

## SUPPORTING INFORMATION

### Triaryl-1,4-diamine based polysquaraines: effect of co-solvent and monomer insertion on optoelectronic properties

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#### Experimental

##### Materials and methods

Toluene, methanol and dimethylsulfoxide (DMSO) were purified from a solvent purification system (MBraun MB-SPS-800) prior to use. Chloroform ( $\text{CHCl}_3$ ) was dried over calcium hydride ( $\text{CaH}_2$ ) and distilled prior to use. Unless otherwise specified, all other solvents and chemicals were purchased from commercial suppliers (Alfa Aesar, Sigma-Aldrich, TCI, Acros Organics) and used as received. All reactions were carried out under argon at 1 atmosphere unless mentioned otherwise. Concerning OLED fabrication, clean ITO on glass substrates were used as the transparent anodes. On top of that, a 40-50 nm thick layer of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) has been deposited by spin-coating to form the hole transport layer. Then, a 50 nm thick polysquaraine emissive layer was spin-coated, followed by thermal deposition of Calcium (20 nm) and Aluminum (100 nm) to form the cathode.

##### Characterizations

The precursors and polymers were characterized by IR, HRMS,  $^1\text{H}$  and  $^{13}\text{C}$  NMR in order to determine their chemical structures. NMR spectra were recorded on a Bruker 400 MHz spectrometer from a deuterated chloroform, tetrahydrofuran, methylene chloride or dimethyl sulfoxide ( $\text{CDCl}_3$ , THF- $d_8$   $\text{CD}_2\text{Cl}_2$  or DMSO- $d_6$ ) solution. IR spectra were recorded with Bruker Tensor 27 spectrometer using a 0.6 mm-diameter beam and a  $4\text{ cm}^{-1}$  resolution. Samples were analyzed with the attenuated total reflectance (ATR) method. High resolution mass spectroscopy analyses were performed on an AutoSpec-Waters spectrometer (EI). Molar masses of the polymers were measured by SEC at  $25\text{ }^\circ\text{C}$  with  $\text{CHCl}_3$  with 1% of triethylamine as eluent, using a Malvern Viscotek TDMax system, and PS standards were used for calibration. Absorption and photoluminescence spectra were recorded for a polymer solution ( $0.01\text{ g L}^{-1}$  in  $\text{CHCl}_3$ ) and a polymer film casted from a  $\text{CHCl}_3$  solution ( $10\text{ g L}^{-1}$ ) using the spectrophotometers UV-3600 of Shimadzu and Fluoromax-4 of Horiba Scientific, respectively. Energetic levels were evaluated by cyclic voltammetry in electrolyte solutions of  $0.1\text{ M TBAPF}_6$  in  $\text{CHCl}_3$ . A platinum/titanium electrode was used both as counter electrode and as working electrode, and a silver wire was used as the reference electrode. The obtained potentials were recalibrated adding ferrocene in the solution. The absolute fluorescence quantum yields of the synthesized polymers were measured with the Quantaaurus-QY setup of Hamamatsu. The performance of the OLEDs

(CIE chromaticity coordinates, electroluminescence spectra, emission-voltage curves) was tested with the External Quantum Efficiency Measurement System (C9920-12) of Hamamatsu, using an integration sphere. .

### Synthesis of precursors

N1,N4-didodecyl-N1,N4-diphenylbenzene-1,4-diamine (TPDA): N1,N4-diphenylbenzene-1,4-diamine (10.00 g, 38.4 mmol) and freshly powdered potassium hydroxide (10.78 g, 192.1 mmol) were introduced in a 500 ml round-bottom flask, and subsequently degassed via three vacuum/argon cycles. 200 ml of dry DMSO was then added under argon, and the mixture was stirred at 90°C for 2 h. 1-bromododecane (23.93 g, 23 ml, 96.0 mmol) was then added dropwise and the reaction was allowed to stir for 4 h. The mixture was poured in 2 L of water, and extracted four times with 100 mL of diethyl ether. The combined organic phases were concentrated under vacuum, washed three times with 50 ml of water and dried over MgSO<sub>4</sub>. The solvent was removed under vacuum. Flash chromatography (heptane:ethyl acetate 95:5) followed by a recrystallization in pentane afforded the pure product as a white powder (15.34 g, 67 %).

<sup>1</sup>H NMR (400 MHz, THF):  $\delta$  (ppm) 7.15 (t,  $J$  = 7.9 Hz, 4H), 6.95 (s, 4H), 6.87 (d,  $J$  = 7.9 Hz, 4H), 6.76 (t,  $J$  = 7.3 Hz, 4H), 3.70 – 3.62 (m, 4H), 1.71 – 1.61 (m, 4H), 1.31 (d,  $J$  = 19.3 Hz, 36H), 0.88 (t,  $J$  = 6.8 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, THF):  $\delta$  (ppm) 149.69, 143.83, 129.89, 124.80, 120.48, 119.65, 53.28, 33.03, 30.80, 30.77, 30.74, 30.73, 30.62, 30.46, 28.62, 28.13, 23.72, 14.59. FT-IR (ATR):  $\nu$  = 3038, 2916, 2848, 1594, 1494, 1467, 1358, 1256, 1143, 1094, 845, 742, 699, 612 cm<sup>-1</sup>.

HRMS (EI+,  $m/z$ ) [M]<sup>+</sup> calculated for C<sub>42</sub>H<sub>64</sub>N<sub>2</sub>: 596.5070, found 596.5080.

1,2-dichlorocyclobutene-3,4-dione (SqCl): In a dried and nitrogen flushed 50 mL flask, 5 g (43.8 mmol) of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) was solubilized in 10 mL of toluene. Then, 2 equivalents of thionyl chloride (6.36 mL, 87.7 mmol) were added as well as a droplet of DMF as catalyst (approximately 200  $\mu$ L). The reaction was heated at reflux temperature for one hour before being allowed to cool down at room temperature. After evaporation of the toluene at room temperature with a small nitrogen flow, the pure yellow compound was recovered after sublimation at 65°C under vacuum (yield: 95%)

The product doesn't present any protons, a <sup>1</sup>H NMR was performed to confirm the absence of impurities.

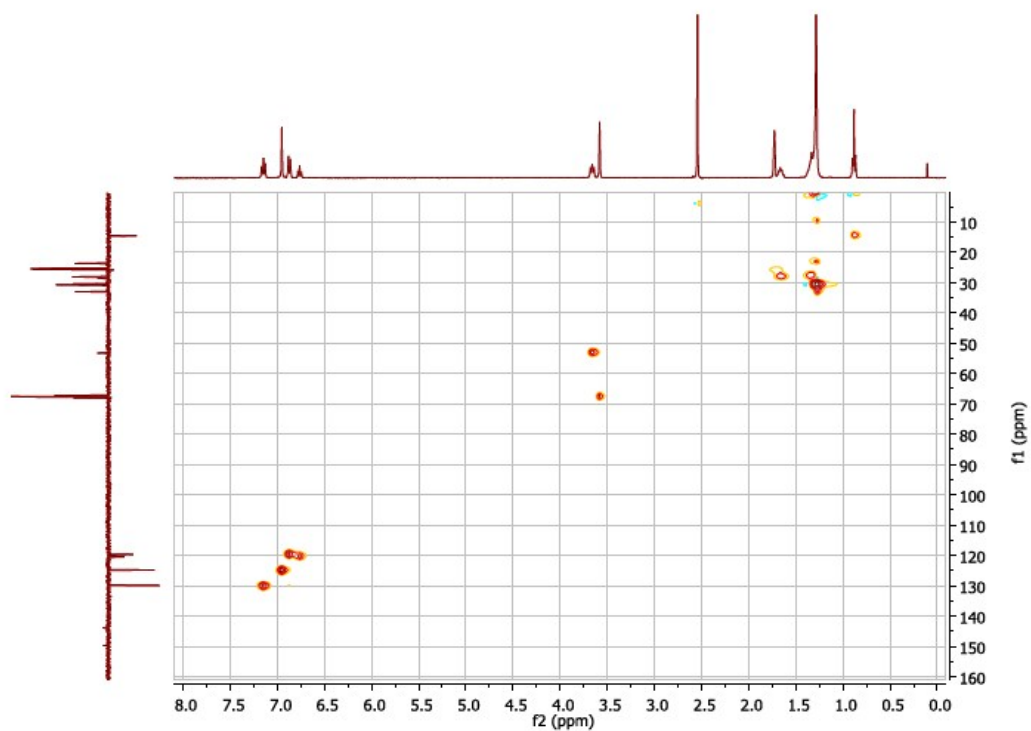
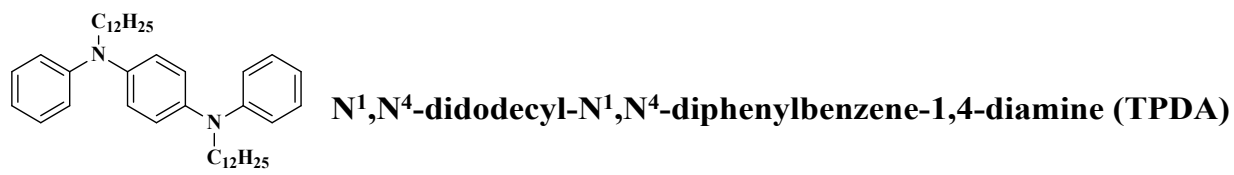
<sup>13</sup>C NMR (101 MHz, THF):  $\delta$  (ppm) 190.12, 185.99

FT-IR (ATR):  $\nu$  = 1810, 1760, 1530, 1171, 1048, 879, 736, cm<sup>-1</sup>.

