

Supporting Information

Synthesis and evaluation of simple multimers based on biosourced central core as donor materials for photovoltaic applications

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1- Material and Methods

NMR spectra were recorded on a 200, 300 or 400 MHz spectrometer (T = 300 K). The spectra were referenced against the internal NMR-solvent standard. Chemical shifts were expressed in parts per million (ppm) and were reported as s (singlet), d (doublet), t (triplet), td (doublet triplet), m (multiplet) and coupling constants *J* were given in Hz. Mass spectra were recorded under EI, CI or ESI mode on mass spectrometer or under MALDI-TOF mode on mass spectrometer. The main peaks are described according to *m/z*. The peak corresponding to molecular mass is expressed as (M^{+}). IR Spectra were also performed in ATR mode on a Bruker spectrometer. HPLC solvents were used for the measurements. Electrochemical experiments were performed on a potentiostat in a standard three-electrodes cell using platinum electrodes and a Ag/AgCl reference electrode. All the chromatograms were drawn against Ferricinium/Ferrocene couple.

2- Syntheses of push-pull based molecular donors

TPA-Br, **1** and **2** were commercially available. The procedure for the synthesis of compound **3** was followed according to the publication of Zhang¹⁴ while the coupling to obtain compound **4** was performed according to the paper of Fan¹⁵.

Syntheses of cyanoesters 5, 6 and 7

To a solution of diol or triol (1 eq.) in toluene (0.7-0.8M) was successively added cyanoacetic acid (2.5-4.0 eq.) and *p*-toluenesulfonic acid (0.1 eq.). The reaction mixture was heated under reflux overnight using a Dean-Stark apparatus. After cooling to r.t., the solution was diluted with dichloromethane and the organic phase was washed with aqueous saturated NaHCO₃ (2 × 10 mL) and brine (1 × 10mL). The organic layer was dried over MgSO₄ and the solvents were evaporated under vacuum. The crude product was then purified either by chromatography or recrystallization.

Cyanoester 5: Following the general procedure, isosorbide (2.00 g, 13.7 mmol) and cyanoacetic acid (2.91 g, 34.3 mmol) led to cyanoester 5 (2.313 g, 8.25 mmol, 60 %) as a slightly yellow oil which was used without purification or after purification by silica gel column chromatography. ¹H NMR (CDCl₃) δ: 5.30-5.23 (m, 2H), 4.92 (t, *J* = 5.3 Hz, 1H), 4.53 (d, *J* = 4.9 Hz, 1H), 4.04-4.01 (m, 2H), 3.96-3.92 (m, 2H), 3.55 (s, 2H), 3.53 (s, 2H). ¹³C NMR (CDCl₃) δ: 162.3, 162.2, 112.6, 112.4, 85.7, 80.7, 80.0, 76.0, 73.0, 70.7, 24.7, 24.5. HRMS calcd for C₁₂H₁₂N₂O₆Na : 303.0588. Found 303.0593.

Cyanoester 6: Following the general procedure, isomannide (2.00 g, 13.7 mmol) and cyanoacetic acid (3.00 g, 35.7 mmol) led to cyanoester 6 (2.22 g, 7.92 mmol, 52 %) as a slightly yellow oil which was used without further purification. ¹H NMR (CDCl₃) δ: 5.23-5.13 (m, 2H), 4.81-4.73 (m, 2H), 4.10 (dd, *J* = 10.1, 6.1 Hz, 2H), 3.95 (dd, *J* = 10.1, 5.8 Hz, 2H), 3.56 (s, 4H). ¹³C NMR (CDCl₃) δ: 162.4, 112.7, 80.2, 75.3, 70.8, 24.5. HRMS calcd for C₁₂H₁₂N₂O₆Na : 303.0588. Found 303.0593.

Cyanoester 7: Following the general procedure, glycerol (1.50 g, 16 mmol) and cyanoacetic acid (5.60 g, 65 mmol) led to cyanoester 7 (2.2 g, 46%) as a white solid after crystallization in CHCl₃. Mp: 85-86°C. ¹H NMR (DMSO-*d*₆): 5.29 (m, 1H), 4.35 (m, 1H), 7.23 (dd, 1H, *J* = 1.1 and 3.6 Hz), 4.03 (m, 6H). ¹³C NMR (DMSO-*d*₆): 164.2, 164.0, 114.8, 114.7, 70.2, 63.1, 24.7, 24.5. IR (cm⁻¹): 2264, 1743, 1331, 1171. HRMS calcd for C₁₂H₁₁N₃O₆Na : 316.0546. Found 316.0540.

Syntheses of **TPA-Isos-F**, **TPA-Isos-T**, **TPA-Isom-T**, **general procedure**.

To a solution of dicyanoester (1eq.) in CHCl_3 (0.15M) was added under Ar, aldehyde (2eq.) and one drop of Et_3N . The reaction mixture was refluxed for 20h. After cooling down to rt, the reaction mixture was taken up in dichloromethane and water. The organic layer was washed with HCl (1M) aqueous solution, dried over MgSO_4 then concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: cyclohexane/EtOAc).

