

SUPPORTING INFORMATION

Fullerene Derivatives with Increased Dielectric Constant

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Table of Contents

1. Experimental section

2. Synthesis

3. UV-vis spectra

4. Electrochemical properties

5. Dielectric constant measurement

6. Electron mobility measurements based on space-charged limited current

7. NMR spectra

General

All reagents and solvents were used as received. All reactions were performed under a nitrogen atmosphere using oven dried glassware (150 °C). The C60 used for the syntheses was 99.5% (purchased from Solenne BV, Groningen, The Netherlands). Column chromatography was performed using silica gel (Kieselgel Merck Type 9385, 230-400 mesh). ¹H NMR and ¹³C NMR were performed on a Varian Unity Plus (500MHz) or on a Varian Unity Plus (400 MHz) instrument, as indicated, at 25 °C; Values are reported in ppm; Multiplicities are denoted as follows: s = singlet, m = multiplet, br = broad and J values are given in Hz. IR measurements were performed on a Nicolet Nexus FT-IR instrument. HPLC analyses were performed on an LC-MS system (Agilent/HP 1100 series) using an analytical Cosmosil Buckyprep® column (4.6 x 250 mm); UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer.

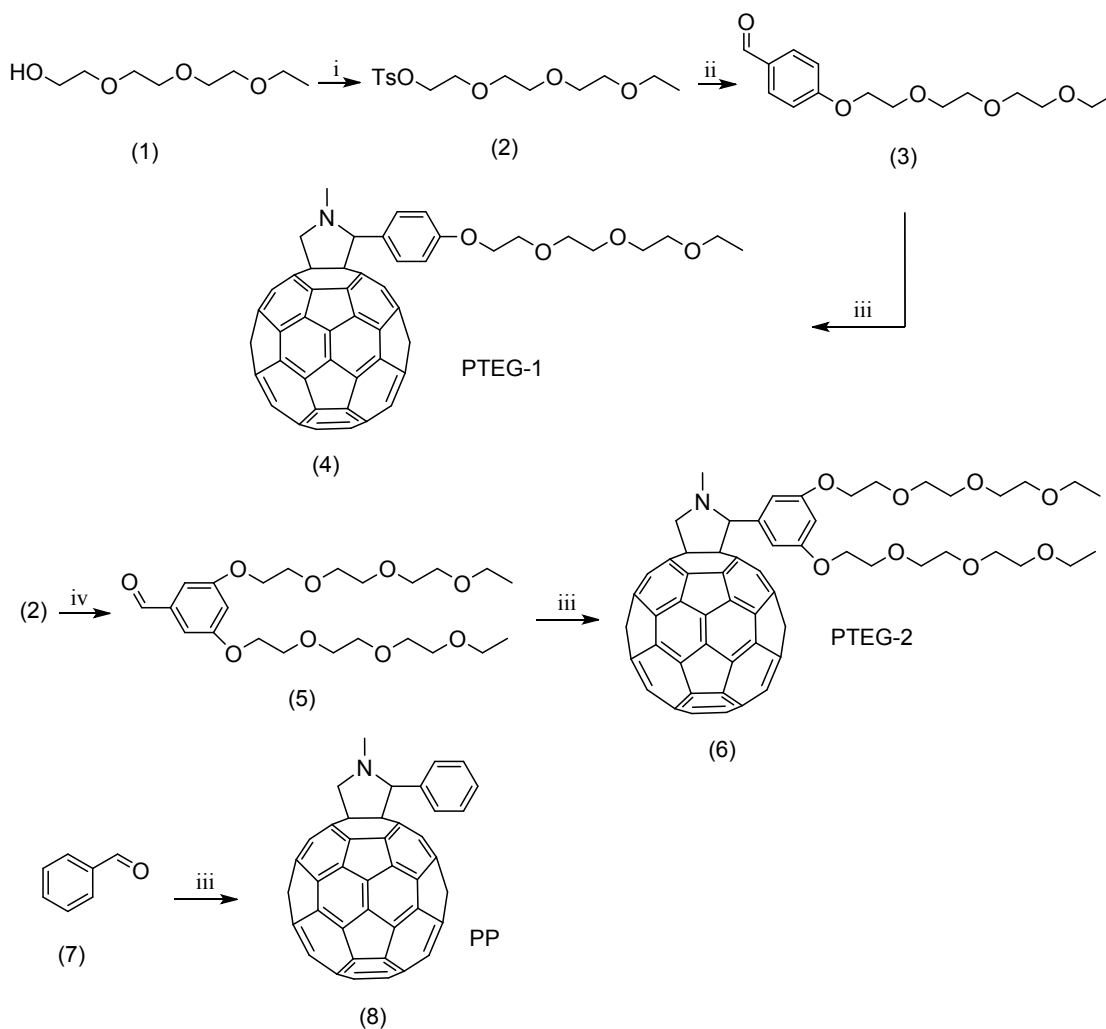
1. Experimental section

Device fabrication: Commercially available glass substrates patterned with Indium Tin Oxide (ITO) in four different dimensions were used to function as bottom electrode for capacitors. The cleaning of substrates was performed by scrubbing with soap/water solution, rinsing with de-ionized water, sonication in acetone and isopropyl alcohol followed by oven drying and UV-ozone treatment. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; VP AI4083, H.C. Starck) was spin cast from an aqueous suspension in ambient condition and oven-dried at 140 °C for 10 minutes. All films were spun from CHCl₃ under an inert, nitrogen atmosphere. Metallic contacts and LiF were deposited at a pressure of $\sim 10^{-6}$ mbar by thermal evaporation.

Device Characterization: Impedance spectroscopy was performed in the range of 10 Hz to 10 MHz using a Solartron 1260 impedance gain-phase analyzer with an AC drive voltage of 10 mV. Current-voltage characterization was conducted with Keithley 2400 source meter. The stability of measurements was established by carrying the tests under inert, nitrogen atmosphere at a stable temperature (295 K) in the dark. Film thicknesses were obtained using a Dektak 6M Stylus Profiler and, in cases the films were too soft for the tip of the profiler, these thicknesses were verified by AFM profile.

