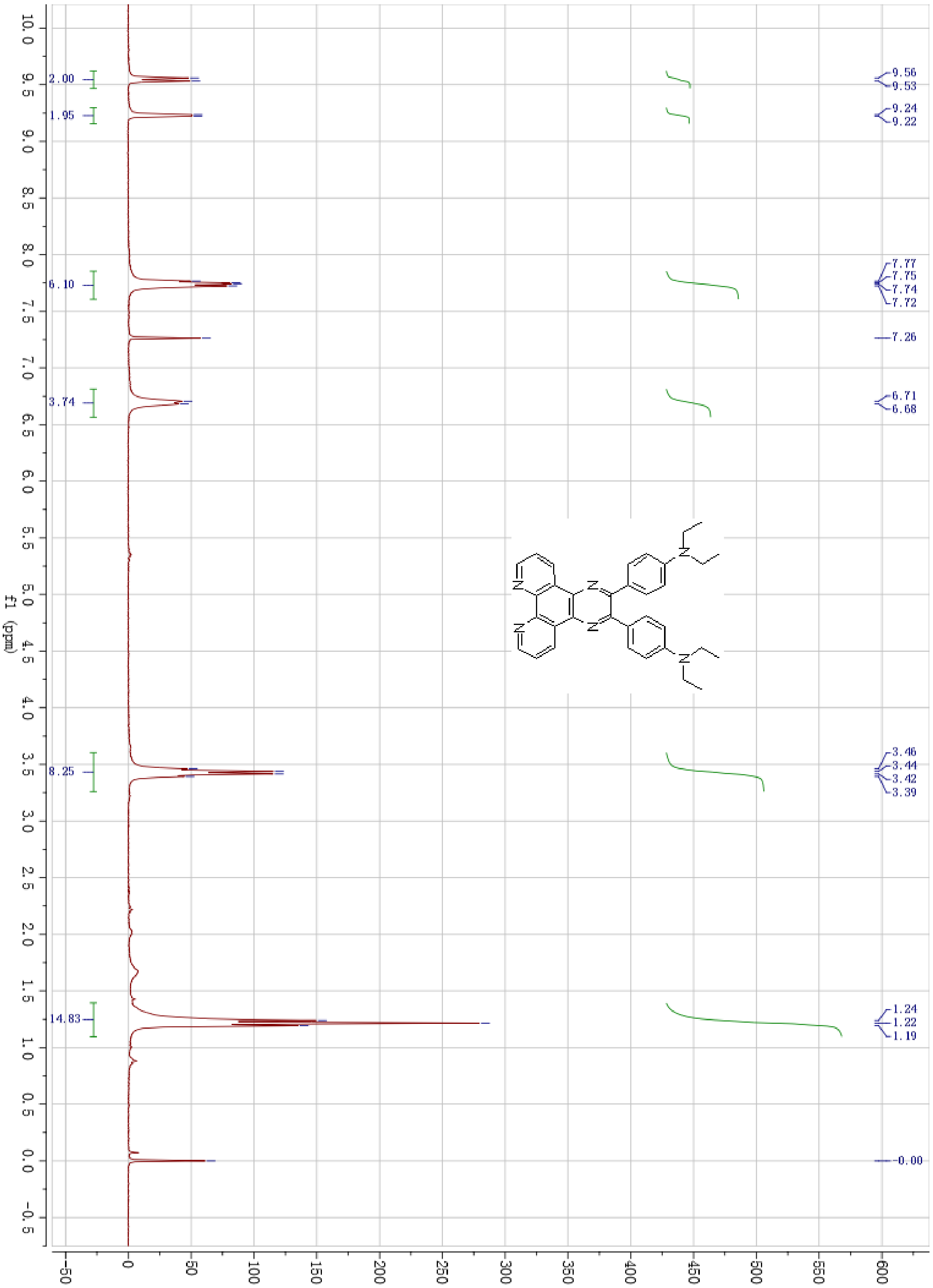

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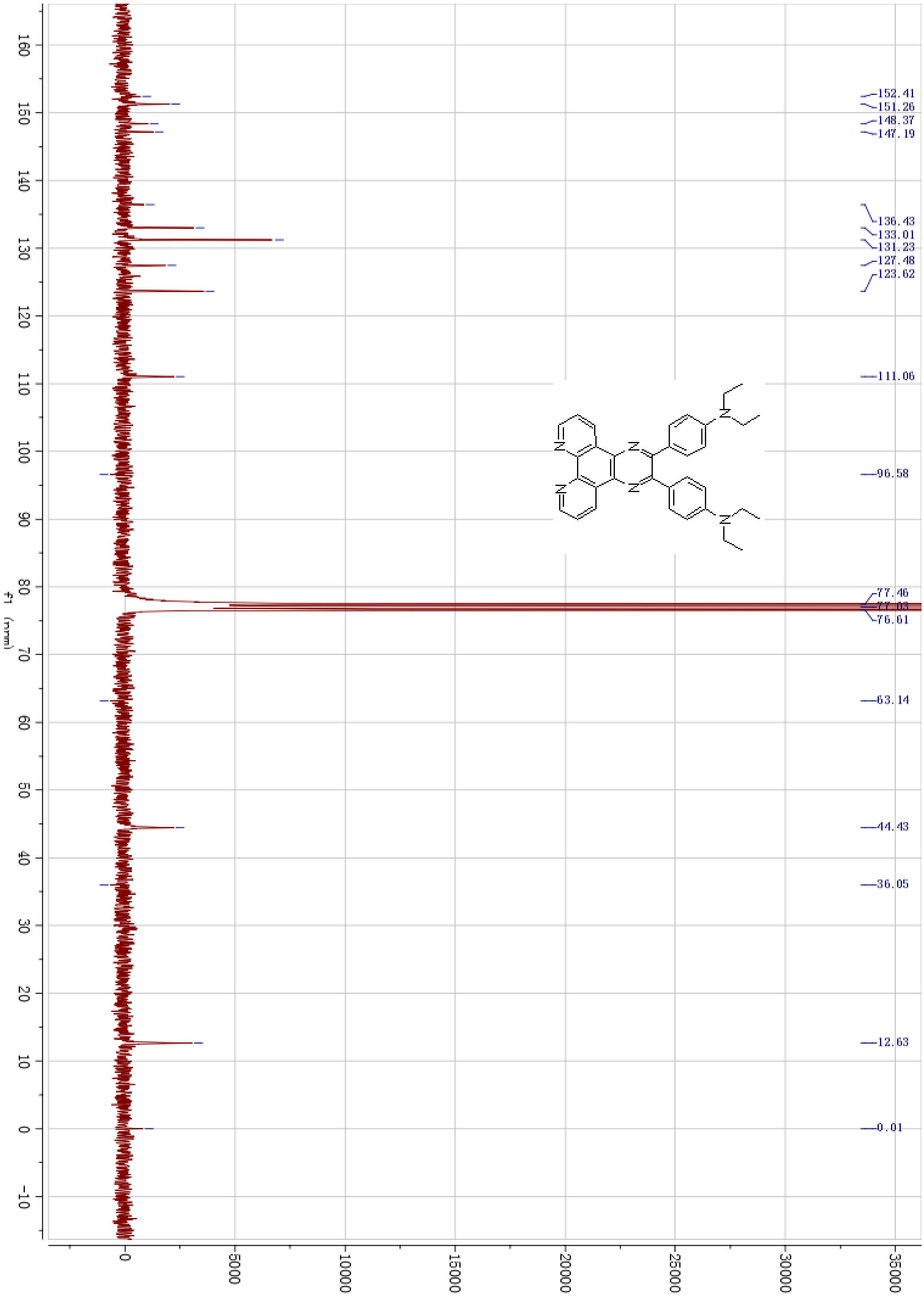
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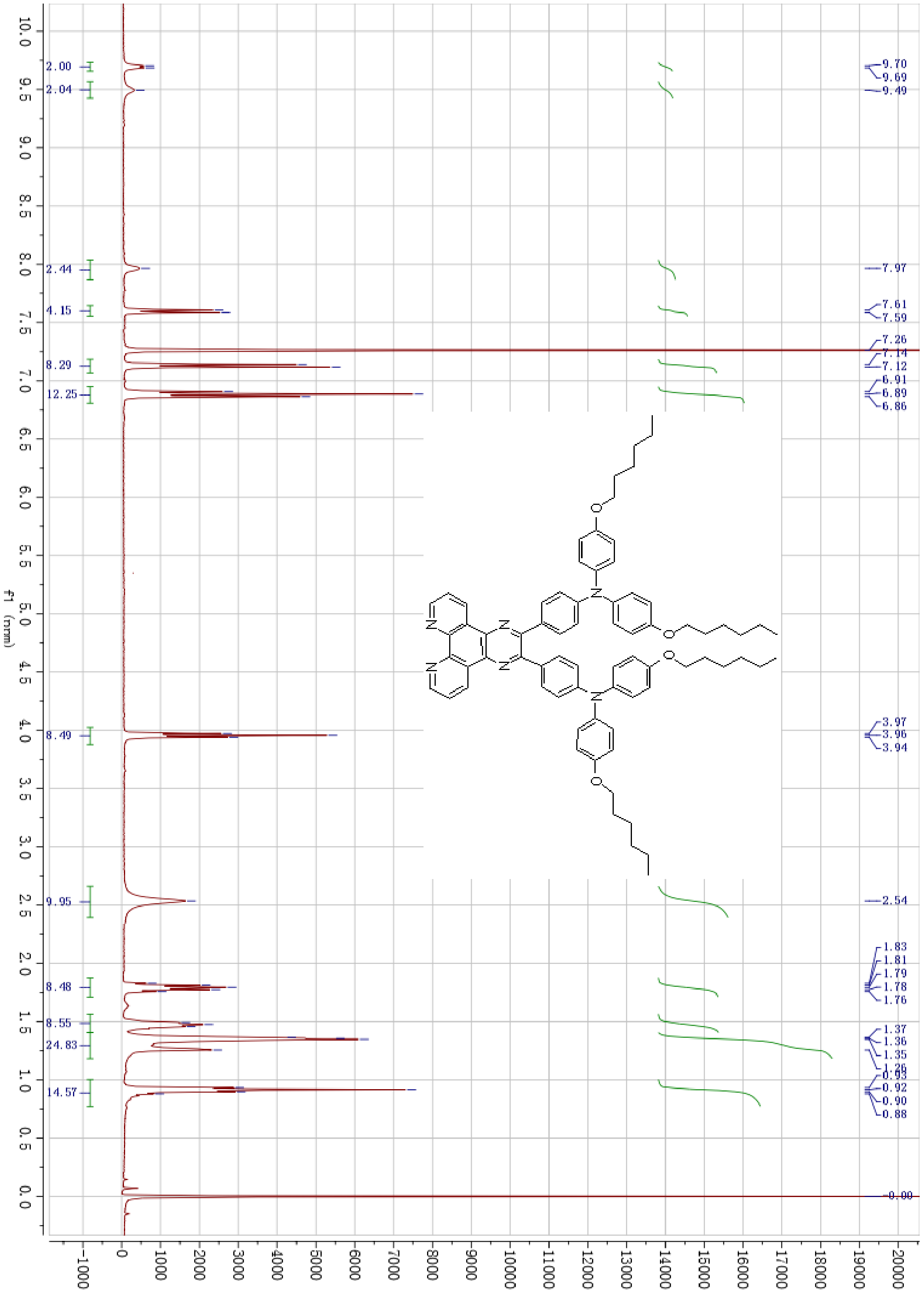
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18000
19000
