

SUPPORTING INFORMATION

Effects of Anchoring and Spacer groups of Asymmetric Zinc Phthalocyanines on Photovoltaic Performance of Dye-Sensitized Solar Cells

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1. Synthesis

1.1. Synthesis of 4-(6-carboxy-2-naphthoxy)phthalonitrile (4)

Phthalonitrile **1** has been synthesized and characterized according to published procedure [1]. 4-Nitrophthalonitrile (0.98 g, 5.66 mmol), 6-hydroxy-2-naphthoic acid (1.06 g, 5.66 mmol), and K_2CO_3 (2.35 g, 16.98 mmol) were dissolved in DMF (40 mL). The reaction mixture was stirred at 60 °C for 76 h under an argon stream. The progress of the reaction was monitored by TLC. The reaction mixture was poured into 200 mL of cold water and the pH of the solution was adjusted to 1 by addition of 1:1 concentrated hydrochloric acid (v/v). After the mixture was left for 1 h, the precipitate was filtered and washed with water until the filtrate was neutral. Finally, the cream-colored product was crystallized from methanol–water. This compound is soluble in chloroform, THF, dichloromethane (DCM), dimethylformamide (DMF), dimethylsulfoxide (DMSO), and acetone. Yield: 75% (1.33 g); m.p. 248 °C. FTIR $\nu_{\max}/\text{cm}^{-1}$: 3103, 3072, 3042 (CH arom.), 2234 ($-C\equiv N$), 1698 (C=O), 1657, 1590, 1577, 1568, 1490, 1473 (Ar C=C), 1405, 1386, 1298, 1280, 1245 (Ar-O-Ar), 1142, 1122, 1097, 969, 834, 821, 765, 633; $^1\text{H-NMR}$ (d_6 - DMSO) δ , ppm: 13,11 (1H, s, -OH), 8,67 (1H, br s, Ar-H), 8,27 (1H, d, $J=9$ Hz, Ar-H), 8,15 (1H, d, $J=9$ Hz, Ar-H), 8,04-7,98 (2H, m, Ar-H), 7,95 (1H, d, $J=3$ Hz, Ar-H), 7,77 (1H, d, $J=2,5$ Hz, Ar-H), 7,55 (1H, dd, $J=2,5$ ve 8,5 Hz, Ar-H), 7,48 (1H, dd, $J=2,5$ ve 8,5 Hz, Ar-H); Anal. Calc. for $C_{19}H_{10}N_2O_3$ (314.294 g/mol): C, 72.61; H, 3.21; N, 8.91; Found: C, 72.30; H, 3.11; N, 8.60%; MS m/z (100%) Calc.: 314, Found: 315 $[M+H]^+$.

1.2. Synthesis of 4-(2,4-di-tert-butylphenoxy)phthalonitrile (5)

Phthalonitrile **2** has been synthesized and characterized according to published procedures [2]. 4-Nitrophthalonitrile (1.73 g, 10 mmol) was dissolved in N, N-dimethylformamide (40 mL) under nitrogen, and 2,4-di-tert-butylphenol (2.06 g, 10 mmol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (5.2 g, 38 mmol) was added in portions for 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at 60 °C for 48 h. Then the mixture was poured into 200 ml water, and extracted with CH_2Cl_2 . The crude product was washed first with 10% $NaHCO_3$, then with water, and dried over anhydrous sodium sulfate. The product was evaporated to dryness. The residue was recrystallized from ethanol. Yield: 78% (2.5 g); m.p. 150–151 °C, FTIR $\nu_{\max}/\text{cm}^{-1}$: 3075 (CH arom.), 2995, 2958, 2868 (-CH, aliph.), 2230 ($-C\equiv N$), 1593- 1484 (arom. $-C=C-$), 1248 (Ar-O-Ar), 1088, 839; $^1\text{H-NMR}$ (d_6 -DMSO) δ , ppm: 8,08 (1H, d, $J=9$ Hz, Ar-H), 7,77 (1H, br d, $J=2,5$ Hz, Ar-H), 7,46 (1H,

br d, J= 2 Hz, Ar-H), 7,33-7,30 (2H, m, Ar-H), 6,92 (1H, d, J=8,4 Hz, Ar-H), 1,31 (18H, s, t-BuCH₃); Anal. Calc. for C₂₂H₂₄N₂O (332,439 g/mol): C, 79.48; H, 7.28; N, 8.43; Found: C, 79.40; H, 7.34; N, 8.39%; MS m/z (100%) Calc.: 332.43, Found: 355.17 [M+Na]⁺.