2. Synthesis

Scheme S1. Synthetic route for the preparation of PTEG-1, PTEG-2, and PP.

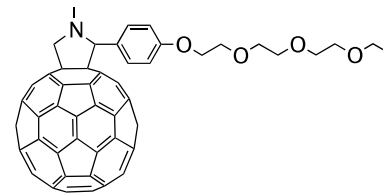


i) TsCl, NaOH, THF, *ii*) *p*-hydroxybenzaldehyde, K₂CO₃, DMF *iii*) C₆₀, sarcosine, ODCB, 90 °C, *iv*) 3,5-dihydroxybenzaldehyde, K₂CO₃, DMF

Treatment of triethylene glycol monoethyl ether (**1**) with toluene-*p*-sulfonyl chloride (TsCl) and NaOH, followed by a Williamson-type reaction of the resulting tosylate (**2**) with *p*-hydroxybenzaldehyde in the presence of K₂CO₃ in DMF at 90 °C afforded the corresponding benzaldehyde (**3**). The target fulleropyrrolidine (PTEG-1) (**4**) was prepared by 1,3-dipolar cycloaddition of the aldehyde (**3**), *N*-methylglycine and C₆₀, according to the Prato method in ODCB at 90 °C in 39% yield. PTEG-2 (**6**) was synthesized from 3,5-dihydroxybenzaldehyde by following a similar synthetic approach as described above in 32% yield. For comparison, we also prepared PP (**8**), which lacks TEG chains, starting from benzaldehyde.

PTEG-1 (4):

An oven-dried three-necked, 250 mL round-bottom flask was charged with C₆₀ (1.08 g, 1.5 mmol), 4-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy) benzaldehyde (452 mg, 1.6 mmol), sarcosine (435 mg, 4.9 mmol) and *o*-dichlorobenzene (100 mL). The reaction mixture was stirred under N₂ at 90 °C for 72 h. The mixture was concentrated *in vacuo* to ~15 mL, and



the crude residue was purified by column chromatography (Silica gel; toluene/ethyl acetate 4:1) to afford the pure compound as a brown solid. The product was redissolved in 7 mL of chlorobenzene, precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried *in vacuo* at 50 °C. This procedure gave 600 mg (0.58 mmol, 39%) of PTEG-1.

¹H NMR (400 MHz, CDCl₃) δ = 7.69 (br s, 2H), 6.96 (d, *J* = 8.6, 2H), 4.97 (d, *J* = 9.4, 1H), 4.87 (s, 1H), 4.23 (d, *J* = 9.4, 1H), 4.13 (t, *J* = 5.0, 2H), 3.84 (t, *J* = 5.0, 2H), 3.73-3.71 (m, 2H), 3.65-3.63 (m, 4H), 3.60 – 3.55 (m, 2H), 3.51 (q, *J* = 7.0, 2H), 2.78 (s, 3H), 1.19 (t, *J* = 7.0, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 158.80, 156.36, 154.09, 153.63, 153.61, 147.29, 147.27, 146.77, 146.51, 146.32, 146.29, 146.24, 146.19, 146.13, 146.11, 146.07, 145.92, 145.90, 145.76, 145.52, 145.47, 145.44, 145.31, 145.29, 145.25, 145.21, 145.12, 144.68, 144.61, 144.37, 143.12, 142.96, 142.65, 142.56, 142.53, 142.52, 142.27, 142.24, 142.14, 142.10, 142.06, 142.01, 142.00, 141.94, 141.82, 141.66, 141.52, 140.13, 140.09, 139.88, 139.58, 136.75, 136.54, 135.78, 135.76, 130.42, 129.09, 114.65, 83.14, 77.22, 70.82, 70.70, 70.63, 69.97, 69.80, 69.73, 68.95, 67.33, 66.63, 39.99, 15.18.

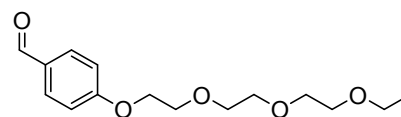
IR (cm⁻¹): 2848, 1609, 1509, 1309, 1259, 1225, 1174, 1126, 1103, 846, 600, 573, 551, 526.

Exact mass: Calcd for C₇₇H₂₇NO₄: 1029.2. Found: 1029.8

Anal. Calcd. For C₇₇H₂₇NO₄: C, 88.60; H, 2.62; N, 1.36. Found: C, 88.93; H, 2.52; N, 1.41

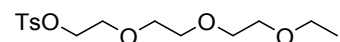
4-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy) benzaldehyde (3):

A three-necked, 250 mL round-bottom flask was charged with *p*-hydroxybenzaldehyde (1.55 g, 12.69 mmol), 2-[2-(2-ethoxyethoxy) ethoxy]ethyl *p*-tosylate (4.78 g, 14.38 mmol), K₂CO₃ (5.3 g, 38.4 mmol) and DMF (60 mL). The reaction mixture was stirred overnight at 90 °C. After cooling, the crude reaction mixture was poured into water (100 mL, pH = 2) in a 250 mL Erlenmeyer flask and extracted with dichloromethane. The organic layer was washed subsequently with water (3x 25 mL) and brine (1x 25 mL) and dried over Na₂SO₄. The solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to give pure compound as light yellow oil (3.0 g, 10.64 mmol, 83%).



¹H NMR (400 MHz, CDCl₃) δ = 7.80 (d, *J* = 8.7, 2H), 6.99 (d, *J* = 8.7, 2H), 4.19 (t, *J* = 4, 2H), 3.87 (t, *J* = 4, 2H), 3.71 (m, 3.4, 2H), 3.68 – 3.60 (m, 4H), 3.56 (m, 2H), 3.49 (q, *J* = 7.0, 2H), 1.18 (t, *J* = 7.0, 3H).

