The first selenophene containing phthalocyanine analogue and its application in transistor devices

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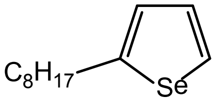
S1 Experimental section

All other chemicals were purchased from Aldrich and used as received except selenophene which was purchased from Frontier Scientific, Inc. All reactions were carried out in under Argon using solvents and reagents as commercially supplied, unless otherwise stated. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of $CDCl_3$ or TMS as an internal reference and are given in ppm. Electrospray mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. MALDI was performed with a Micromass MALDI micro MX. UV-vis spectra were recorded on a UV-1601 Shimadzu S2 UV-vis spectrometer. IR spectra were recorded as neat samples on a Perkin Elmer Precisely Spectrum 100 FT-IR spectrometer with a universal ATR sampling accessory. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh). Thin Layer Chromatography (TLC) was performed on Merck aluminium-backed plates precoated with silica (0.2 mm, 60 F254). Microwave experiments were performed in a Biotage initiator V 2.3. Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5nW and a power number of 0.5. Samples for PESA were prepared by spin-coating a solution of the sample on glass substrates from chlorobenzene at a concentration of 5mg mL^{-1}.

OFETs were fabricated on a highly-doped silicon substrate, which acted as a common gate electrode. A thermally grown 200 nm layer of silicon dioxide was then used as the gate dielectric. Gold source and drain electrodes were patterned using standard photolithography. The SiO_2 layer was treated with the primer hexamethyldisilazane (HMDS) to before semiconductor depostion. Solutions of the SePc were made in chlorobenzene at a concentration of 10 mg / ml and then spin-cast (1000 rpm for 60 sec) onto the substrates under atmospheric-pressure N_2. The samples were then annealed for 30 min at 50˚C. Electrical characterisation was carried out in N_2 at atmospheric pressure using a Keithley 4200 semiconductor parameter analyser.

S2 Synthetic Procedures

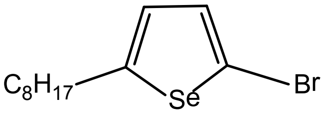
2-Octylselenophene (1)



1

To a solution of selenophene (5 g, 38.15 mmol) in THF (50 mL) at -78°C was added a solution of *n*-BuLi (2.5M solution in hexanes, 18.3 mL , 45.79 mmol) dropwise. The solution was allowed to warm to room temperature over 1.5 h, and then cooled to -78°C upon when 1-bromooctane (7.91 mL, 45.79 mmol) was added. The reaction was left to reach room temperature and stirred for 16 h. Water (130 mL) was added and the organic layer was extracted with diethyl ether (3 x 50 mL). The organic phase was combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The crude product was purified by distillation (10 mbar, 115°C) to afford **1** as a pale yellow oil (3.37g, 36.24%). R_f 0.43 (hexane); IR ν_{max} (neat)/cm^{-1}: 2959 (m), 2927 (s), 2856 (m), 1463 (m), 1381 (w), 1241 (w), 1149 (w), 1027 (w), 824 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.77 (dd excl. Se satellites, *J* = 5.6 , 1.1 Hz, 1H), 7.11 (dd, *J* =5.6, 3.6 Hz, 1H), 6.92 (dd, *J* = 3.6, 1.1 Hz, 1H), 2.86 (t, *J* = 7.41 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.39 – 1.21 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 153.52, 129.10, 127.94, 126.17, 32.75, 32.59, 31.88, 29.37, 29.25, 29.15, 22.69, 14.13; ^{77}Se {^{1}H} NMR (76 MHz, $CDCl_3$) δ_{Se} 602.51; HRMS (E.I): Calculated for $C_{12}H_{20}Se$: 244.0730; found: 244.0729.

