Supporting Information

Efficient Nonlinear-Optical Behaviors of Chiral-Amide-Bonded Porphyrin Noncovalent Functionalized MWCNTs by Terminated Pyrene Units

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1. Experimental Section

General

^{1}HNMR spectra was recorded on a Bruker AVANCE 400 spectrometer (operating at 400.03 MHz). Residual solvent peaks were used to provide internal references for the ^{1}H NMR spectra (δ = 7.26 ppm for $CDCl_3$, δ = 5.32 ppm for CD_2Cl_2). All reagents and solvents used were of reagent grade and were used as received unless noted otherwise. Cyclic voltammetry was carried out on a Chi-730D electrochemistry station with a three-electrode cell. A glassy carbon disk, a platinum wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. The UV and visible regions of the electronic absorption spectra were recorded with an HP 8453A diode array spectrophotometer. A JASCO J-815 spectrodichrometer was used to measure circular dichroism spectra. Electrochemical impedance spectroscopy (EIS) was recorded at frequencies ranging from 10-2 to 106 Hz with an amplitude of 6 mV. Steady-state fluorescence spectra were measured on a Fluoro-Max-P instrument; samples with a concentration of 5.0 ×10^{-5} mol/L were dissolved in dry DMSO, filtered, transferred to a long quartz cell, and then capped and deoxygenated by bubbling with N_2 before measurement.

The open-aperture Z-scan measurements were carried out by using a mode-locked Nd:YAG laser (Continuum, Surelite II) operating at 532, with a 4 ns pulse width. All samples with the concentration of 0.1 mg/mL in DMSO were tested in 1 mm quartz cells at room temperature by using 30 cm focal length lens. The incident energy and transmittance were monitored by two energy detectors (Rjp-765 energy probes), which were linked to an energy meter (Rj-7620 Energy Ratiometer, Laser probe). The sample positioned at the focal point (z = 0) is moved along the z-axis of the incident beam, and the normalized transmittance of the sample as a function of position can be obtained. The laser intensity is 0.3 J. A low pulse repletion frequency of 2 Hz and single shot mode were employed to fire the laser pulses in order to void the thermal effects in the NLO measurements.

5-*p*-Aminophenyl-10,15,20-triphenylporphyrin 1.

Nitrosonitric acid (3.2 mL) was slowly added to 300 mL CH_2Cl_2 of 5,10,15,20-tetrahenylporphyrin (3.00 g, 4.88 mmol), and the mixture was stirred at 0–5°C in an ice-bath for 4 h. The reaction mixture was neutralized with ammonia solution to ca. pH = 7.0, and the organic layer was washed with brine and dried with anhydrous $MgSO_4$. After removal of the solvent, the residue was recrystallized from CH_2Cl_2 and MeOH and finally purified by Al_2O_3 gel chromatography (eluent: CH_2Cl_2/hexane = 2:1) to give 5-*p*-nitrophenyl-10,15,20-triphenylporphyrin as a purple solid. $SnCl_2{\cdot}2H_2O$ (2.0 g, 1.62 mmol) was then added to a 100 mL conc. HCl solution of 5-*p*-nitrophenyl-10,15,20-triphenylporphyrin (916 mg, 0.400 mmol). The mixture was vigorously stirred in a preheated oil bath 70°C for 2 h, and then neutralized to around pH = 8.0 with ammonia solution. The reaction mixture was quenched by 50 mL ice-water and the water phase was extracted with ethylacetate (3 × 100 mL). The combined organic layers were dried with anhydrous $MgSO_4$. After removal of the organic solvent, the residue was purified through recrystallization by adding MeOH to the CH_2Cl_2 solution to afford pure 5-*p*-aminophenyl-10,15,20-triphenylporphyrin **1** as a purple solid. Yield: 767 mg, 87.3%. ^{1}H NMR ($CDCl_3$, 298 K): δ = 8.93 (d, J = 4.0 Hz; 2H), 8.84 (s, 6H), 8.20 (d, J = 8.0 Hz; 2H), 7.98 (d, J = 8.0 Hz; 2H), 7.74~7.80 (m, 9H), 7.06 (d, J = 8.0 Hz; 2H), 4.02 (s, 2H), –2.76 (s, 2H).

Synthesis of L-3a. 5-*p*-aminophenyl-10,15,20-triphenylporphyrin **1** (0.28 g, 0.0004 mol), BOC-L-alanine (0.189 g, 0.002 mol) and dicyclohexylcarbodiimide (DCC, 0.3 g, 0.015 mol) was mixed in 35 mL CH_2Cl_2 and stirred at room temperature for 6 h, after removal the solvent, the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2) to give the target compound. After removal of the solvent, the residue was dissolved in 30 mL CH_2Cl_2 again and 10 mL concentrated HCl was added. The mixture was stirred at room temperature for 1 h and neutralized by amino solution. The organic phase was collected and purified by silica gel column chromatography (CH_2Cl_2:MeOH = 98:2; v:v) to give target compound **L-3a** in 57% yield (150 mg). ^{1}H NMR ($CDCl_3$, 298 K) δ_H, ppm 9.93 (s, 1H), 8.86 (d, *J* = 16.0 Hz, 9H), 8.20 (t, J = 8.6 Hz, 9H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 9H), 3.86 (s, 1H), 1.61 (d, *J* = 6.8 Hz, 3H), –2.78 (s, 2H).

