Electronic Supporting Information

Experimental Methods

Analyical methods

NMR analyses. ^1H and ^{29}Si NMR were measured in diethyl ether or chloroform-*d* with TMS (0.00 ppm) as the internal reference on a Varian spectrometer. ^1H NMR spectra were collected on Varian MR 400 and at 500 MHz using a 7998.4 Hz spectral width, a pulse width of 45°, relaxation delay of 0.5 s, 65K data points. ^{13}C NMR spectra were collected on Varian MR 400 and at 100 MHz using a 25,000 Hz spectral width, a pulse width of 40°, relaxation delay of 1.5 s, and 75K data points. ^{29}Si NMR spectra were collected on Varian VNMRS 500 MHz and were collected at 99.35 MHz using a 4960 Hz spectral width, a pulse width of 7°, a relaxation delay of 15 s, and 4K data points.

Mass spectroscopy (MS). Electron impact (EI) analyses were conducted using a VG 70-250-S magnetic sector instrument (Waters) by electron impact ionization (EI). The instrument was calibrated with perfluorokerosene-H. The samples were run in EI mode at 70 eV electron energy with an ion source temperature of 240 °C. The mass range was scanned from *m/z* 1000 to 35. Hi-Res mass spec analysis was conducted on the same instrument.

Electrospray ionization (ESI) was performed on an Agilent Q-TOF system with a dual ESI ion source. The mobile phase consisted of a 9:1 mixture of acetonitrile:water with 0.1% formic acid. Lockmass correction was used to obtain mass accuracy.

Matrix assisted laser desorption ionization time of flight (MALDI-TOF) was performed on a Micromass TofSpec-2E equipped with a 337 nm nitrogen laser in positive-ion reflectron mode using poly(ethylene glycol) as calibration standard, dithranol as matrix, and $AgNO_3$ as ion source. Sample was prepared by mixing solution of 5 parts matrix (10 mg/mL in THF), 5 parts sample (1 mg/mL in THF), and 1 part of $AgNO_3$ (2.5 mg/mL in water) and then spotting the mixture on a stainless steel target plate.

Gel permeation chromatography (GPC). GPC analyses were run on a Waters 440 system equipped with Waters Styragel columns (7.8 x 300, HT 0.5, 2, 3, 4) with a Waters 2410 refractometer for detection, with THF as the solvent. The system was calibrated using polystyrene standards and toluene as reference. Analyses were performed using PL Caliber 7.04 software (Polymer Labs, Shropshire UK).

Fourier-transform infrared spectroscopy (FTIR). Diffuse reflectance Fourier transform (DRIFT) spectra were recorded on a Nicolet 6700 Series FTIR spectrometer (Thermo Fisher Scientific, Inc., Madison, WI). Optical grade, random cuttings of KBr (International Crystal Laboratories, Garfield, NJ) were ground (400 mg) with 5 mg of sample to be analyzed. For DRIFT analyses, samples were packed and smoothed off to ensure little scattering. The FTIR sample chamber was flushed continuously with N_2 prior to data acquisition in the range 4000-400 cm^{-1} with a precision of ± 4 cm^{-1}.

Materials. The compounds $[PhSiO_{1.5}]_{8,12}$ were received as a gift from Mayaterials Inc. $[PhSiO_{1.5}]_{10}$ was prepared as follows. Bromine, ICl (1.0 M in dichloromethane) and other synthetic reagents were purchased from Sigma Aldrich and used as received. Dichloromethane (CH_2Cl_2) was purchased from Fisher Scientific and distilled from CaH_2 under N_2 prior to use. Dioxane and THF were purchased from Fisher Scientific and distilled from Na/benzophenone under N_2 prior to use.

DecaphenylSQ. To a 2 L round bottom flask under N_2 was added 16 g (0.12 mol) $[PhSiO_{1.5}]_n$ or 20 mL (0.08 mol) phenyltriethoxysilane, 1.75 L of methylene chloride, 5.2 mL of TBAF (nBu_4NF), and 2.5 mL of H_2O and magnetic stirrer. The reaction was stirred for 2-3 days, or until the reaction mixture became transparent. The reaction was then worked up by one of two methods. a. Aqueous workup: 5x wash with H_2O in a separatory funnel, of which the organic layer was then dried over Na_2SO_4, and filtered. b. The reaction was quenched with 50 g of $CaCl_2$ and stirred for 1 day to remove the fluoride ion and then filtered through Celite. The solvent was then removed by rotary evaporation. The resulting white solid was then partially dissolved in 50 mL of a 1:1 THF:acetonitrile. The resulting suspension was then filtered. The resulting solvent was then removed from the resulting solution. It was then redissolved in a minimum amount of THF, precipitated into methanol, filtered and dried under vacuum. DodecaphenylSQ: white solid, 7.8 g, 49% details will be reported elsewhere.[41]