TPA-Isos-F: Following the general procedure, **5** (62 mg, 0.221 mmol) and **3** (150 mg, 0.442 mmol) led to **TPA-Isos-F** (151 mg, 0.164 mmol, 74%) as a red solid after chromatography (eluent: cyclohexane/EtOAc, 8:2 toward 1:1). ^1H NMR (CDCl_3) δ : 7.94 (s, 1H), 7.89 (s, 1H), 7.71-7.68 (m, 4H), 7.32-7.28 (m, 10H), 7.15-7.06 (m, 16H), 6.79-6.78 (m, 2H), 5.39-5.35 (m, 2H), 5.04 (t, $J = 5.4$ Hz, 1H), 4.65 (d, $J = 4.9$ Hz, 1H), 4.20-4.06 (m, 3H), 4.00-3.96 (m, 1H). ^{13}C NMR (CDCl_3) δ : 162.9, 162.6, 161.1, 161.0, 149.7, 149.6, 147.3, 147.2, 146.7 (2°C), 138.2, 129.5, 126.7, 125.5, 124.2 (2°C), 121.7 (2°C), 121.4, 121.3, 116.0, 115.7, 108.1 (2°C), 94.3 (2°C), 86.1, 81.1, 79.6, 77.3, 75.4, 73.3, 71.0. HRMS calcd for $\text{C}_{58}\text{H}_{42}\text{N}_4\text{O}_8$: 922.2997; Found 922.2991.

TPA-Isos-T: Following the general procedure, **5** (39 mg, 0.141 mmol) and **3** (100 mg, 0.281 mmol) led to **TPA-Isos-T** (72 mg, 0.075 mmol, 53%) as a red solid after chromatography (eluent: cyclohexane/EtOAc, 85:15 toward 1:1). ^1H NMR (CDCl_3) δ : 8.30 (s, 1H), 8.25 (s, 1H), 7.75-7.73 (m, 2H), 7.56-7.53 (m, 4H), 7.32-7.28 (m, 10H), 7.16-7.04 (m, 16H), 5.40-5.34 (m, 2H), 5.05 (t, $J = 5.3$ Hz, 1H), 4.65 (d, $J = 5.0$ Hz, 1H), 4.19-4.06 (m, 3H), 4.00-3.96 (m, 1H). ^{13}C NMR (CDCl_3) δ : 162.7, 162.4, 156.0, 155.8, 149.5 (2°C), 147.3, 147.2, 146.8 (2°C), 140.1, 140.0, 133.8, 133.7, 129.5, 127.4, 125.6 (2°C), 125.3, 124.1(2°C), 123.3, 122.1 (2°C), 116.0, 115.8, 95.8, 95.7, 86.1, 81.0, 79.7, 75.5, 73.3, 71.0. HRMS calcd for $\text{C}_{58}\text{H}_{42}\text{N}_4\text{NaO}_6\text{S}_2$: 977.2438; Found 977.2430.

TPA-Isom-F: Following the general procedure, **6** (62 mg, 0.221 mmol) and **3** (150 mg, 0.442 mmol) led to **TPA-Isom-F** (144 mg, 0.156 mmol, 71%) as a red solid after chromatography (eluent: cyclohexane/EtOAc, 85:15 to 6:4). ^1H NMR (CDCl_3) δ : 7.95 (s, 1H), 7.73-7.68 (m, 4H), 7.35-7.26 (m, 10H), 7.16-7.05 (m, 16H), 6.80-6.76 (m, 2H), 5.30-5.21 (m, 2H), 4.97-4.80 (m, 2H), 4.17-4.10 (m, 2H), 4.09-4.03 (m, 2H). ^{13}C NMR (CDCl_3) δ : 162.9, 161.0, 149.6, 147.3, 147.3, 146.8, 138.0, 129.5, 126.7, 125.5, 124.2, 121.8, 121.4, 116.0, 108.5, 94.4, 80.3, 74.9, 70.7. HRMS (ESI) calcd for $\text{C}_{58}\text{H}_{42}\text{N}_4\text{NaO}_8$: 945.2895; Found 945.2856.

Synthesis of **TPA-Gly-T**

4 (189 mg, 0.53 mmol, 3.9 eq) and **7** (40 mg, 0.13 mmol) were dissolved in 4 ml DMF at RT. 1 drop of triethylamine was added. The solution turned red and was stirred overnight at RT. 30 ml of ethyl acetate was added as well as 30 ml of brine. The organic phase was then dried over MgSO_4 , filtered and evaporated. The crude mixture was purified on silica gel using dichloromethane as eluent. A red powder was recovered with a yield of 74% (132 mg). mp: 248-249 °C. ^1H NMR (CDCl_3): 8.37 (s, 1H), 8.32 (s, 2H), 7.78 (d, 1H, $J = 4.0$ Hz), 7.75 (d, 2H, $J = 4.0$ Hz), 7.52 (m, 6H), 7.31 (m, 15H), 7.16 (m, 18H), 7.05 (m, 6H), 5.65 (m, 1H), 4.74 (dd, 2H, $J = 3.3$ and 12.1 Hz), 4.74 (dd, 2H, $J = 3.3$ and 12.1 Hz), 4.60 (dd, 2H, $J = 3.9$ and 12.1 Hz). ^{13}C NMR (CDCl_3): 162.7, 162.3, 155.8, 155.7, 147.4, 147.1, 140.5, 140.3, 133.7, 129.4, 127.3, 125.5, 125.4, 125.1, 124.0, 123.2, 121.9, 115.8, 95.5, 70.3, 63.3. IR (cm^{-1}): 2216, 1716, 1520, 1178, 1058. HRMS calcd for $\text{C}_{81}\text{H}_{56}\text{N}_6\text{O}_6\text{S}_3$: 1304.3405; Found 1304.3405.