2-Bromo-5-octylselenophene (2)

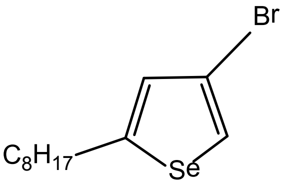


2

To a solution of 2-octylselenophene (3.36 g, 13.8 mmol) in THF (40 mL) at 0°C in the absence of light, was added N-bromosuccinimide (2.58 g, 14.4 mmol) in small portions over 1 h. The mixture was left to reach room temperature and stirred for 16 hours. Water (40 mL) was added and the mixture extracted with diethyl ether (3 x 50 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO_2, eluent: hexane) to give **2** as a yellow oil (3.94 g, 88%). R_f 0.62 (hexane); IR ν_{max} (neat)/cm^{-1}: 2957 (m) , 2926 (s), 2855 (m), 1556 (w), 1468 (s), 1377 (w), 1240 (w), 1144 (w), 1020 (w), 918 (s); ^{1}H

NMR ($CDCl_3$) δ_H 7.01 (d excl. Se satellites, *J* 3.9 Hz, 1H), 6.62 (d, *J* 3.9 Hz, 1H), 2.78 (t, *J* 7.5 Hz, 2H), 1.67 – 1.55 (m, 2H), 1.39 – 1.17 (m, 10H), 0.86 (t, *J* 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ_C 155.67, 132.31, 126.22, 111.97, 33.02, 32.34, 31.85, 29.30, 29.21, 28.99, 22.67, 14.11; ^{77}Se {^{1}H} NMR (76 MHz, $CDCl_3$) δ_{Se} 672.58; HRMS (E.I): Calculated for $C_{12}H_{19}BrSe$ 321.9835; found 321.9832.

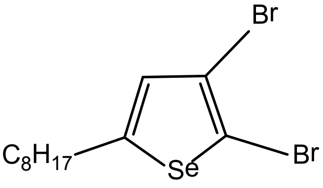
3-Bromo-5-octylselenophene (4)



4

A solution of LDA was prepared by the addition of n-BuLi (2.5M in hexanes, 8.4 mL, 21 mmol) to a solution of diisopropylamine (21.36 mmol, 3.01 mL) in THF (30 mL) at -78°C. After addition the solution was stirred for 20 min at -78°C, warmed to RT and stirred for a further 20 min. The solution was cooled to -78°C, and added dropwise to a solution of 2-bromo-5-octylselenophene (3.44 g, 10.6 mmol) in anhydrous THF (140 mL) at -78°C. The resultant mixture was stirred at -78°C for 2 h and then quenched by slow addition of MeOH (140 mL). After stirring for 1 h, the mixture was warmed to RT, saturated NaCl added (100 mL) and extracted with hexane (4 x 100 mL). The combined organics washed with water (4x100 mL), dried ($MgSO_4$), filtered and the solvent removed under reduced presurre. The crude product was purified by column chromatography (SiO_2, eluent: hexane) to give **4** as a pale yellow oil (3.13 g, 90.8%). R_f 0.71 (hexane); IR ν_{max} (neat)/cm^{-1}: 2960 (m), 2921 (s), 2854 (m), 1756 (w), 1648 (w), 1536 (m), 1465 (m), 1438 (w), 1381 (w), 1331 (m), 1183 (m), 1136 (w), 1084 (w), 1062 (w), 837 (s), 824 (s); ^{1}H NMR ($CDCl_3$) δ_H 7.61 (d excl. S , *J* 1.4 Hz, 1H), 6.87 (d excl. Se satellites, *J* 1.3 Hz, d), 2.8 2 (t excl. Se satellites, *J* 8.0 Hz, 2H), 1.70 – 1.58 (m, 2H), 1.41 – 1.19 (m, 10H), 0.87 (t, *J* 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ_C 154.19, 128.89, 123.48, 109.30, 32.46, 32.18, 31.85, 29.30, 29.19, 28.99, 22.67, 14.13; ^{77}Se {^{1}H} NMR ($CDCl_3$) δ_{Se} 638.58; HRMS (E.I): Calculated for $C_{12}H_{19}BrSe$ 321.9835; found 321.9834.

