Highly Fluorescent One-handed Nanotubes from a Chiral Asymmetric Perylene Diimide

Xiaojie Ma[a‡], Yibin Zhang[a‡], Yingxuan Zheng[a], Yifan Zhang[a], Xia Tao[b], Yanke Che[a]*, Jincai Zhao[a]

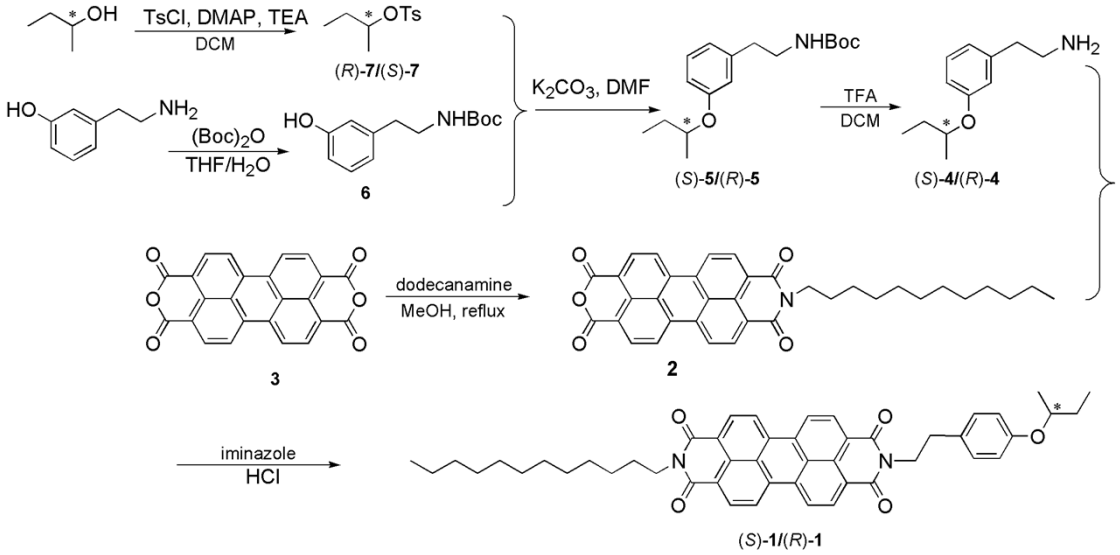
[a] *Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: ykche@iccas.ac.cn*

[b] *State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China*

‡ These authors contributed equally to this work.

Contents

1. General procedure for synthesis of the chiral asymmetric PDI molecules (*R/S*)-1



Scheme S1. Synthesis procedure for chiral asymmetric PDI molecules (*R/S*)-**1**.

All reagents and solvents were purchased from commercial sources and used without further purification.

Compound (*R*)-7. A solution of (*R*)-butan-2-ol (5.008 g, 67.57 mmol) in dichloromethane (100 mL) was added dropwise to a stirred solution of 4-toluene sulfonyl chloride (14.13 g, 74.13 mmol), 4-dimethylaminopyridine (825 mg, 6.76 mmol), and triethylamine (13.64 g, 134.8 mmol) in dichloromethane (120 mL) at 0 °C. Then the mixture was cooled to room temperature and stirred overnight. The solution was then washed with saturated $NaHCO_3$ (100 mL) and H_2O (3 × 100 mL). The combined aqueous layers were extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over sodium sulfate, and concentrated under vacuum. The residue was purified by column chromatography (silica, hexanes : ethyl acetate = 20 :1) to afford (***R***)-**7** (11.5 g) as a colorless oil. (*S*)-**7** was obtained by the same procedure**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 2H), 7.31 (d, 2H), 4.33-4.37 (m, 1H), 2.42 (s, 3H), 1.51-1.61 (m, 2H), 1.22 (d, 3H), 0.78 (t, 3H).