2-[2-(2-ethoxyethoxy) ethoxy]ethyl *p*-tosylate (2):

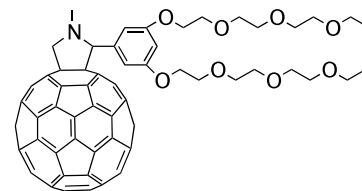


Sodium hydroxide (800 mg, 20 mmol) dissolved in water (4 mL) and 2-[2-(2-ethoxyethoxy) ethoxy]ethanol (2.49 g, 14 mmol) in THF (4mL) were placed in a three-necked, 50 mL flask. The mixture was cooled on an ice bath. *p*-Toluenesulfonyl chloride (2.44 g, 13 mmol) in THF (4 mL) was added drop-wise to the mixture over 1 h. The solution was stirred at 0 °C for an additional 3h., then poured into ice-water (150 mL) and extracted with ethyl acetate. The organic layer was washed with water and dried over Na₂SO₄. The solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to give the pure compound as colorless oil (4.0 g, 12.04 mmol, 92%).

¹H NMR (400 MHz, CDCl₃) δ = 7.78 (d, *J* = 8.3, 2H), 7.32 (d, *J* = 8.0, 2H), 4.14 (t, *J* = 4.8, 2H), 3.67 (t, *J* = 4.8, 2H), 3.61 – 3.53 (m, 8H), 3.49 (q, *J* = 7.0, 2H), 2.42 (s, 3H), 1.18 (t, *J* = 7.0, 3H).

¹³C NMR (100 MHz, CDCl₃) δ = 144.75, 132.99, 129.78, 127.94, 70.71, 70.67, 70.49, 69.75, 69.22, 68.63, 66.58, 21.60, 15.12.

PTEG-2 (6):



A three-necked, 250 mL round-bottom flask was charged with C₆₀ (720 mg, 1.0 mmol), 3,5-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy) benzaldehyde (458 mg, 1mmol), sarcosine (270 mg, 3.0 mmol) and *o*-dichlorobenzene (100 mL). The reaction mixture was stirred under N₂ at 90 °C for 72 h. The reaction mixture was concentrated *in vacuo* to ~15 mL, and the crude residue was purified by column chromatography (silica gel; chloroform/ethyl acetate 3:2) to afford the pure compound as a brown solid. The product was redissolved in 7 mL of chlorobenzene, precipitated with MeOH, washed repeatedly with MeOH and pentane, and dried *in vacuo* at 50 °C. This gave 267 mg (0.22 mmol, 32%) of PTEG-2.

¹H NMR (400 MHz, CDCl₃) δ = 6.99 (br, 2H), 6.45 (t, *J* = 2.1, 1H), 4.95 (d, *J* = 9.4, 1H), 4.81 (s, 1H), 4.23 (d, *J* = 9.4, 1H), 4.10 (m, 4H), 3.82 (t, *J* = 4.9, 4H), 3.74 – 3.60 (m, 12H), 3.58 (m, 4H), 3.51 (q, *J* = 7.0, 4H), 2.80 (s, 3H), 1.19 (t, *J* = 7.0, 6H).

¹³C NMR (100 MHz, CDCl₃) δ = 158.91, 155.11, 153.06, 152.57, 152.40, 146.27, 145.95, 145.41, 145.28, 145.24, 145.19, 145.12, 145.08, 145.07, 145.05, 144.94, 144.91, 144.74, 144.52, 144.50, 144.45, 144.30, 144.25, 144.23, 144.22, 144.21, 144.12, 143.67, 143.59, 143.36, 143.35, 142.11, 141.94, 141.65, 141.54, 141.20, 141.17, 141.13, 141.10, 141.01, 140.91, 140.78, 140.65, 140.59, 139.14, 139.09, 138.83, 138.58, 138.22, 135.56, 135.46, 134.74, 134.69, 101.01, 82.60, 76.20, 75.90, 69.80, 69.68, 69.58, 68.90, 68.79, 68.56, 68.02, 66.52, 65.62, 39.04, 14.17.

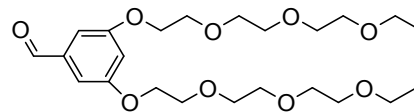
IR (cm⁻¹): 2861, 1591, 1443, 1347, 1330, 1293, 1103, 1066, 938, 848, 766, 746, 755, 726, 690, 597, 573, 552, 526.

Exact mass: Calcd for C₈₅H₄₃NO₈: 1205.3. Found: 1205.8

Anal. Calcd. For C₈₅H₄₃NO₈ : C, 84.56; H, 3.56; N, 1.16. Found : C, 83.25; H, 3.63; N, 1.24.

3,5-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy) benzaldehyde (5):

A three-necked, 50 mL round-bottom flask was charged with 3,5-dihydroxybenzaldehyde (500 mg, 3.63 mmol), 2-[2-(2-ethoxyethoxy)ethoxy]ethyl *p*-tosylate (2.85 g, 8.58 mmol), K₂CO₃ (1.6 g, 11.58 mmol), and DMF (25 mL). The reaction mixture was stirred over night at 90 °C. After cooling, the crude reaction mixture was poured into water (100 mL, pH = 2) in a 250 mL Erlenmeyer flask and extracted with dichloromethane. The organic layer was washed subsequently with water (3 x 25 mL) and brine (1 x 25 mL) and dried over Na₂SO₄. The solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, dichloromethane/ ethyl acetate 3:1) to give pure compound as colorless oil (1.3 g, 2.83 mmol, 78%).



¹H NMR (400 MHz, CDCl₃) δ = 9.83 (s, 1H), 6.97 (d, *J* = 2.3, 2H), 6.71 (t, *J* = 2.3, 1H), 4.11 (t, *J* = 4.0, 4H), 3.82 (t, *J* = 4, 4H), 3.70 – 3.66 (m, 4H), 3.65 – 3.58 (m, 8H), 3.54 (m, 4H), 3.47 (q, *J* = 7.0, 4H), 1.15 (t, *J* = 8.0, 6H).

¹³C NMR (100 MHz, CDCl₃) δ = 191.74, 160.34, 138.24, 108.22, 107.91, 70.80, 70.67, 70.59, 69.76, 69.48, 67.79, 66.55, 15.11.

