Supplementary Material for:

Planar *Meso* Pentafluorophenyl Core Modified Isophlorins

J. Sreedhar Reddy[a] and Venkataramanarao G. Anand[b]
Chemical Sciences &Technology Division,
National Institute for Interdisciplinary Science & Technology, NIIST (Formerly RRL)
CSIR, Trivandrum - 695019
India.
[b]Indian Institute of Science Education & Research, (IISER)
900, NCL Innovation Park, Dr. Homi Bhabha Road,
Pune - 411 008, Fax: +91-20-25898022; Tel: +91-20-25898021,
E-mail: vg.anand@iiserpune.ac.in
India.

General notes and procedure:

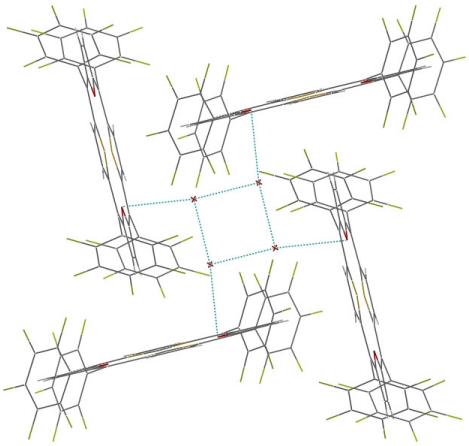
^{1}H NMR spectra were recorded on a 300 MHz Bruker Advance DPX spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent ($CHCl_3$, s, δ, 7.26). Mass spectroscopic analysis of **1** was carried out on a Voyager-De-STR (Applied Biosystems). Mass spectroscopic analysis of **2** was carried out on JEOL JMS 600H spectrometer. Electronic spectra were recorded on a Perkin-Elmer Lambda 20 spectrophotometer. Chromatographic separations were performed on basic alumina and silica gel (230-400) in glass columns.

Single Crystal Structure Determination: The single crystal X-ray diffraction data were collected on a Bruker AXS Kappa Apex 2 CCD diffractometer at 173(2) K for **2** and 248(2) K for **1**. Good quality single crystals were grown by slow evaporation of n-hexane into chloroform solutions of **1** and **2**.

Crystallographic data of **1**: $C_{44}H_8F_{20}O_4$, Mw = 980.01, Rhombohedral, space group R-3, a = b = 19.8252(5) Å, c = 24.8223(9) Å, $\alpha=\beta=90$, $\gamma=120$, V = 8449.0(4) Å^3, Z = 9, D_{calc} = 1.734 g/cm^{-3}, T = 248(2) K, R1 = 0.0359, $R2_w$ = 0.0877.

Crystallographic data of **2**: $C_{44}H_8F_{20}S_2O_2$, Mw = 1011.96, Tetragonal, space group I-4, a = b = 12.1454(3) Å, c = 27.8101(16) Å, $\alpha=\beta=\gamma=90$, V = 4102.3(3) Å^3, Z = 4, D_{calc} = 1.795 g/cm^{-3}, T = 173(2) K, R1 = 0.0593, $R2_w$ = 0.1938.

The water oxygen O2, in **2**, and its four fold equivalents form a square shaped hydrogen bonded cluster positioned around the four fold axis in the body center and at the unit cell origin. Even though, the water hydrogens could not be located in the difference Fourier map, O2-O2 # (#: 1-y, -1+x, z) distance of 2.809 Å shows strong hydrogen bonding interaction between the water molecules. Further, the square water (O2) is bound to the oxygens (O1) of the furan rings of four molecules generated by four fold rotation. The O1-O2 distance of 3.037 Å shows a weak hydrogen bonding interaction.



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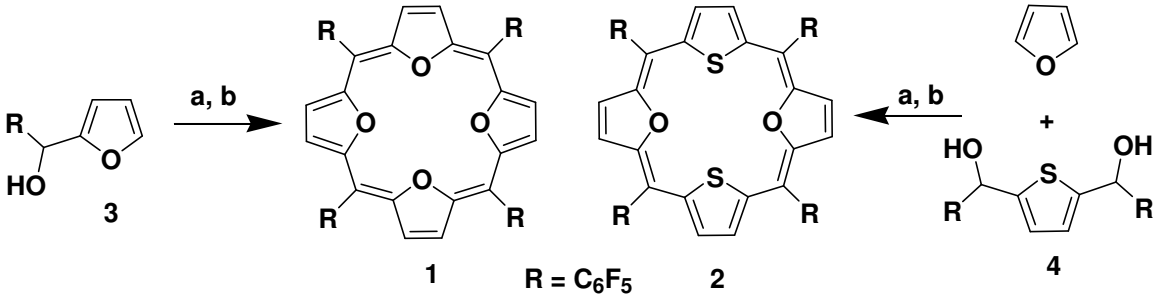
Scheme