Synthesis of D-3a. The general synthetic procedure was similar with that of **L-3a**, only the BOC-D-lalanine was used instead. **D-3a** was obtained in 85.9% yield (280 mg). ^{1}H NMR ($CDCl_3$, 298 K) δ_H, ppm 10.02 (s, 1H), 8.84 (d, *J* = 19.9 Hz, 9H), 8.12 (dd, *J* = 57.0, 11.2 Hz, 11H), 7.71 (d, *J* = 20.4 Hz, 9H), 3.97 (s, 1H), 1.65 (s, 3H), –2.79 (s, 2H).

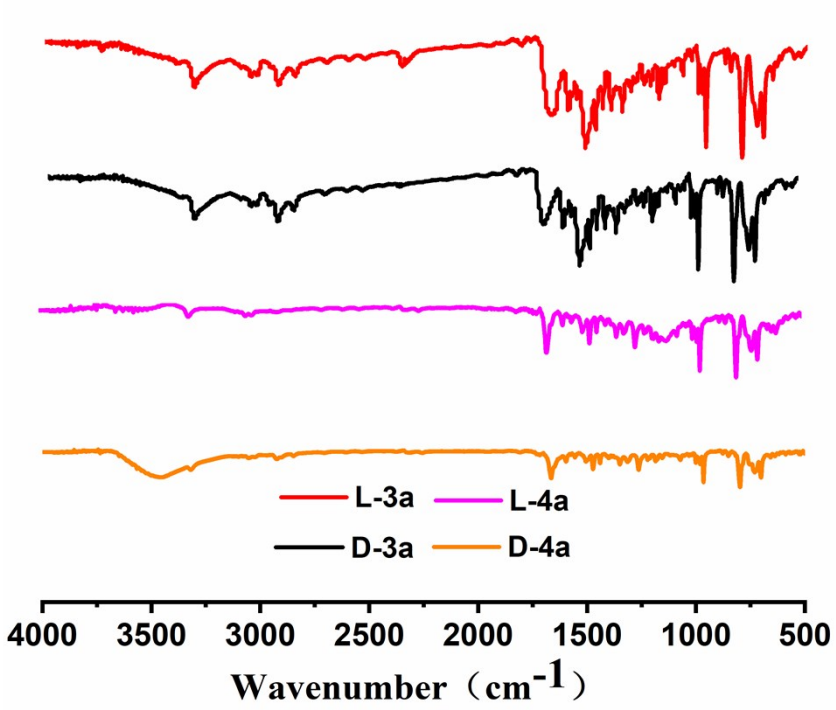

Figure S1 FT-IR spectra of **L/D-3a** and **L/D-4a**.

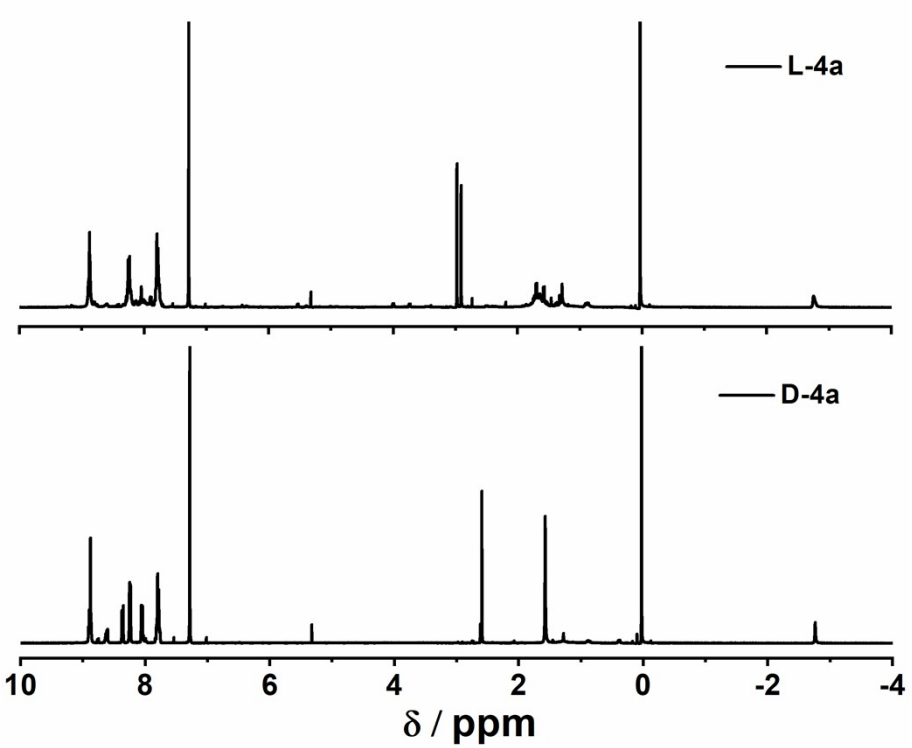

Figure S2 ^{1}HNMR spectrum of chiral porphyrins **L/D-4a** in $CDCl_3$.