2. DSSC fabrications and measurements

TCO22-15 fluorine-doped tin oxide coated glasses, TiO₂ paste (Ti-Nanoxide D/SP), platisol T/SP, Iodolyte AN-50, Chenodeoxycholic Acid (CDCA) and Ruthenizer 535-bisTBA (N719) were supplied from Solaronix and TiCl₄ was supplied from Sigma Aldrich. The surface of FTO glasses was cleaned with acetone, isopropyl alcohol, and DI water in an ultrasonic bath. The FTO glass plates were immersed in 40 mM TiCl₄ aqueous solution at 70 °C for 30 min and washed with water and ethanol. TiO₂ paste was coated onto the FTO plates by the doctor-blade technique on an active square area of 0.25 cm² (5 × 5 mm²) and sintered at 450 °C for 30 min. Screen printing was used to apply a scattering layer paste comprising 400 nm anatase particles, which was then dried for 1h at room temperature. Then the TiO₂ photo anodes were sintered at 450 °C for 30 min again. The resulting layer was composed of 10 μm thickness of TiO₂ layer and 4 μm thickness of scattering layer. Then they were treated again with TiCl₄ at 70 °C for 30 min and sintered at 450 °C for 30 min. After cooling to around 50 °C following the sintering step, FTO glasses were soaked in 0.4 mM ZnPc(6) and ZnPc(7) dichloromethane (DCM) with 10-fold chenodeoxycholic Acid (CDCA) for 24 h at room temperature. Pt-coated FTO glasses were used as the cathode of the DSSCs. Pre-drilled FTO glasses were coated with platisol T/SP platinum paste and sintered at 420 °C for 15 min. Then the counter electrodes were sandwiched with photo electrodes by using Meltonix 1170-60 (Solaronix) 60 μm thick hot-melt sealing and Iodolyte AN-50 liquid electrolyte was syringed between two electrodes.

For photovoltaic measurements, a Gamry Reference 600 potentiostat/galvanostat was used to collect the current density (J_{sc}) -voltage (V) responses of DSSCs under an illumination intensity of 100 mW/cm². An Asahi Spectra HAL-320 – Solar Simulator (350-1100nm) was used to illuminate the devices. J-V curves were analyzed to determine the current density, open circuit potential, fill factor, and efficiency of the DSSCs.

Reference

- 1 S. N. Işık, G. K. Karaoğlan, B. C. Ömür, A. Altındal and G. G. Köse, *Synth. Met.*, 2018, **246**, 7-15.
- 2 M. S. Ağırtaş, *Dyes Pigm.*, 2007, **74**, 490-493.