Compound 6. Di-tert-butyldicarbonate (3.56 g, 16.3 mmol) was added to a solution of 3-(2-aminoethyl)phenol (2.23 g, 16.3 mmol) in H_2O (25 mL) and tetrahydrofuran (60 mL) at room temperature. The mixture was stirred overnight at room temperature. Then tetrahydrofuran was removed by rotary evaporation and the resulting aqueous residue was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over sodium sulfate, and concentrated under vacuum. The residue was purified by column chromatography (silica, hexanes: ethyl acetate = 5:1) to afford **6** (3.2 g).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (br, 1H), 7.13 (t, 1H), 6.73 (d, 1 H), 6.67-6.69 (m, 2H), 4.73 (br, 1H), 3.49 (t, 2H), 2.70 (t, 2H), 1.44 (s, 9H).

Compound (*S*)-**5.** K_2CO_3 (121 mg, 0.880 mmol) was added to a solution of (*R*)-**7** (200 mg, 0.880 mmol) and **6** (208 mg, 0.880 mmol) in N,N-dimethylformamide (6 mL), the mixture was stirred overnight at 80 °C under N_2. The reaction was quenched by the addition of H_2O (10 mL) and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over sodium sulfate, and concentrated under vacuum. The residue was purified by column chromatography (silica, hexanes: ethyl acetate = 5:1) to afford compound (*S*)-**5** (80 mg). **Compound** (*R*)-**5** was obtained by the same procedure**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, 1H), 6.72-6.76 (m, 3H), 4.54 (br, 1H), 4.32-4.37 (m, 1H), 3.37 (t, 2H), 2.75 (t, 2H), 1.70-1.77 (m, 1H), 1.59-1.65 (m, 1H), 1.43(s, 9H), 1.28 (d, 3H), 0.96 (t, 3H).

Compound (*S*)-**4.** Compound (*S*)-**5** (80 mg, 0.27 mmol) was added to a mixture solution of dichloromethane (5 mL) and trifluoroacetic acid (3 mL). The reaction was stirred for 3 h at room temperature, then trifluoroacetic acid was removed by rotary evaporation. After the addition of saturated $NaHCO_3$ (20 mL), the resulting solution was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over sodium sulfate, and concentrated under vacuum to afford compound (*S*)-**4,** which was not purified and used directly for the following reaction. **Compound** (*R*)-**4** was obtained by the same procedure**.**

Compound 2. Compound **3** (200 mg, 0.510 mmol) was added to a solution of dodecylamine (1 g, 5.4 mmol) in methanol (30 mL). The mixture was refluxed for 7 hours under N_2. After the reaction was cooled to room temperature, ethanol (20 mL) and concentrated HCl (12 N, 20 mL) was added. The mixture was stirred overnight at room temperature to afford a dark red precipitate. The resulting red solid was collected by vacuum filtration through a 0.45 μm membrane filter, rinsed thoroughly with water and ethanol, and then concentrated under vacuum to afford **2** that was not purified due to its poor solubility in common organic solvents and was used directly for the following reaction.

Compound (*S*)-**1.** A mixture of **2** (30 mg) and (*S*)-**4** (50 mg) in imidazole (3 g) was heated to 150 °C under N_2 and stirred for 3 hours. After cooling to room temperature, ethanol (50 mL) and concentrated HCl (12 N, 50 ml) were added to the mixture and stirred overnight. The resulting red solid was collected by vacuum filtration through a 0.45 μm membrane filter and rinsed thoroughly with water and ethanol. The residue was purified by column chromatography (silica, chloroform : acetone =100 :1) to afford **(*S*)-1** (20 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68-8.71 (m, 4H), 8.61-8.63 (m, 4H), 7.20-7.23 (m, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.92 (s, 1H), 6.77 (d, J = 7.2 Hz, 1H), 4.44 (d, J = 8.0 Hz, 2H), 4.26-4.34 (m, 1H), 4.21 (t, J = 7.6 Hz, 2H), 3.03 (t, J = 8.0 Hz, 2H), 1.61-1.78 (m, 4H), 1.28-1.43 (m, 3H), 1.26-1.28 (m, 18H), 0.96 (t, J = 7.6 Hz, 3H), 0.88-0.90(m, 3H); MALDI-MS: (m/z)= 734.7.