$[o\text{-}BrPhSiO_{1.5}]_8$. To a dry 100 mL Schlenk flask under N_2 was added 5.0 g $[PhSiO_{1.5}]_8$ (4.85 mmol, 38.5 mmol phenyl) followed by 10 mL dichloromethane. A condenser was attached followed by an addition funnel. The flask was then heated to 60°C in an oil bath. To the addition funnel were added 3.3 mL of Br_2 (64 mmol) and finally an additional 2 mL of CH_2Cl_2, to wash the graduated cylinder. Following this, the N_2 flow was stopped, and a vent to a bubbler containing aqueous base was added. At this point, the Br_2 solution was added dropwise, to the dispersion of OPS. The solution was stirred for 1 d. At this point, the flask was placed in an ice bath and a saturated 2:1 sodium metabisulfite : sodium carbonate was added to the top of the solution with vigorous stirring, until the Br_2 color disappeared (10 to 20 mL). The mixture was transferred to a separatory funnel, and the organic layer was extracted and washed sequentially with a 50 mL portion of water. The organic layer was removed, and charcoal and celite were added and stirred for 10 min. The black mixture was filtered, then dried with sodium sulfate, and filtered again to give a clear, colorless liquid. The CH_2Cl_2 was removed by rotary evaporation, the resulting solid was redissolved in 10 mL of THF, and subsequently precipitated into 200 mL stirred, cold methanol. The precipitate is recovered by filtration and dried under vacuum to yield white powder.

$[BrPhSiO_{1.5}]_{10}$ was synthesized under N_2 in an oven dried Schlenk flask topped with a reflux condenser. To the flask were added a mixture of 5.0 g $[PhSiO_{1.5}]_{10}$ (4.85 mmol, 38.5 mmol phenyl) and 10 mL of CH_2Cl_2. An addition funnel was then attached and the apparatus was heated to 40 ± 2°C in an oil bath. The N_2 flow was stopped briefly and 3.3 mL of Br_2 (50 mmol) was added dropwise. At the same time, a "T" connected to a bubbler containing aqueous base was added. The solution was stirred for 16 h at 40 ± 2 °C.

At this point, the reaction was quenched with 10 to 20 mL of saturated aqueous solution of 2:1 sodium metabisulfite:sodium carbonate until the Br_2 color disappeared. The organic layer was extracted and washed sequentially with a 50 mL portion of water. Then charcoal and celite were added and the mixture stirred for 10 min. The black mixture was filtered to remove solid, then dried over sodium sulfate, and filtered again to give a clear, colorless liquid.

CH_2Cl_2 was removed by rotary evaporation, the resulting solid was dissolved in small amount of THF, and subsequently precipitated into 200 mL of stirred, cold methanol. The precipitate was recovered by filtration and dried under vacuum at 50 ± 2 °C over night.

$[o\text{-}BrPhSiO_{1.5}]_{12}$.. The reaction was run as above; however 2.6 mL of Br_2 (39 mmol) were added dropwise to $[PhSiO_{1.5}]_{12}$ (4.85 mmol, 38.5 mmol phenyl) and 10 mL of dichloromethane. The reaction was run and worked up as above.

Table S1. Bromination of $[PhSiO_{1.5}]_x$ (x = 8, 10 or 12) and F^-/H_2O_2 Si-C cleavage† products.

characterization SQ	Max in MALDI	Temp. ° C	Area %† Ortho	†% 2-bromophenol[25]
Ph_8SQ	$BrPh_8SQ$	30-40	85	≈ 90
$Ph_{10}SQ$	$Br_4Ph_{10}SQ$	30-40	78	75
$Ph_{10}SQ$	$Br_9Ph_{10}SQ$	30-40	75	75
$Ph_{12}SQ$	$Br_6Ph_{12}SQ$	40	60	60
$Ph_{12}SQ$	$Br_6Ph_{10}SQ$	40	60	60
$Ph_{12}SQ$	$Br_9Ph_{10}SQ$	50-55	62	60
$PhSiCl_3$	$BrPhSiCl_3$		5††	
$Br_{16}Ph_8SQ$				90 % 2,5 dibromo phenol
I_8Ph_8SQ, $I_{10}Ph_{10}SQ$, $I_{12}Ph_{12}SQ$				90 % 4-iodophenol

†From GPC analysis of F^-/H_2O_2 cleavage of Phenyl Si-C bond.[25] ††70 % meta, 25 % para.[26]

Table S2. Ipso ^{13}C for $[PhSiO_{1.5}]_{8,10,12}$ and $[BrPhSiO_{1.5}]_{8,10,12}$ and selected model compounds.