2. Figures

FT-IR Spectra

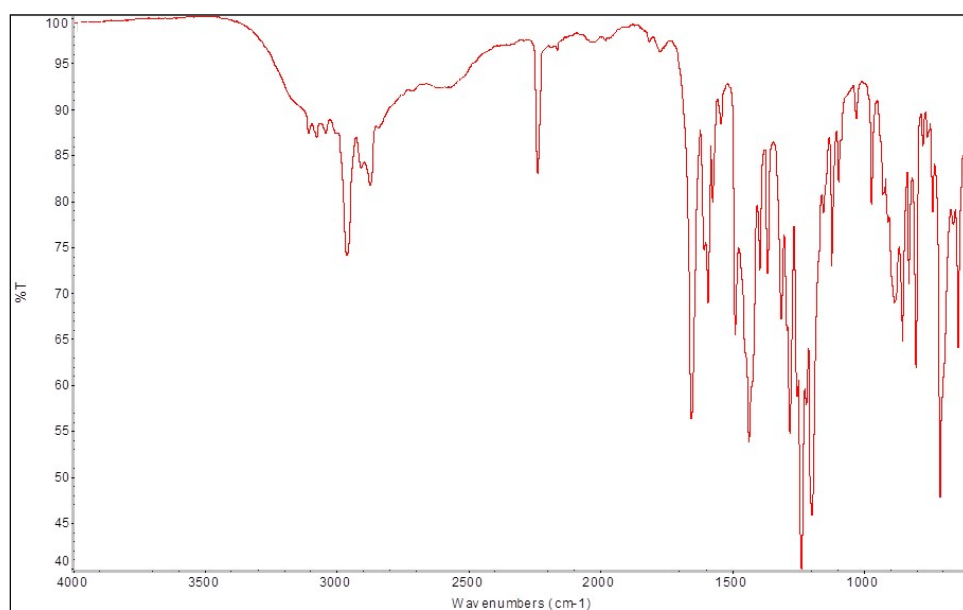


Fig. S1. FT-IR spectrum of compound **3**

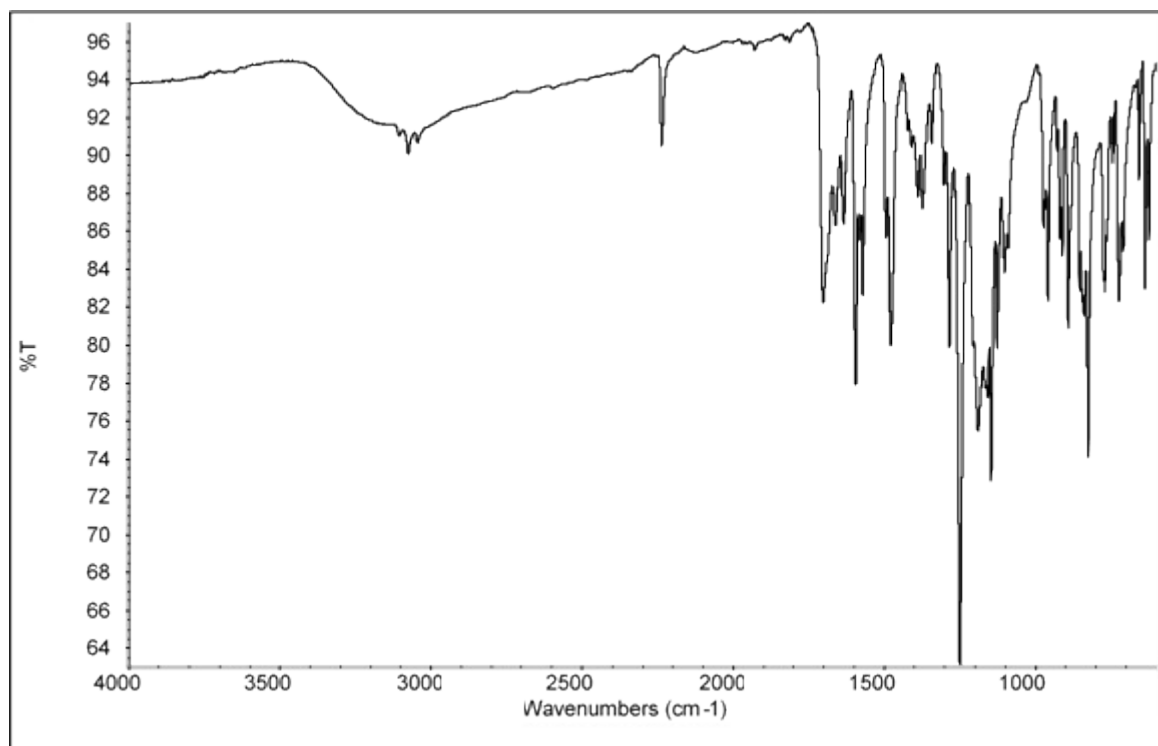


Fig. S2. FT-IR spectrum of compound 4