(*R*)-1 was also obtained by the same procedure.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68-8.69 (m, 4H), 8.61-8.63 (m, 4H), 7.20-7.23 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.91 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.44 (d, *J* = 8.0 Hz, 2H), 4.27-4.34 (m, 1H), 4.21 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H), 1.62-1.80 (m, 4H), 1.28-1.54 (m, 3H), 1.26-1.28 (m, 18H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.88-0.90(m, 3H); MALDI-MS: (m/z)= 734.6.

The ^{1}H NMR and MALDI-MAS spectra of **compounds (*R/S*)-1** are attached at the end.

2. Self-assembly of chiral asymmetric PDI molecules (*R/S*)-1

The chiral asymmetric PDI molecules (*S*)-**1** and (*R*)-**1** were self-assembled by injecting a chloroform solution (0.5 mL) of the corresponding compound (0.1 mM) into 4 mL of ethanol (poor solvent) in a test tube or vial, followed by aging for variable periods. The time-dependent self-assembly process was monitored and recorded by circular dichroism (CD). The nanotubes aged in ethanol for 7 days after the initiation of self-assembly, were dropped into 10 mL of acetonitrile and aged for 9 days to unwind them into nanocoils completely.

3. Structural and property characterizations

CD spectra and UV-vis absorption spectra were measured on a JASCO J-815 spectropolarimeter at room temperature. Fluorescence spectra were obtained on PerkinElmer LS 55 luminescence spectrophotometer with an excitation wavelength of 450 nm. Transmission electron microscopy (TEM) measurements were performed with FEI TecnaiG^2 T20 (120 KV). The fluorescence quantum yields of the nanotubes were determined by the integrating sphere method performed on Hamamatsu Absolute PL Quantum Yield spectrometer C11247.

4.

Supporting figures

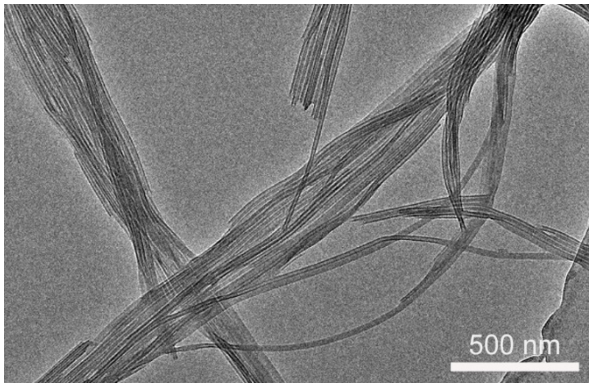


Figure S1. TEM image of nanotubes assembled from (*S*)-**1** at 24 h after the initial of self-assembly process.