Synthetic procedure for 1: 2-pentafluorophenylhydroxy methyl furan (264 mg, 1 mmol), **3**, in 100 ml of dry CH_2Cl_2 was degassed with argon for 10 min, then $BF_3.OEt_2$ (0.12 ml, 1 mmol) was added under dark, and the resulting solution was stirred for 2h. After adding five equivalents of $FeCl_3$, solution was opened to air and stirred for additional two hours. The reaction mixture was washed with water and passed through a short alumina column. This mixture was separated by repeated silica gel column chromatography by using CH_2Cl_2/n-hexane as eluant. A green color band obtained was identified as **1** in 2.5% yields (7 mg).

^{1}H NMR (300MHz, $CDCl_3$, 298K): $\delta = 2.49$ (s, 8H); UV-Vis (CH_2Cl_2): λ_{max} (ε) = 320 (22,121), 357 (30,654), 409 (331), 434 (378), 463 (370), 498 (275); MALDI-TOF Mass m/z: Calcd. For $C_{44}H_8F_{20}O_4$: 980.01; Observed: 980.55(100.0%, M^+).

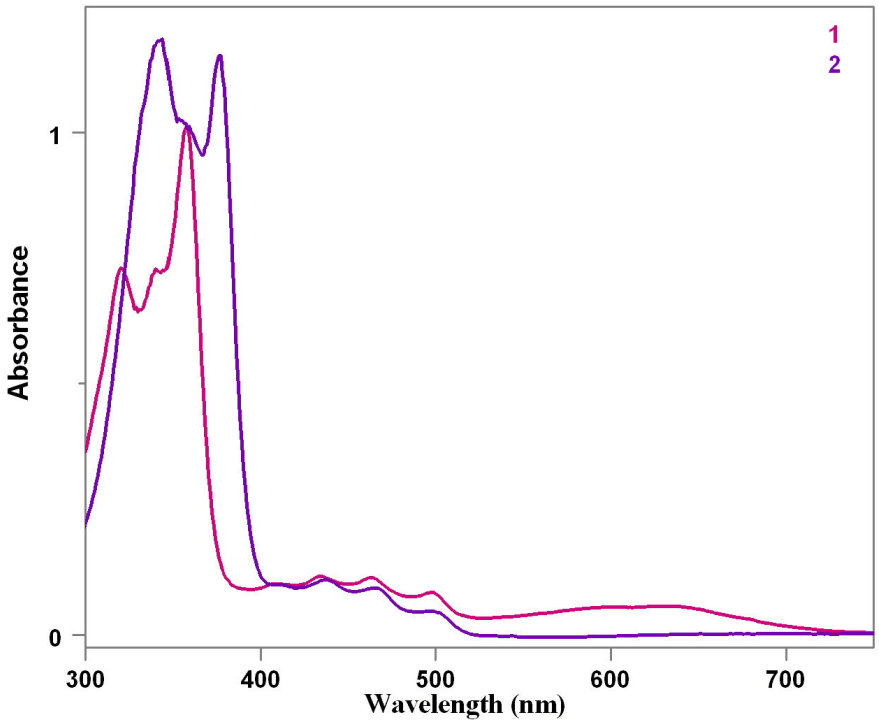
Synthetic procedure for 2: A similar procedure as mentioned for **1** was followed with 2,5-bis(pentafluorophenylhydroxymethyl) thiophene, **4**, (476 mg, 1 mmol) and furan (0.072 ml, 1 mmol). **2** was obtained in 6% yields (15 mg).

^{1}H NMR (300MHz, $CDCl_3$, 298K): $\delta = 3.33$ (s, 4H), 3.37 (s, 4H); UV-Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 344 (30,996), 376 (46,333), 409 (336), 437 (369), 465 (313), 497 (159); FAB Mass m/z: Calcd. For $C_{44}H_8F_{20}S_2O_2$: 1011.96; Observed: 1012.27 (100.0%, M^+).

2-(pentafluorophenylhydroxymethyl) furan (3): To a stirred solution of freshly distilled furfural [10mmol, 0.83ml in 40 ml THF] under argon atmosphere at 0^{o}C, freshly prepared Grignard Reagent [C_6F_5MgBr, (12.5mmol)] was added. Stirring was allowed for 2 hours to attain room temperature and the reaction mixture was quenched with saturated NH_4Cl solution. The organic layer was extracted with Et_2O (50 ml) three times and combined organic layers was washed with water and brine solution. After drying over Na_2SO_4, the solvent was removed under vacuum and purified through silica gel(100-200 mesh) column chromatography with CH_2Cl_2:n-Hexane (1:3) as eluant, to yield the pure compound as light yellow solid.(2.0 grams Yield: 76%.)