Cage	Ipso carbon ^{13}C (ppm)	Cage	Ipso carbon ^{13}C (ppm)
PhT_8	130.92	$BrPhT_8$	129.06
PhT_{10}	130.55	$BrPhT_{10}$	129.01
PhT_{12}	130.83	$BrPhT_{12}$	128.99
$NO_2C_6H_5$	148.30	o-$BrNO_2C_6H_4$	152.80
$CF_3C_6H_5$	130.90	o-$CF_3BrC_6H_4$	130.2[27]
$PhSi(OEt)_3$	131.77	$PhSiCl_3$	131.55
$[Ph_2SiO]_4$	134.42		

Table S3. Calculated HOMO, LUMO and band gap of HT_8, HT_{10} and HT_{12} at the B3LYP/6-31G* level of approximation.[38]

	HOMO (eV)	LUMO (eV)	Band Gap (eV)
T_8	-8.477	0.420	8.897
T_{10}	-8.621	0.455	9.076
T_{12}	-8.624	0.502	9.126

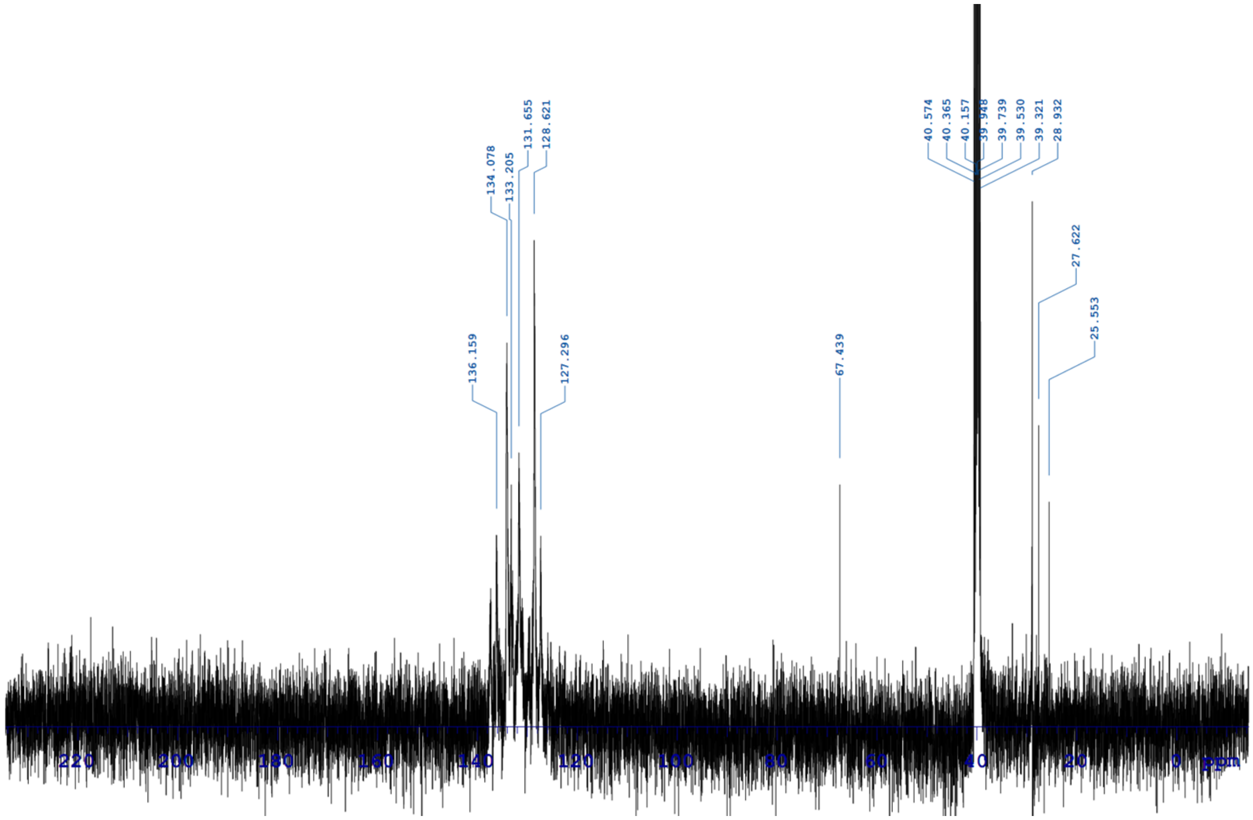

Figure 1. ^{13}C-NMR of $Br_5Ph_{10}SQ$ in DMSO-d_6