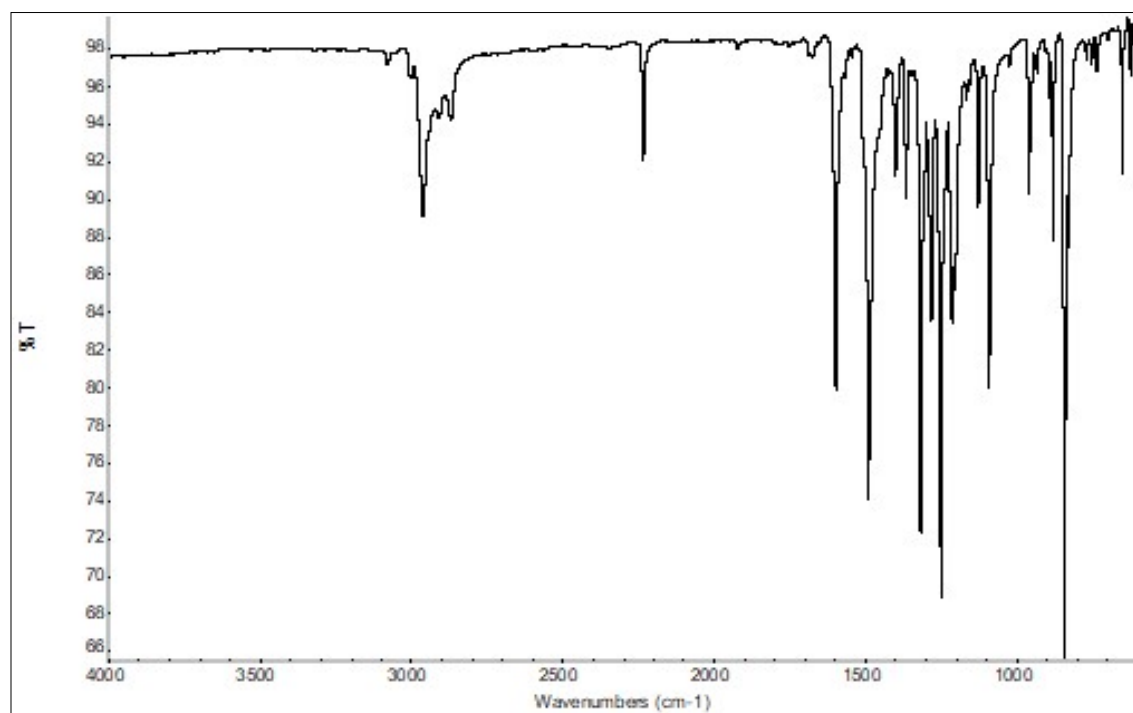


Fig. S3. FT-IR spectrum of compound 5

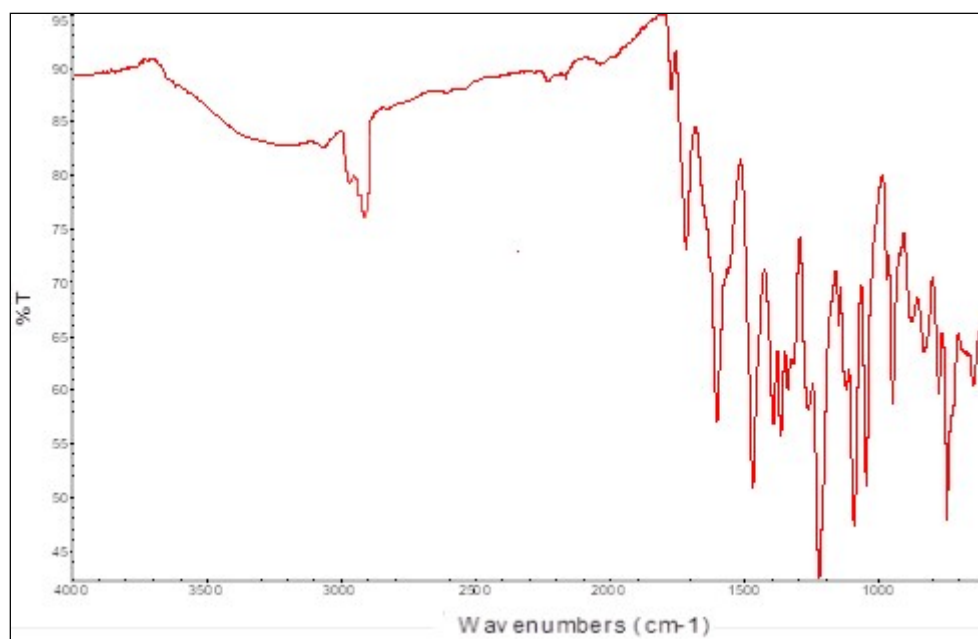


Fig. S4. FT-IR spectrum of compound **6**