20000
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8.29
12.25
8.49
9.95
8.48
8.55
24.83
14.57
9.70
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9.49
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7.61
7.59
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7.14
7.12
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6.89
6.86
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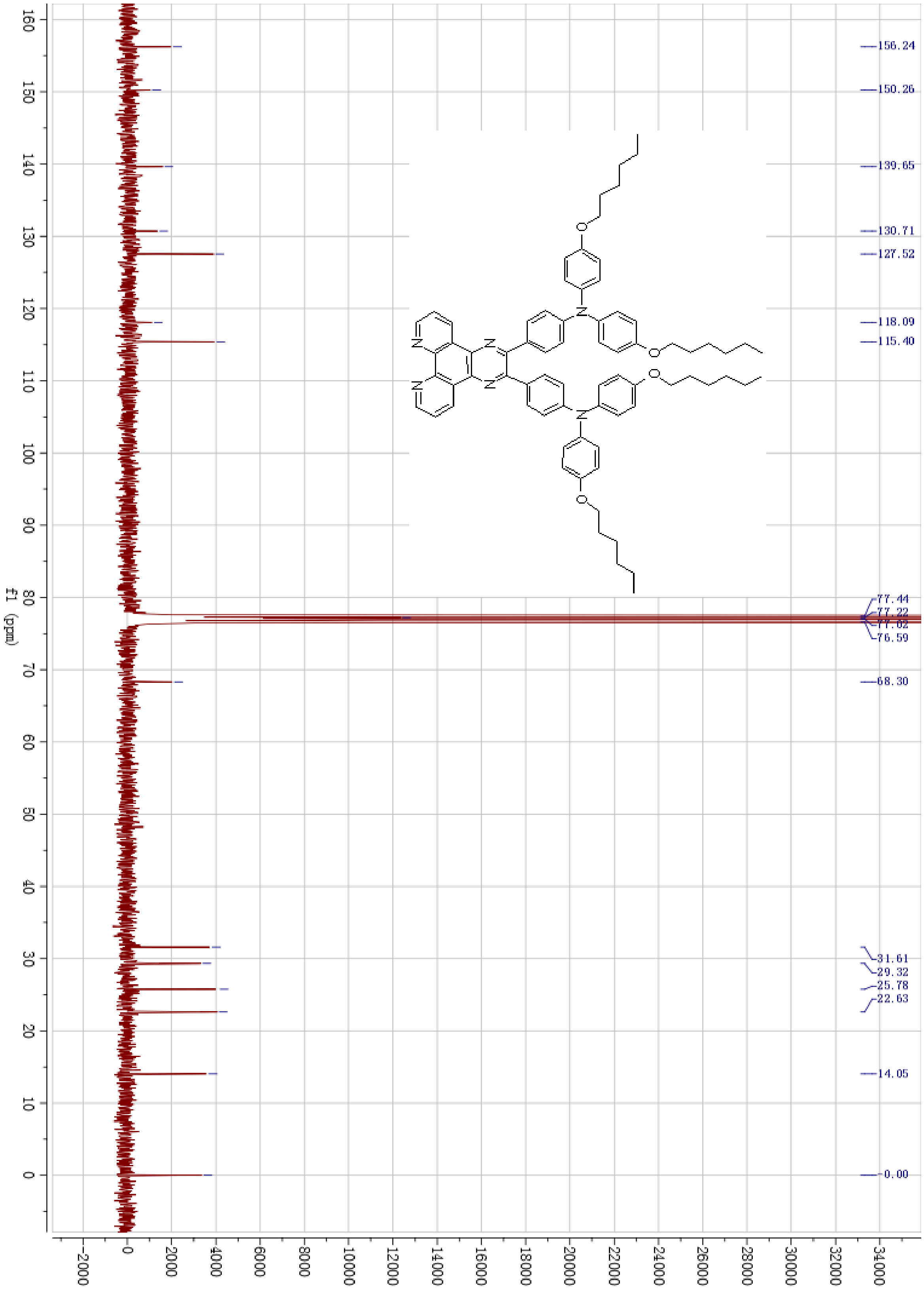
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f1 (ppm)
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Dye desorption experiment