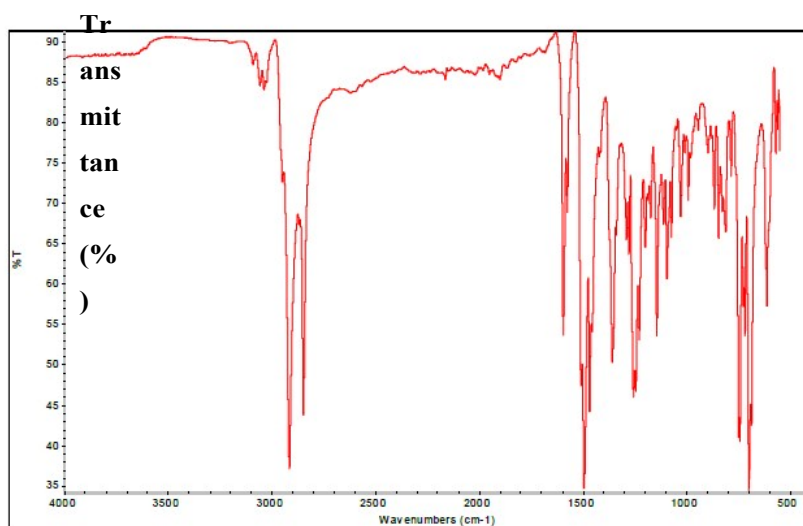
HRMS (EI+,  $m/z$ ) [M]<sup>+</sup> calculated for C<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>: 150.93536, found 150.93586

### General procedure for polysquaraines synthesis:

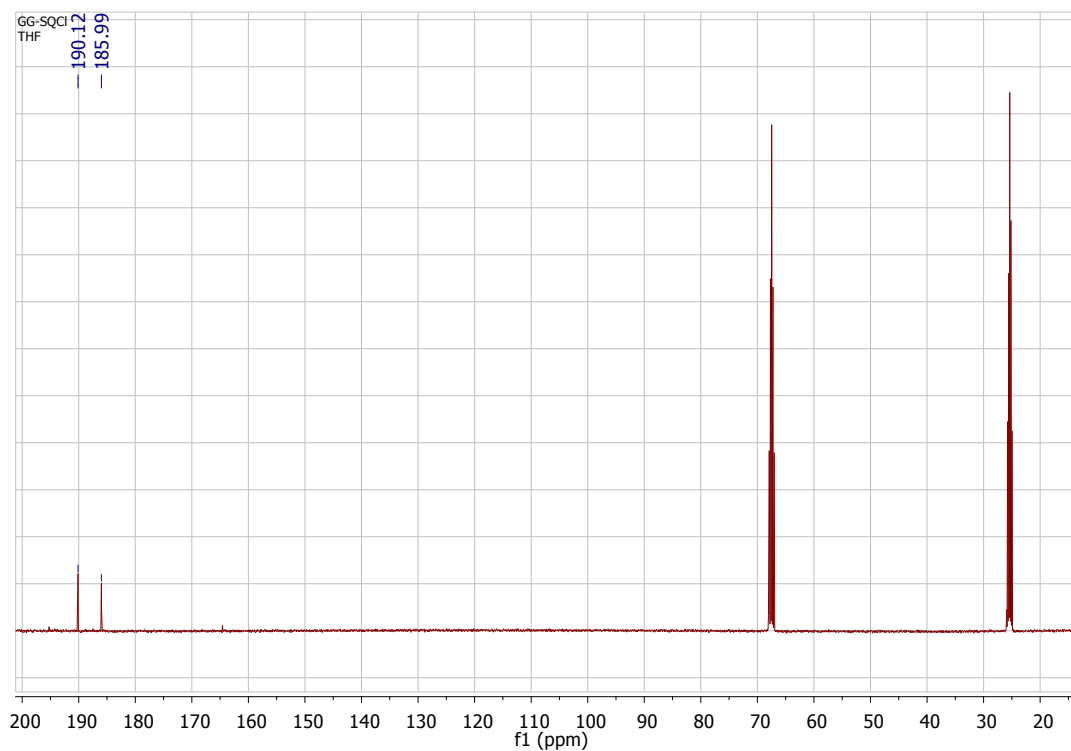
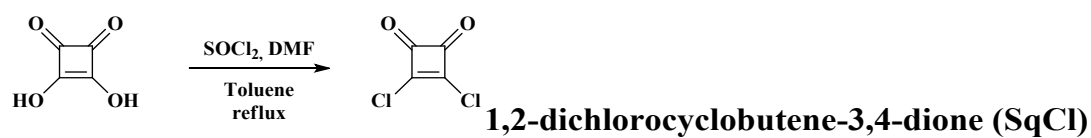
Squaric acid or SqCl and previously synthesized TPDA were solubilized in stoichiometric amount in a mixture of toluene and an alcohol. Type of alcohol (1-butanol, 1-dodecanol or 1,3-propanediol) and amounts were chosen to control and tune polymers' structures. The reaction mixture was heated for 4 hours under  $\mu$ -wave irradiation and the polymer was purified by soxhlet, first with methanol then chloroform. No monomer was recovered, indicating a conversion above 99%.



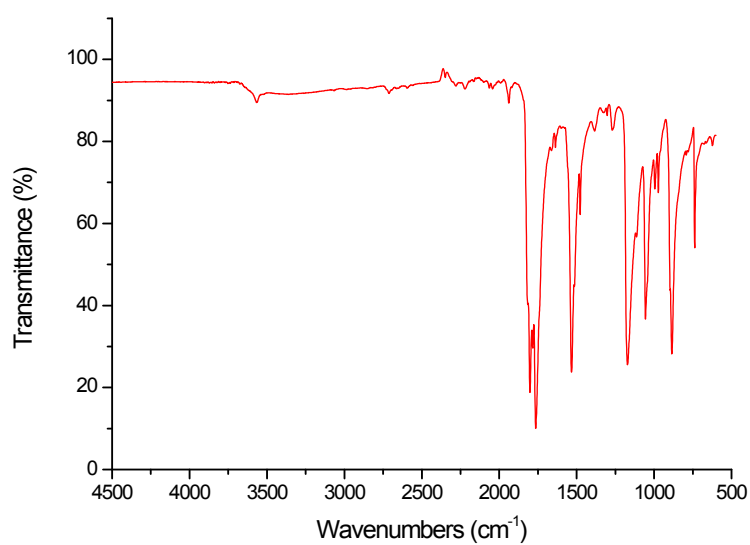
**Figure S1: <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum of TPDA (in THF-d<sub>8</sub>).**



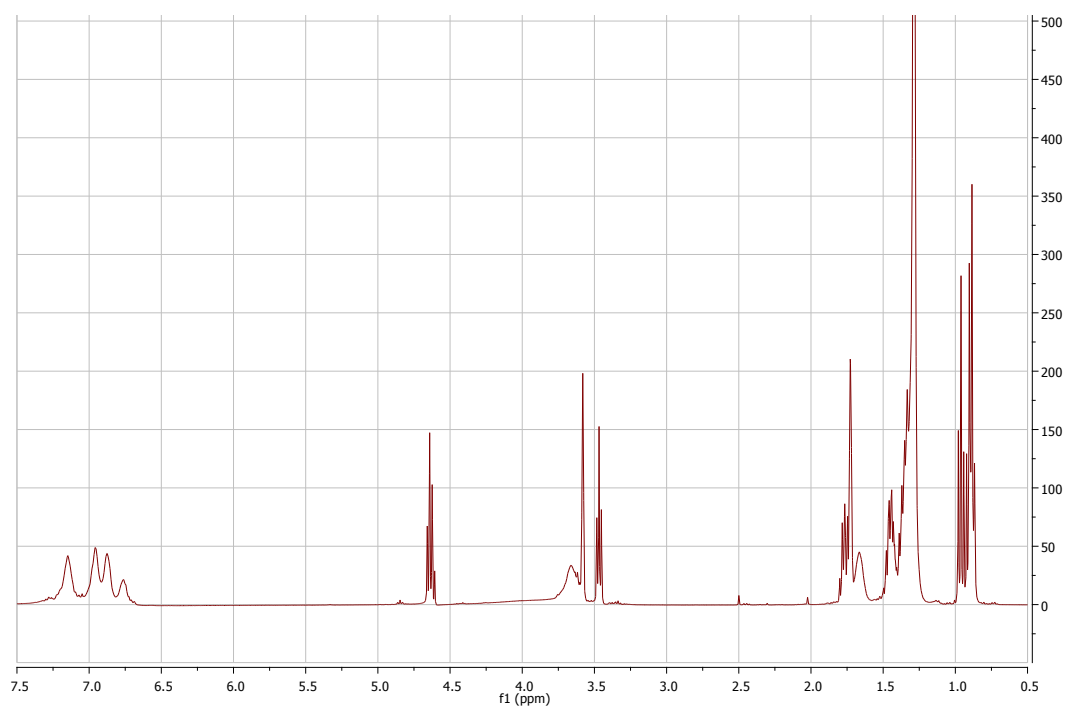
**Figure S2: ATR-FTIR spectrum of TPDA.**



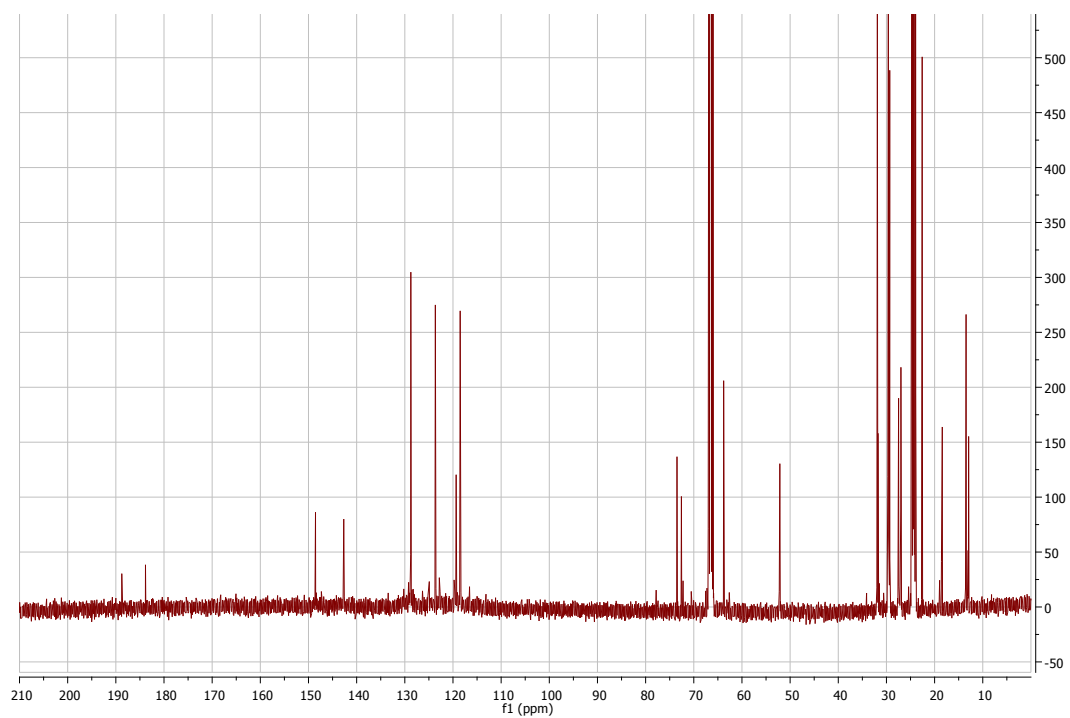
**Figure S3:**  $^{13}\text{C}$  NMR spectrum (101 MHz) of SqCl in  $\text{THF-d}_8$ .



