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Perfluorinated *cyclo*-tetrakis(phenylene sulfides): synthesis and structure

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Contents

1. General information

Dimethylformamide (DMF) and triethylamine were kept over NaOH and distilled immediately before use. Hexafluorobenzene and pentafluorothiophenol were obtained from P&M Invest (Dolgoprudny, Russia). Perfluoro-*m*-xylene **7** was a ~2.7 : 1 mixture with its *para*-isomer (according to the ^{19}F NMR data) which is considerably less reactive.[S1] This mixture was a byproduct in the synthesis of octafluorotoluene by the reaction of hexafluorobenzene with Teflon chips.[S2,S3] Perfluoro-1,4-bis(phenylthio)benzene **5** and tetrafluorobenzene-1,4-dithiol **1** were synthesized according to the literature procedures.[S4,S5]

The ^{19}F spectra were recorded for solutions in $CDCl_3$ and $OC(CD_3)_2$ on a Bruker AV300 spectrometer at 282.36 MHz, ^{13}C NMR spectra were recorded on a Bruker AV-400 instrument (100.6 MHz). Chemical shifts are given in δ ppm from CCl_3F (^{19}F) and TMS (^{13}C), *J* values in Hz; C_6F_6 (–162.9 ppm from CCl_3F), $CDCl_3$ (76.9 ppm from TMS) were used as internal standards. IR spectra were taken on a Bruker Vector 22 IR spectrophotometer.

Gas chromatographic–mass spectrometric analysis (GC-MS) was performed on a Hewlett Packard HP 5890 Series II chromatograph coupled with an HP 5971 mass-selective detector [HP-5MS capillary column, 30 m×0.25 mm, film thickness 0.25 μm; carrier gas helium, flow rate 1 ml min^{-1}; oven temperature programming from 50 °C (2 min) to 280 °C at a rate of 10 deg min^{-1} and finally 5 min at 280 °C; injector temperature 280 °C; ion source temperature 175 °C; electron impact, 70 eV; 1.2 scan s^{-1}, a.m.u. range 30–800].

The elemental compositions of macrocycle **8** were determined by classical method and for macrocycle **2** from the high-resolution mass spectra (electron impact, 70 eV) which were obtained with a Thermo Scientific DFS instrument. The progress of reactions was monitored by TLC on silica gel 60 F_{254} plates (Merck). Silica gel with a particle size of 0.063–0.200 mm (Merck) was used for column chromatography.

Experimental section

*Synthesis of macrocycle **2**.*

4,5,9,10,14,15,19,20,21,22,23,24,25,26,27,28-Hexadecafluoro-2,7,12,17-tetrathiapentacyclo [16.2.2.2^{3,6}.2^{8,11}.2^{13,16}]octacosa-1(20),3,5,8,10,13,15,18,21,23,25,27-dodecaene **2.** a) A solution of perfluoro-1,4-bis(benzenethio)benzene **5** (0.55 g, 1 mmol) and tetrafluorobenzene-1,4-dithiol **1** (0.21 g. 1 mmol) in acetonitrile (200 ml) was added dropwise in a period of ~12 h with stirring into a boiling solution of triethylamine (1.21 g, 12 mmol) in acetonitrile (50 ml). The mixture was stirred under reflux for 10 h, and the solvent was evaporated. Silica gel column chromatography (eluent $CHCl_3$) gave 0.67 g of a solid material containing (GC-MS) 91% of compound **2** and 8% of the initial compound **5**, crystallization of which from a mixture of ethanol/acetone gave 0.49 g (68%) pure macrocycle **2**. Mp 280-287 ^oC. IR (KBr) ν, cm^{-1}: w 1620, vs 1466, w 1437, w 1387, m 1248, s 957, m 810, w 742, w 621. NMR ^{13}C ($CDCl_3$), δ: 146.5 (dm, $^1J_{CF}$ = 257.5 Hz, C-F), 115.9 (m, C-S). NMR ^{19}F ($CDCl_3$), δ: -133.7 (s). HRMS m/z: 719.8619 (M^+). $C_{24}F_{16}S_4$. Calculated: M = 719.8622.