The prepared nanocrystalline TiO_2 electrodes were heated at 500 °C for 30 min, followed by treating with a 40 mM aqueous solution of $TiCl_4$ for 30 min at 75 ^{0}C and subsequent sintering at 500 ^{0}C for 30 min. The electrodes were immersed in a dye bath containing 0.2 mM **PPL-1** or **PPL-2** and **N719** in anhydrous ethanol and kept for 24 h at room temperature. For determining the absorption abilities of dyes on the film, the dye-coated FTO electrodes were immersed in an aqueous NaOH solution of 0.3 wt% at r.t. for 12h. Figure S1 is the UV spectra of **PPL-1**, **PPL-2** and **N719** on the film. Black, red, and blue lines represent the absorption amounts of dyes **N719, PPL-1**, and **PPL-2**, respectively, while pink line and green line represent the absorption amount of dye **PPL-1** and **PPL-2** after desorption in the aqueous NaOH solution for 12 h. **N719** with the carboxylic group as anchoring moiety was desorbed completely when being immersed in NaOH solution in less than 30 seconds. The difference of the absorption amounts before and after desorption of dye **N719**, **PPL-1** and **PPL-2** indicates that pyrazino-[2,3-f][1,10]phenanthroline containing dyes have stronger binding strength onto TiO_2 electrodes than the classical carboxyl group-containing dye **N719**.

