Imide linked '4+4' macrocycles formed by condensation of isophthaloyl dichloride and tetra- and penta-fluoroanilines

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Electronic Supplementary Information

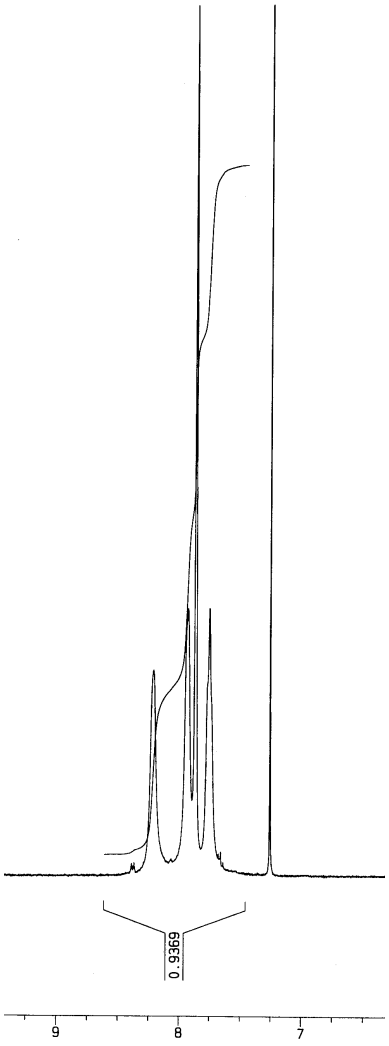

Figure S1 ^{1}H NMR spectrum of compound **1** in $CDCl_3$

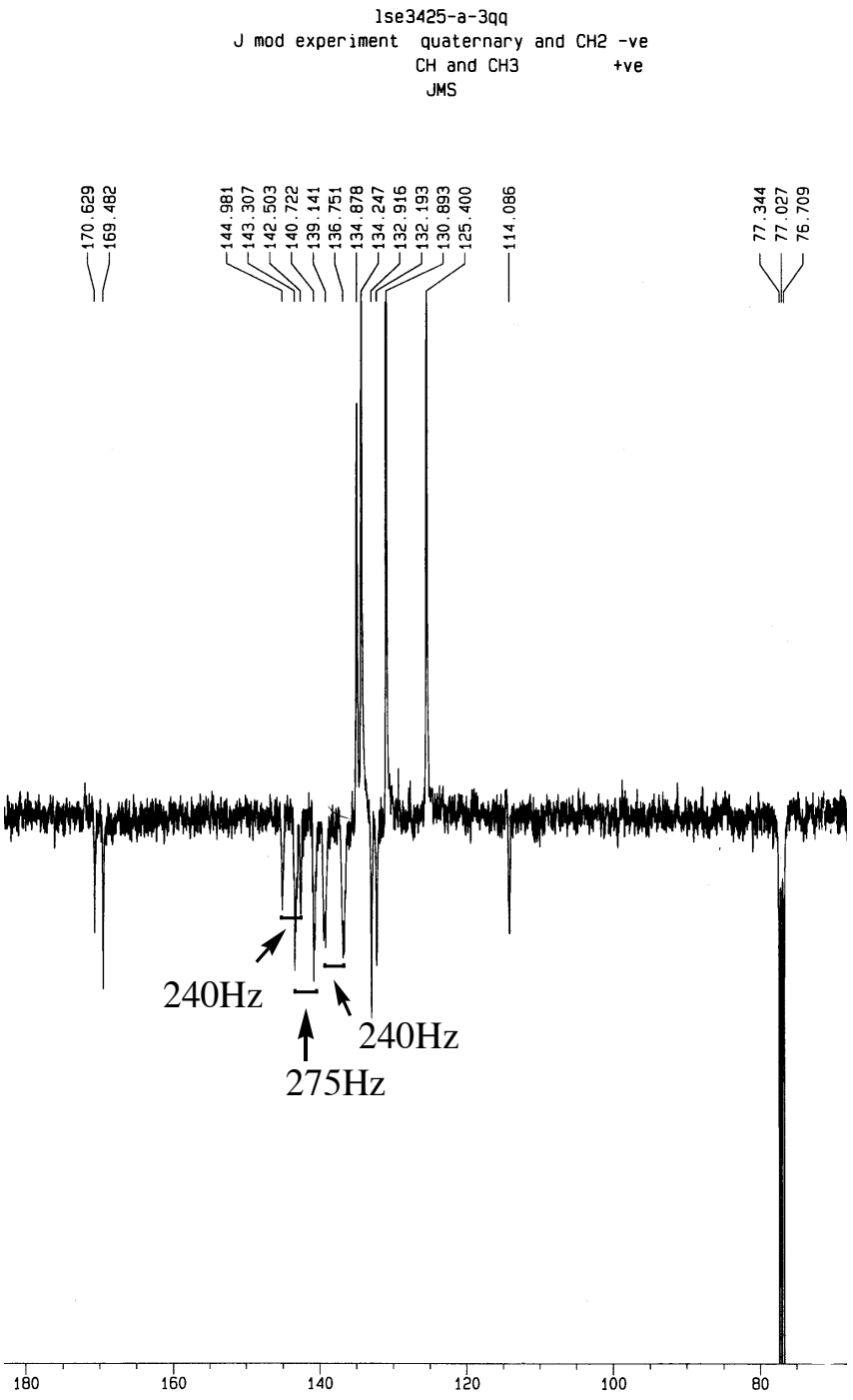