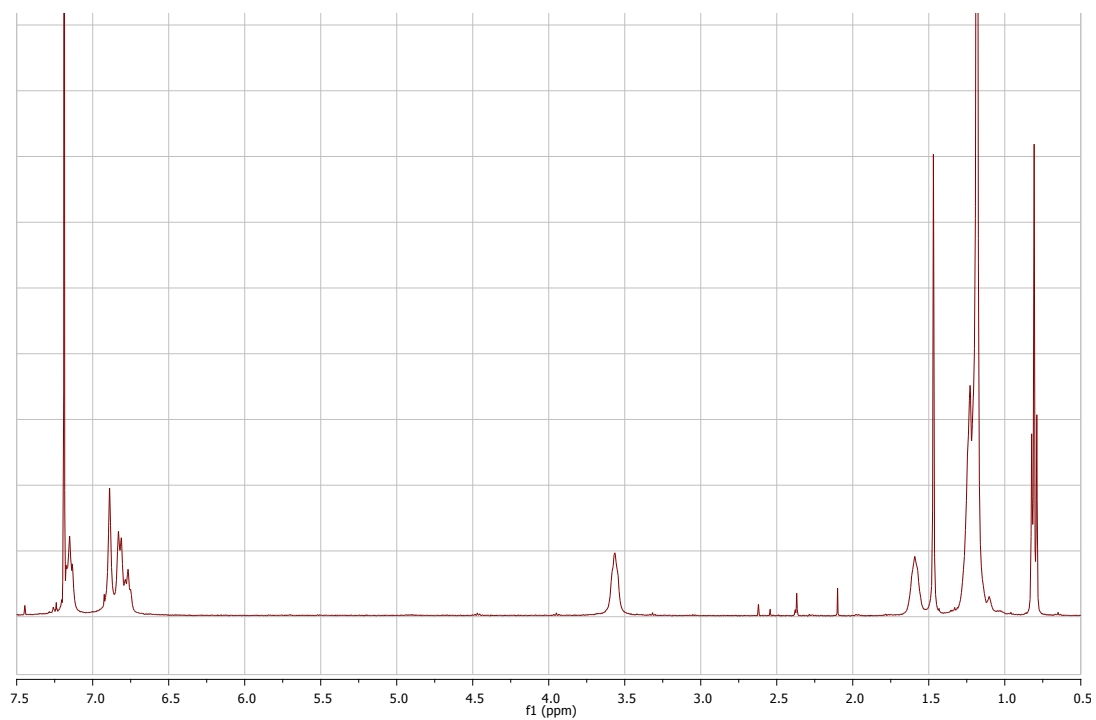
**Figure S4:** ATR-FTIR spectrum of SqCl



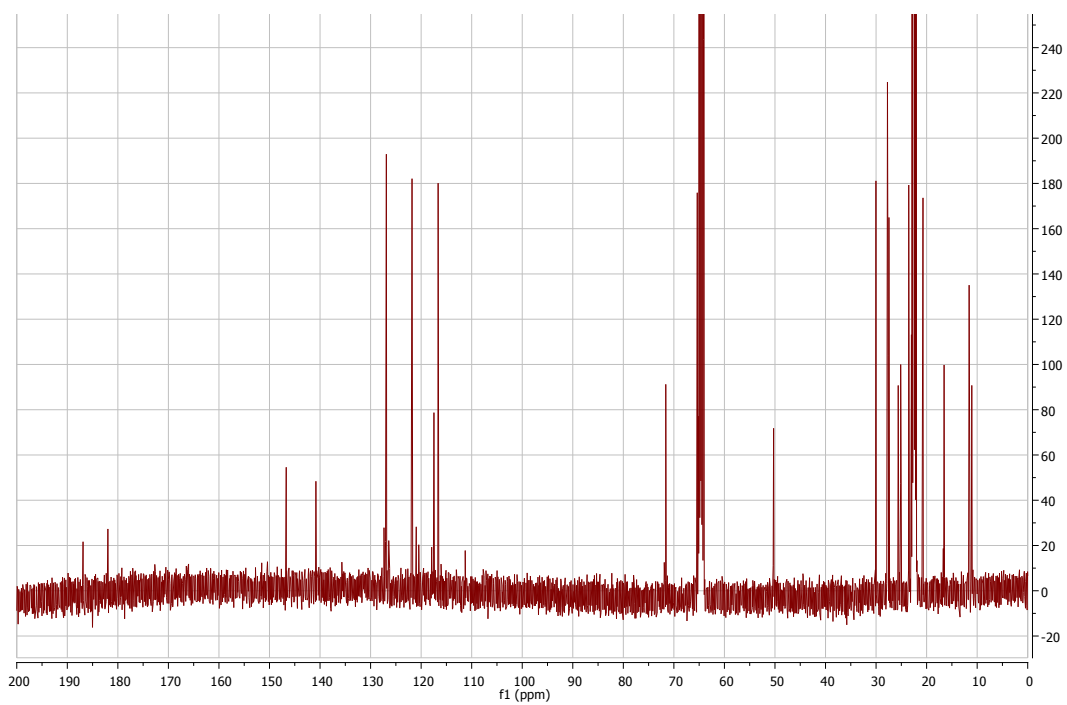
**Figure S5:  $^1\text{H}$  NMR spectrum (400 MHz) of PSQ-C4 in  $\text{THF-d}_8$ .**



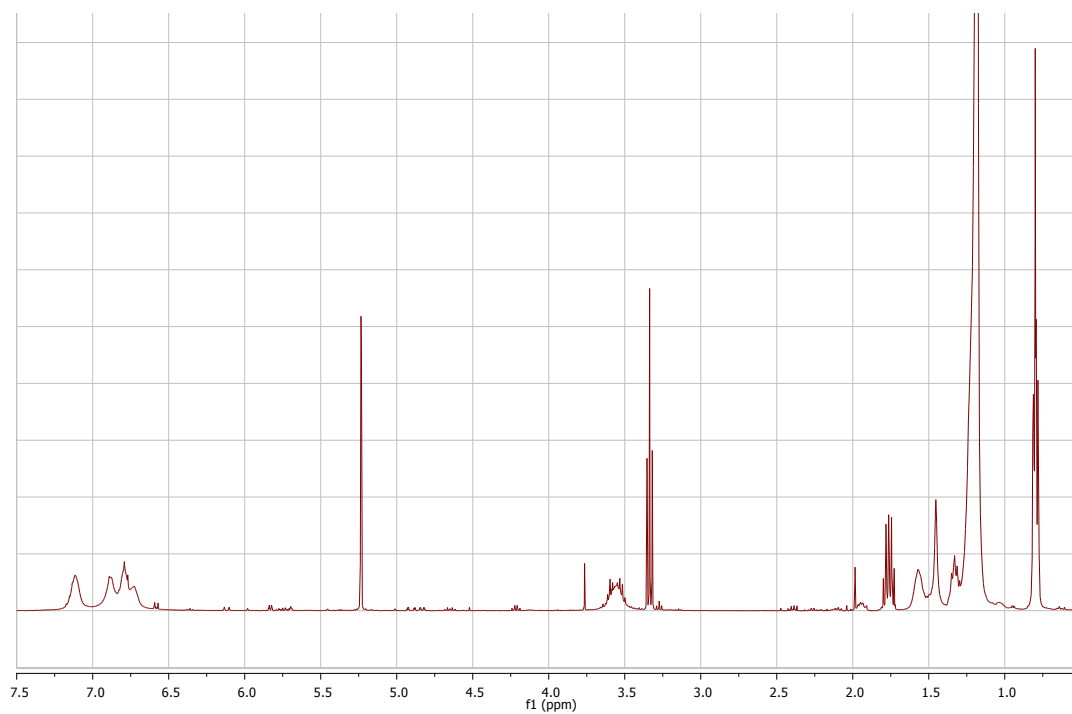
**Figure S6:  $^{13}\text{C}$  NMR spectrum (101 MHz) of PSQ-C4 in  $\text{THF-d}_8$ .**



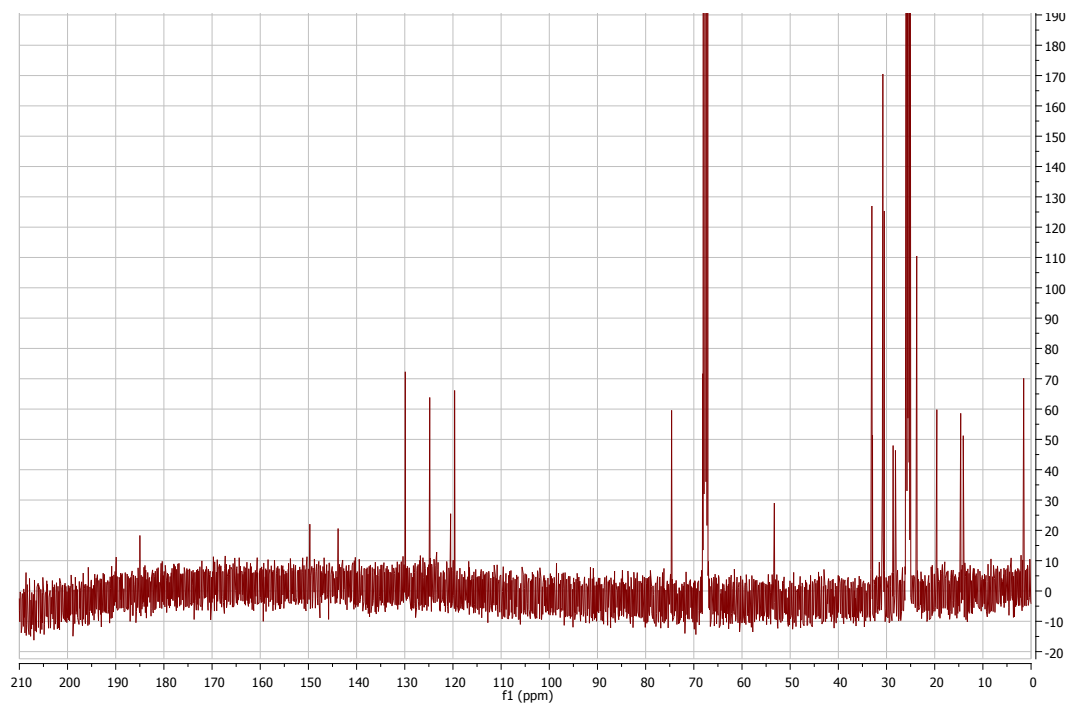
**Figure S7:**  $^1\text{H}$  NMR spectrum (400 MHz) of PSQ-C12 in  $\text{CDCl}_3$ .