3- Preparation of the solar cells

Indium-tin oxide coated glass slides of $24 \times 25 \times 1.1$ mm with a sheet resistance of $RS = 10 \Omega/\text{sq}$ were purchased from VisionTek Systems Ltd. The substrates were cleaned by a series of subsequent 15 minute ultrasonic treatments in distilled water with several drops of detergent (Deconex® 12 PA-x solution), distilled water alone, acetone, and finally in ethanol. Once dried with hot air, a UV-ozone plasma treatment (UV Ozone cleaner, Ossila) was performed for 15 min. A filtered aqueous solution of poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate) (PEDOT:PSS; Clevios P VP. AI 4083) through a $0.45 \mu\text{m}$ RC membrane (Millex®) was spun-cast onto the patterned ITO surface at 5000 rpm for 40 s before being baked at $110 \text{ }^\circ\text{C}$ for 15 min. The best devices were obtained with films spun-cast at 1300 rpm from bulk solution in chloroform of $10 \text{ mg}\cdot\text{mL}^{-1}$ with a donor:acceptor ratio of 1:4 w/w, the acceptor being PC71BM. Finally, OSCs were completed by the successive thermal deposition of LiF and aluminum (80 nm) at a pressure of 10^{-6} Torr through a shadow mask defining two cells of 27 mm^2 each. J vs V curves were recorded in the dark in a N_2 glove box and under illumination using a Keithley 236 source-measure unit and a home-made acquisition program. The light source is an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttechnik, equipped with a metal halogen lamp). The light intensity was measured by a broad-band power meter (13PEM001, Melles Griot). EQE was recorded under ambient atmosphere using a halogen lamp (Osram) with an Action Spectra Pro 150 monochromator, a lock-in amplifier (Perkin-Elmer 7225) and a S2281 photodiode (Hamamatsu).

4- UV-Vis spectra

Solutions of different compounds were prepared at 10^{-5} mol/L in DCM. The films were prepared from solutions at 10^{-3} mol/L and spun cast at 800 rpm onto glass sheets.

Fig 1. Comparison of UV-Vis spectra of TPA-Gly-T in solution (yellow line) and in film (dashed yellow line).

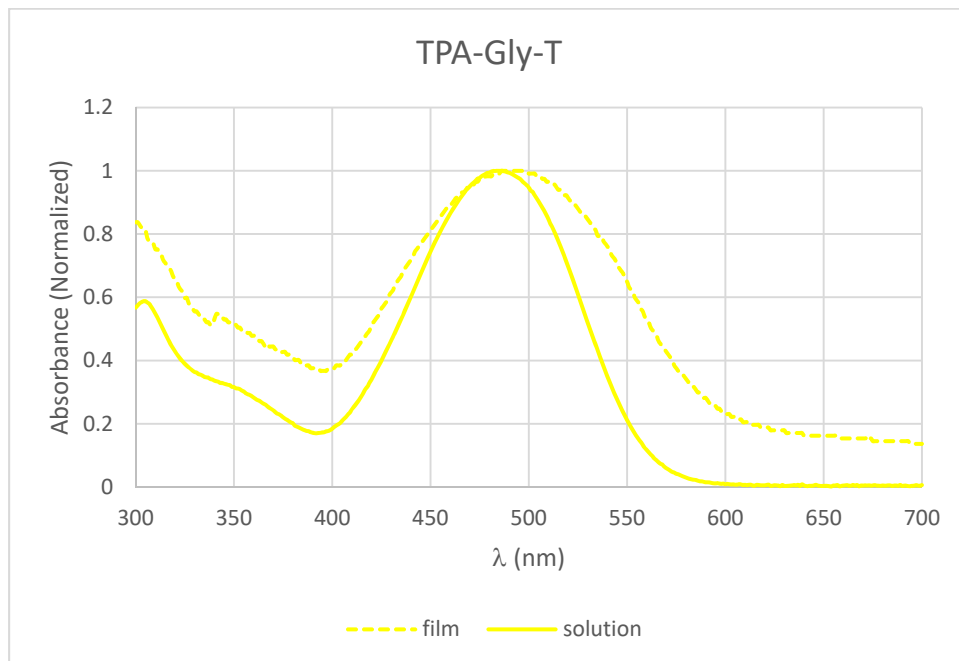


Fig 2. Comparison of UV-Vis spectra of TPA-ISOM-F in solution (grey line) and in film (dashed grey line).