Figure S2 J MOD ^{13}C NMR (Quaternary and CH_2 carbons negative and CH carbons positive) for compound **1** in $CDCl_3$. Inequivalencies are introduced by the conformational locking of the macrocycle.

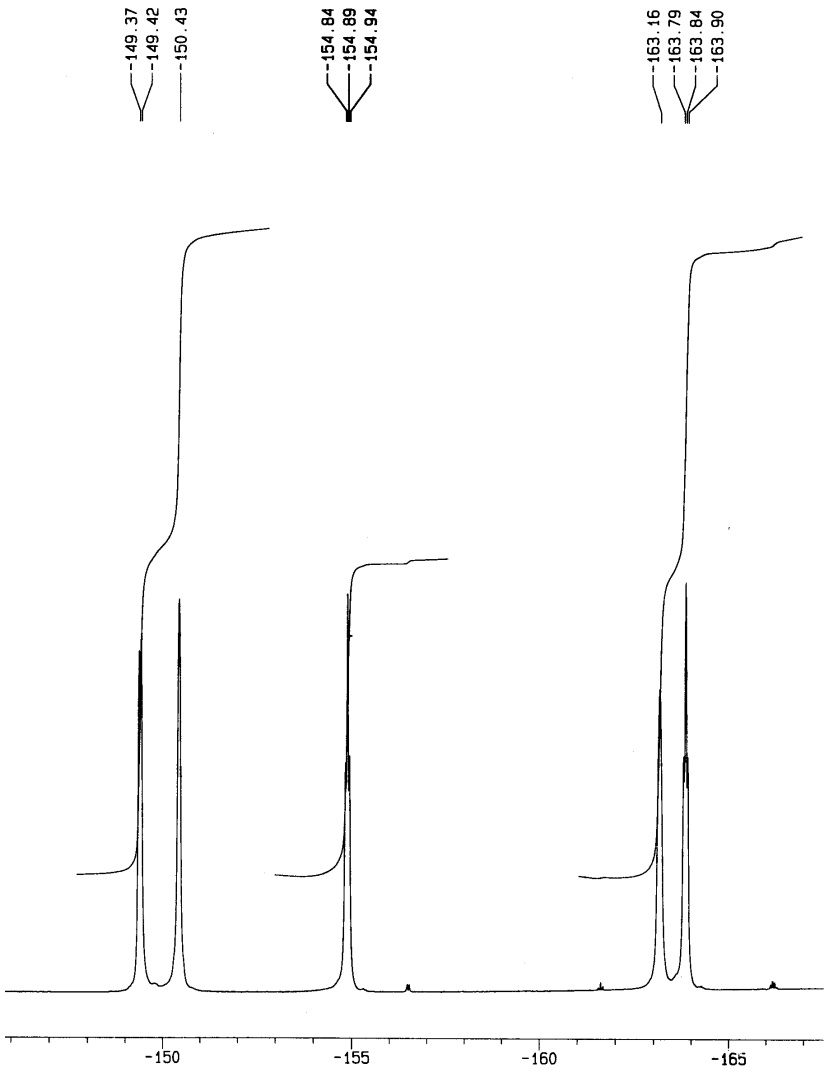

Figure S3 ^{19}F NMR of compound **1** in $CDCl_3$. Five different fluorine environments are observed presumably due to hindered rotation of the pendant pentafluorophenyl groups.