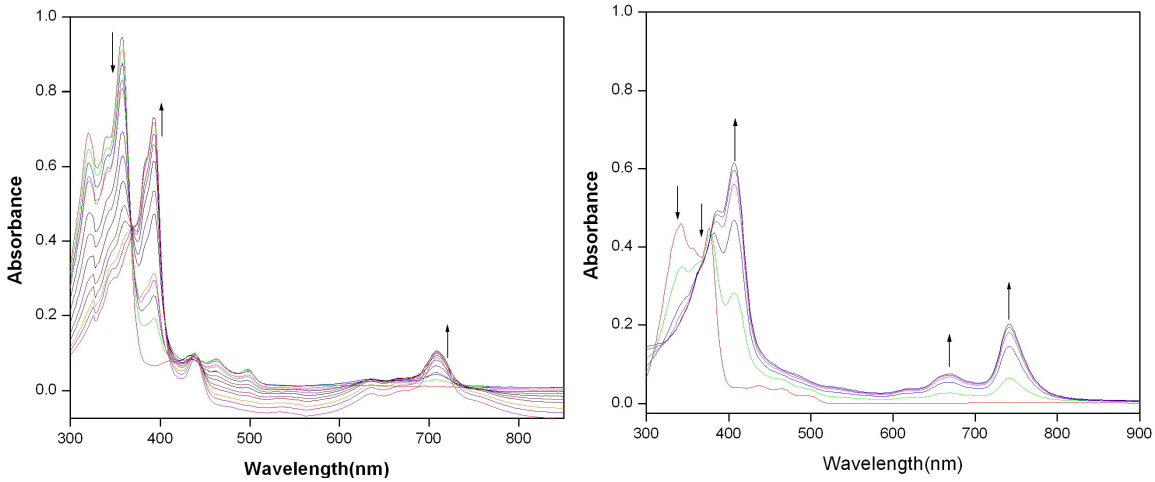
^{1}H NMR: (400MHz, $CDCl_3$, 298K): $\delta = 7.4$ (s, 1H), 6.37(m, 1H), 6.30(d, J= 4.0Hz, 1H), 6.16(d, J=11.2Hz 1H), 2.79 (d, J=11.2Hz, 1H). **EI MS** m/z**:** 264.08(100.0%, M^+)

Electronic Absorption Studies:

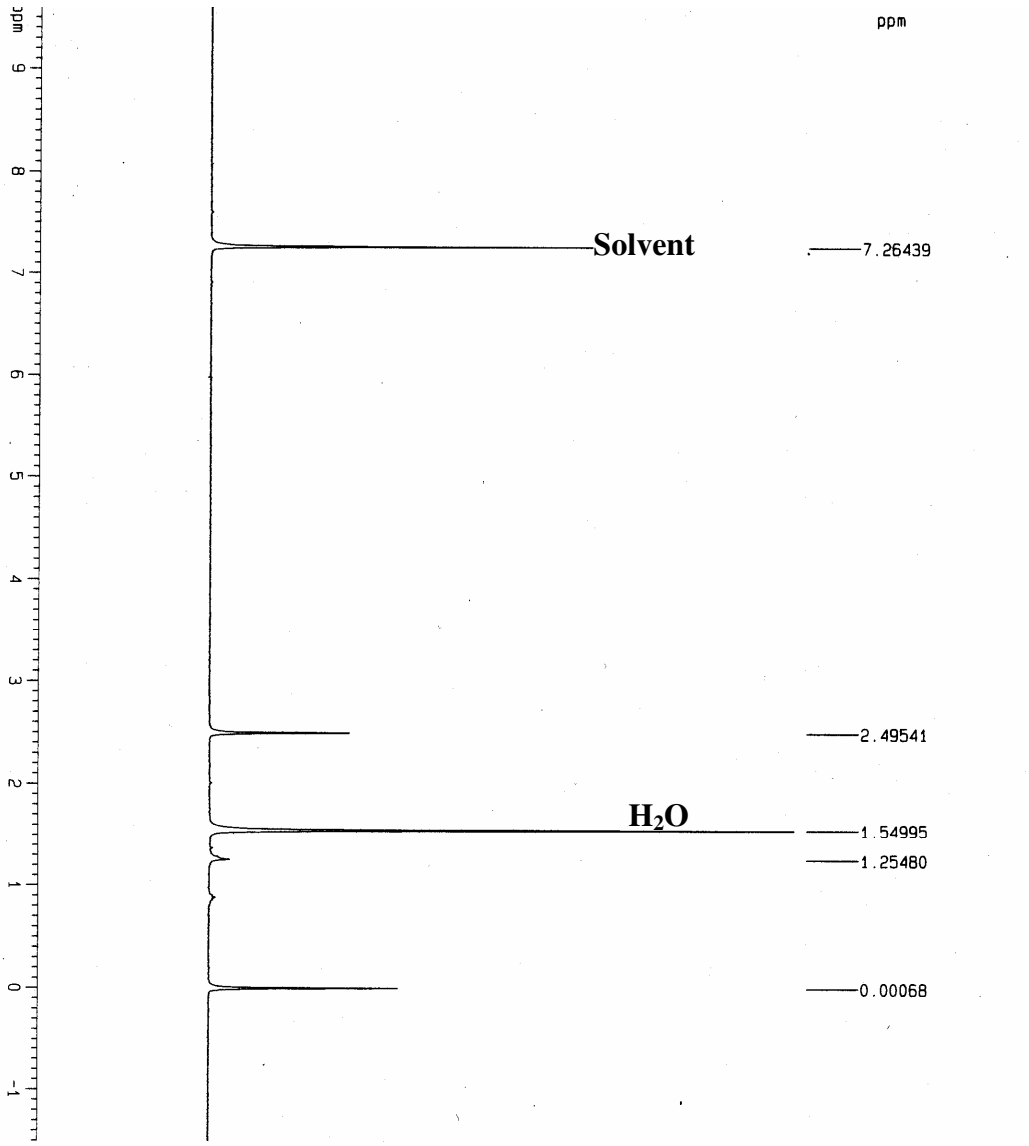


Electronic absorption spectra of 10^{-5} M solutions of **1** and **2** in dichloromethane.

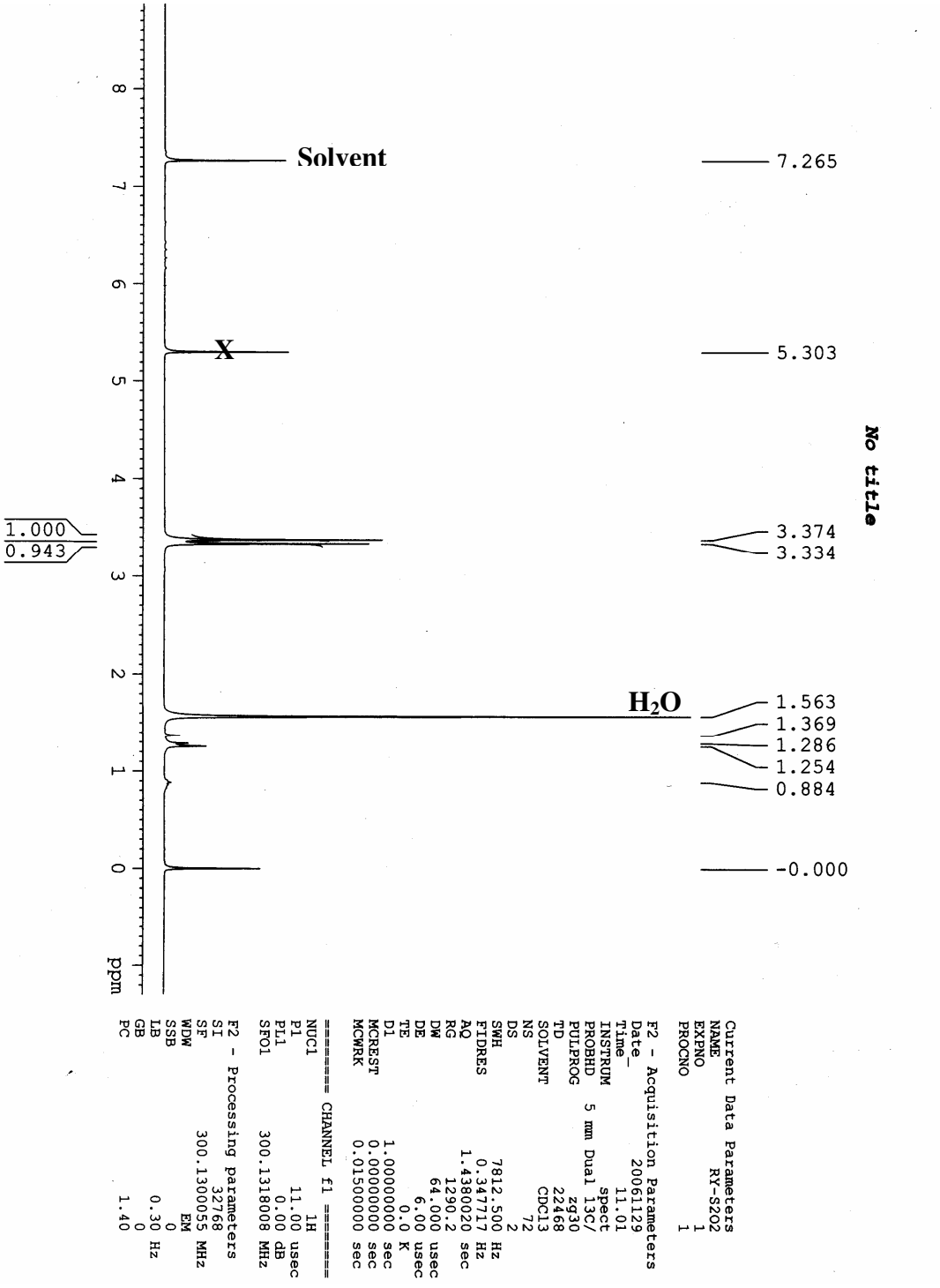
Titration with $HClO_4$:



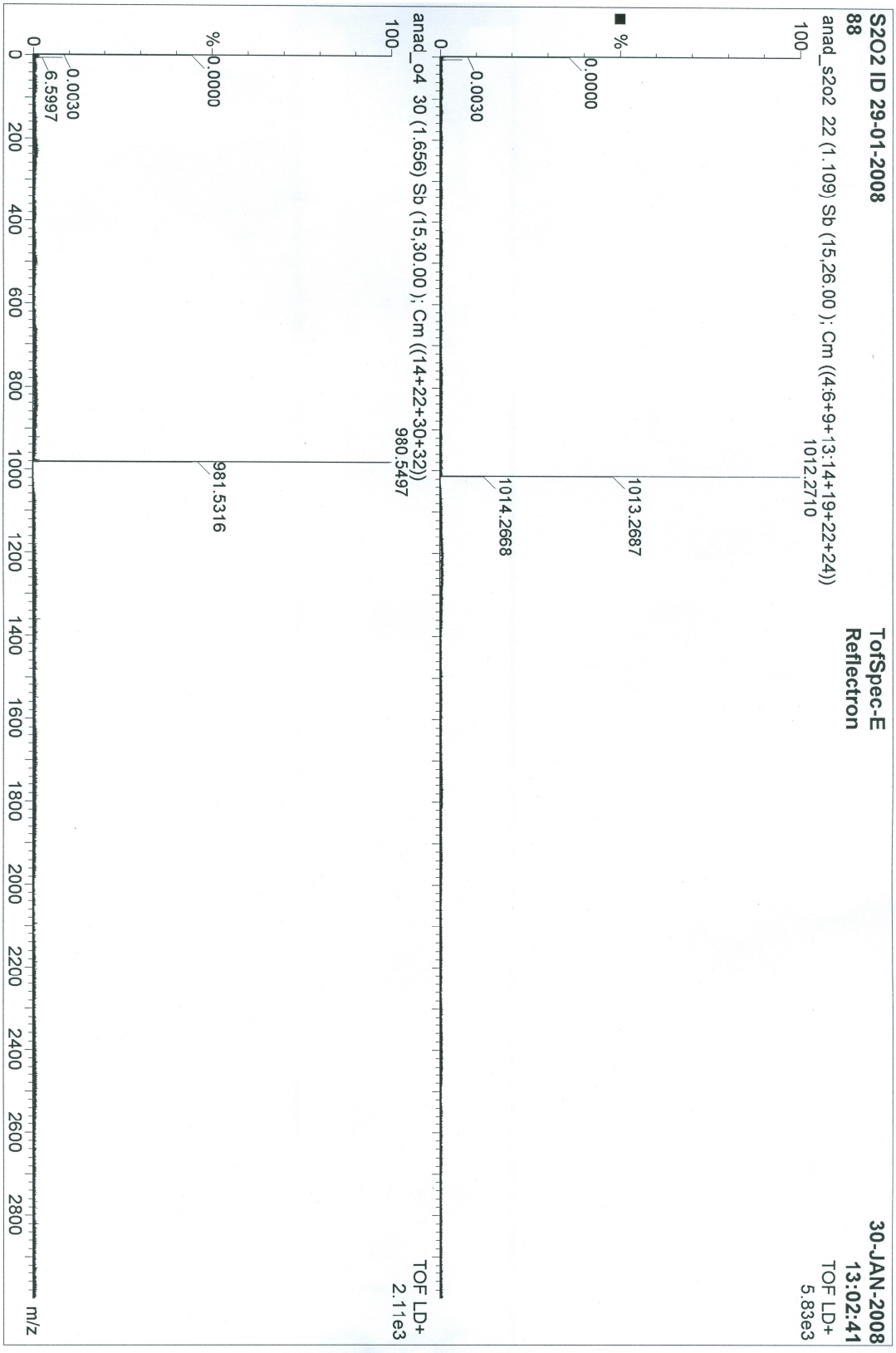
Changes in Electronic Absorption Spectrum upon addition of $HClO_4$ to **1** (left) and **2** (right)