b) Hexafluorobenzene (0.37 g, 2 mmol) was added with stirring into solution of tetrafluorobenzene-1,4-dithiol **1** (0.43 g, 2 mmol) and triethylamine (2.00 g, 20 mmol) in DMF (100 ml). The mixture was stirred at 80 ^oC for 42 h, and the solvent was evaporated. Silica gel column chromatography (eluent CCl_4) gave 0.10 g of a solid material containing (GC–MS) 92% of compound **2**, crystallization of which from a mixture of ethanol/acetone gave 0.08 g (11%) pure macrocycle **2**.

c) Hexafluorobenzene (0.37 g, 2 mmol) was added with stirring into solution of tetrafluorobenzene-1,4-dithiol **1** (0.43 g, 2 mmol) and triethylamine (2.00 g, 20 mmol) in acetonitrile (100 ml). The mixture was stirred at 80 ^oC for 16 h, and the solvent was evaporated. The residue was treated with 5% HCl (60 ml) and then with CH_2Cl_2 (3×50 ml). The extract was dried with Na_2SO_4 and evaporated. The residue was treated with boiling acetonitrile (20 ml) and filtered. Evaporation gave 0.21 g solid material containing (NMR ^{19}F, GC-MS) 24% of compound **2** and 73% of tetrafluorobenzene-1,4-dithiol **1**.

d) A solution of pentafluorothiophenol (0.80 g, 4 mmol) in DMF (50 ml) was stirred at room temperature for 52 h and then at 80 ^oC for 4 h. Filtration and evaporation of the solvent gave 0.60 g of white solid material containing (GC-MS) 65% $C_6F_5SC_6F_4SH$ **3** (M^+ 380), 6% $C_6F_5SC_6F_4SC_6F_4SH$ **4** (M^+ 560) and 9% of macrocycle **2** (M^+ 720).

*Synthesis of macrocycle **8**.*

Perfluoro-1,4-bis(2,4-dimethylbenzenethio)benzene **7**. A solution of tetrafluorobenzene-1,4-dithiol **1** (0.43 g, 2 mmol) of and triethylamine (1.01 g, 10 mmol) of in acetone (80 ml) was added dropwise in period of 6 h with stirring into a solution of a mixture of perfluorinated *m*- and *p*-xylenes (*m*/*p* 2.7:1, ~5 mmol of the *meta*-isomer **6**, 1.96 g) in acetone (20 ml) at 0 ^oC. The mixture was stirred at room temperature for 2 h, and the solvent was evaporated. Silica gel column chromatography (eluent CCl_4/$CHCl_3$ 3:1) gave 1.24 g of solid material containing (NMR ^{19}F, GC–MS) 95% of compound **7** (M^+ 746) and 3% of macrocycle **8** (M^{++} 460). NMR ^{19}F ($(CD_3)_2CO$), δ: -131.4 (s, 4F, F-2,3,5,6), -125.9 (dd, 2F, $J_{F(6')-F(5')}$ = 22 Hz, $J_{F(6')-F(3')}$ = 13 Hz,

F-6′,6′′), -125.0 (qd, 2F $J_{F(5')\text{-}CF_3(4')}$ = 23 Hz, $J_{F(5')\text{-}F(6')}$ = 22 Hz, F-5′,5′′), -114.1 (qqd, 2F, $J_{F(3')\text{-}CF_3(2')}$ = 33 Hz, $J_{F(3')\text{-}CF_3(4')}$ = 23 Hz, $J_{F(3')\text{-}F(6')}$ = 13 Hz, F-3′,3′′), -55.8 (t, 6F, $J_{CF_3(4')\text{-}F(3',5')}$ = 23 Hz, CF_3(4′,4′′)), -53.0 (d, $J_{CF_3(2')\text{-}F(3')}$ = 33 Hz, CF_3(2′,2′′)).