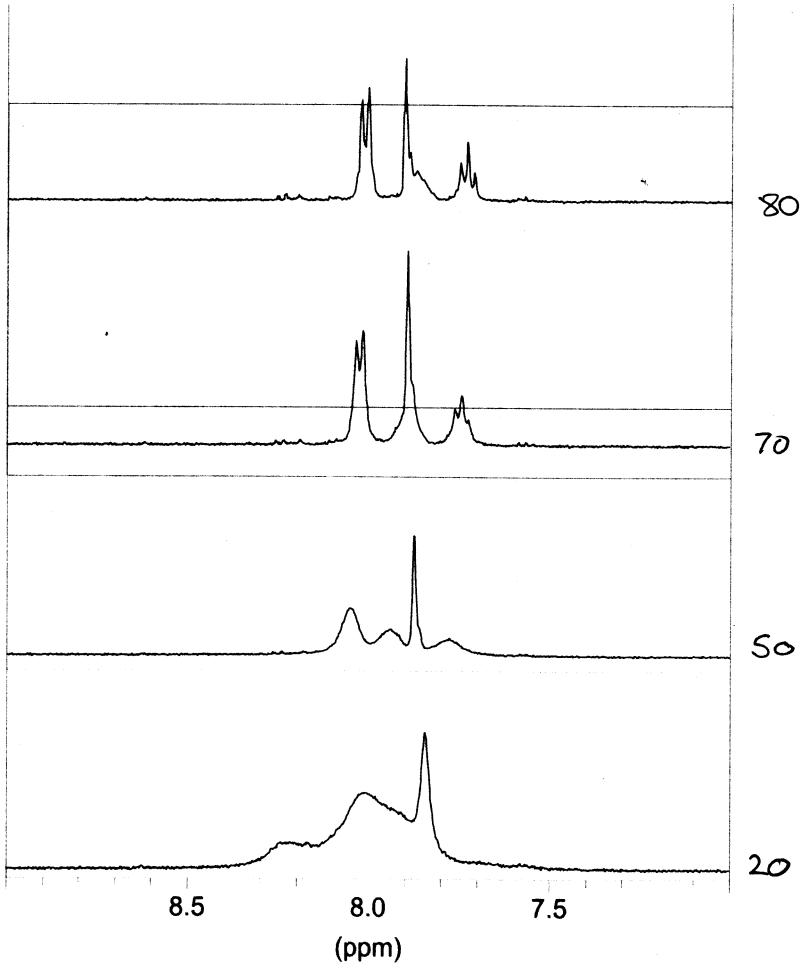

Figure S4 ^{1}H NMR spectrum of compound **2** in DMSO-d_6 at 20, 50, 70 and 80°C

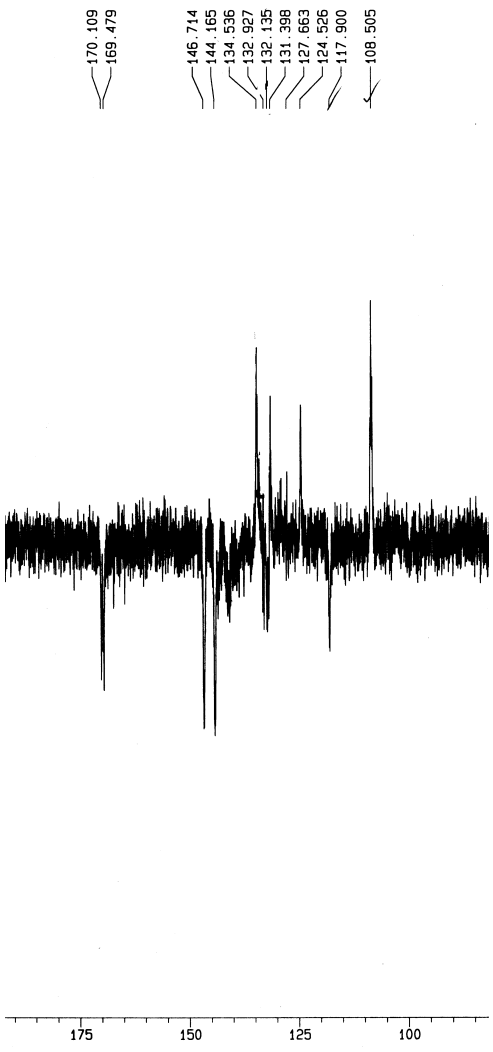

Figure S5 J MOD ^{13}C NMR (Quaternary and CH_2 carbons negative and CH carbons positive) for compound **2** in DMSO-d_6. Inequivalencies are introduced by the conformational locking of the macrocycle.