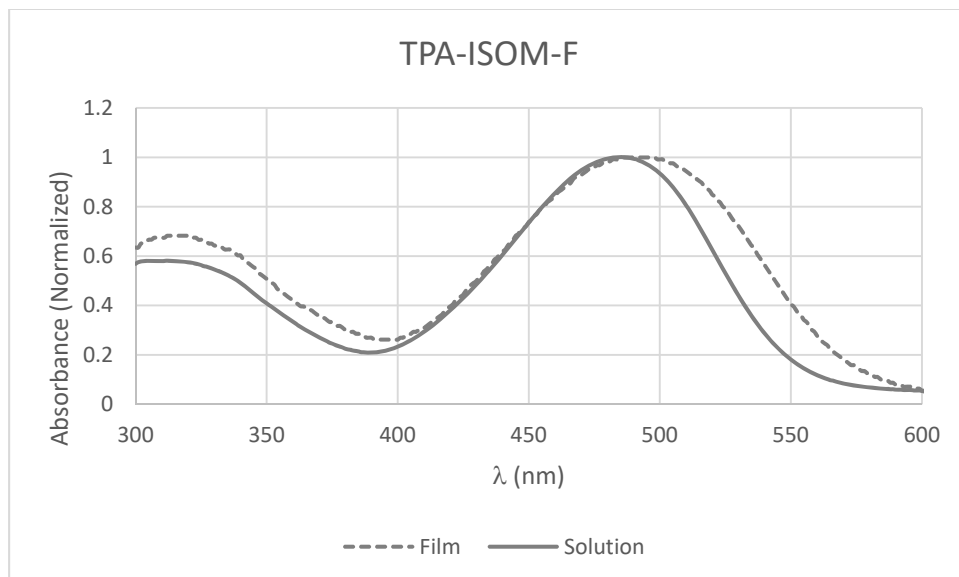
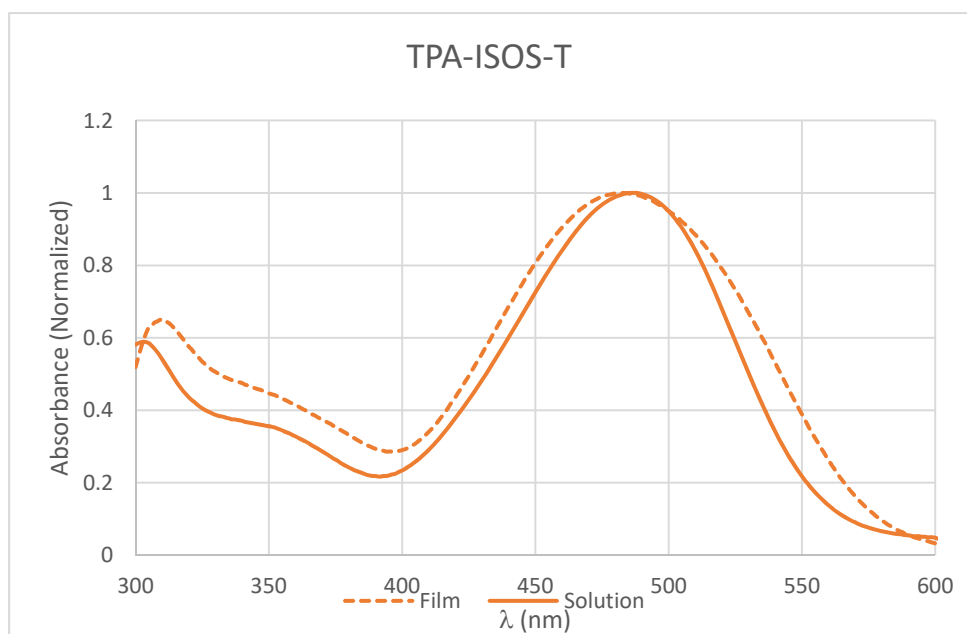


Fig 3. Comparison of UV-Vis spectra of TPA-ISOS-T in solution (orange line) and in film (dashed orange line).



5- SCLC measurements

Space charge limited current (SCLC) measurements

A solution of molecular donor (20 mg/mL) in chloroform was spun cast at 800 rpm onto ITO substrates prepared and coated with PEDOT:PSS as described above. This yielded organic layers of ca 130 nm. Gold cathodes (150 nm) were thermally evaporated under a vacuum of 10^{-6} Torr, through a shadow mask defining active area of 12.60 mm², 3.10 mm² and 0.78 mm² per substrates. Hole mobilities μ_h were evaluated using the Mott-Gurney law, ie, $J_{\text{SCLC}} = (9/8)\epsilon_0\epsilon_r \mu_h(V^2/d^3)$ where ϵ_0 is the permittivity of free space, ϵ_r is the static dielectric constant of the medium (ϵ_r is approximated to 3), V is the voltage applied and d the thickness of the active layer.

Fig 4. SCLC measurements of TPA-Gly-T.

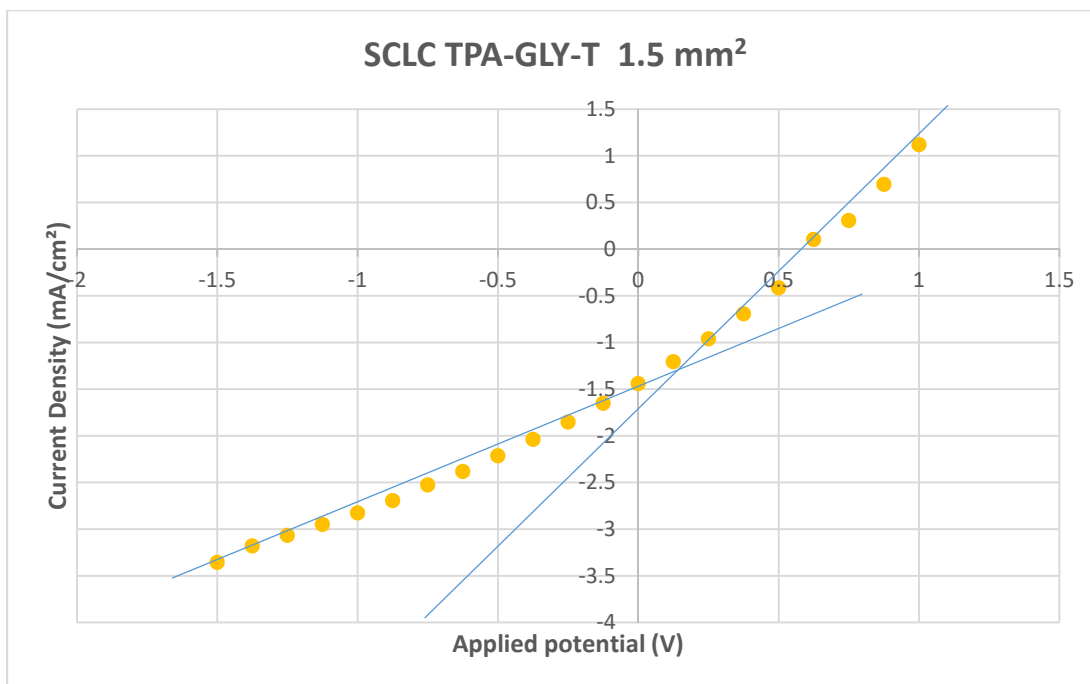


Fig 5. SCLC measurements of TPA-ISOS-T.