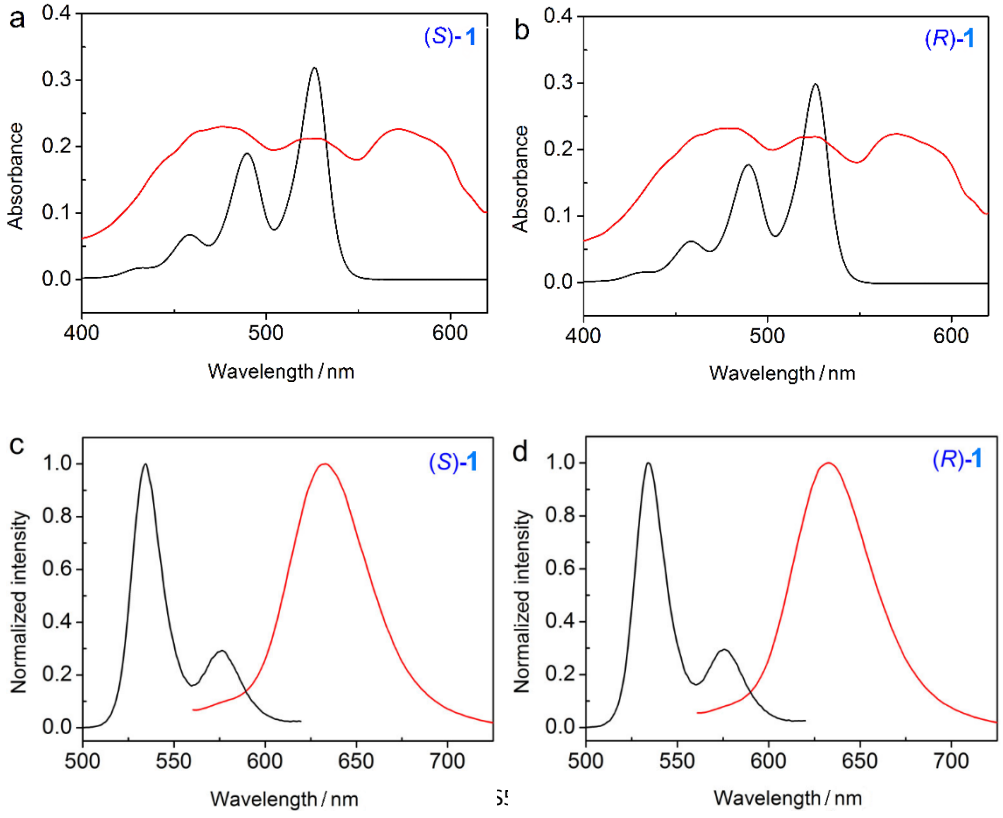


Figure S2. Absorption (a, b) and fluorescence spectra (c, d) of (*S*)-**1** (a, c) and (*R*)-**1** (b, d) in chloroform (3 μM, black) and in a mixed solvent containing 0.5 mL of a chloroform solution of 0.1 mM (*S*)-**1** or (*R*)-**1** in 4 mL ethanol (i.e., nanotubes formed after 330 h of aging, red).