3. UV-vis spectra

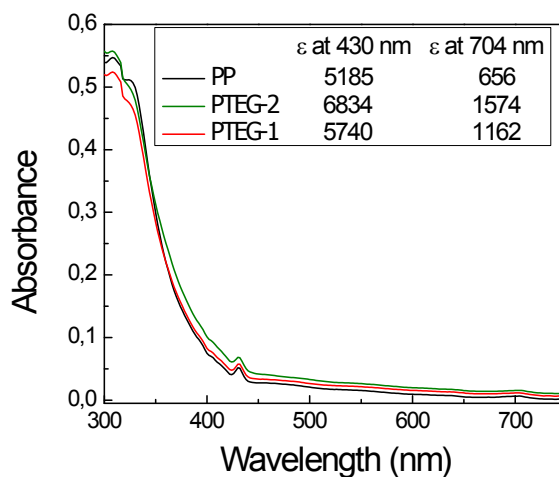


Figure S1. UV-vis absorption spectra of PTEG-1, PTEG-2 and PP in 10⁻⁵ M CHCl₃ solution

4. Electrochemical properties

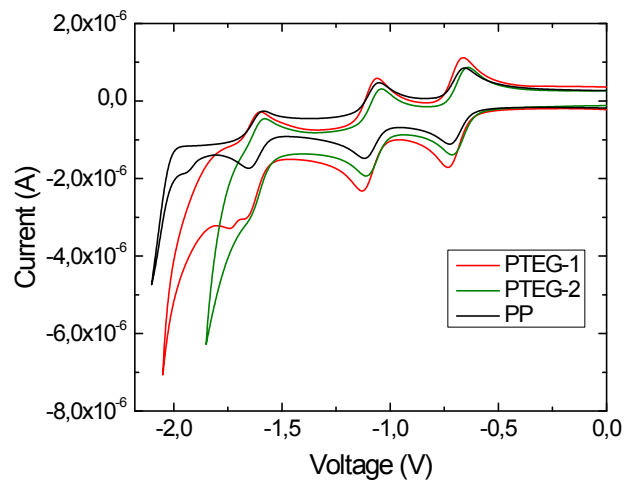


Figure S2. Cyclic voltammograms of PTEG-1, PTEG-2 and PP; experimental conditions: Bu_4NPF_6 (0.1 M) as the supporting electrolyte, ODCB/ CH_3CN (4:1) as solvent; Pt, working electrode; Pt wire, counter electrode; Ag/AgCl, reference electrode; scan rate 10 mV/s, potentials are relative to Fc/Fc^+ .

5. Dielectric constant measurement

Dielectric constant is obtained by spectral impedance measurements in the following device architecture: ITO/PEDOT:PSS/fullerene film/Al (Figure S3). The samples comprised glass substrates patterned with ITO in four different configurations.

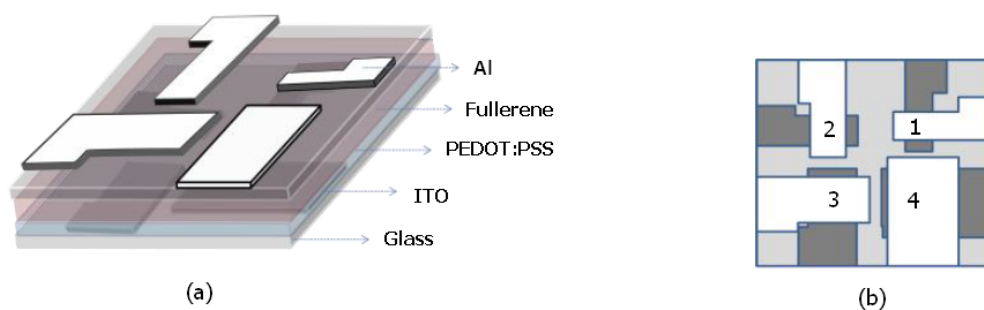


Figure S3. (a) General layout of the device (b) 9.5 mm^2 , 16.16 mm^2 , 35.7 mm^2 , 99.5 mm^2 defined areas for four parallel plate capacitors on one substrate.

The capacitance was determined from equivalent circuit (Figure S4) fit over impedance response of fabricated capacitors. The dielectric constant was determined by:

$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

where A is the capacitor's area (m^2), d is thickness of the fullerene film (m) and ϵ_0 is the permittivity of a vacuum (8.85×10^{-12} F/m).

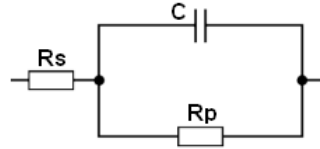


Figure S4. Equivalent circuit to fit the measurement data, with capacitance C , parallel resistance R_p and serial resistance R_s .

6. Electron mobility measurements based on space-charged limited current

The experimental J - V curves show that current density quadratically depends on the voltage, which is characteristic behavior for space-charge limited current (SCLC) and is described by

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_e \frac{V^2}{L^3}$$

where ϵ_r is the dielectric constant of fullerene derivative obtained from impedance spectroscopy and L is the thickness of the film. We calculated mobility values from SCLC fits of the current density-voltage response of the devices determined.