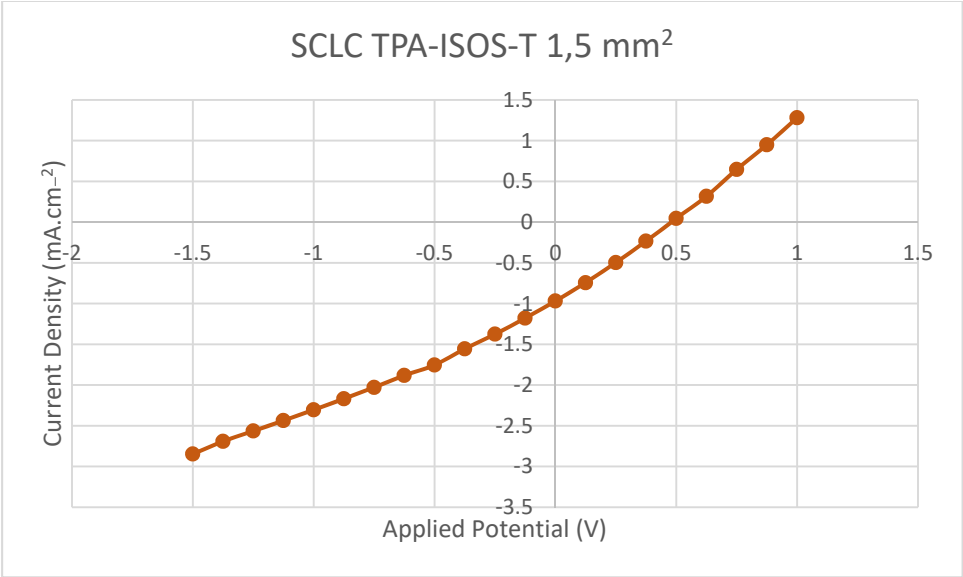


Fig 6. SCLC measurements of TPA-ISOS-F.

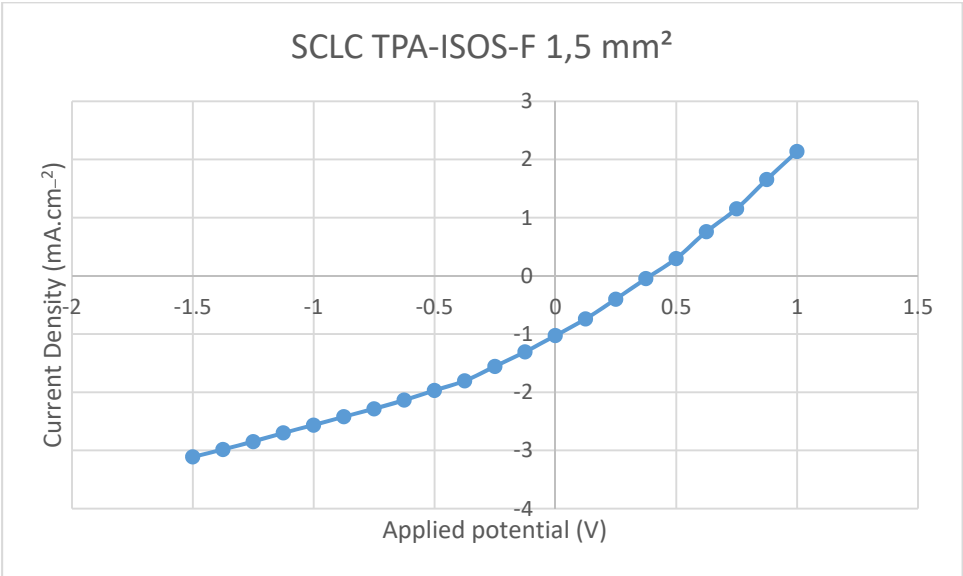
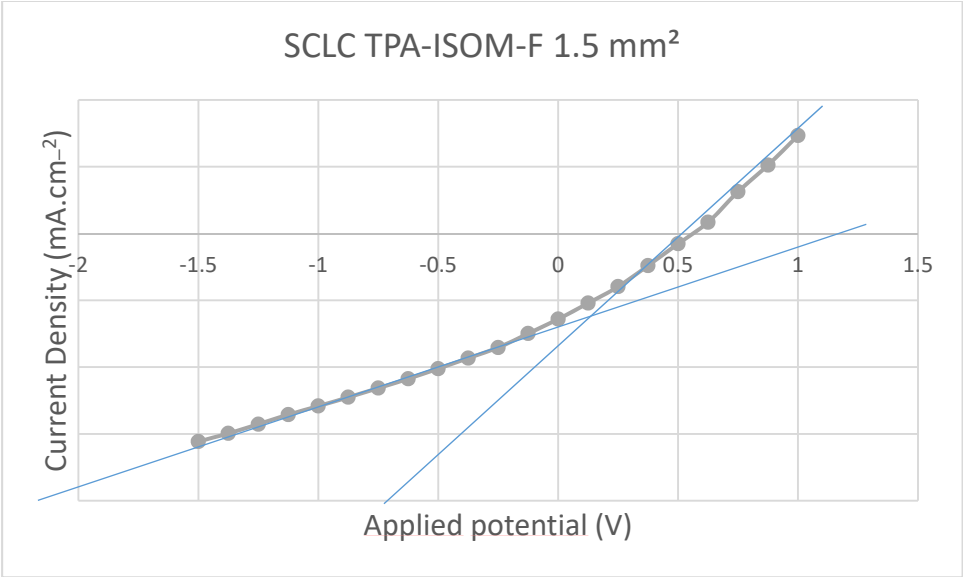


Fig 7. SCLC measurements of TPA-ISOM-F.



6- NMR spectra

Fig 8. ^1H NMR Spectrum of TPA-Isos-F in CDCl_3 .