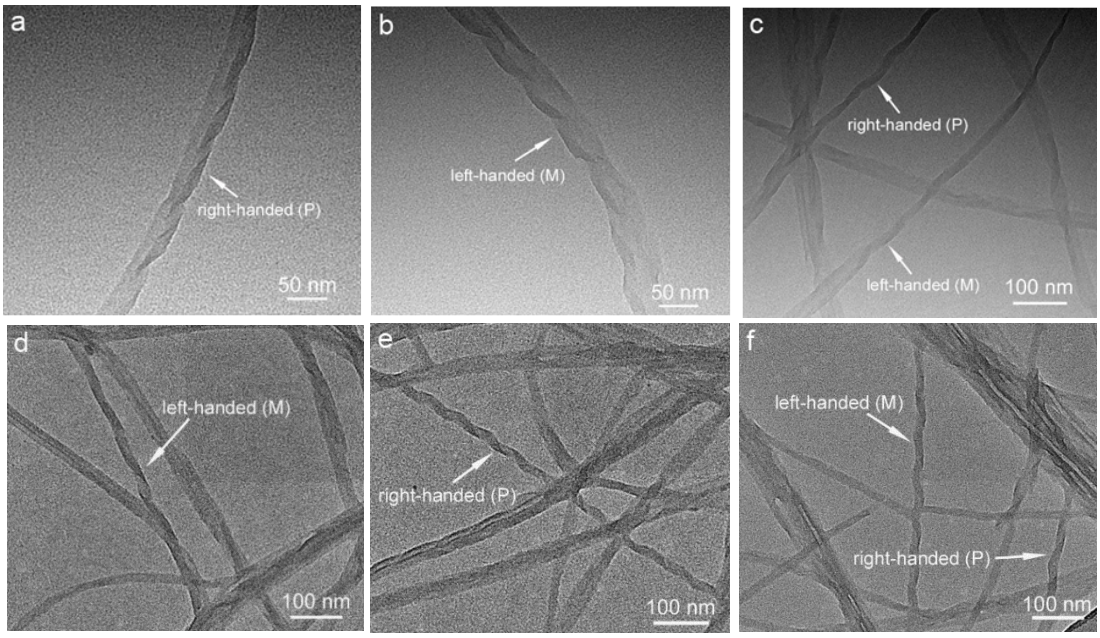
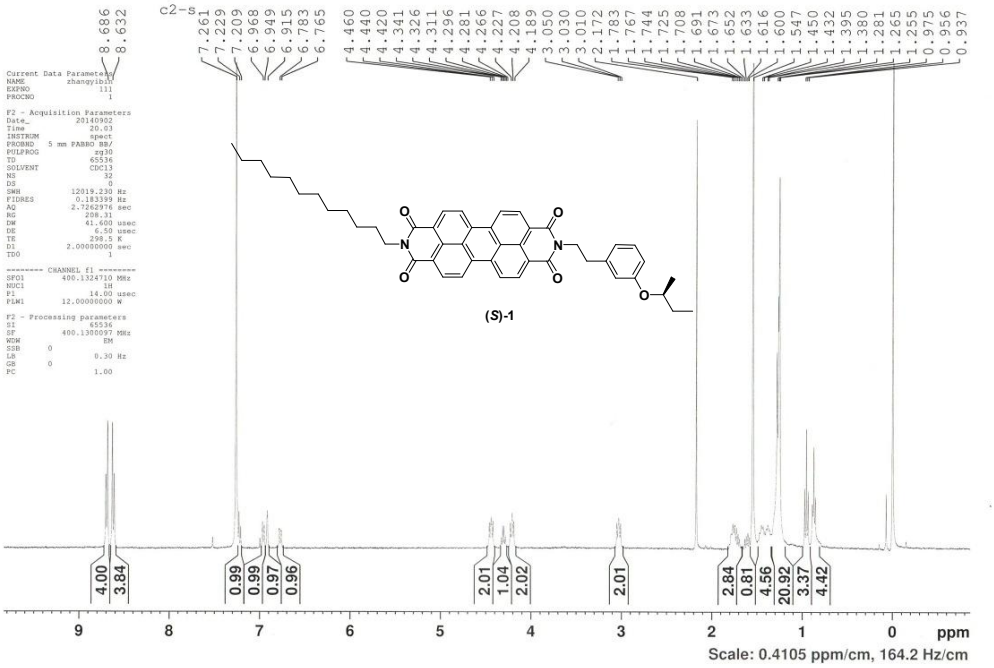
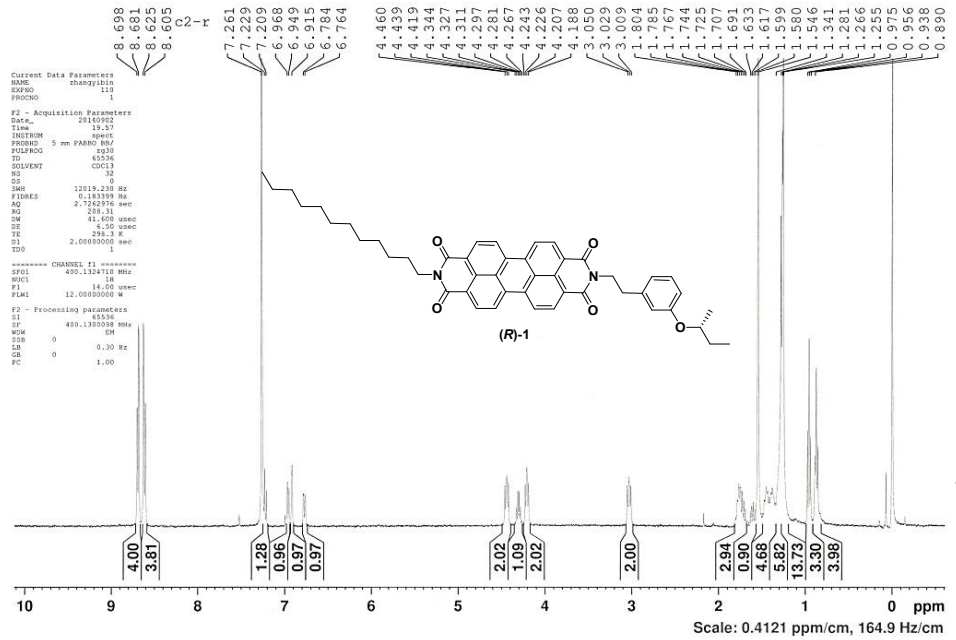