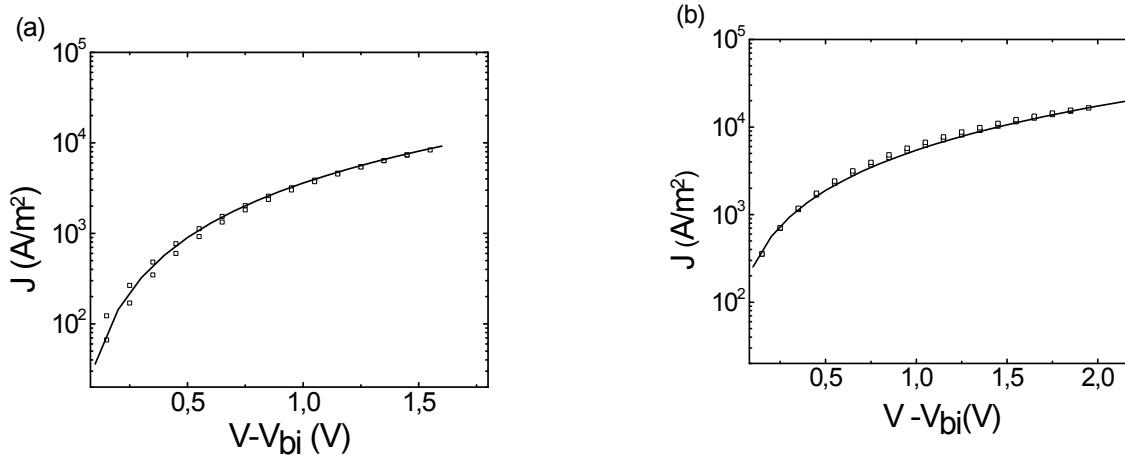
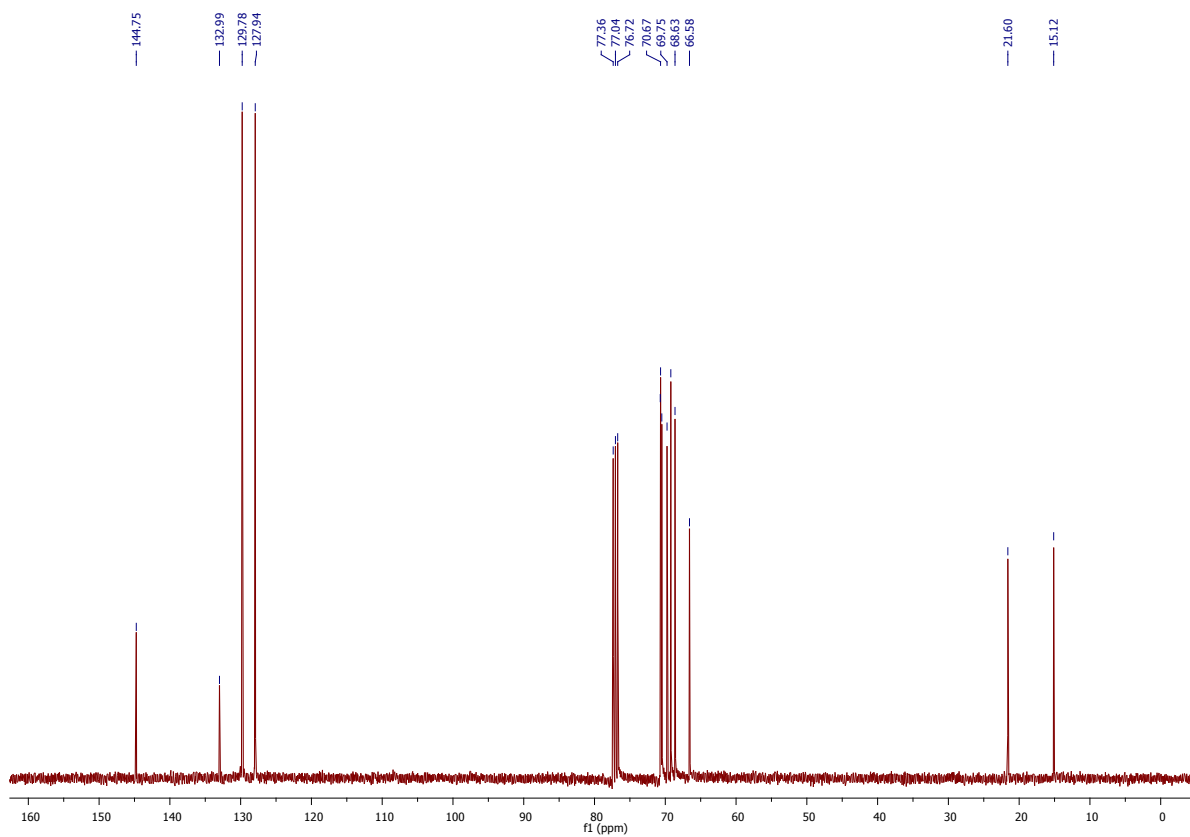
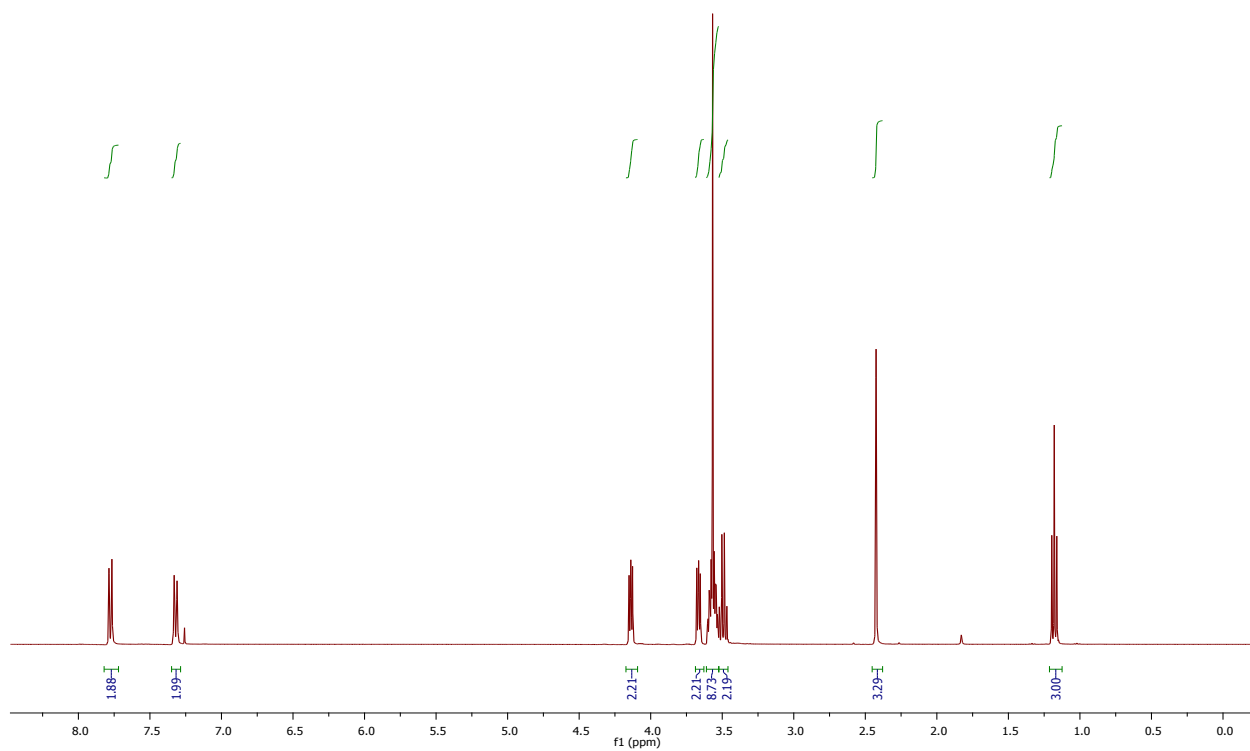