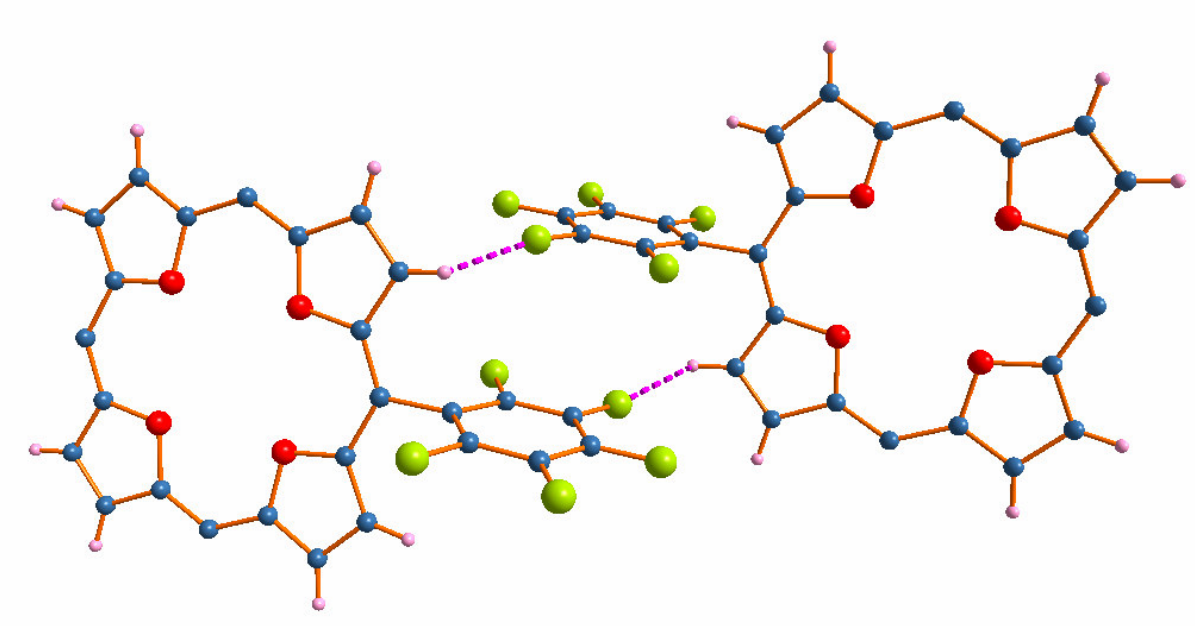
^{1}H NMR Spectrum of 1 at 298K



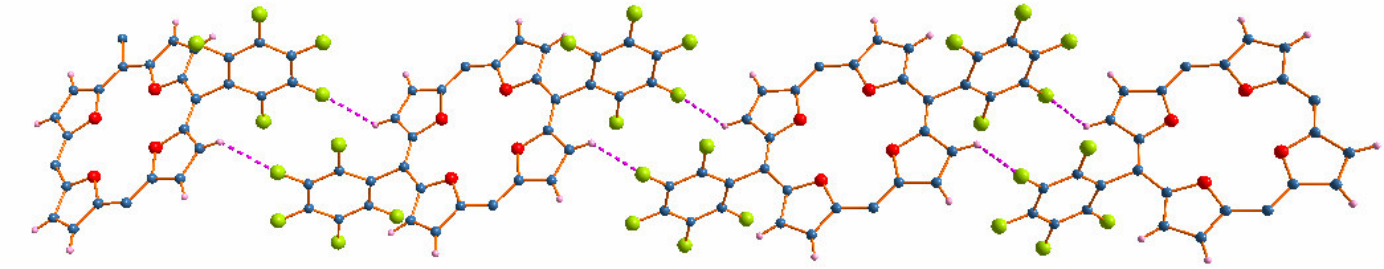
^{1}H NMR Spectrum of 2 at 298K



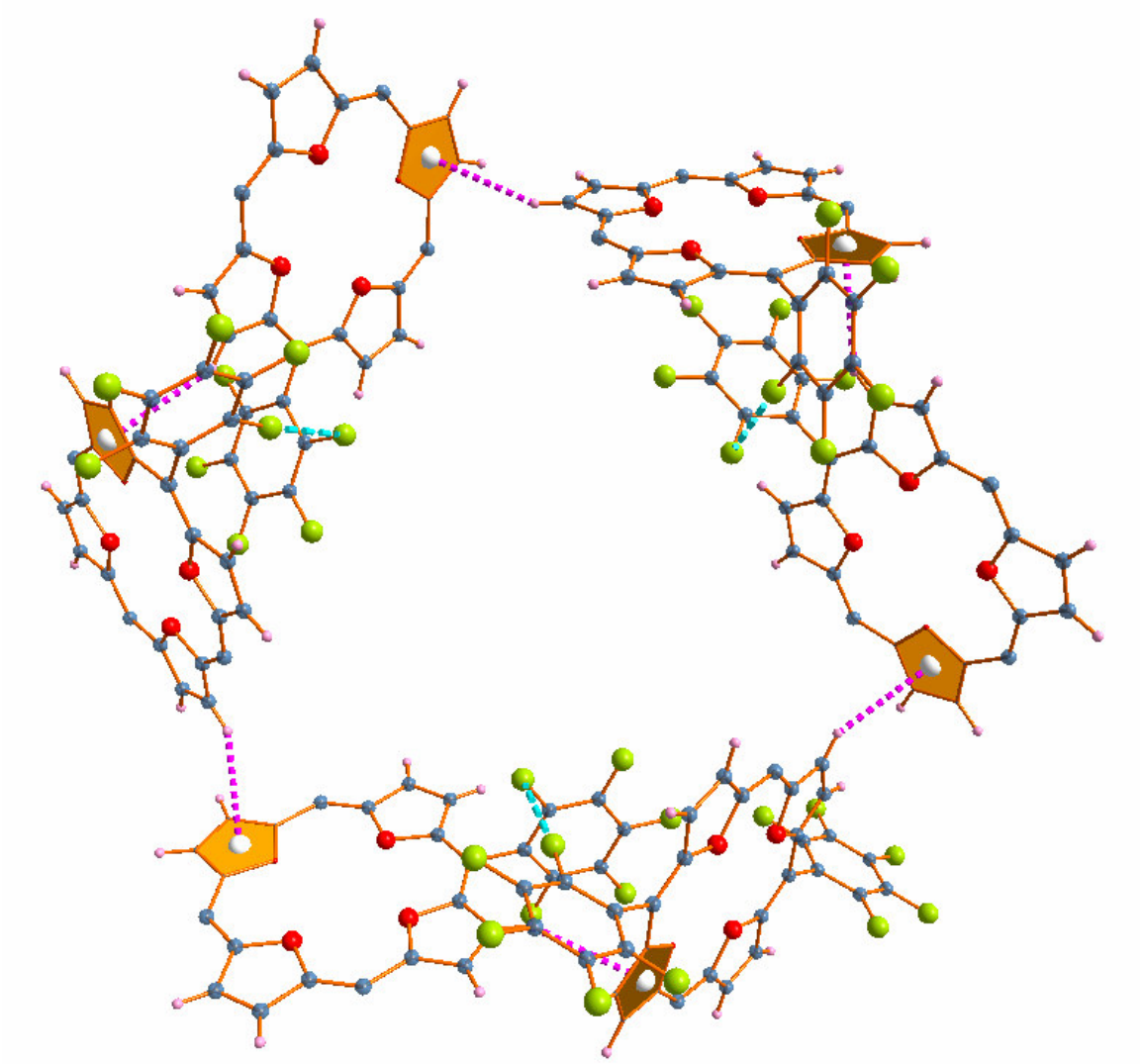