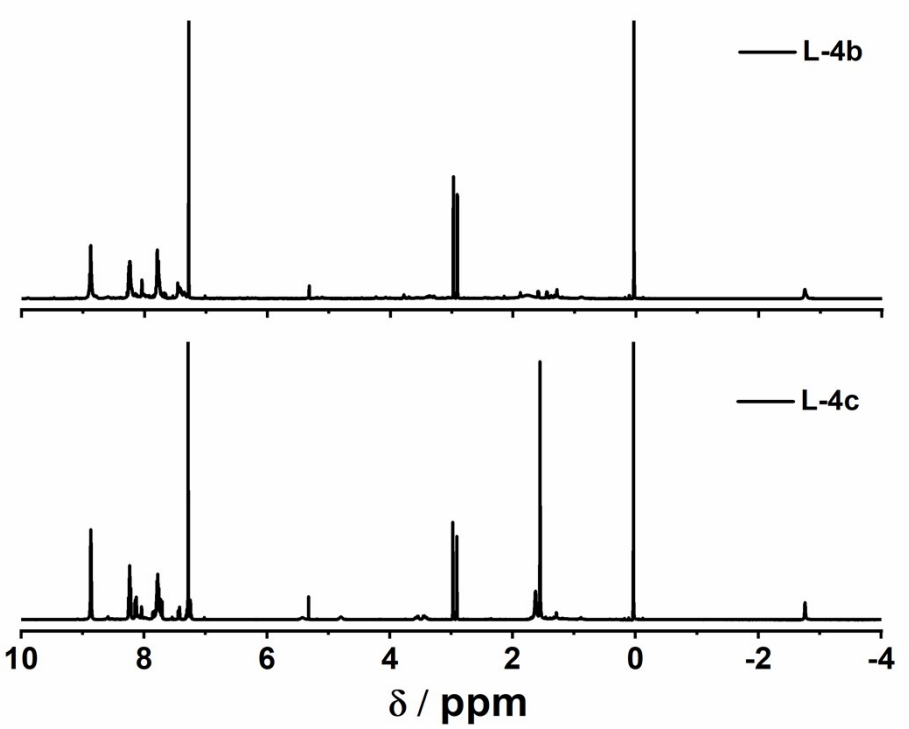

Figure S3 ^{1}HNMR spectrum of chiral porphyrins **L-4b** and **L-4c** in $CDCl_3$.

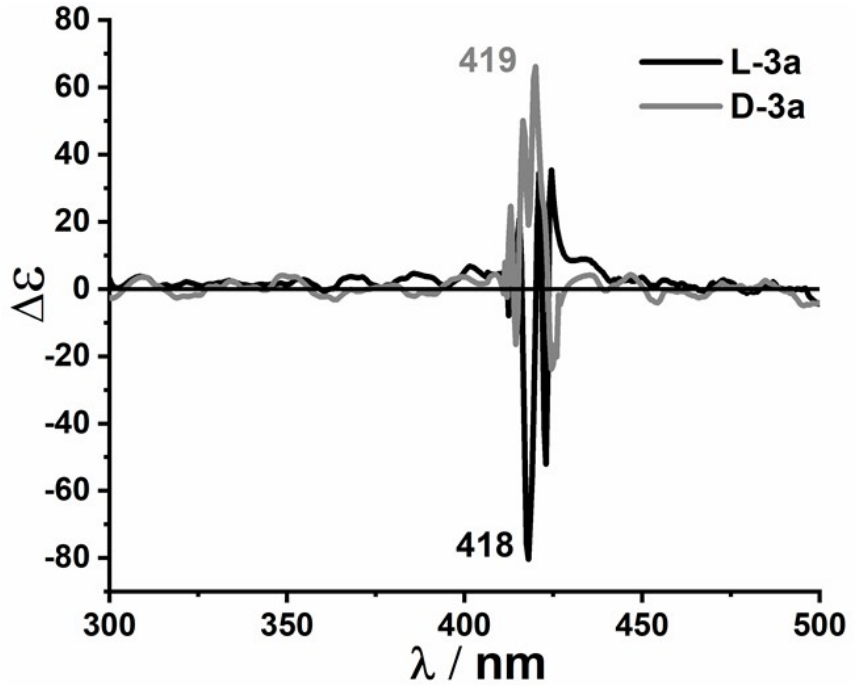

Figure S4 Circular dichroism (CD) spectra of **L/D-3a**