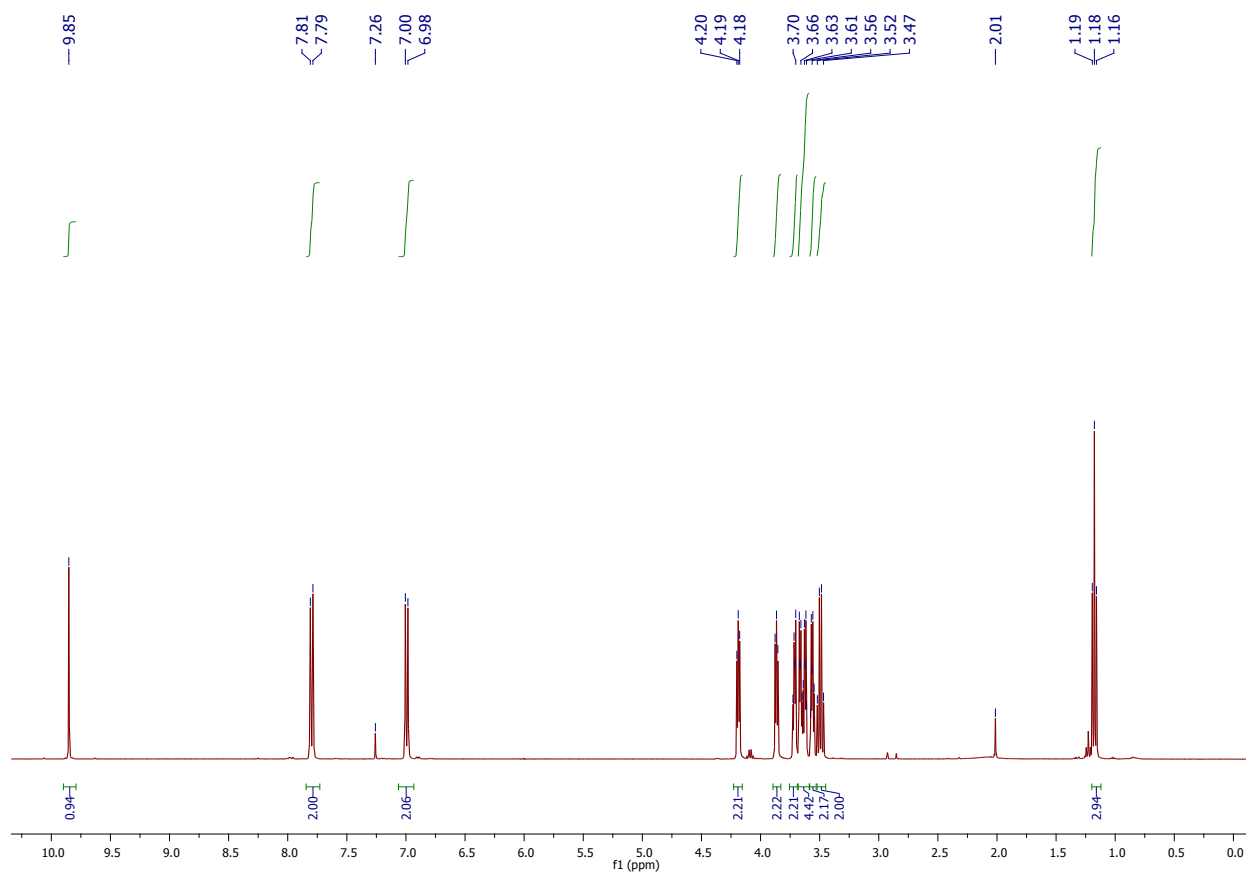
Figure S5. Current density versus voltage corrected for (a) $V_{bi} = 0.5$ of Au /PTEG-1/LiF/Al and (b) $V_{bi} = 0.05$ of Al /PTEG-2/Al at room temperatures 295K. Experimental data (symbols) are fitted with SCLC current (solid lines).