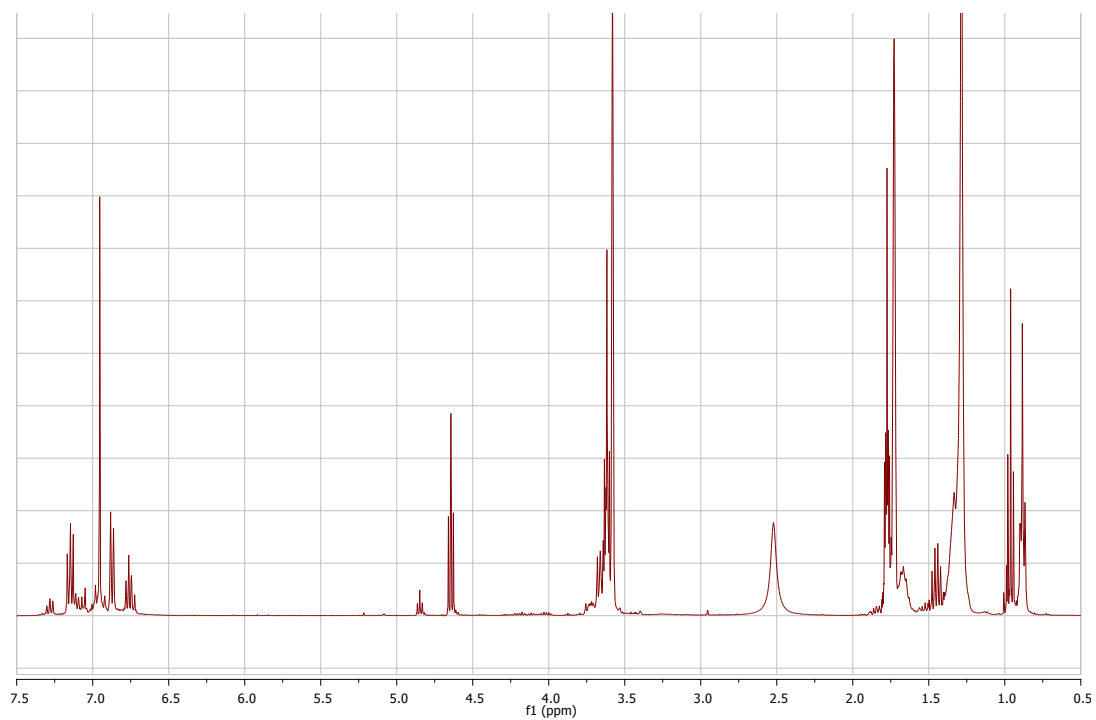
**Figure S8:**  $^{13}\text{C}$  NMR spectrum (101 MHz) of PSQ-C12 in  $\text{THF-d}_8$ .



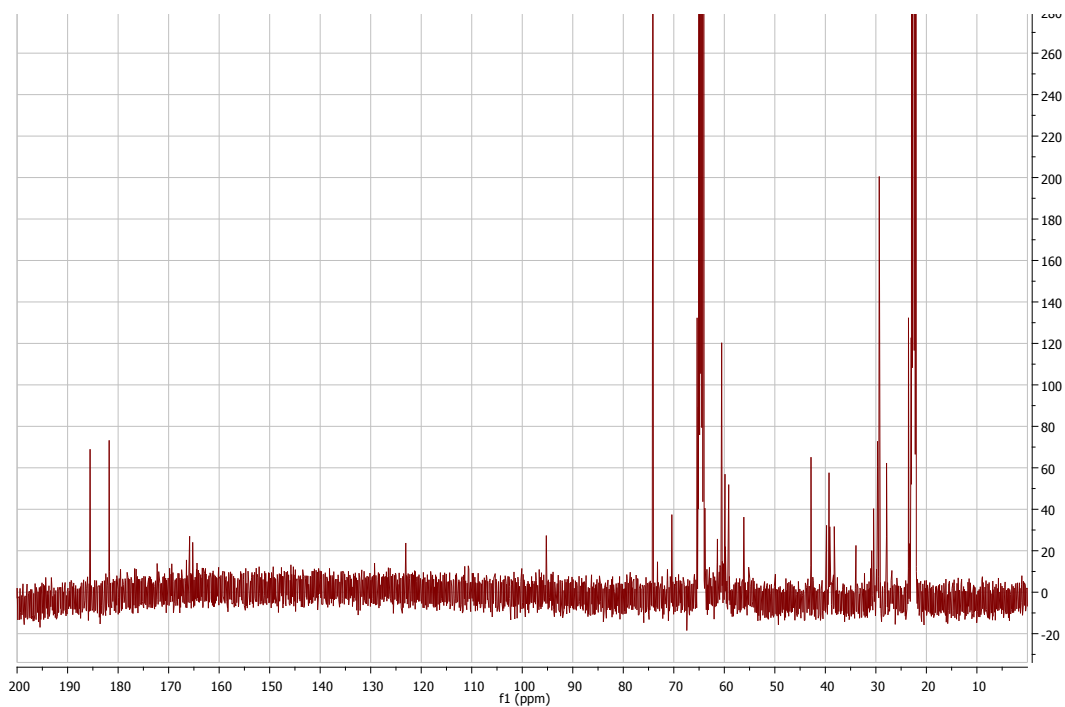
**Figure S9:**  $^1\text{H}$  NMR spectrum (400 MHz) of PSQ-SqCl in  $\text{THF-d}_8$ .