MALDI-TOF Mass spectrum of **2** and **1**



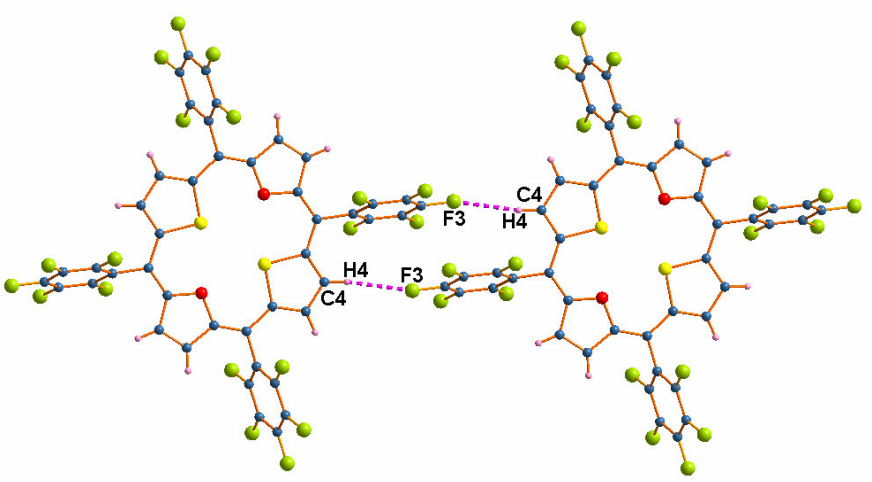
Two molecules of **1** interact through two C3-H3…F2 (2.5 Å, 115^{o}) hydrogen bonds.
Other *meso* aryl groups are omitted for clarity.