7. NMR spectra

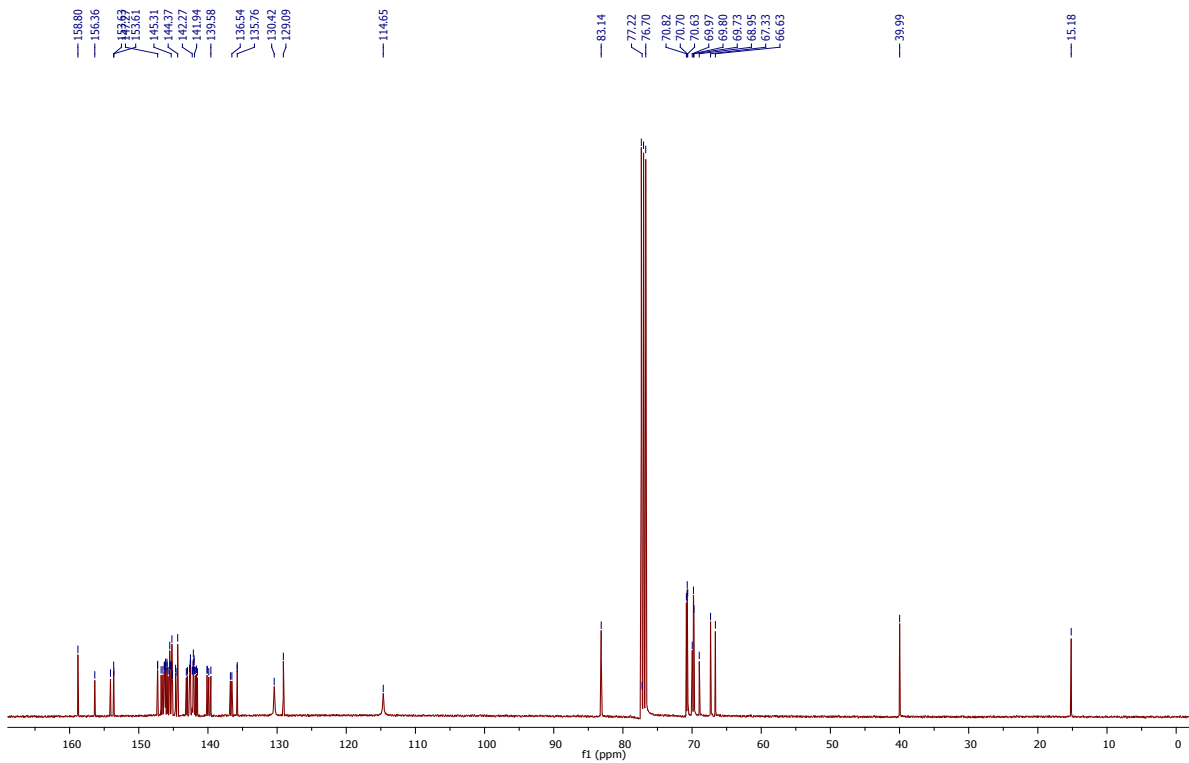
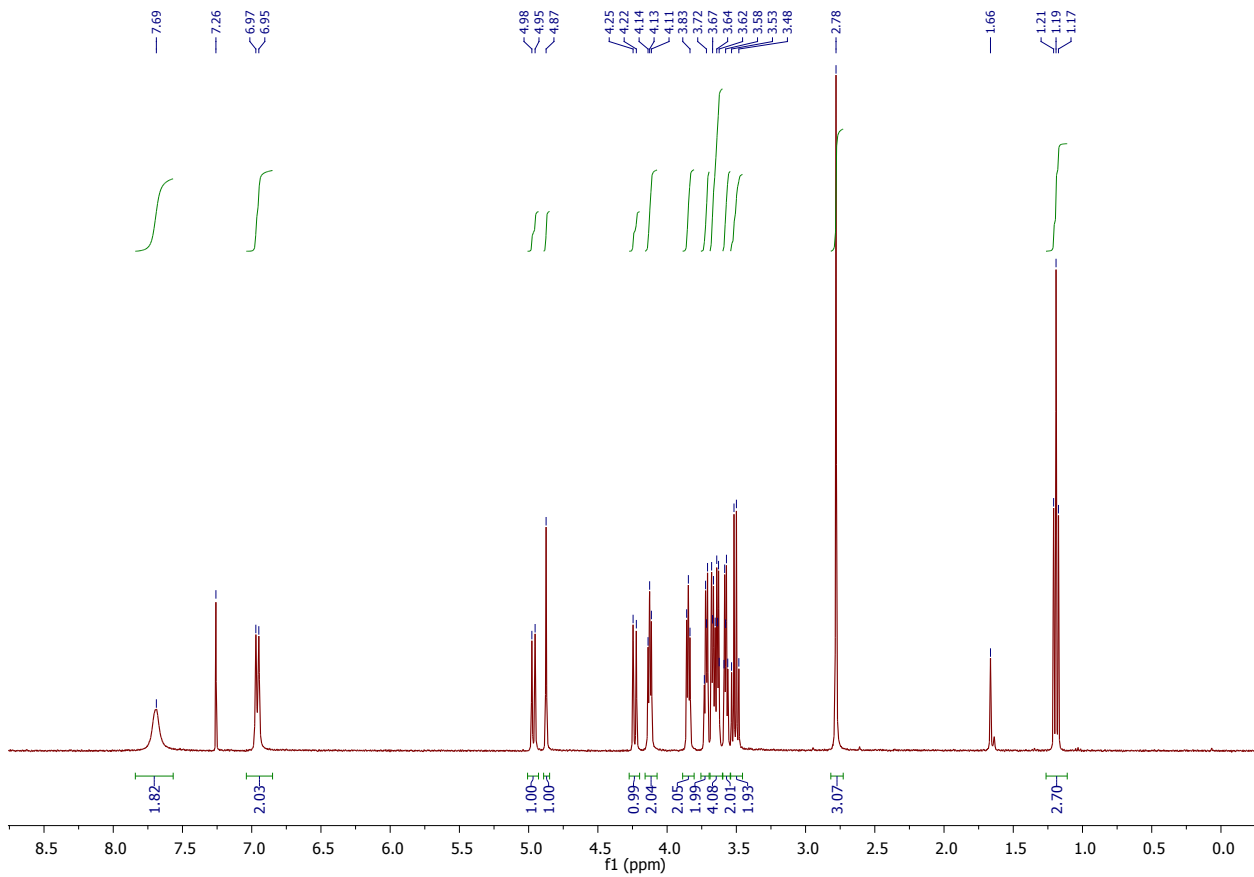
2-[2-(2-ethoxyethoxy) ethoxy]ethyl *p*-tosylate (2):