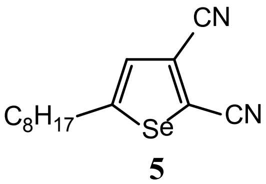
2,3-Dibromo-5-octylselenophene (3)



3

To a solution of 3-bromo-2-octylselenophene (2.60 g, 8.07 mmol) in anhydrous DMF (80 mL) at 0°C in the dark was added N-bromosuccinimide (1.58 g, 8.88 mmol) portionwise over 1 h. The mixture was left to reach room temperature and stirred for 16 hours. Water (100 mL) was added and the mixture extracted with hexane (3 x 100 mL). The combined organics were washed with water (3 x 100 mL), dried ($MgSO_4$), filtered and the solvent under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluent: hexane) to give **3** as a yellow oil (2.60 g, 80.4%). R_f 0.54 (hexane); IR ν_{max} (neat)/cm^{-1}: 2957 (m), 2924 (s), 2854 (m), 1543 (m), 1464 (m), 1378 (w), 1309 (w), 1172 (s), 1149 (m), 1131 (w), 1082 (w). 943 (s), 819 (s); ^{1}H NMR ($CDCl_3$) δ_H 6.74 (t, *J* 1.2 Hz, 1H), 2.78 (dt, *J* 9.8, 1.0 Hz, 2H), 1.64 – 1.54 (m, 2H), 1.41 – 1.19 (m, 10H), 0.87 (t, *J* 6.9 Hz, 3Ht); ^{13}C NMR ($CDCl_3$) δ_C 154.29, 128.94 (ArH), 114.02, 109.10, 32.88, 31.84 (2C), 29.26, 29.16, 28.91, 22.66, 14.12; ^{77}Se {^{1}H} NMR (76 MHz, $CDCl_3$) δ_{Se} 705.98; ^{77}Se NMR (76 MHz, $CDCl_3$) δ_{Se} 705.98 (dt, J 5.68, 9.64 Hz, 1Se); HRMS (E.I): Calculated for $C_{12}H_{18}Br_2Se$ 399.8940; found 399.8928.

2,3-Dicyano-5-octylselenophene (5)

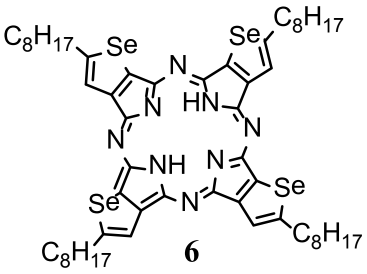


5

A solution of 2,3-dibromo-5-octylselenophene (0.20 g, 0.49 mmol) and CuCN (0.14g, 1.57mmol) in anhydrous DMF (18mL) was heated at reflux for 6 hours. After cooling to RT with mixture was poured into concentrated ammonia hydroxide solution (40 mL) and stirred overnight. The mixture was filtered through a glass sinter to remove any precipitate, and then extracted with DCM (4 x 50 mL). The combined organics were combined washed with water (50ml x 6) until the aqueous washings reached pH 7. The organic phase was dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluent 10:1 hexane: DCM to 1:1 hexane:DCM). This step was repeated to further separate mixed fractions obtained. Pure fractions were combined to give **5** as a pale yellow solid (0.09 g, 59.9%). R_f 0.28 (1:3 hexane:DCM); mp 41-43 °C ; IR ν_{max} (neat)/cm^{-1}: 2958 (m), 2928 (s), 2854 (m), 2213 (s), 1454 (m), 1361 (w), 1261 (w), 840 (w); ^{1}H NMR ($CDCl_3$) δ_H 7.22 (t, *J* 0.8 Hz, 1H), 2.90 (t, *J* 7.5 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.41 – 1.18 (m, 10H), 0.86 (t, *J* 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ_C 164.38, 127.89, 121.52, 119.79, 113.58, 113.12, 32.70, 32.15, 31.75, 29.11, 29.07, 28.89, 22.61, 14.09; ^{77}Se {^{1}H} NMR (76

MHz, $CDCl_3$) δ_{Se} 757.21; ^{77}Se NMR (76 MHz, $CDCl_3$) δ_{Se} 757.21 (dt, *J* 6.2, 10.4 Hz, 1Se); *m/z* 294 (M^+); HRMS (E.I): Calculated for $C_{14}H_{18}N_2Se$ 294.0635; found 294.0638.