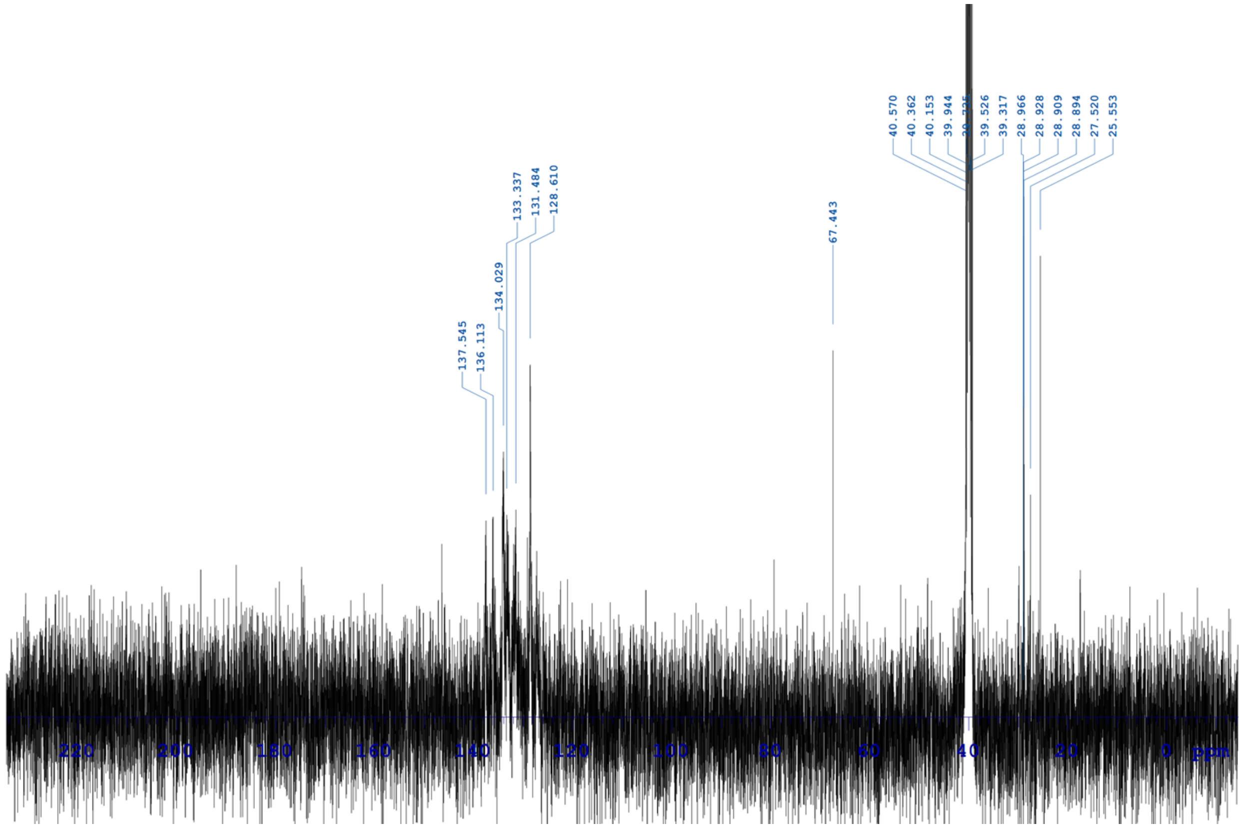

Figure 2. ^{13}C-NMR of $Br_9Ph_{10}SQ$ in DMSO-d_6

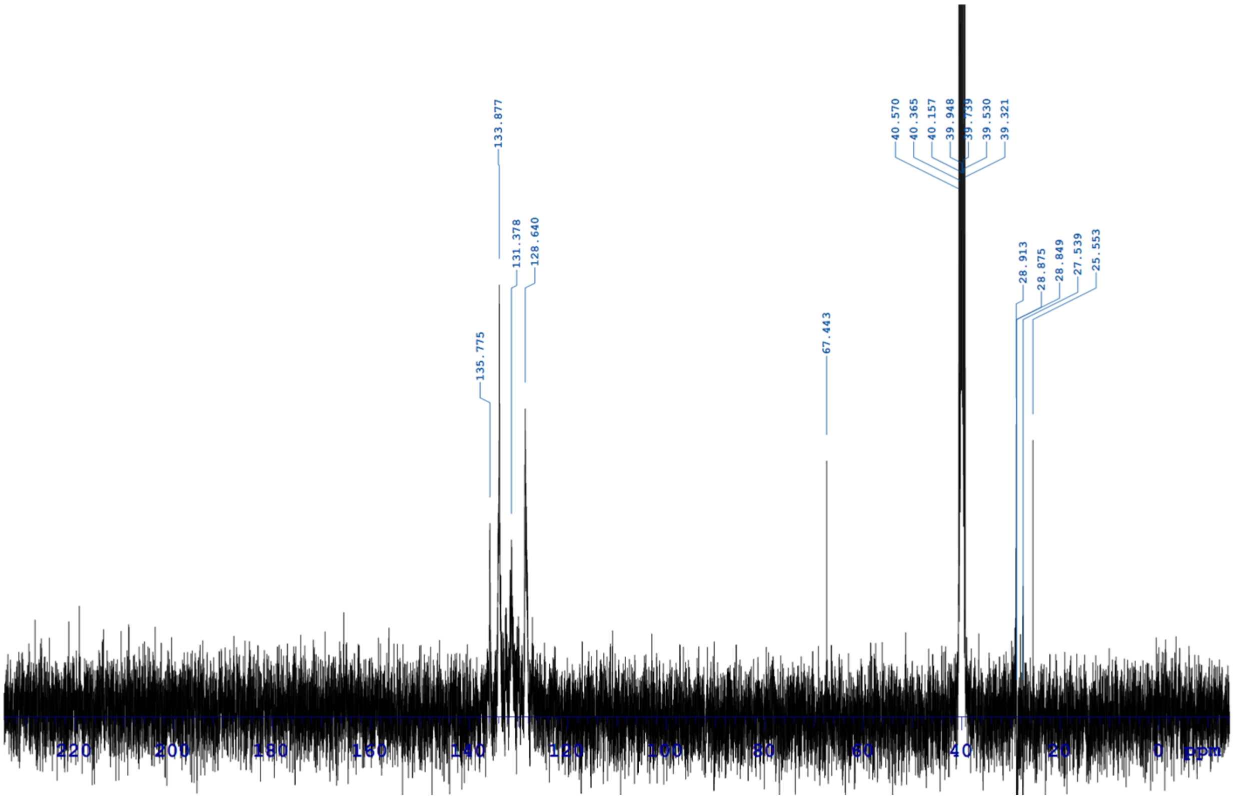

Figure 3. ^{13}C-NMR of $Br_6Ph_{12}SQ$ in DMSO-d_6

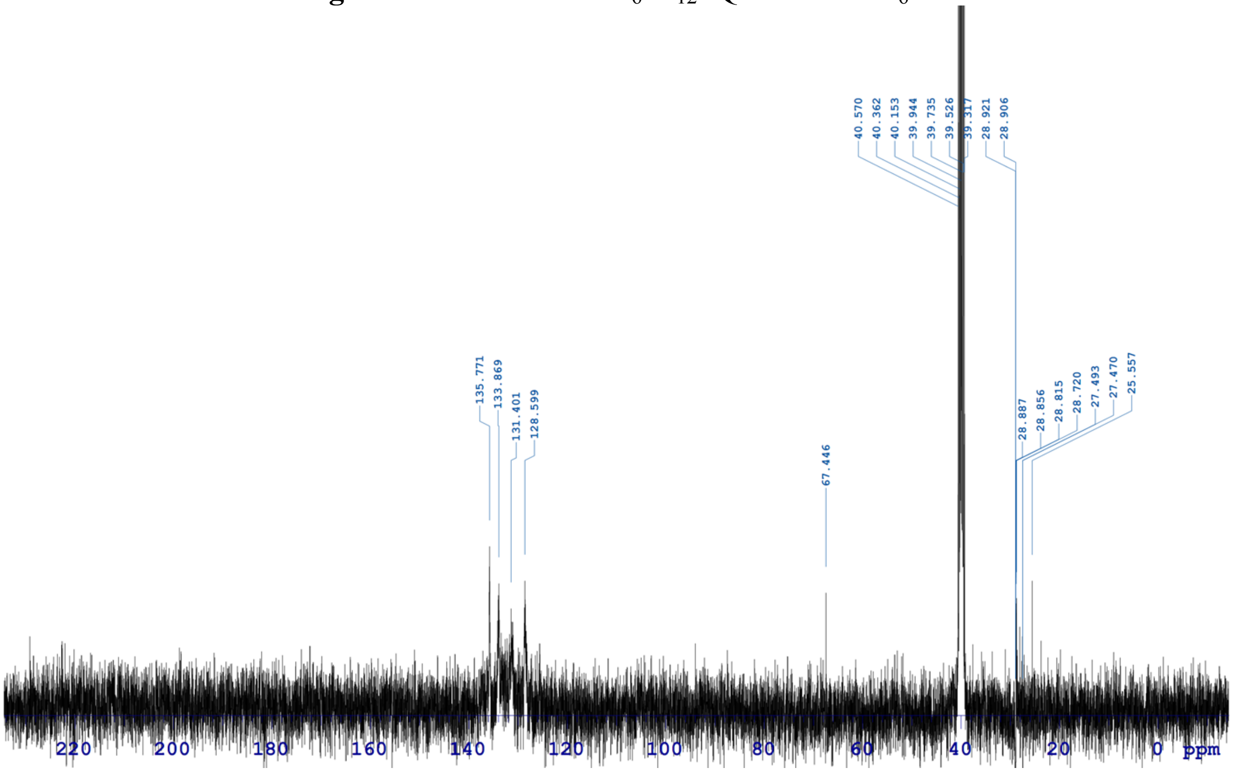