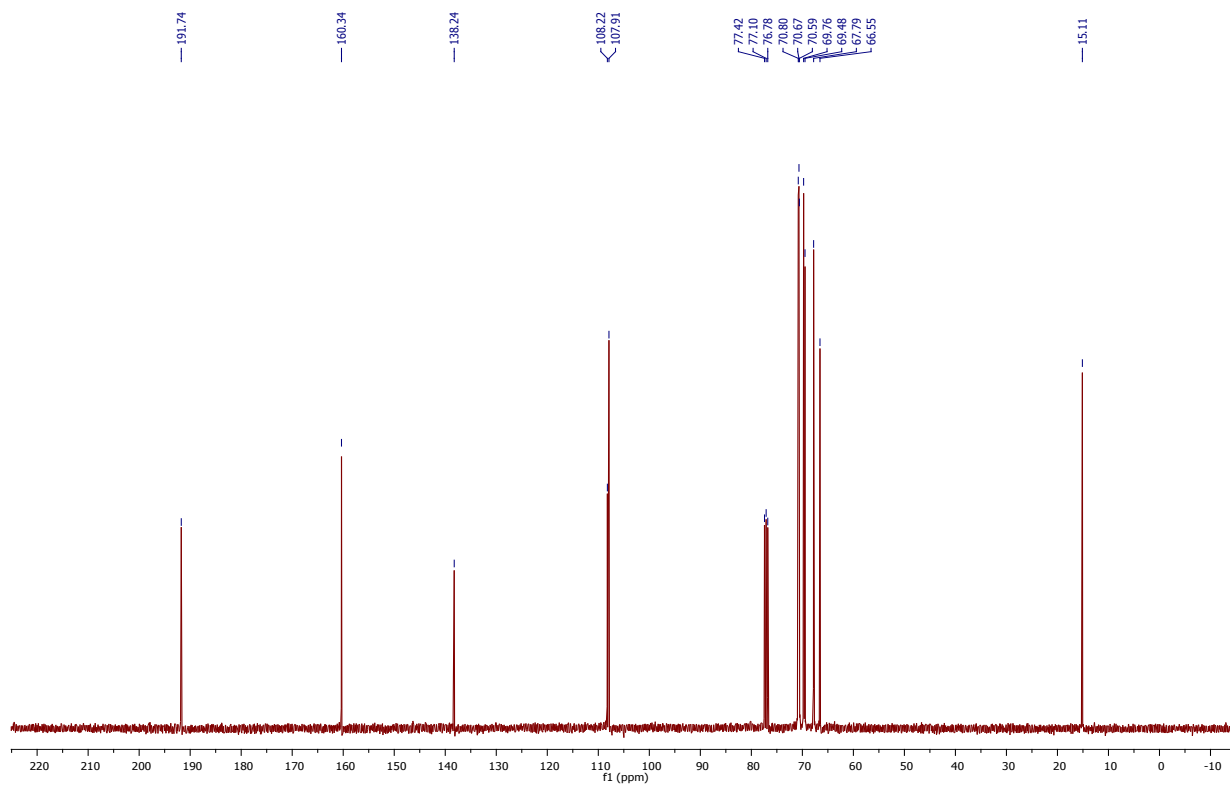
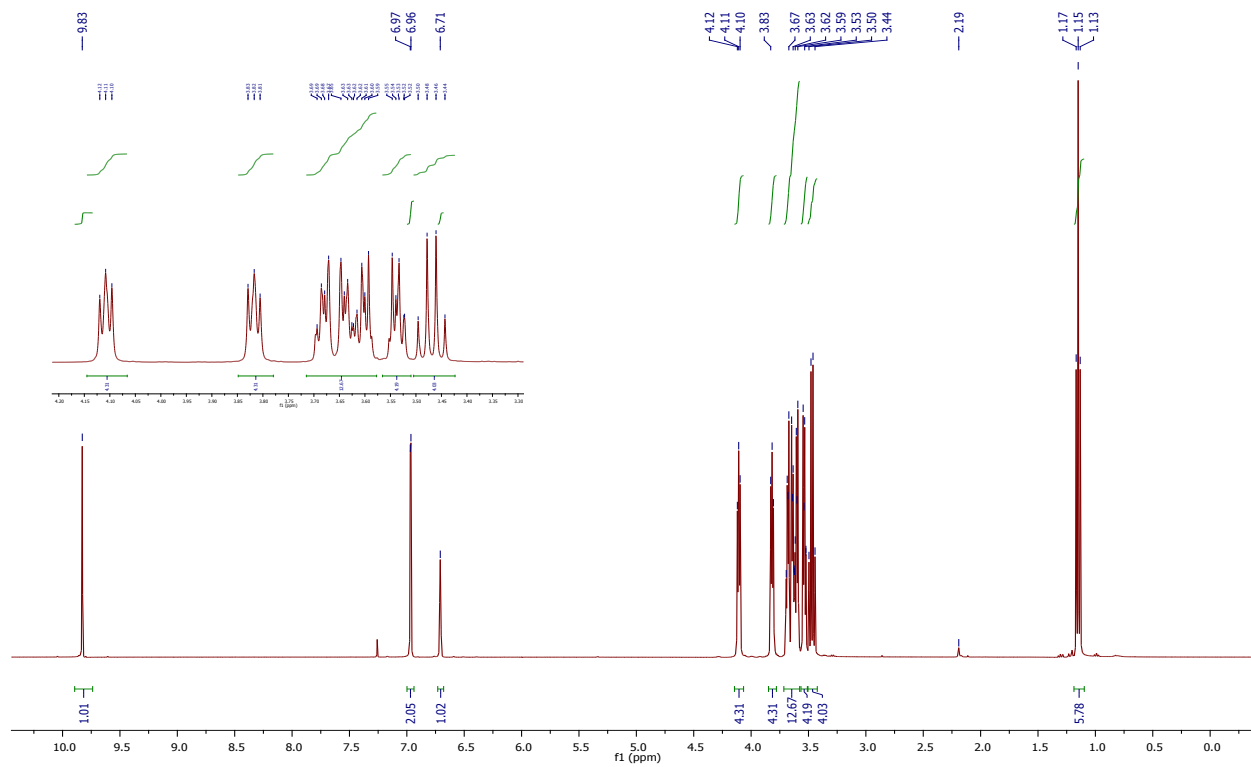
4-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy) benzaldehyde (3)



PTEG-1 (4)



3,5-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzaldehyde (5)



PTEG-2 (6)