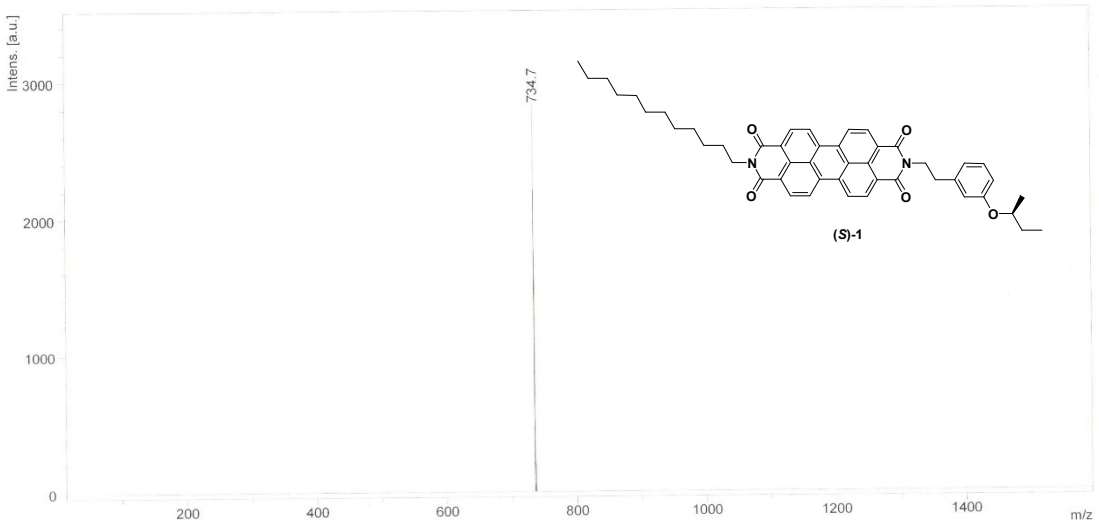
Figure S3. TEM images of assemblies formed from (*S*)-**1** (a, b, c) and (*R*)-**1** (d, e, f) at 5 min after the initial of self-assembly process.

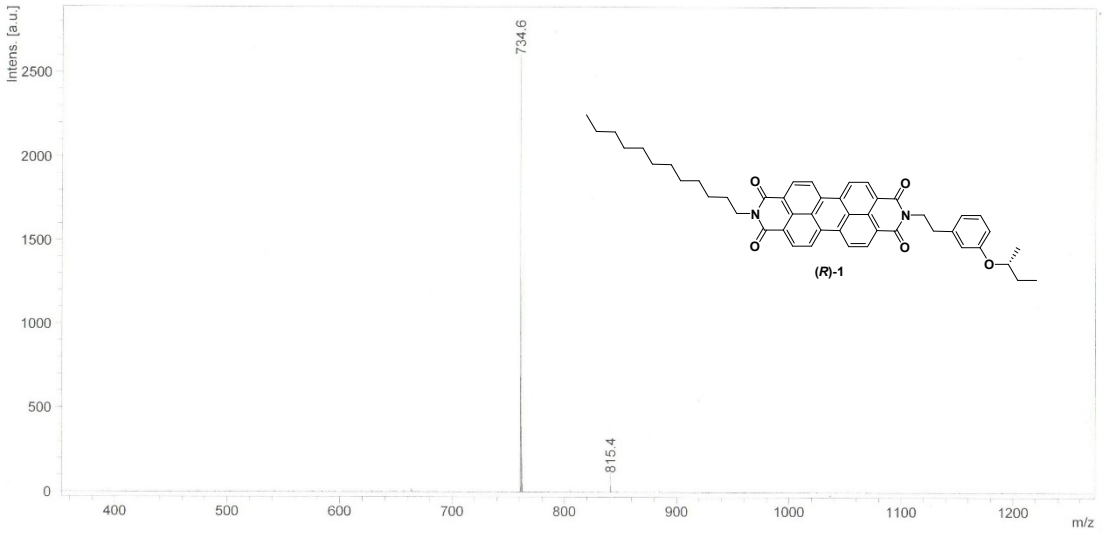
5. NMR spectra





6. MALDI-TOF mass spectra




Intens [a.u.]
2500
2000
1500
1000
500
0
734.6
815.4
400
500
600
700
800
900
1000
1100
1200
m/z
O
N
O
O
N
O
O
(R)-1