**Figure S10:**  $^{13}\text{C}$  NMR spectrum (101 MHz) of PSQ-SqCl in  $\text{THF-d}_8$ .

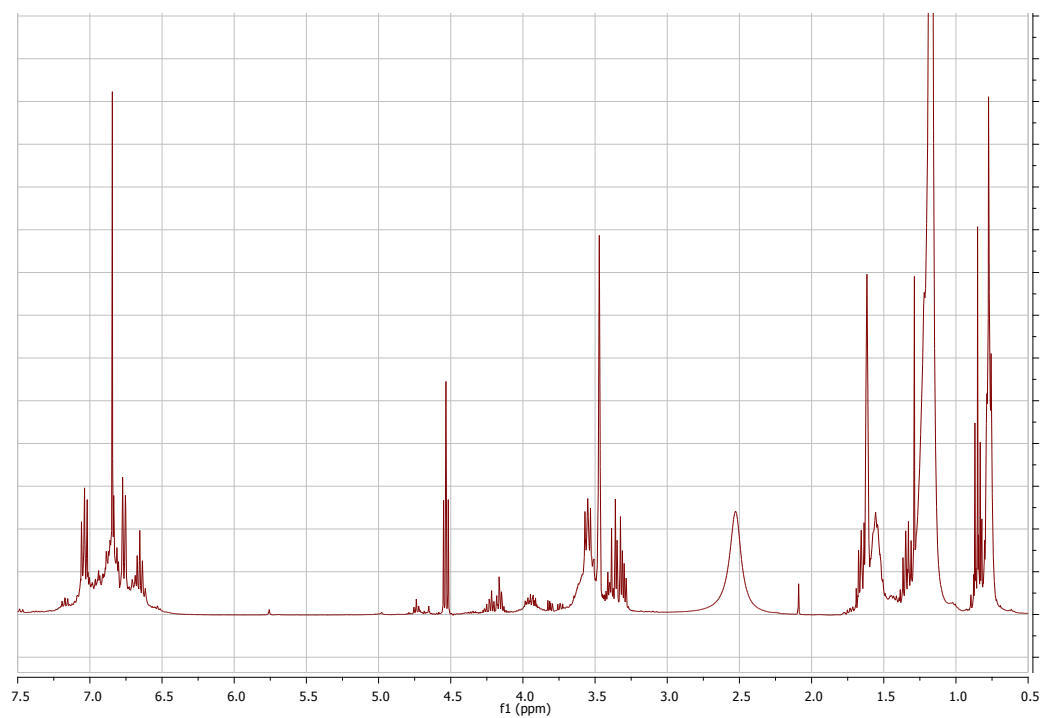


**Figure S11:  $^1\text{H}$  NMR spectrum (400 MHz) of PSQ-PD2 in  $\text{THF-d}_8$ .**

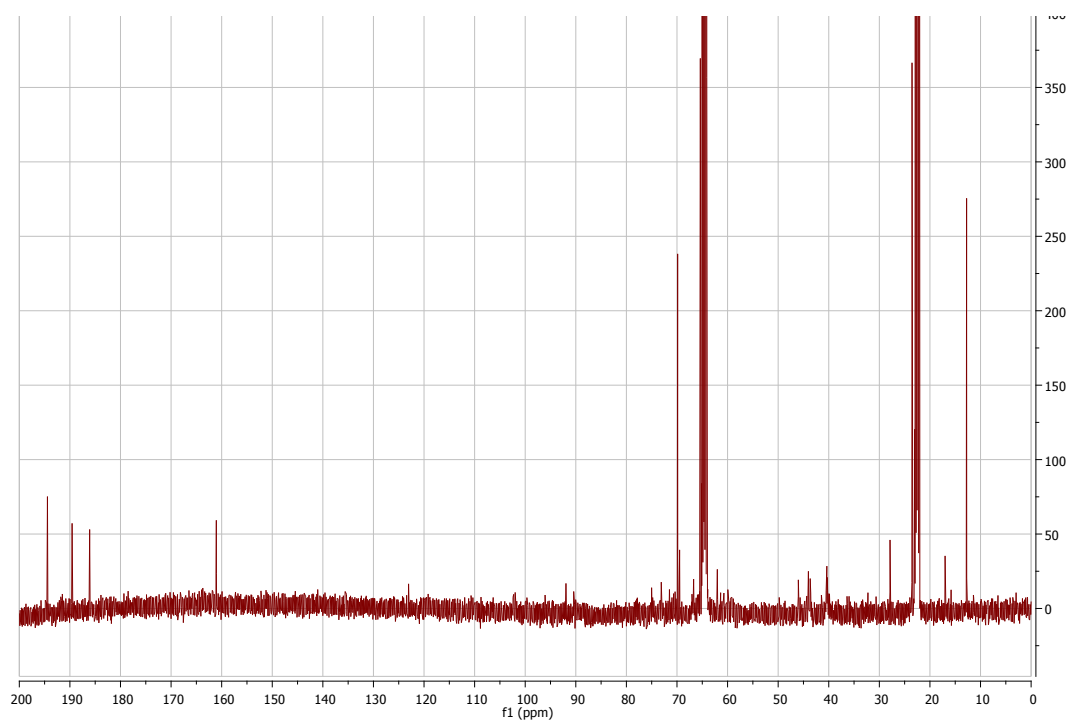


**Figure S12:  $^{13}\text{C}$  NMR spectrum (101 MHz) of PSQ-PD2 in  $\text{THF-d}_8$ .**

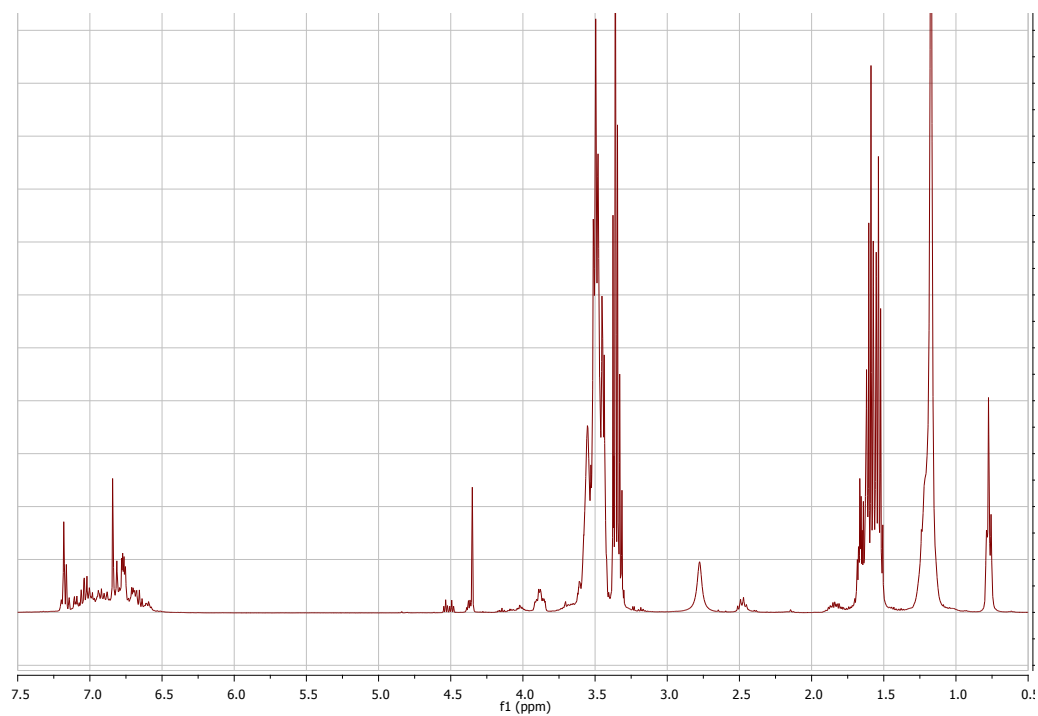




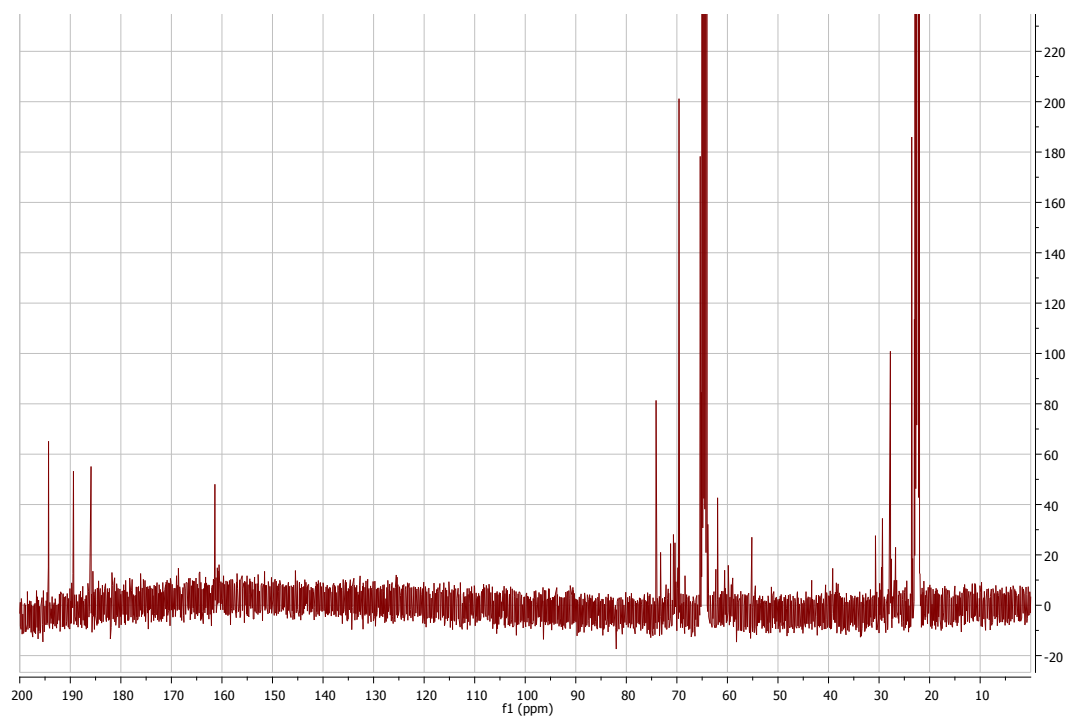
**Figure S13:  $^1\text{H}$  NMR spectrum (400 MHz) of PSQ-PD3 in  $\text{THF-d}_8$ .**



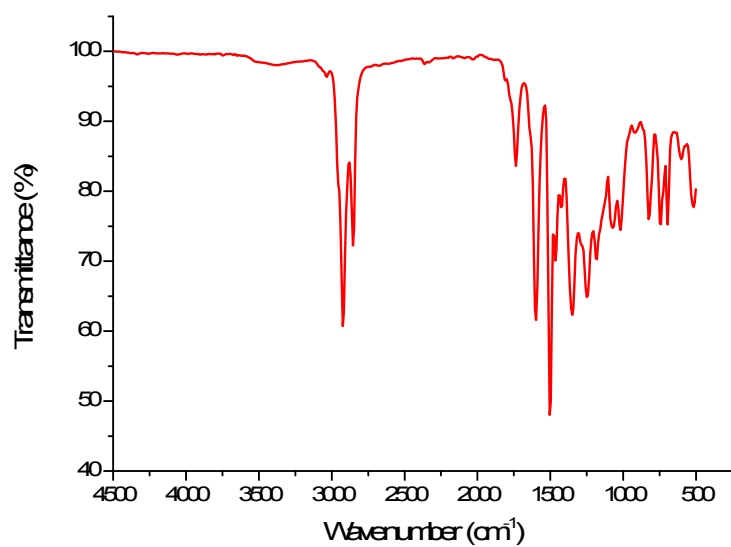
**Figure S14:  $^{13}\text{C}$  NMR spectrum (101 MHz) of PSQ-PD3 in  $\text{THF-d}_8$ .**



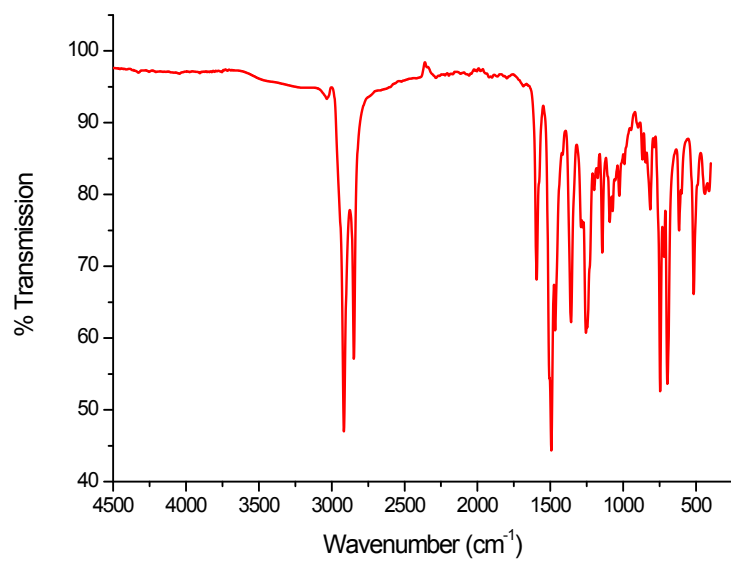
**Figure S15:  $^1\text{H}$  NMR spectrum (400 MHz) of PSQ-PD10 in  $\text{THF-d}_8$ .**



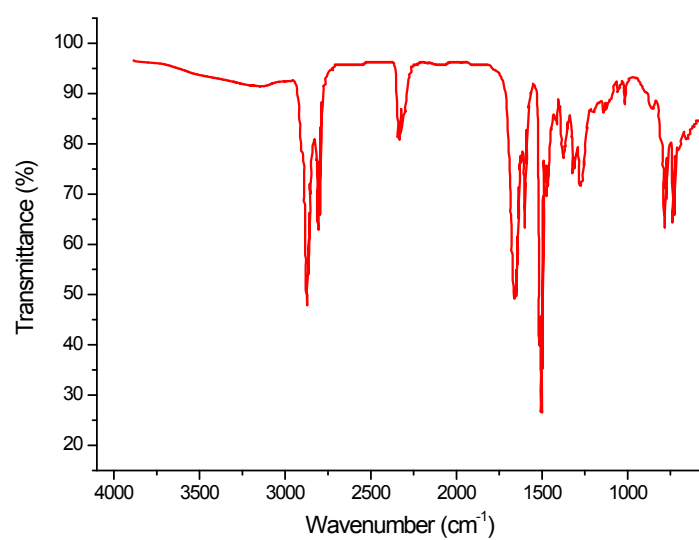
**Figure S16:  $^{13}\text{C}$  NMR spectrum (101 MHz) of PSQ-PD10 in  $\text{THF-d}_8$ .**



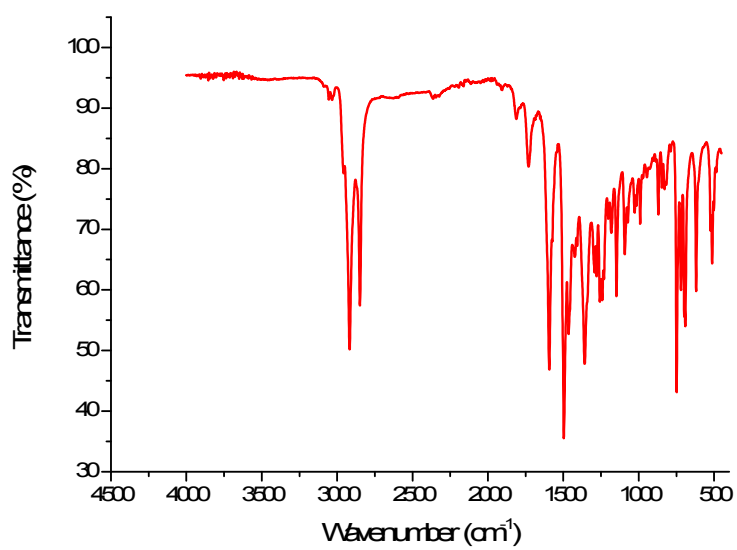
**Figure S17: ATR-FTIR spectrum of PSQ-C4.**



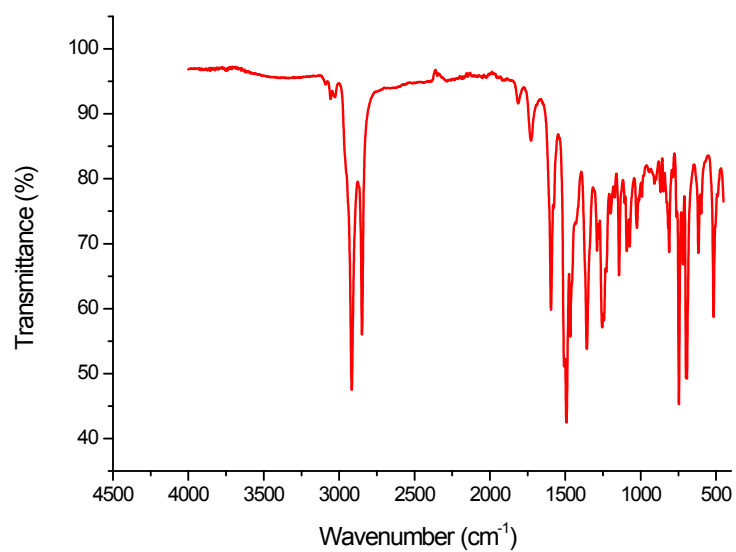
**Figure S18: ATR-FTIR spectrum of PSQ-C12.**