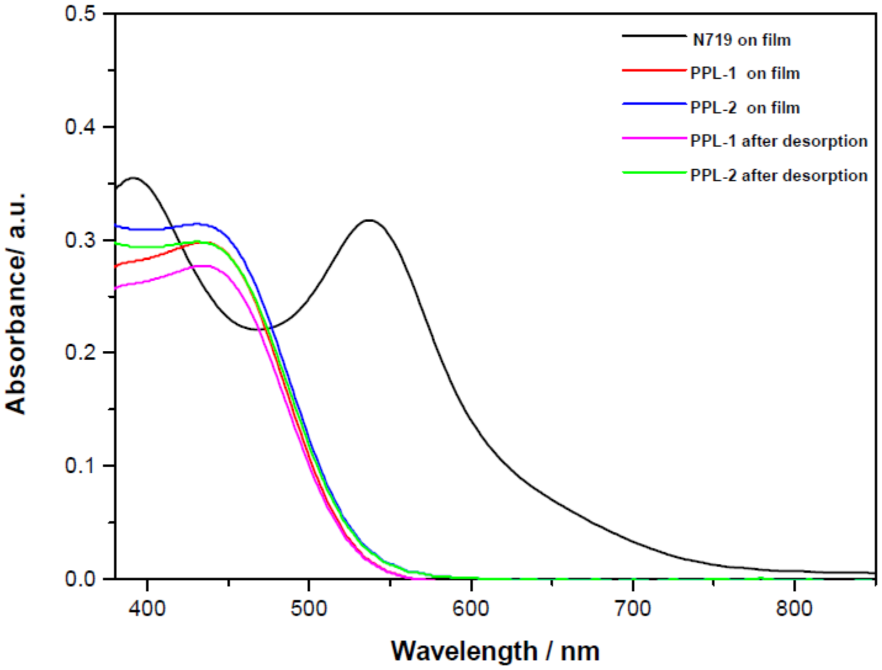

Fig.S1 The UV spectrum of **PPL-1**, **PPL-2** and **N719** on film.

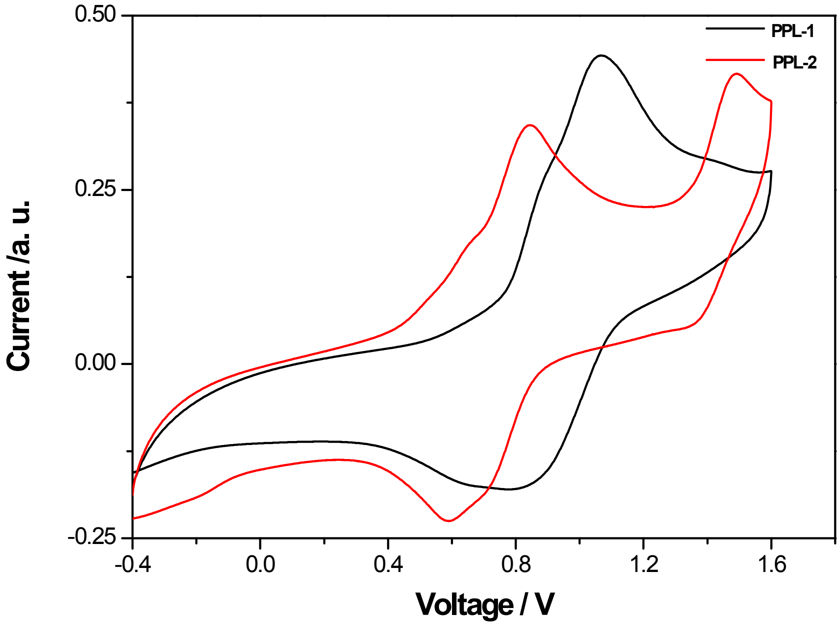

Fig.S2 The cyclic voltammetry grams of **PPL-1** and **PPL-2**.

References

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(2) P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker and M. Gr¨atzel, *J. Phys. Chem. B*, 2003, **107**, 14336.

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