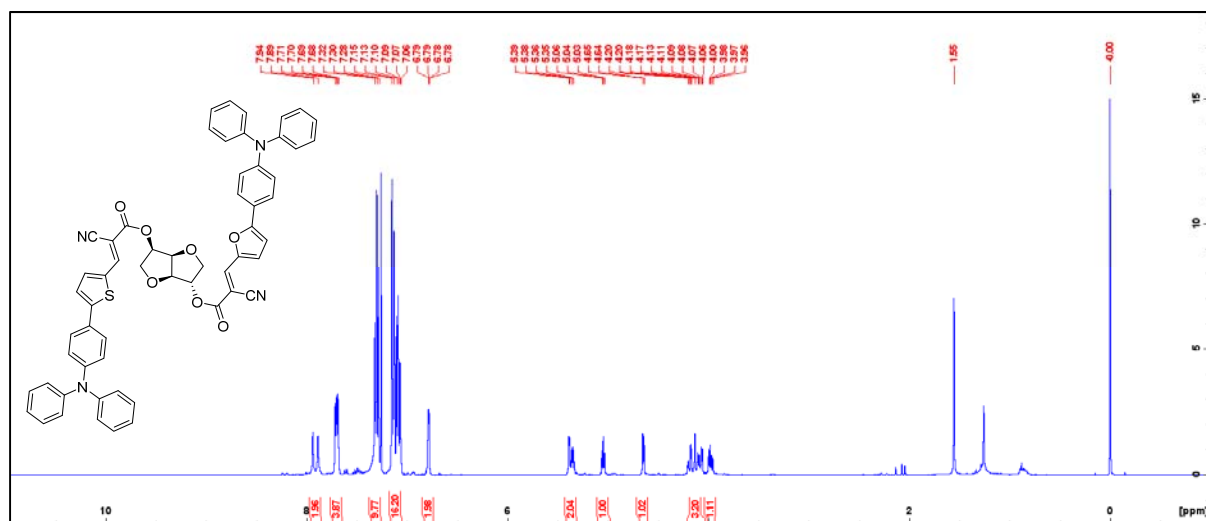


Fig 9. ^{13}C NMR Spectrum of TPA-Isos-F in CDCl_3 .

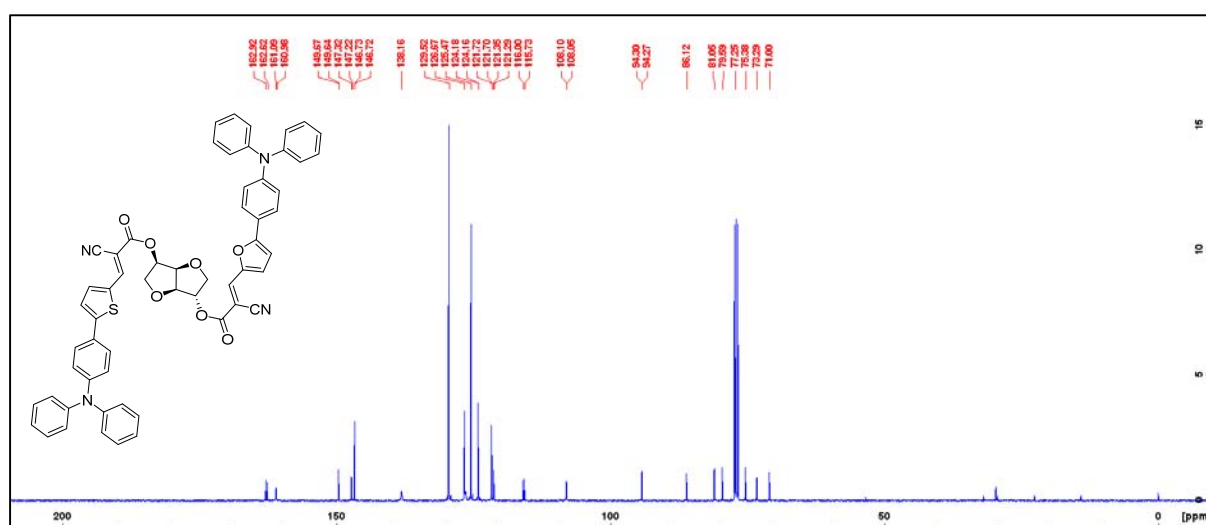


Fig 10. ¹H NMR Spectrum of TPA-Isos-T in CDCl₃.