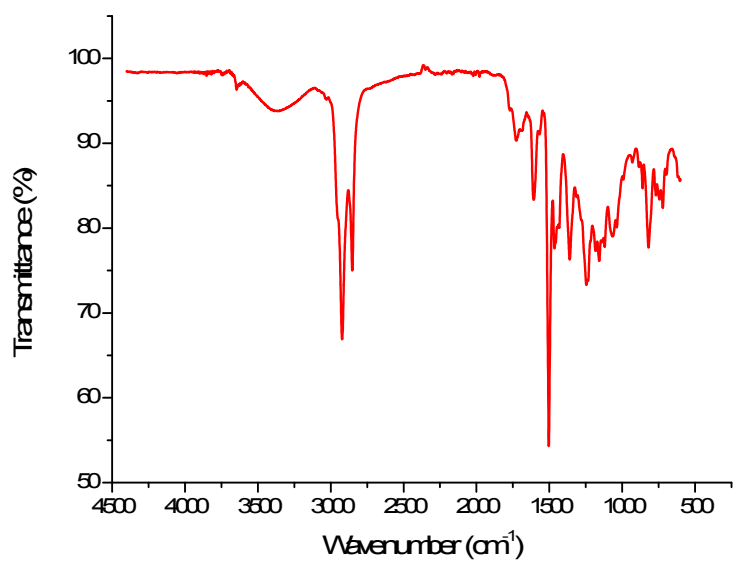
**Figure S19: ATR-FTIR spectrum of PSQ-SqCl.**



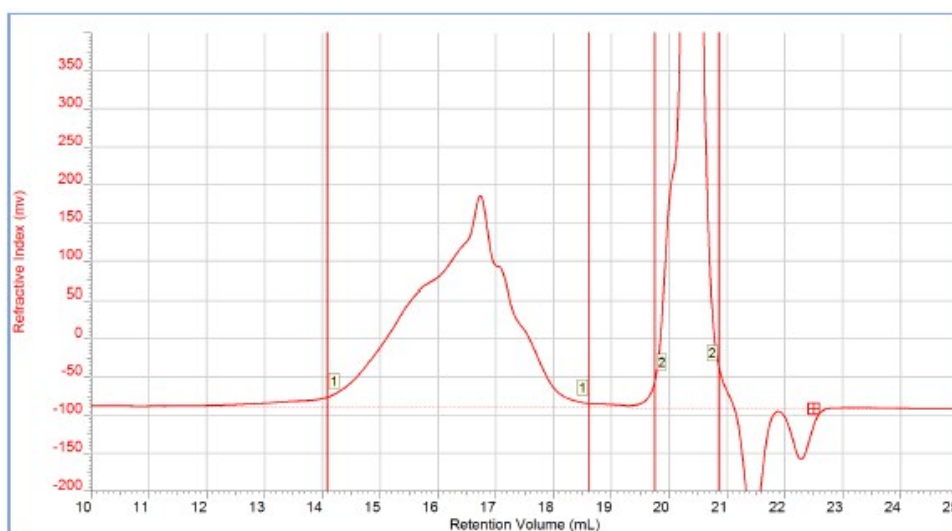
**Figure S20: ATR-FTIR spectrum of PSQ-PD2.**



**Figure S21: ATR-FTIR spectrum of PSQ-PD3.**

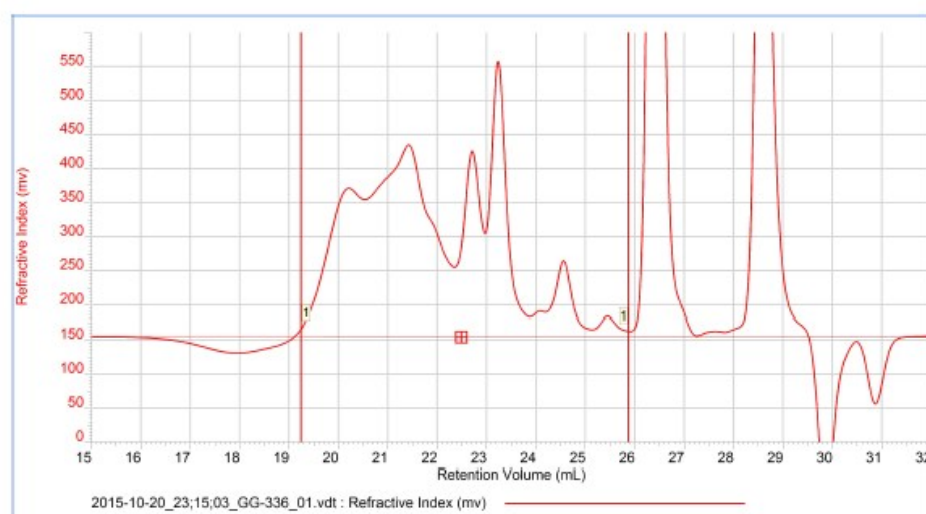


**Figure S22: ATR-FTIR spectrum of PSQ-PD10.**



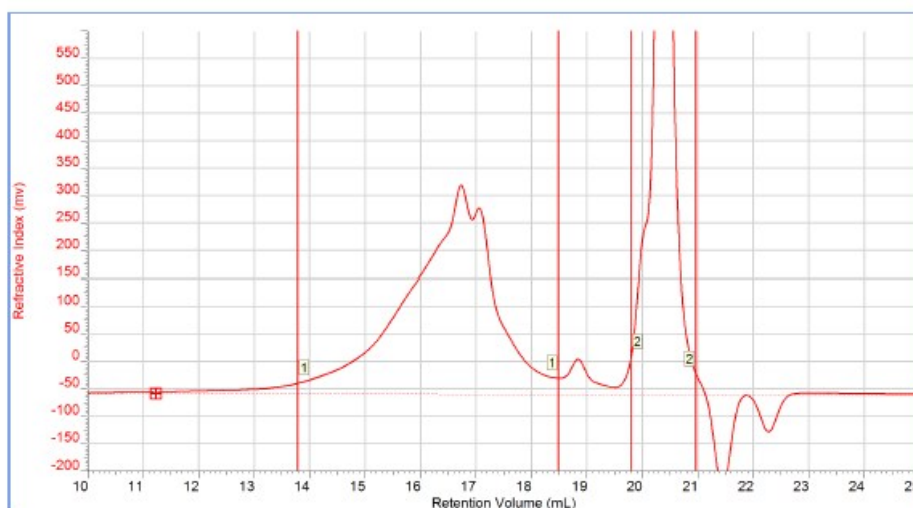
Peak	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
1	2 759	6 699	15 067	2 710	2.428	16.720

**Figure S23: SEC profile of PSQ-C4 (in CHCl<sub>3</sub>, polystyrene standard).**



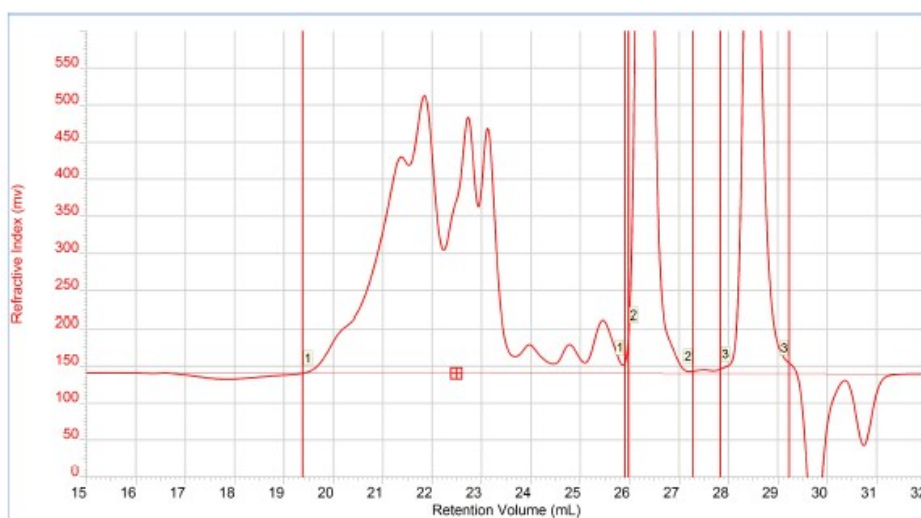
Peak	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
1	2 407	7 200	14 703	1 434	2.991	23.223

**Figure S24: SEC profile of PSQ-C12 (in CHCl<sub>3</sub>, polystyrene standard).**



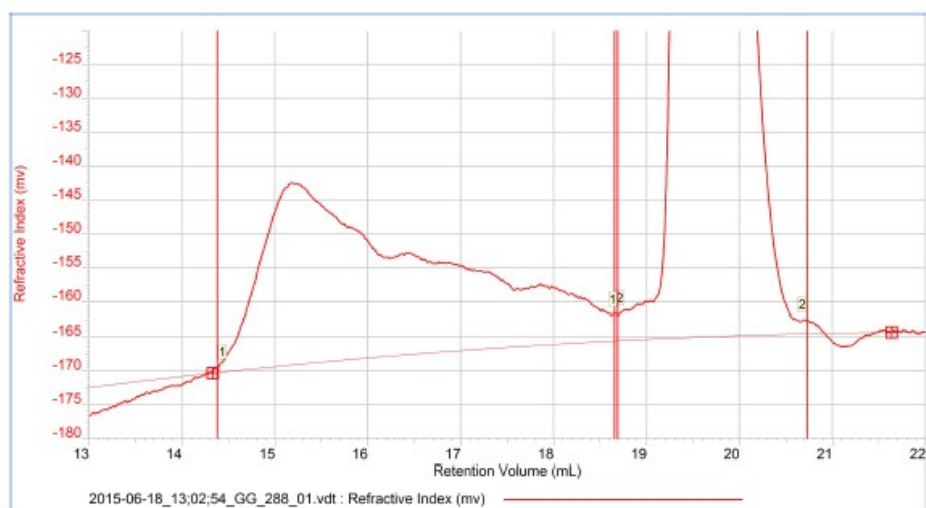
Peak	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
1	2 476	6 752	20 470	2 706	2.727	16.720