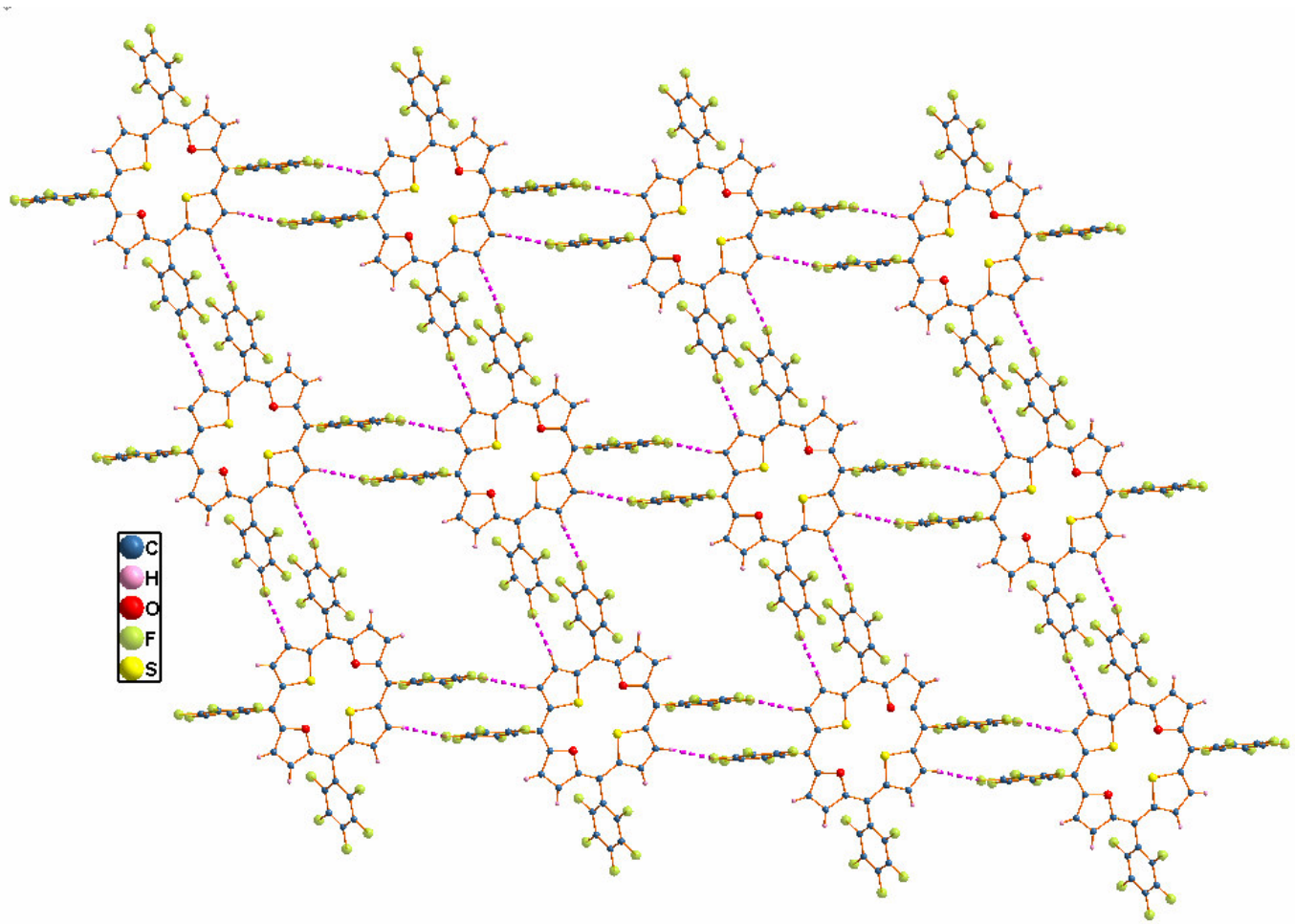
One dimensional hydrogen bonded chain of **1** through C-H…F hydrogen bonding.
Other *meso* aryl groups are omitted for clarit



Cyclic hexamer of **1** formed due to six C-H…π(pink dotted line) along with three F…F interactions (cyan dotted lines). Other *meso* aryl groups are omitted for clarity.



Two molecules of **2** interact through two C4-H4…F3 (2.68 Å, 170.5^{o}) hydrogen bonds.



Two dimensional supramlolecular grid of **2** formed due to C-H…F hydrogen bonding.