Figure 4. ^{13}C-NMR of $Br_{12}Ph_{12}SQ$ in DMSO-d_6

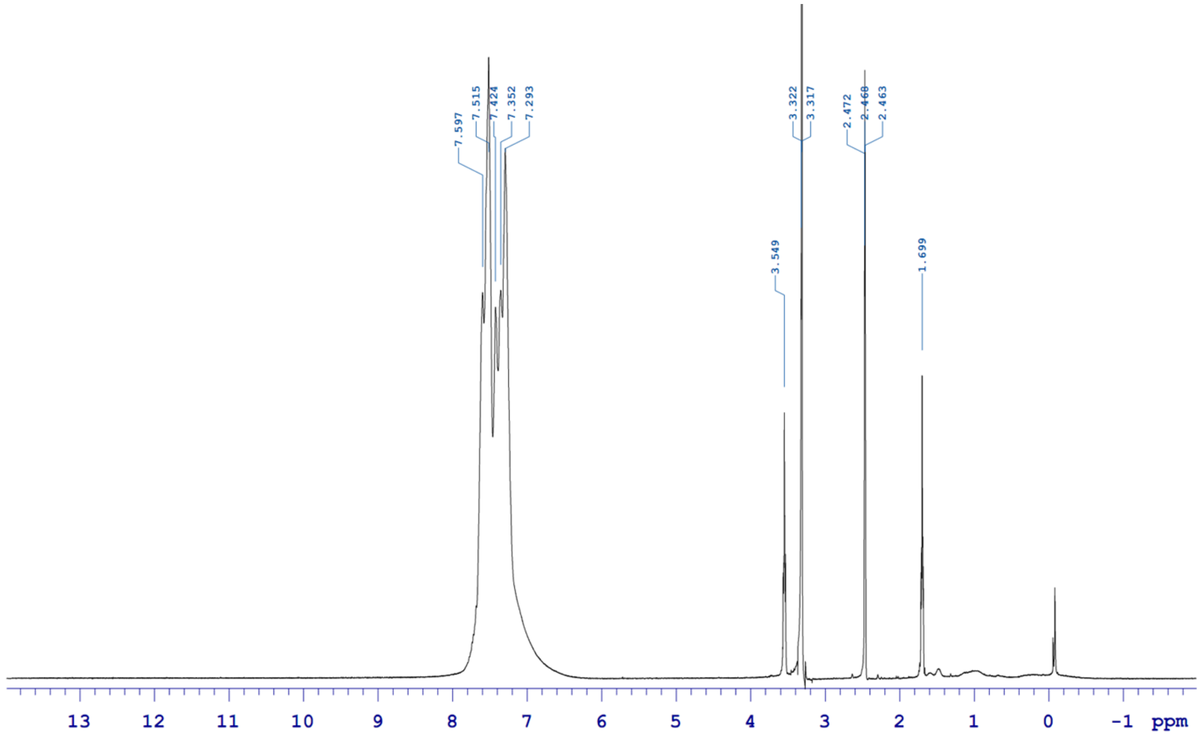

Figure 5. ^{1}H-NMR of $Br_5Ph_{10}SQ$ in DMSO-d_6

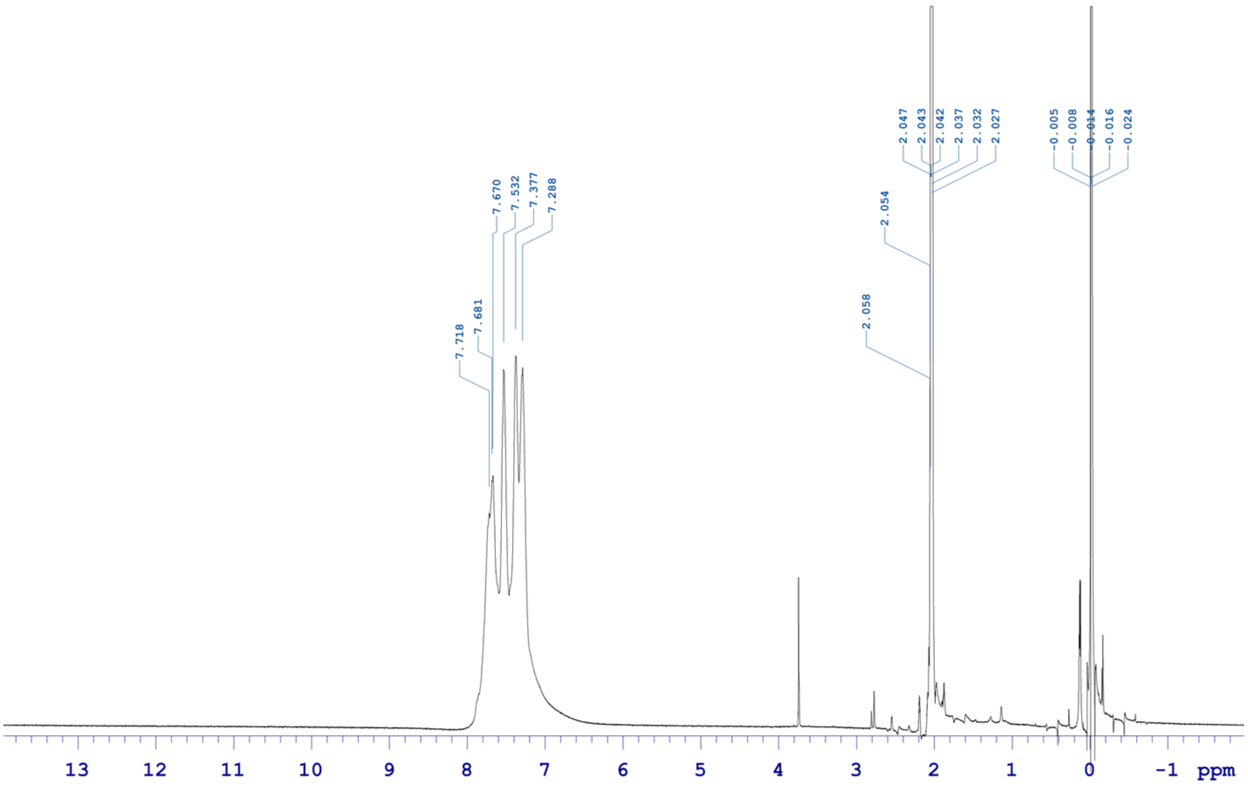