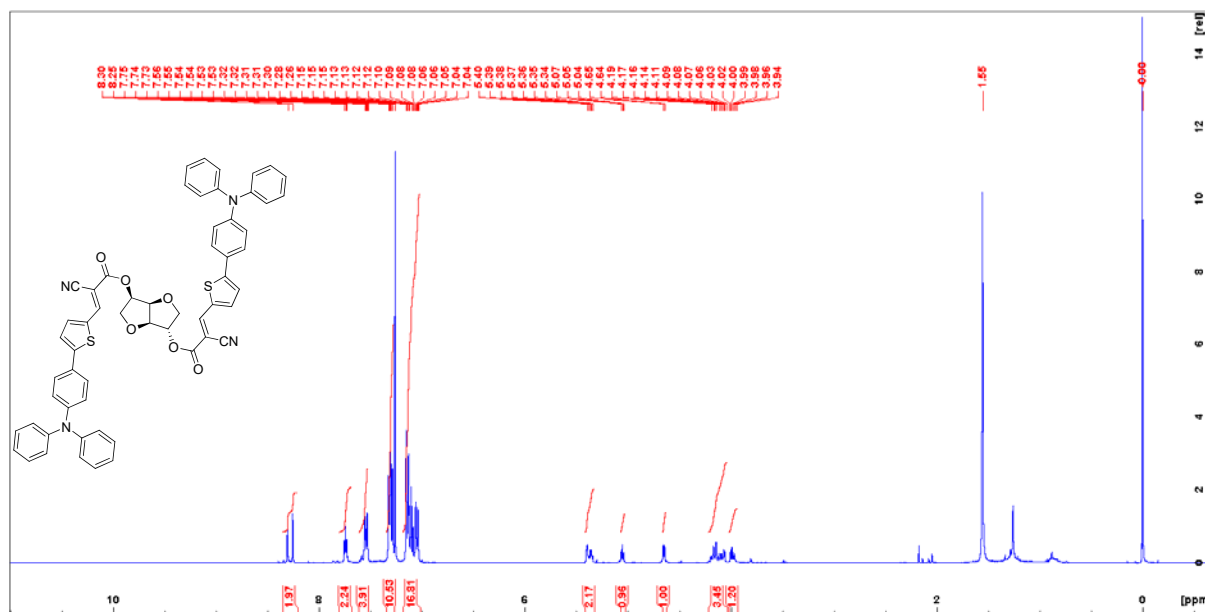


Fig 11. ¹³C NMR Spectrum of TPA-Isos-T in CDCl₃.

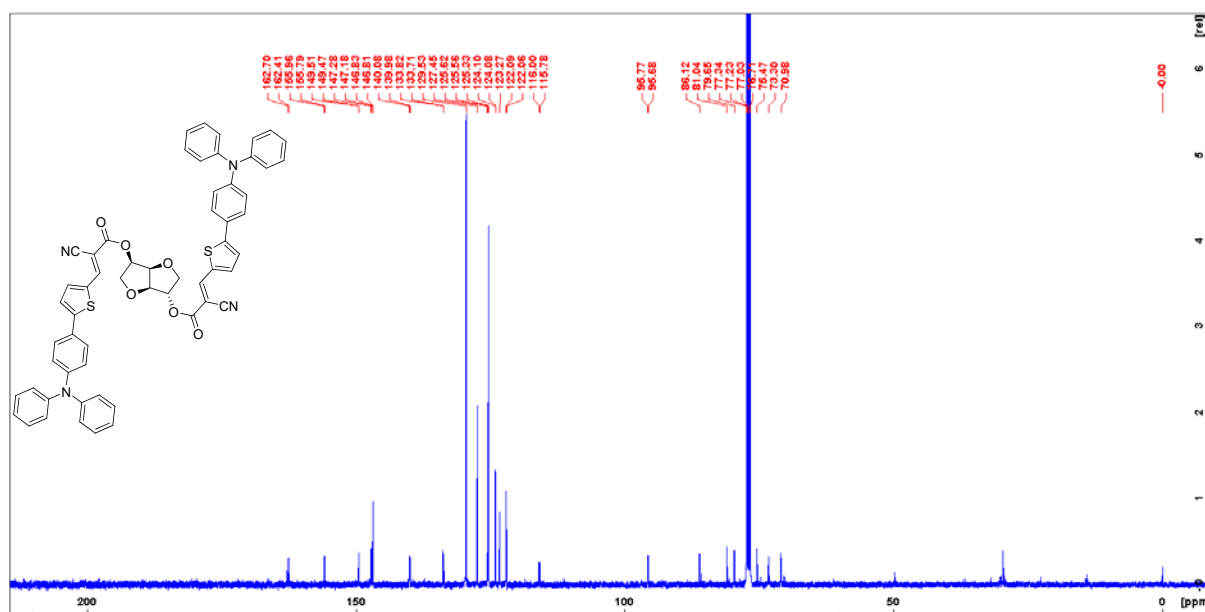


Fig 12. ^1H NMR Spectrum of TPA-Isom-F in CDCl_3 .

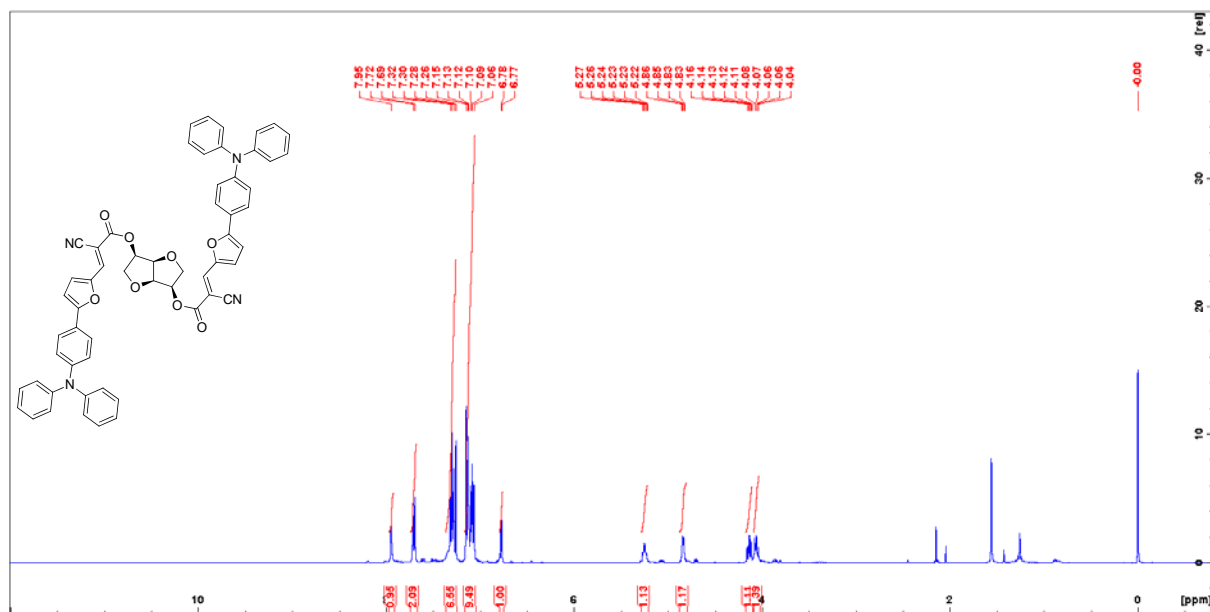


Fig 13. ^{13}C NMR Spectrum of TPA-Isom-F in CDCl_3 .