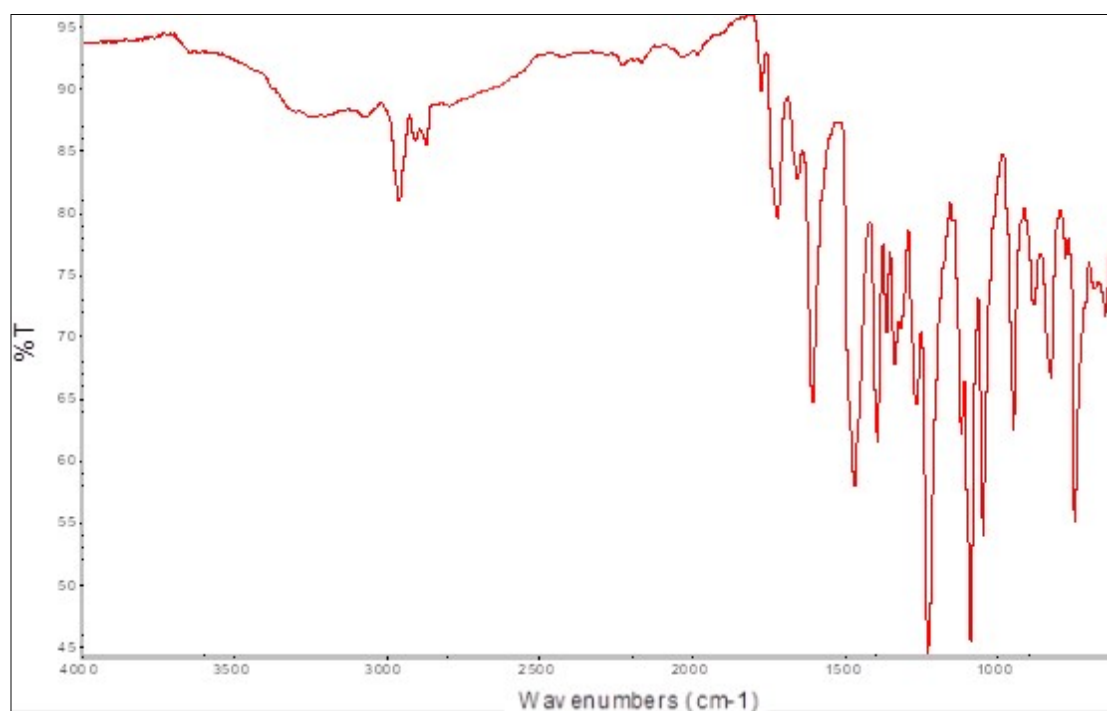


Fig. S5. FT-IR spectrum of compound **7**

MS Spectra

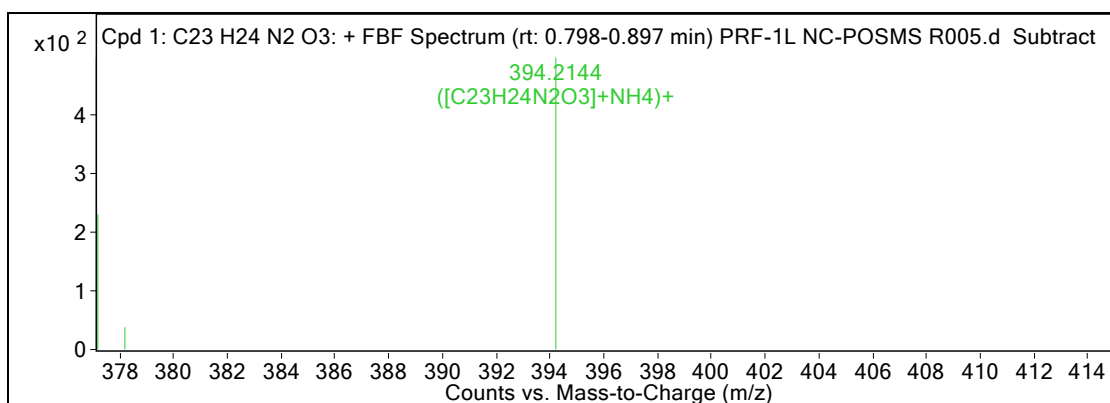


Fig. S6. LC-MS spectrum of compound 3