**Figure S25: SEC profile of PSQ-SqCl (in  $\text{CHCl}_3$ , polystyrene standard).**



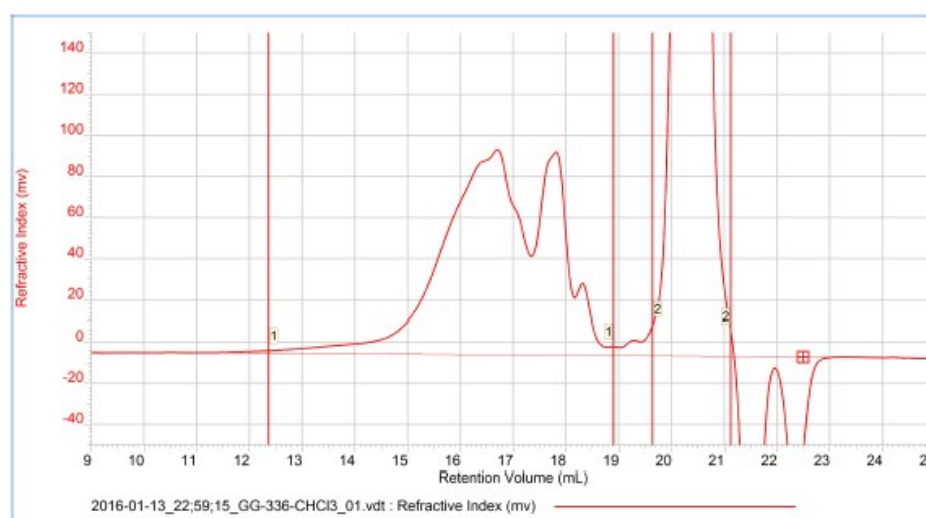
Peak	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
1	2 110	4 511	8 158	4 025	2.137	21.833

**Figure S26: SEC profile of PSQ-PD2 (in  $\text{CHCl}_3$ , polystyrene standard).**



Peak	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
1	3 720	12 686	22 289	22 728	3.410	15.187

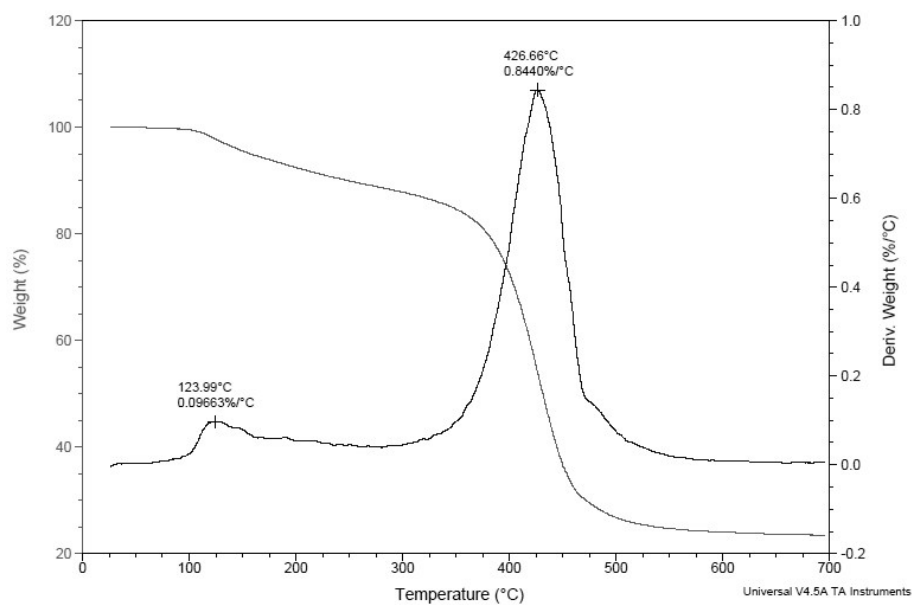
Figure S27: SEC profile of PSQ-PD3 (in  $\text{CHCl}_3$ , polystyrene standard).



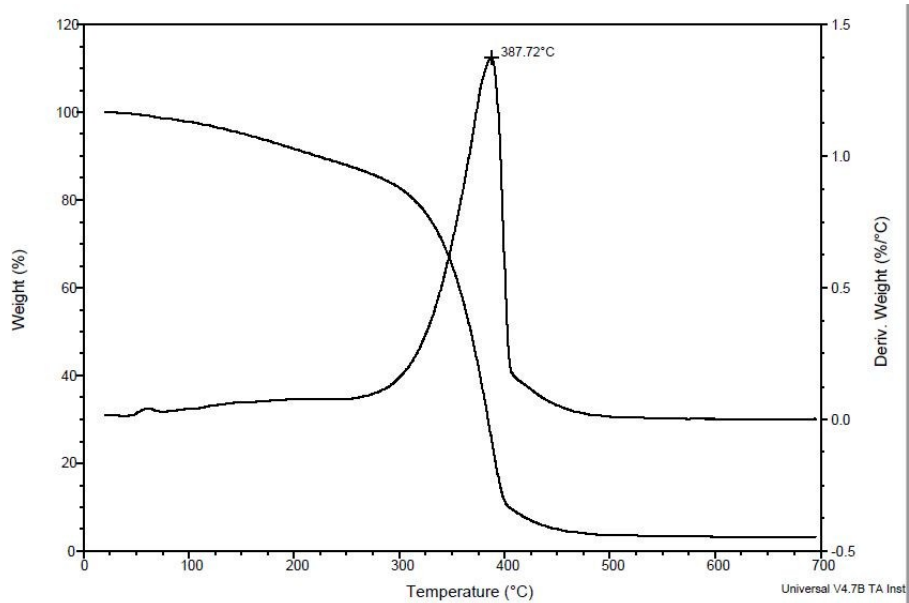
Peak	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
1	1 782	8 064	88 450	3 036	4.525	16.683

Figure S28: SEC profile of PSQ-PD10 (in  $\text{CHCl}_3$ , polystyrene standard).

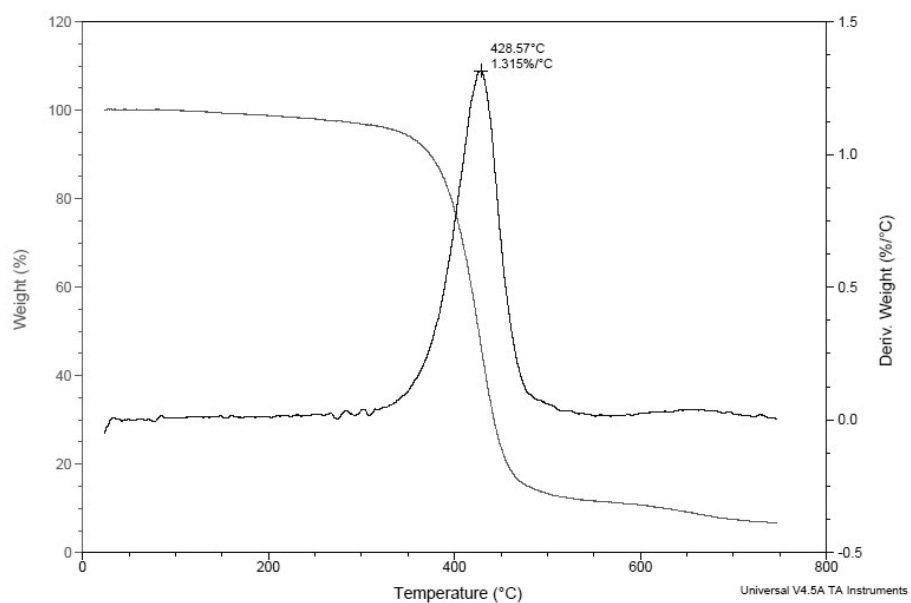




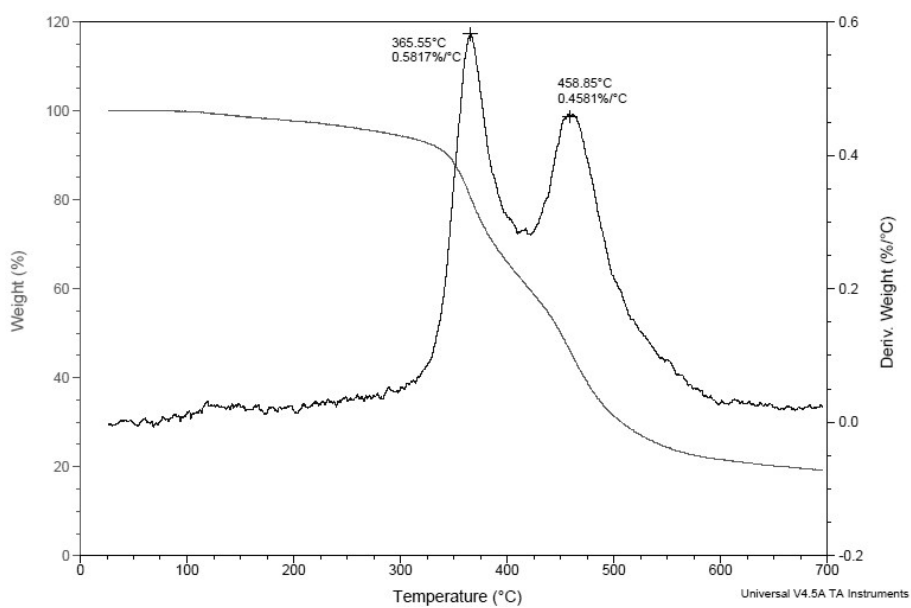
**Figure S29: TGA of PSQ-C4 (scan rate of 10°C.min<sup>-1</sup>).**



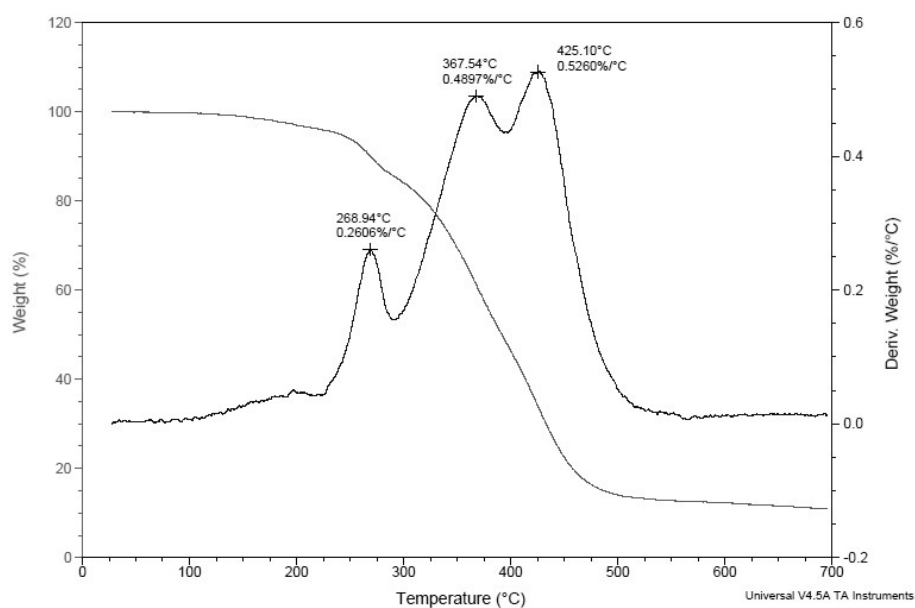
**Figure S30: TGA of PSQ-C12 (scan rate of 10°C.min<sup>-1</sup>).**