2,8,14,20-Tetraoctyl-25*H*,27*H*-tetraseleno[2,3-*b*][2'3'-*g*][2''3''-*l*][2'''3'''-*q*]porphyrazine (6)



6

To a solution of 2,3-dicyano-5-octylselenophene (0.49g, 1.6 mmol) in *n*-pentanol (10 mL) at 100°C was added a solution of 3M lithium pentanoxide (5.50 mL, 17mmol). The resultant dark solution was heated at 130°C for 15 h, cooled to room temperature and acetic acid (30 mL) added. After stirring at room temperature for 30 min, the solvents were removed under reduced pressure and the residue was triturated with methanol. The resulting solid was further purified by column chromatography (Al_2O_3, eluent: DCM) to obtain crude **6** as a black solid (78 mg, 15.9%). A pure sample was obtained for analysis by washing with acetone. R*f* 0.86 (DCM); mp 220-224°C; λ_{max} ($CHCl_3$, 4.25 x 10^{-6} M)/nm 363 (Ɛ/M^{-1} cm^{-1} 121000), 653 (135000), 701 (219000); IR ν_{max} (ATR)/cm^{-1}: 3298 (w), 2958 (m), 2952 (s), 2856 (m), 1529 (w), 1467 (w), 1135 (w), 1106 (w), 1055 (w), 1012 (w), 921 (w), 843 (w), 791 (w), 737 (w); ^{1}H NMR ($CDCl_3$) δ_H 8.32-8.22 (m, 4H), 3.36 (t, *J* 7.3 Hz, 8H, t), 2.12-2.02 (m, 8H), 1.71-1.21 (m, 40H), 0.92 (t, *J* 6.8 Hz, 12H), -3.04 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ_C 161.39, 148.77, 146,71, 142.35, 119.31, 119.04, 34.19, 32.44, 32.35, 32.05, 29.68, 29.49, 22.80, 14.22. ^{77}Se {^{1}H} NMR (76 MHz, $CDCl_3$) δ_{Se} 558.53 (2 Se, m), 555.57 (2 Se, m); (MALDI TOF) *m/z* 1178 (M^+).

Alternative synthesis for 2,8,14,20-Tetraoctyl-25*H*,27*H*-tetraseleno[2,3-*b*][2'3'-*g*][2''3''-*l*][2'''3'''-*q*]porphyrazine (6)

Li (0.0412 g, 5.94 mmol) was added to *n*-pentanol (5 mL) under an argon atmosphere with stirring. The mixture was heated to 100°C, after 1 hour, when the Li had fully dissolved, **5** (0.29 g, 0. 99mmol) was added and the mixture was heated to 130 °C. The resultant dark mixture was left under reflux overnight. The reaction mixture was then left to reach room temperature and poured into MeOH (30 mL) with a pipette of 37 % HCl and left to stir for 30 minutes. The mixture was then filtered and the black precipitates were purified using column chromatography (Al_2O_3, eluted in DCM) to obtain crude **6** as a black solid (51 mg, 17.5%). A pure sample was obtained for analysis by washing with acetone.