5,10,11,16,21,22,23,24,25,26,27,28-Dodecafluoro-4,6,15,17-tetrakis(trifluoromethyl)-2,8,13,19-tetrathiapentacyclo[18.2.2.2^{9,12}.1^{3,7}.1^{14,18}]octacosa-1(22),3(28),4,6,9,11,14(25),15,17,20,23,26-dodecaene **8.** A solution of compound **7** (1.24 g, 1.7 mmol) in acetonitrile (80 ml) and a solution of tetrafluorobenzene-1,4-dithiol **1** (0.36 g, 1.7 mmol) in acetonitrile (80 ml) were simultaneously added dropwise within 7 h with stirring into a boiling solution of triethylamine (0.61 g, 6 mmol) in acetonitrile (30 ml). The mixture was stirred under reflux for 20 h, and the solvent was evaporated. The solid residue was placed into the Soxhlet apparatus, and the product was extracted with boiling benzene. Double-play crystallization of the extract from benzene gave 0.84 g (55%) pure macrocycle **8**. The analytical sample was obtained by sublimation at 270 ºC (10^{-2} Torr). Mp 332.7 ºC (decomp.). IR (KBr) ν, cm^{-1}: w 1620, w 1589, m 1552, vs 1466, s 1423, w 1389, vs 1346, m 1282, m 1259, s 1219, vs 1196, vs 1159, m 1126, s 960, m 876, w 735, w 606. NMR ^{19}F (C_6H_6+$(CD_3)_2CO$), δ: -132.9 (s, 8F, F-10,11,21,22,23,24,26,27), -113.2 (septet d, 2F, $J_{F(5)\text{-}2CF_3}$ = 35 Hz, $J_{F(5)\text{-}F(28)}$ = 15 Hz, F-5,16), -68.8 (d, 2F, $J_{F(28)\text{-}F(5)}$ = 15 Hz, F-25,28), -53.9 (d, 12F, $J_{CF_3\text{-}F(5)}$ = 35 Hz, CF_3). Found, %: C 36.16; F 49.79; S 13.78. GC-MC, m/z: 460 (M^{++}). $C_{28}F_{24}S_4$. Calculated, %: C 36.53; F 49.53; S 13.93. M 920.

References

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Spectral data of obtained compounds

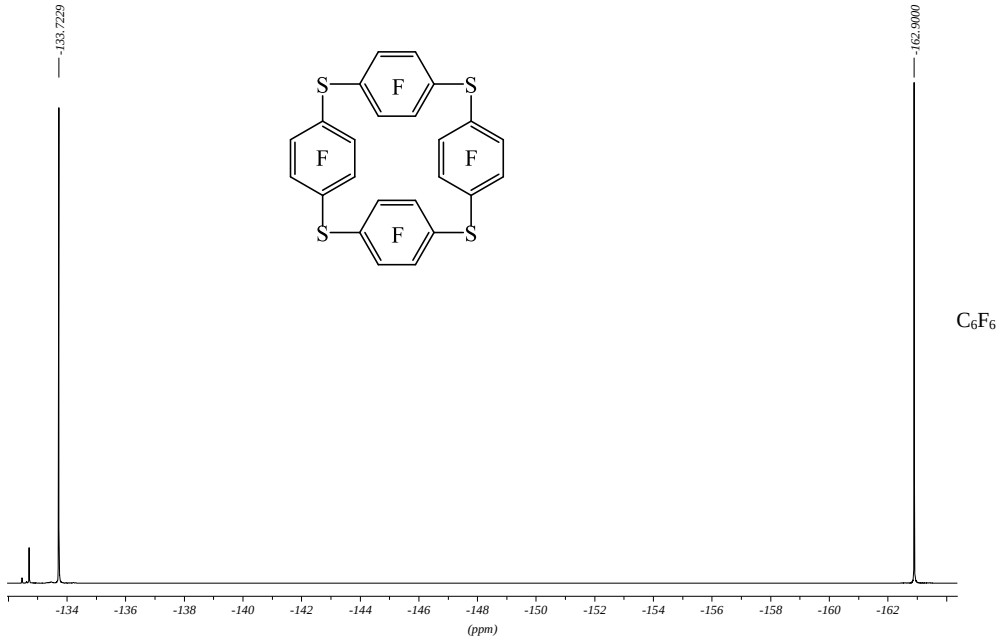

Figure S1. ^{19}F NMR spectrum ($CDCl_3$) of perfluoro-*cyclo*-tetrakis(1,4-phenylene sulfide) **2**.