Figure 6. ^{1}H-NMR of $Br_9Ph_{10}SQ$ in Acetone-d_6

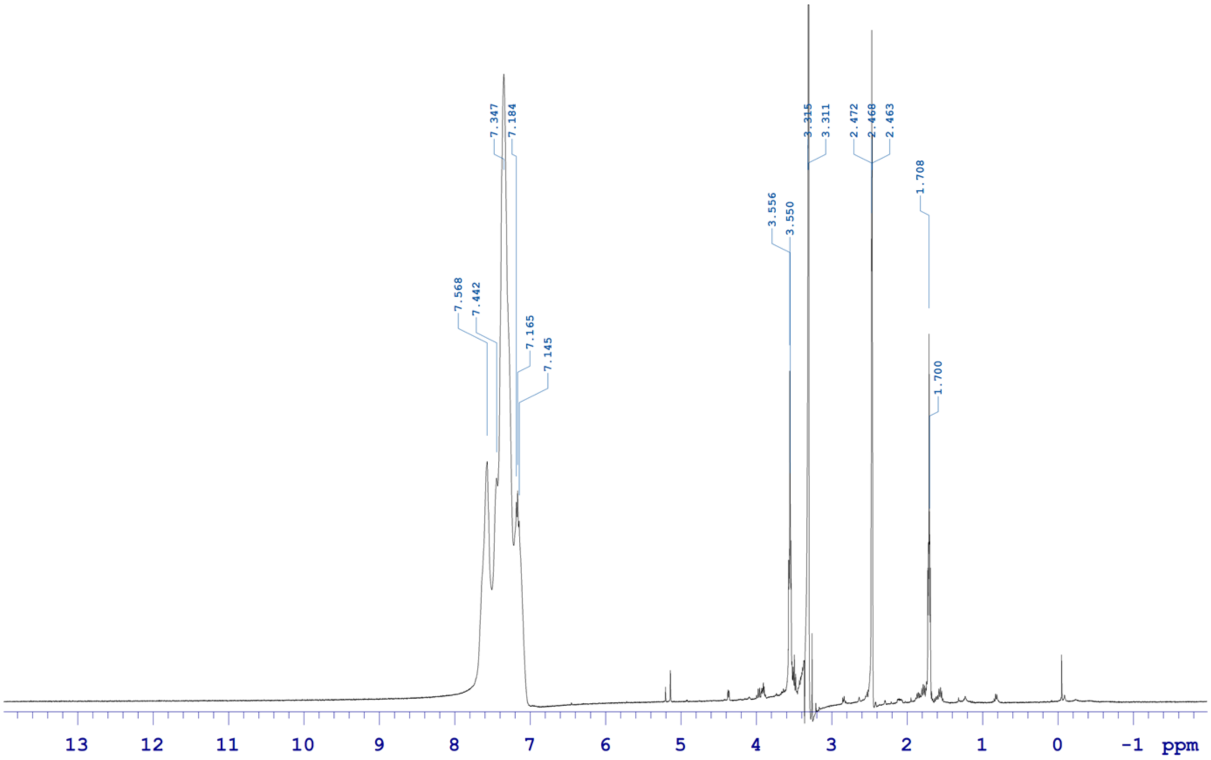

Figure 7. ^{1}H-NMR of $Br_6Ph_{12}SQ$ in DMSO-d_6

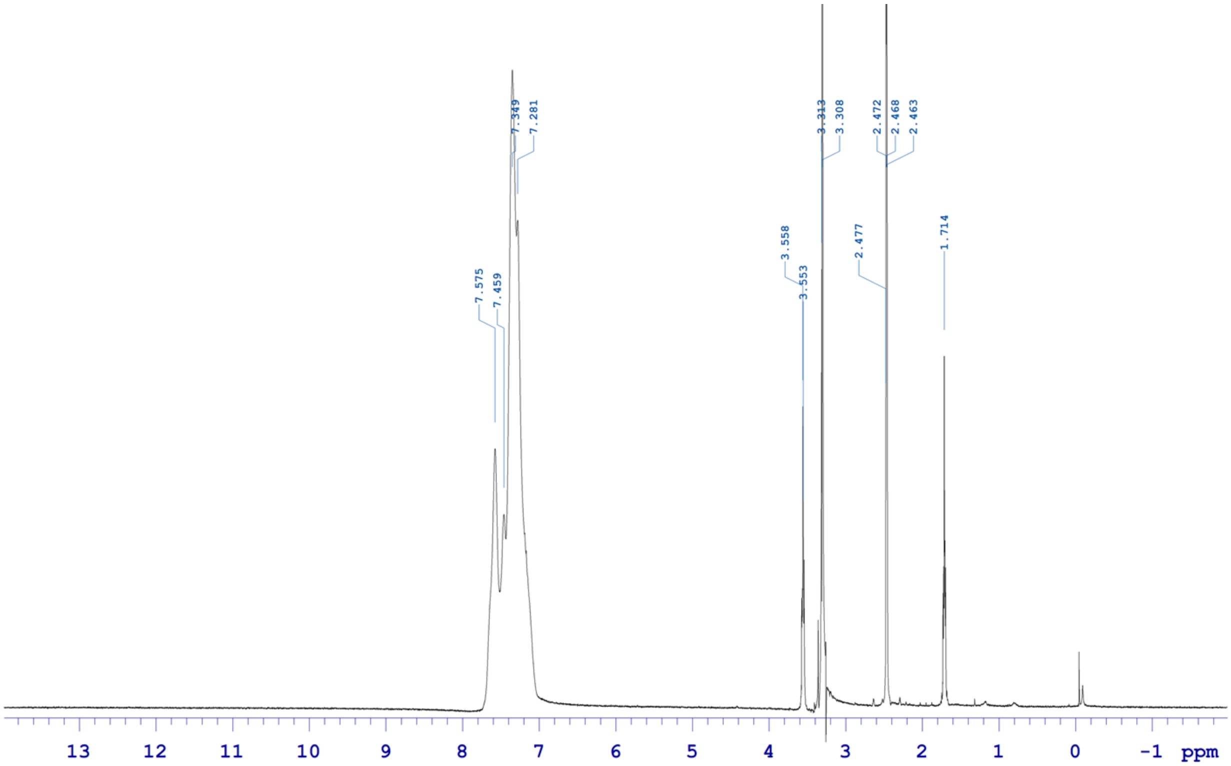

Figure 8. ^{1}H-NMR of $Br_{12}Ph_{12}SQ$ in DMSO-d_6