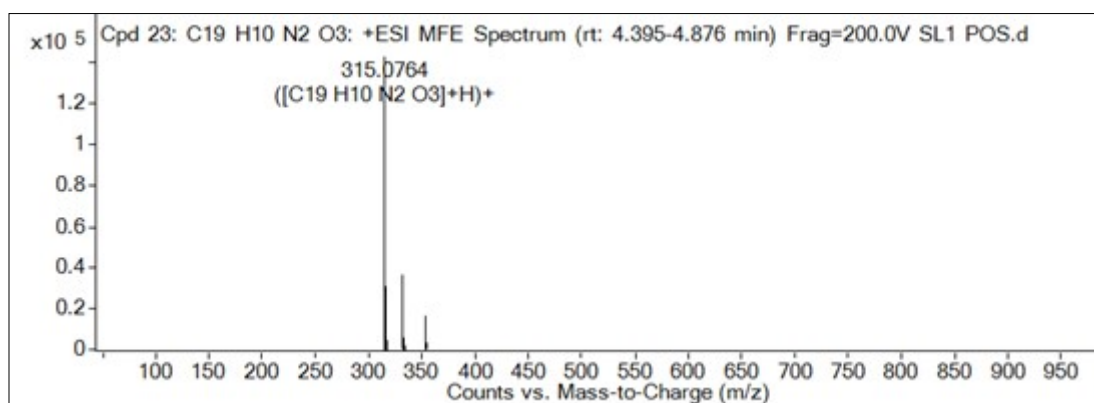


Fig. S7. LC-MS spectrum of compound 4

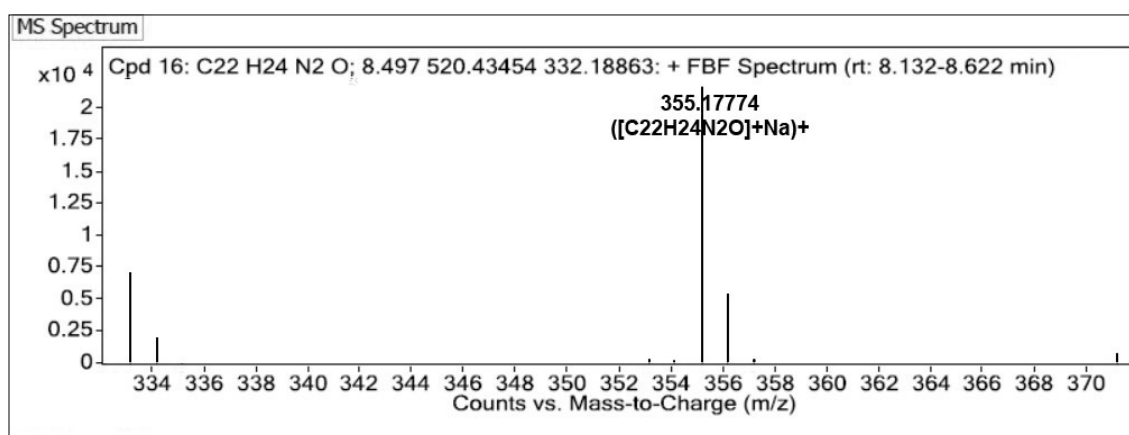


Fig. S8. LC-MS spectrum of compound 5