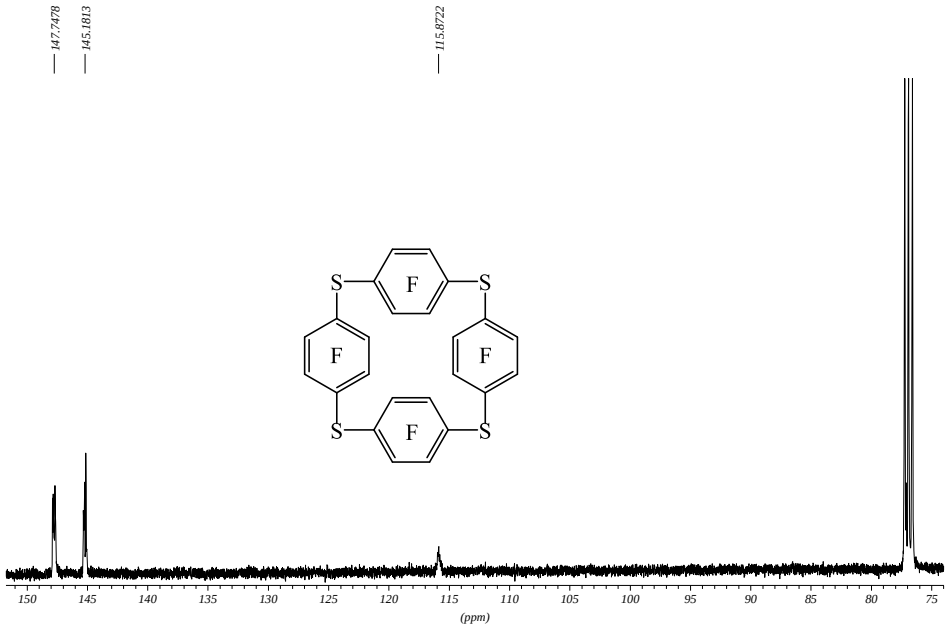

Figure S2. ^{13}C NMR spectrum ($CDCl_3$) of perfluoro-*cyclo*-tetrakis(1,4-phenylene sulfide) **2**.