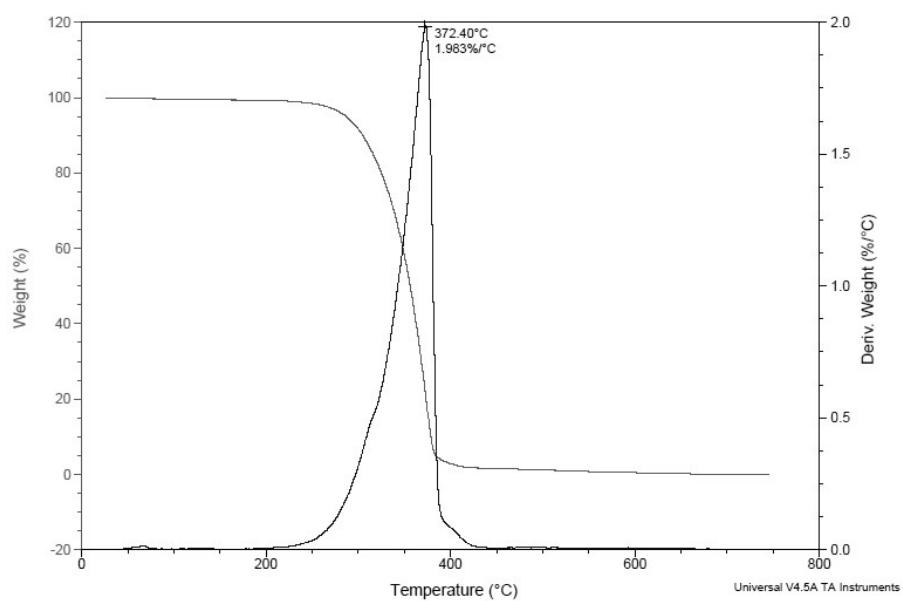
**Figure S31: TGA of PSQ-SqCl (scan rate of 10°C.min<sup>-1</sup>).**



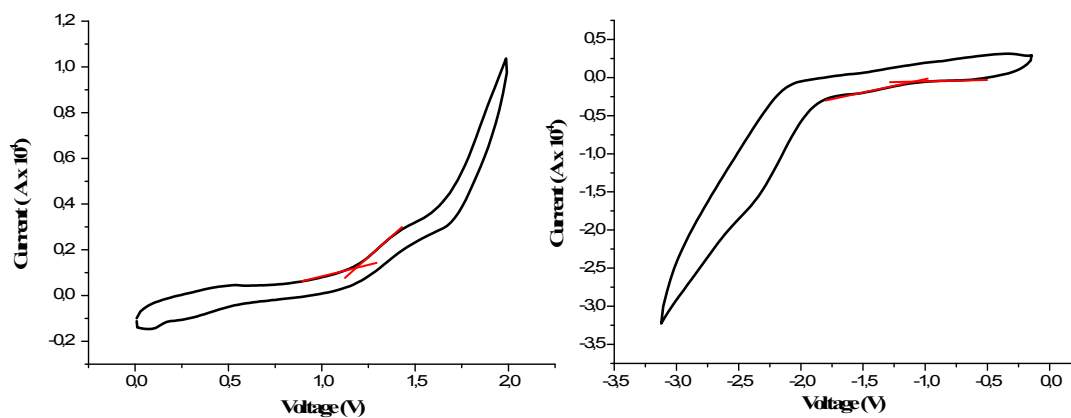
**Figure S32: TGA of PSQ-PD2 (scan rate of 10°C.min<sup>-1</sup>).**



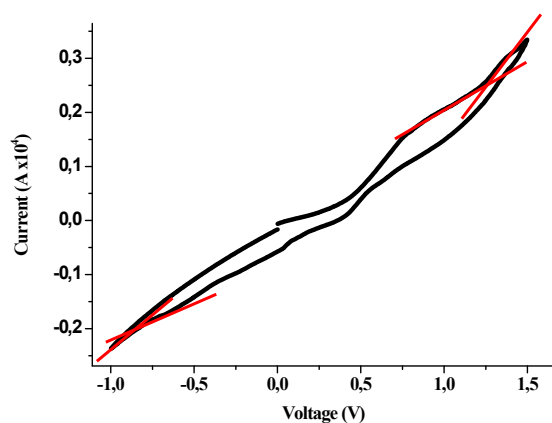
**Figure S33: TGA of PSQ-PD3 (scan rate of 10°C.min<sup>-1</sup>).**



**Figure S34: TGA of PSQ-PD10 (scan rate of 10°C.min<sup>-1</sup>).**



**Figure S35:** Cyclic voltammograms of PSQ-PD10 in  $\text{CH}_2\text{Cl}_2$  solution ( $0.1 \text{ g.l}^{-1}$  with  $\text{TBAPF}_6$  as electrolyte); left-oxidation; right-reduction.



**Figure S36:** Cyclic voltammograms of PSQ-PD10 in film (drop cast on ITO) with  $\text{TBAPF}_6$  as electrolyte

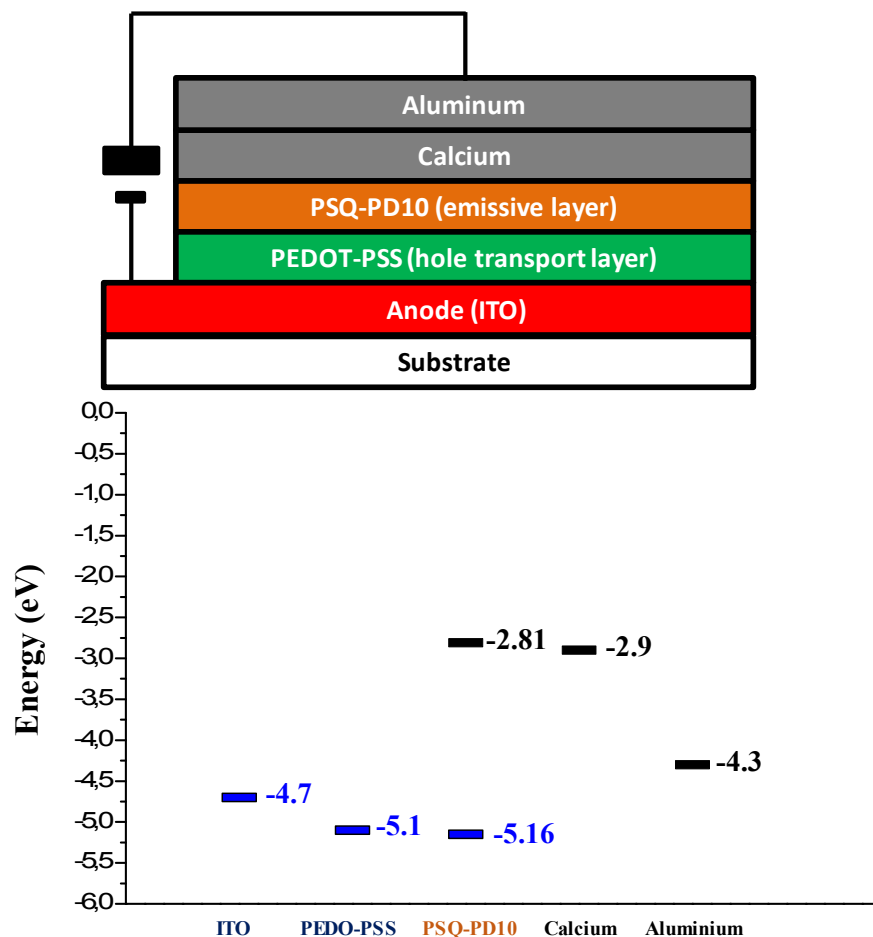


Figure S37: General structure of an OLED designed in this work (top) and energetic levels (bottom).

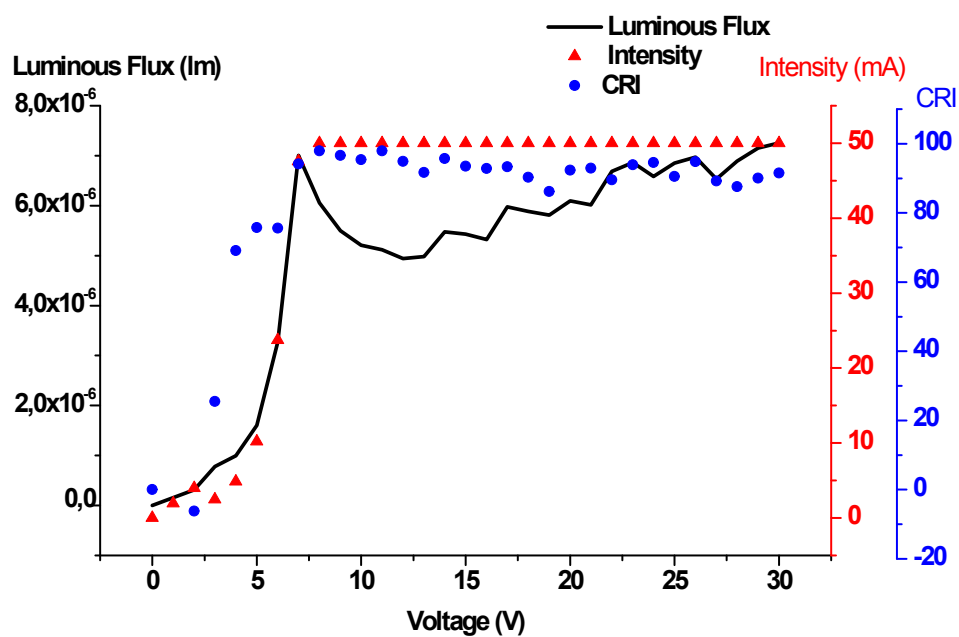
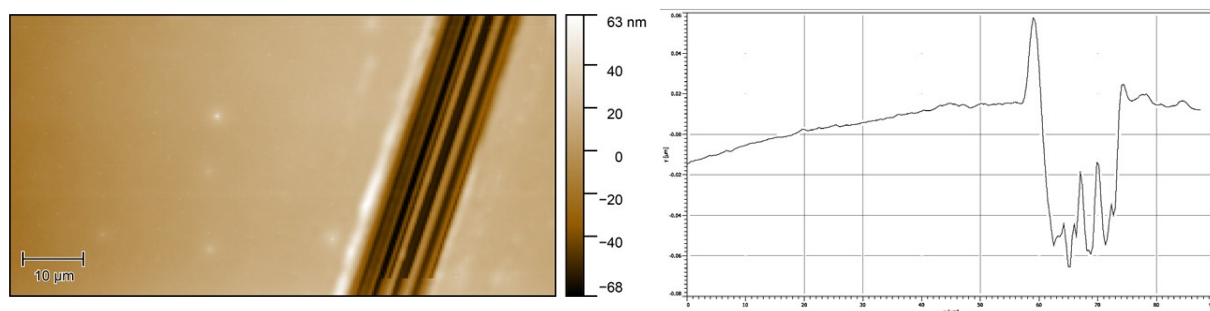


Figure S38: OLED Luminous flux (black, plain), Intensity (red, triangle) and CRI (blue, dot) depending on the applied voltage



**Figure S39: AFM image (left) and profilometry (right) of the PSQ-PD10 polymer film spin-coated on 10 nm PEDOT-PSS layer.**