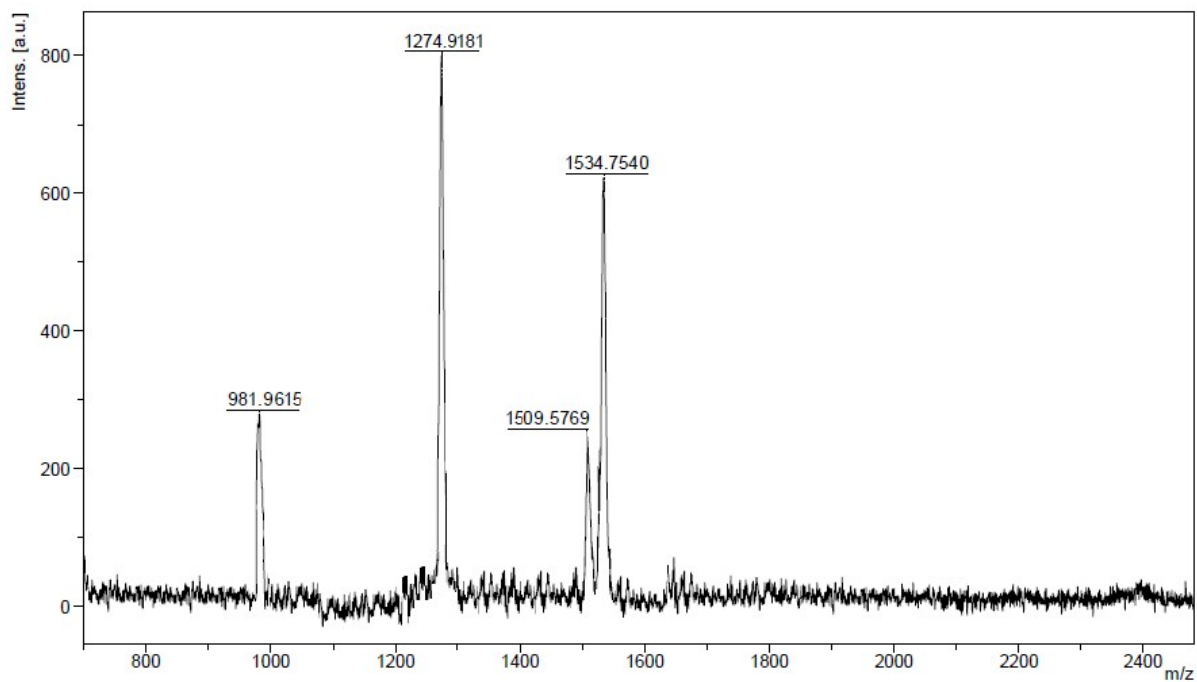


Fig. S9. MS (MALDI-TOF) spectrum of compound 6

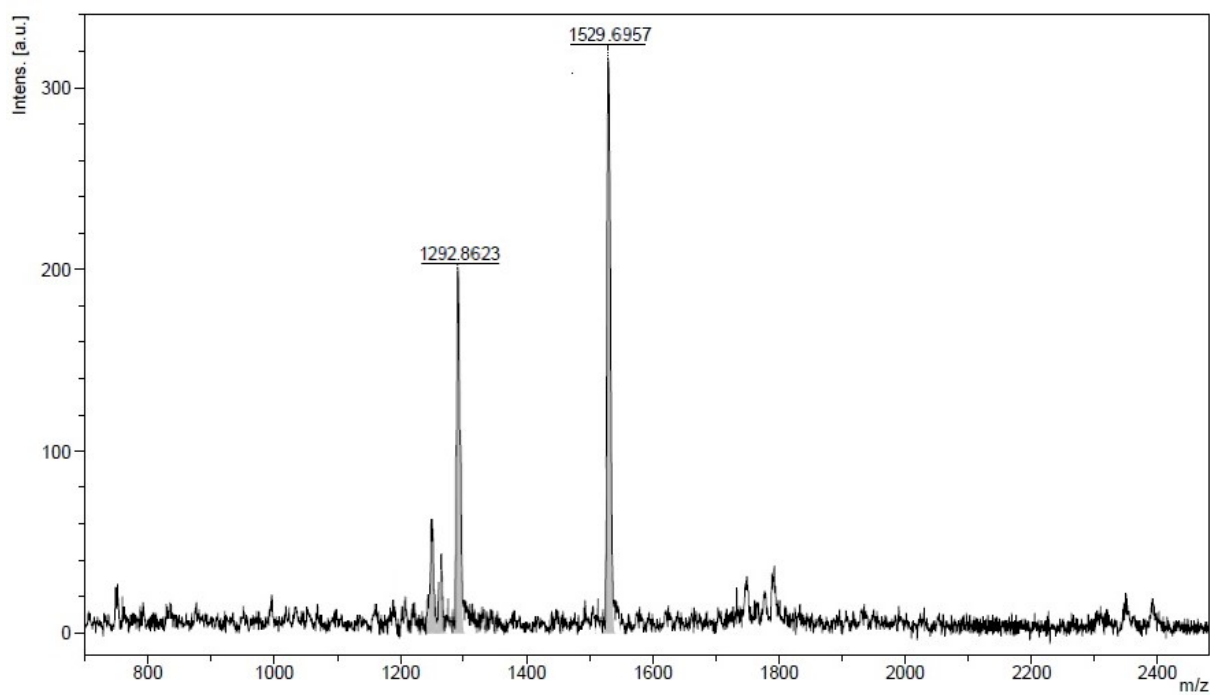


Fig. S10. MS (MALDI-TOF) spectrum of compound 7