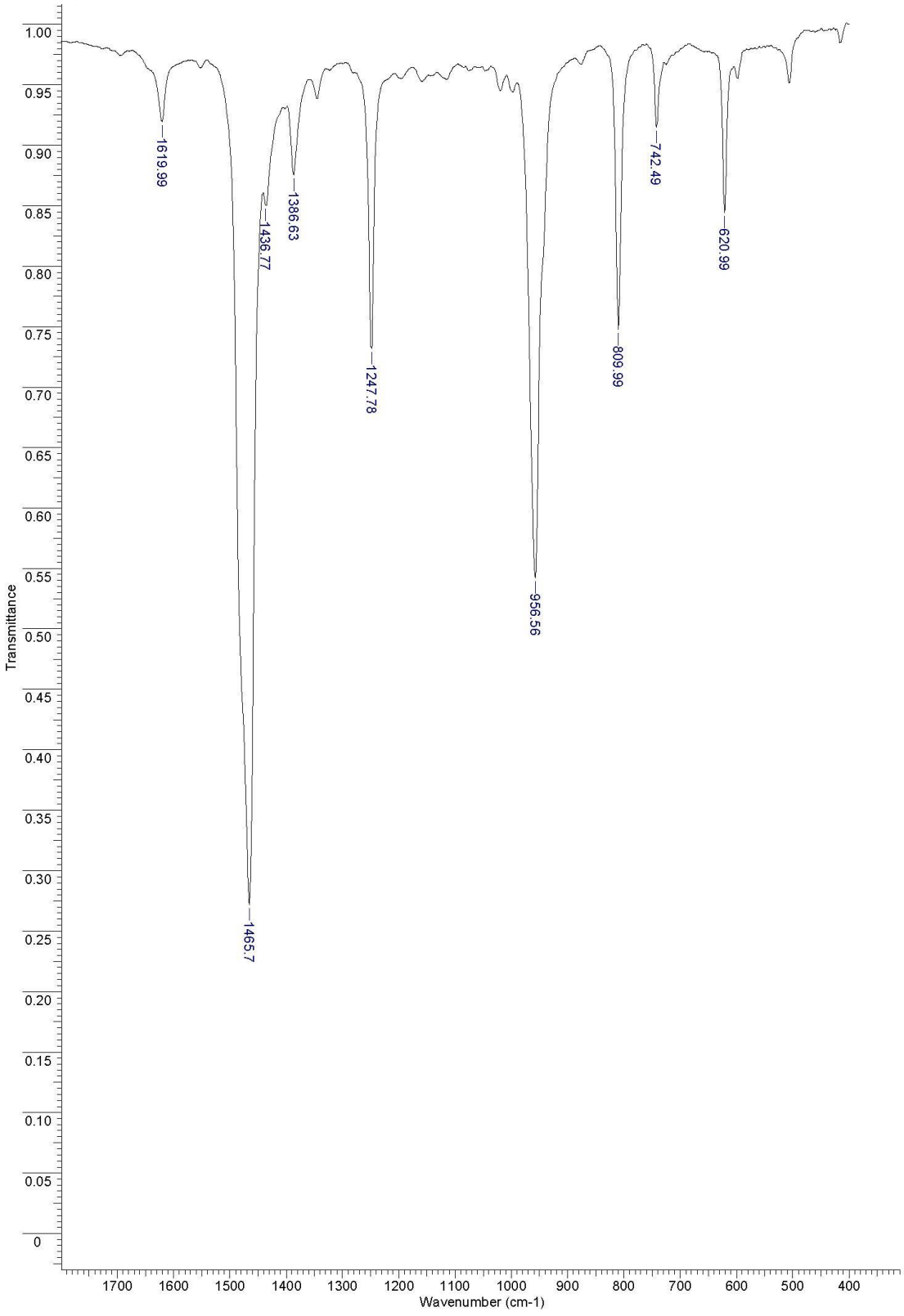

Figure S3. IR spectrum (KBr) of perfluoro-*cyclo*-tetrakis(1,4-phenylene sulfide) **2**.