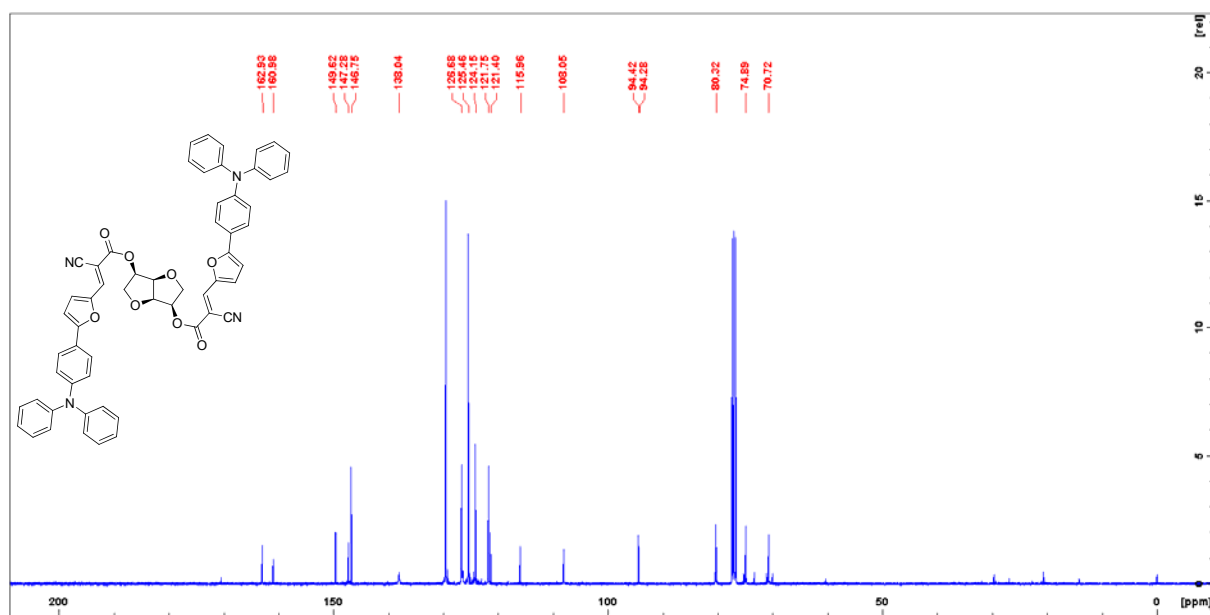


Fig 14. ¹H NMR Spectrum of TPA-Gly-T in CDCl₃.

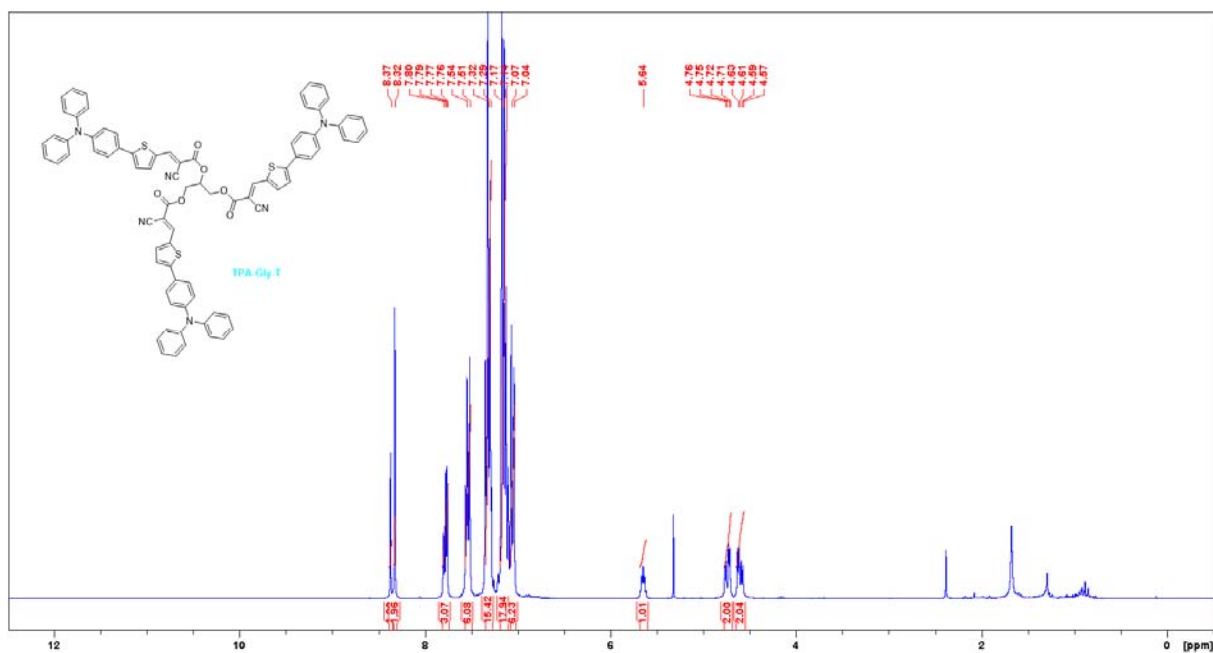


Fig 15. ¹³C NMR Spectrum of TPA-Gly-T in CDCl₃.