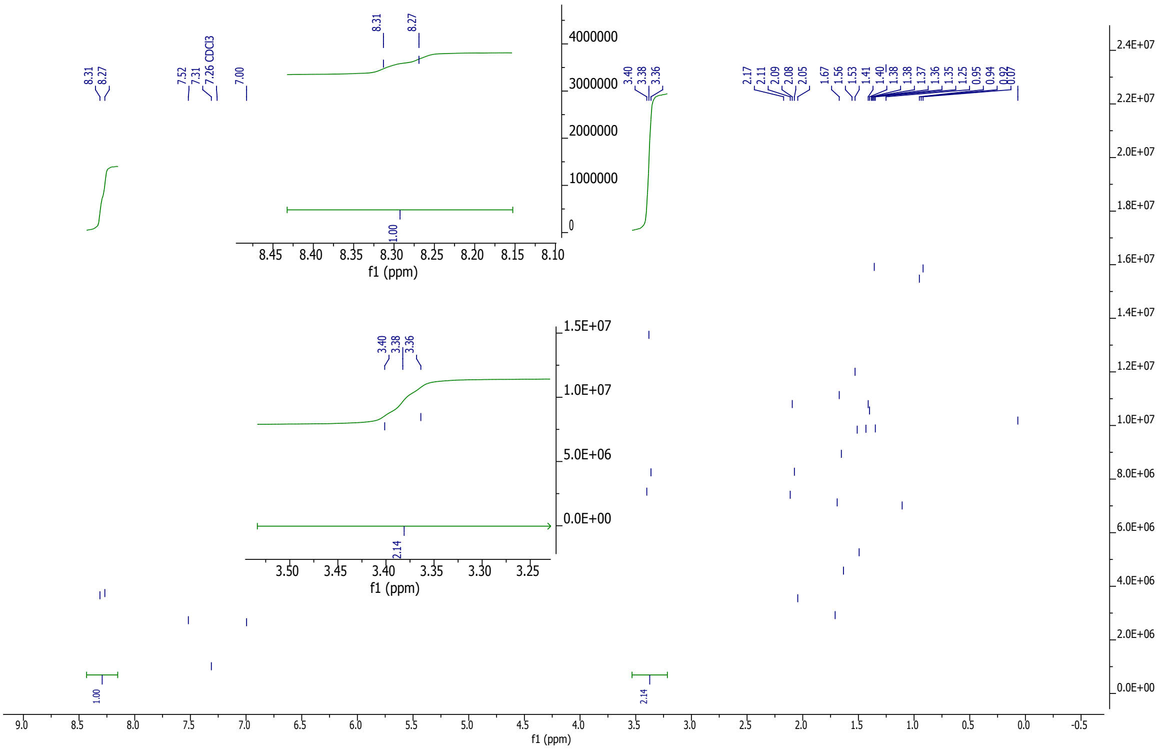


Figure S1. ^{1}H NMR of SePc in $CDCl_3$.