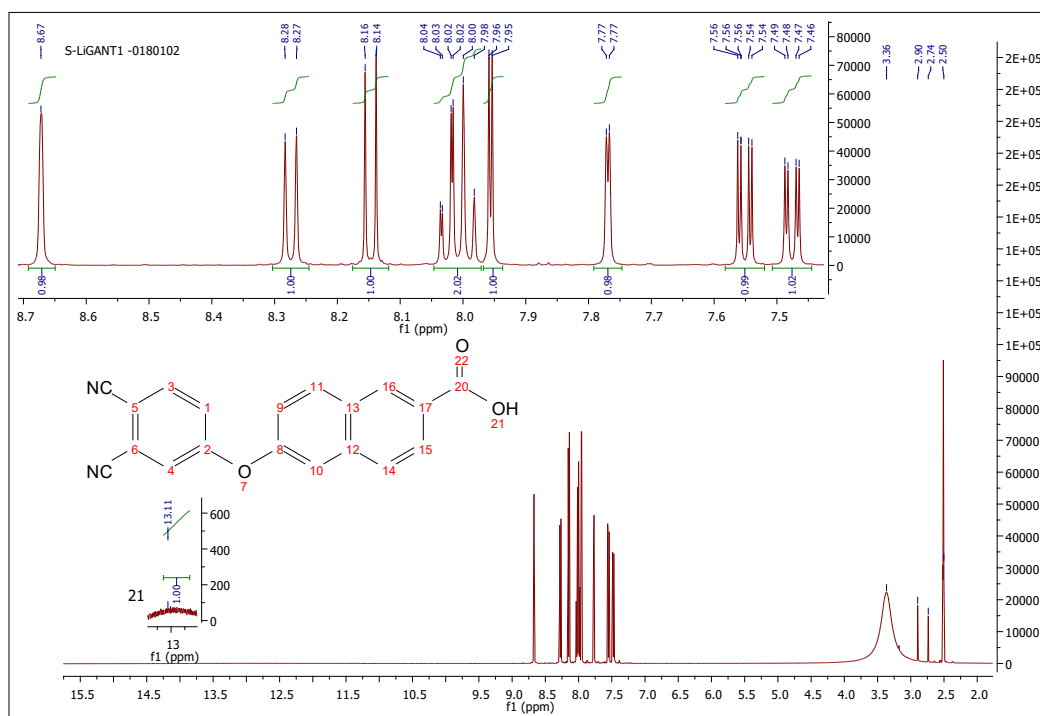


Fig. S11. $^1\text{H-NMR}$ spectrum of compound 4

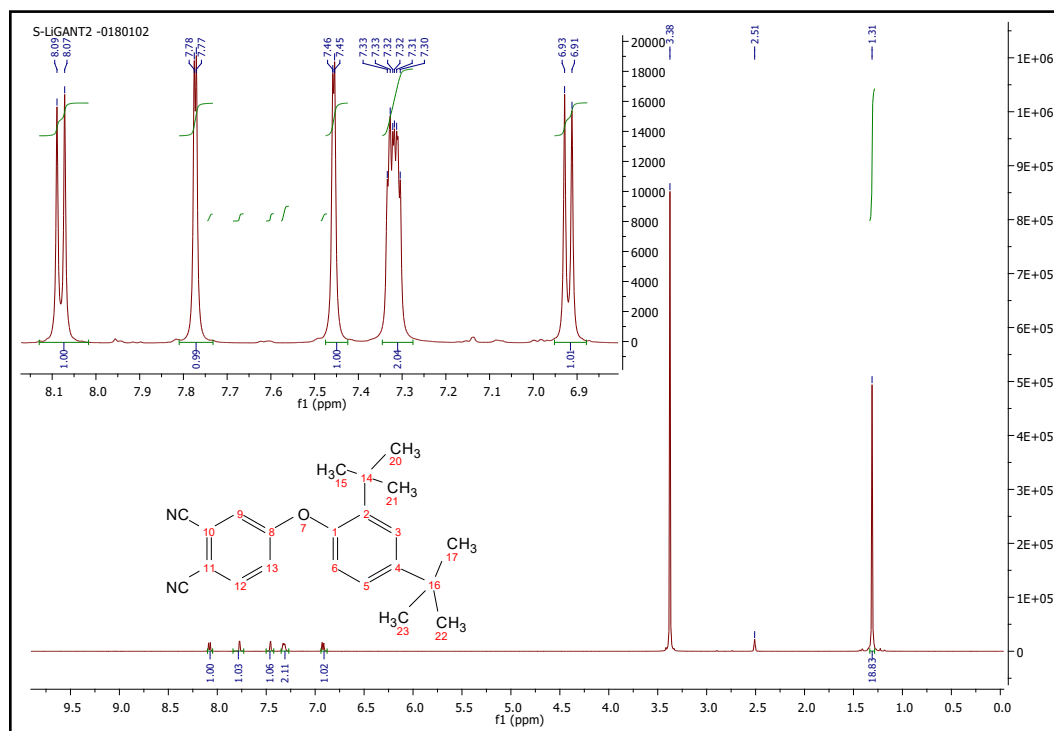


Fig. S12. $^1\text{H-NMR}$ spectrum of compound 5