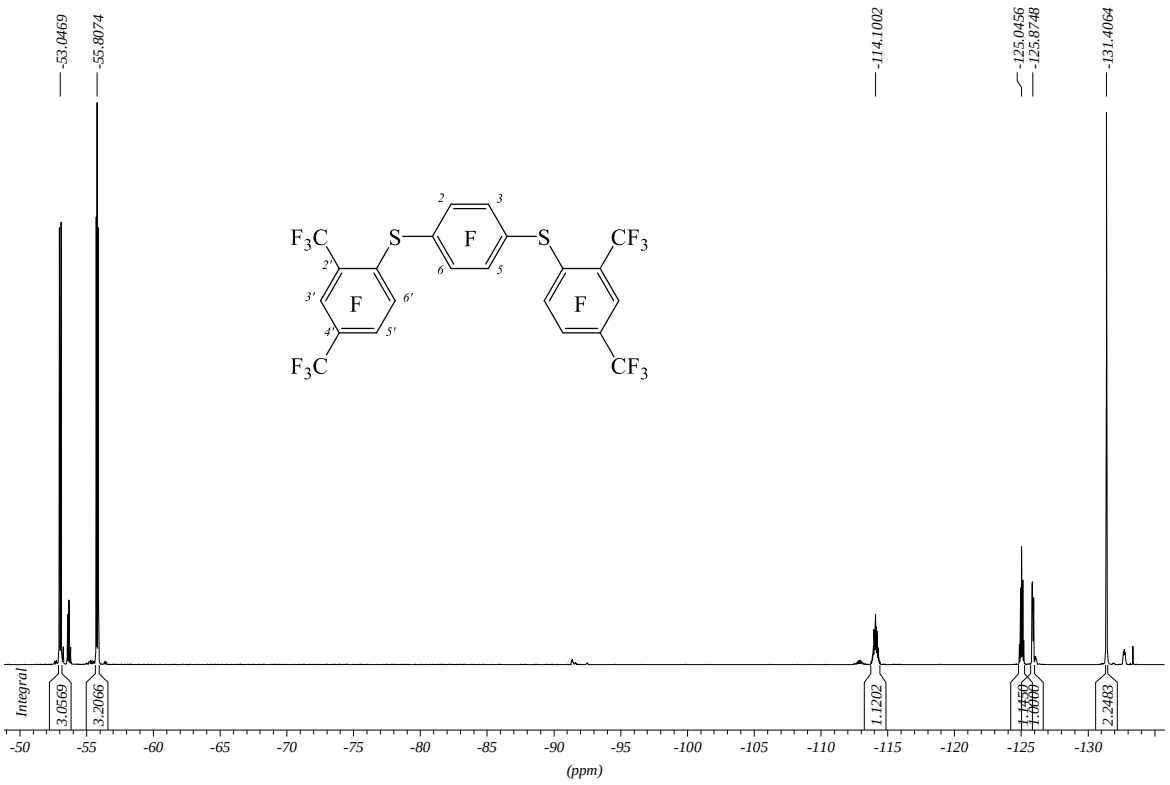

Figure S4. ^{19}F NMR ($(CD_3)_2CO$) of perfluoro-1,4-bis(2,4-dimethylphenylthio)benzene **7**.

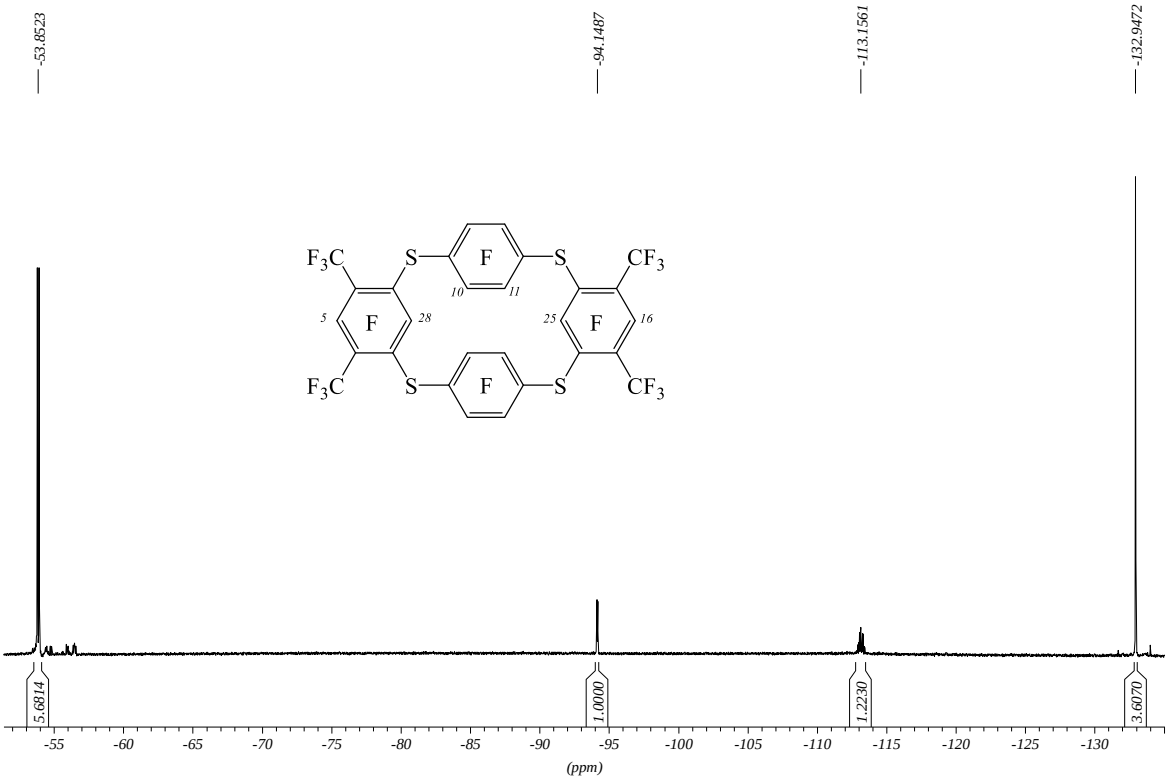

Figure S5. ^{19}F NMR spectrum (C_6H_6 + $(CD_3)_2CO$) of macrocycle **8**.