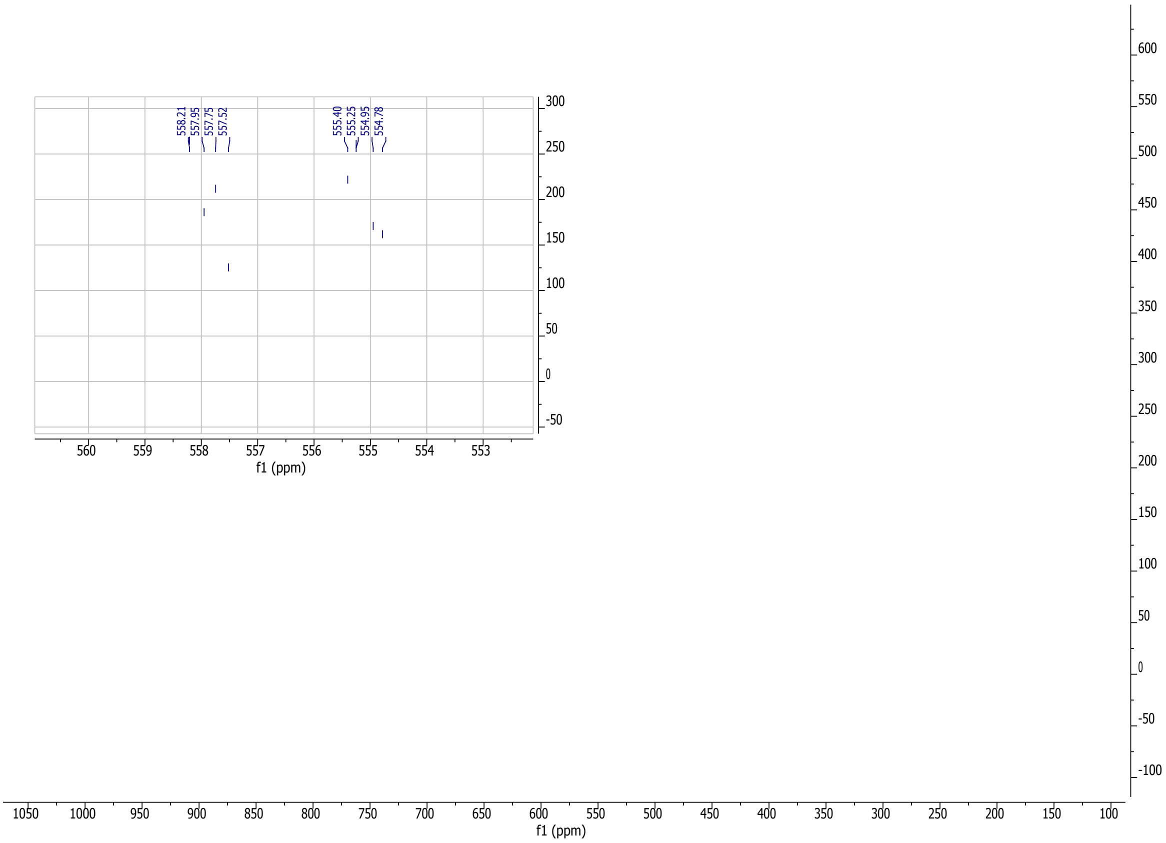


Figure S2. ^{77}Se{^{1}H} NMR of SePc in $CDCl_3$.

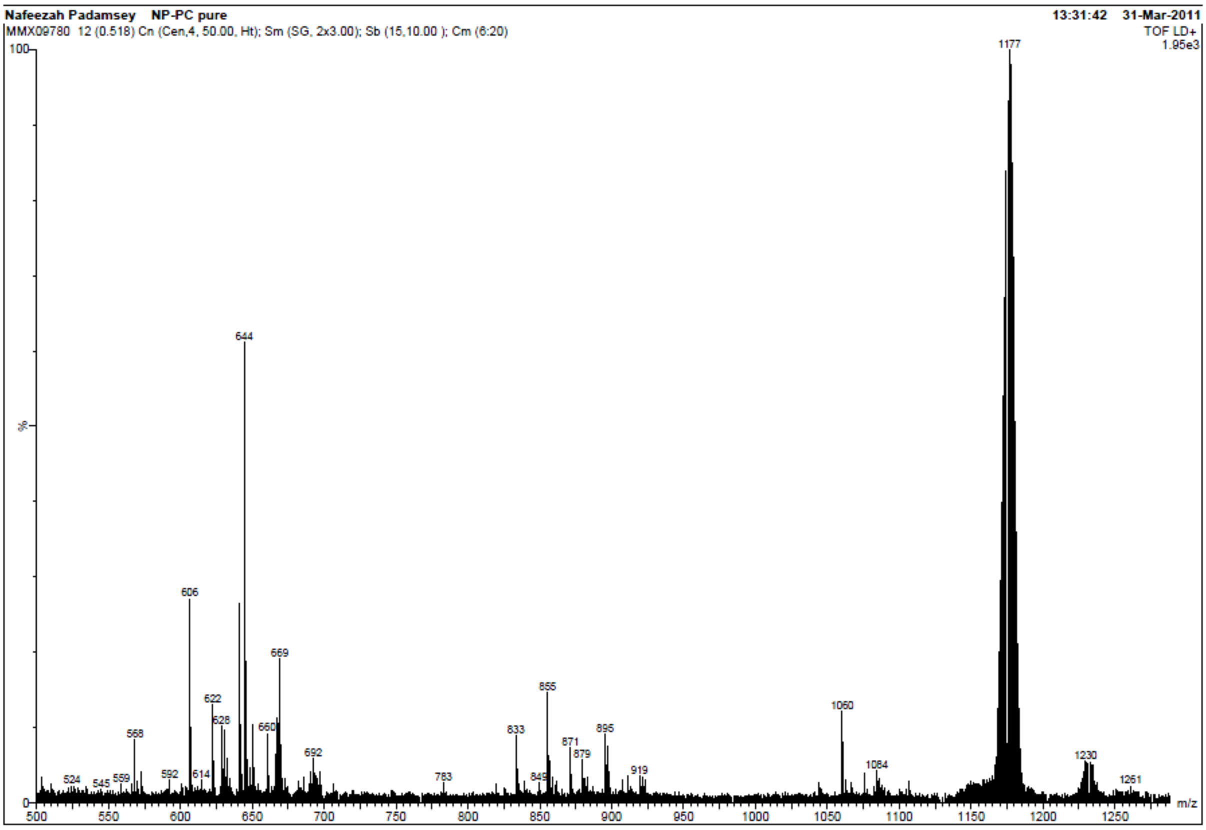


Figure S3. MALDI TOF mass spectrum of SePc