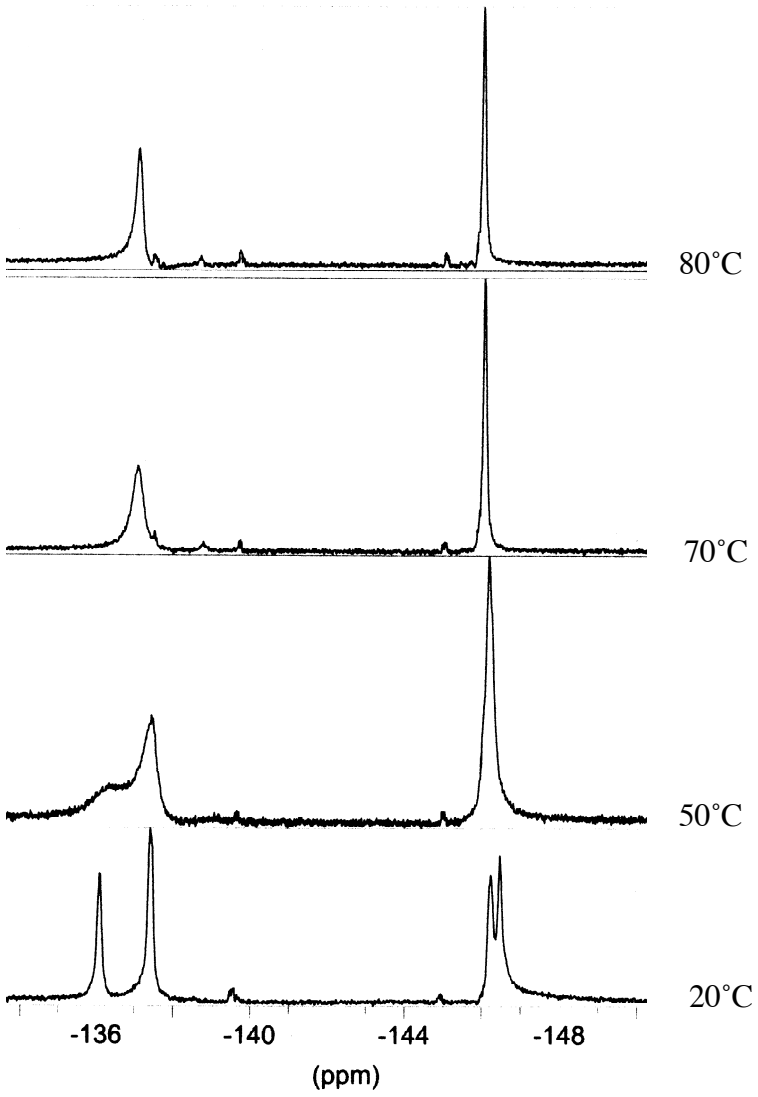

Figure S6 ^{19}F NMR of compound **2** in DMSO-d_6. Four different fluorine environments are observed presumably at 20°C (lowest spectrum) due to hindered rotation of the pendant tetrafluorophenyl groups. At higher temperatures the resonances coalesce into two fluorine signals.

Synthesis of Compound **1**

Isophthaloyl dichloride (0.99g, 4.9 mmol), DMAP (5mg), and triethylamine (1.50 g, 14.9 mmol) were dissolved in dry dichloromethane (50 ml) under N_2. Pentafluoroaniline (0.90g, 4.9 mmol) was added and the reaction was stirred overnight. The reaction mixture washed with water (3 x 40 ml), dried over magnesium sulfate and the solvent

reduced *in vacuo* affording a yellow residue. The residue was purified by column chromatography on silica gel eluting with dichloromethane to afford macrocycle **1** as a white powder in 13% yield.

^{1}H NMR ($CDCl_3$): δ 8.22 (d, 4H, ArH), δ 7.92 (d, 4H, ArH) δ 7.87 (s, 4H, ArH), δ 7.75 (t, 4H, ArH). ^{13}C NMR ($CDCl_3$): δ 170.63, 169.48, 143.74, 142.01, 137.95, 134.88, 134.25, 132.92, 132.19, 130.89, 125.40, 114.09. ^{19}F NMR ($CDCl_3$): δ -149.4, -150.4, -154.9, -163.2, -163.8. MS: 1275.2 ($M + Na^+$), 1307.3 ($M + Na^+ + MeOH$) Satisfactory microanalysis data was obtained.

Compound **2**

Isophthaloyl dichloride (2.46g, 12mmol), DMAP (10mg), and triethylamine (3.66g, 36mmol) were dissolved in dry dichloromethane (50ml) under N_2. 2,3,5,6-Tetrafluoroaniline (2.01g, 12mmol) was added and the reaction stirred overnight. The organic solution was washed with water (3 x 60ml), dried over magnesium sulfate and the solvent evaporated. The resulting product was solid loaded onto a silica 60 column, eluted with dichloromethane. The product was collected and then purified by filtration through a Sephadex® column (LH-20), eluted with 100% acetonitrile. Macrocycle **2** was isolated in 3% after recrystallisation from acetonitrile solution.

^{1}H NMR (DMSO-d_6 80^{0}C): δ 8.02 (2 d, 8H, 2Ar.H), δ 7.90 (broad s, 4H, Ar.H) δ 7.87 (broad, 4H, Ar.H), δ 7.73 (t, 4H, Ar.H). ^{13}C NMR (DMSO-d_6): δ 170.11, 169.50, 146.71, 144.17, 134.54, 132.93, 132.14, 131.40, 124.53, 117.90, 108.51. ^{19}F NMR (DMSO-d_6): δ -136.10, -137.42, -146.02, -146.36. MS: 1203.75 ($M + Na^+$) Satisfactory microanalysis data was obtained.