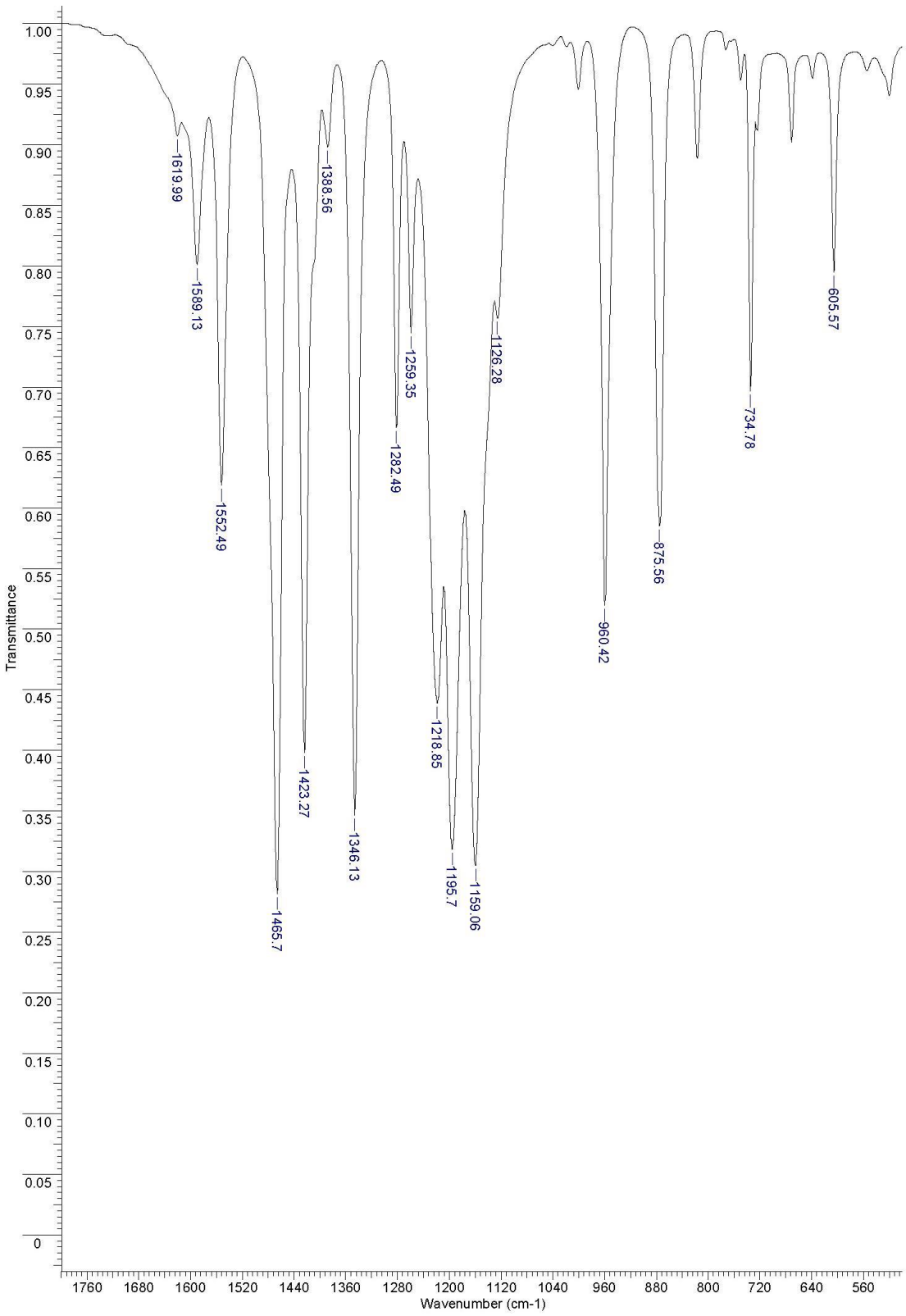

Figure S6. IR spectrum (KBr) of macrocycle **8**.