

Electronic Supplementary Information (ESI)

Functionalised Polyhedral Oligomeric Silsesquioxane with Encapsulated Fluoride – First Observation of Fluxional Si...F Interactions in POSS

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Experimental Procedures

Chemicals and purification methods

Tetrabutylammonium fluoride (TBAF, 1 M solution in THF (containing 5% H₂O), (4-vinylphenyl)trimethoxysilane and dichloromethane (DCM, Analytical Grade) were obtained from Sigma Aldrich, TCI and VWR, respectively, and were used without further purification. All syntheses were undertaken using HPLC-quality water.

The products obtained were purified by recrystallisation in toluene/dichloromethane (VWR, NORMAPUR® and pure 95% respectively) and by flash chromatography in a Buchi Reveleris X2 flash chromatography system, equipped with evaporative light-scattering detection (ELSD) and 254-nm light source, using a mixture of DCM/cyclohexane (VWR, technical grade) as eluent.

Silsesquioxane cage synthesis

In a one-neck flask, a solution of trimethoxy(4-vinylphenyl)silane (11.1 mL, 52.5 mmol) in DCM (1.2 L) was prepared. Water (160 µL, 8.75 mmol) was added to the previous solution, followed by the dropwise addition of the TBAF solution in THF (30 mL, 30 mmol). The reaction mixture was held at 30 °C for 48 h, and the solvent was then evaporated under reduced pressure. The resulting crude product was dissolved in DCM and washed three times with water and the solvent was evaporated. The crude product was taken up in toluene and quickly re-precipitated. The resulting precipitate was then filtered and washed with toluene. The octastyryl T₈-F was obtained as a white powder.

Tetrabutylammonium octastyryl octasilsesquioxane fluoride (white powder): Yield: 26%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.75 – 7.73 (d, CH_{ar}, 16H, J = 8.0 Hz), 7.32 – 7.30 (d, CH_{ar}, 16H, J = 8.0 Hz), 6.74 – 6.67 (dd, CH_{vi}, 8H, J₁ = 17.7 Hz, J₂ = 10.8 Hz), 5.82 – 5.77 (dd, CH_{vi}, 8H, J₁ = 17.7 Hz, J₂ = 0.8 Hz), 5.30 – 5.27 (dd, CH_{vi}, 8H, J₁ = 10.8 Hz, J₂ = 0.8 Hz), 1.92 (t, N-CH₂, 8H, J = 7.5 Hz, J = 7.5 Hz), 1.01 (quint, N-CH₂-CH₂, 8H, J = 7.5 Hz), 0.80 (m, N-CH₂-CH₂-CH₂, 8H, J = 7.5 Hz), 0.73 (t, N-CH₂-CH₂-CH₂-CH₃, 12H, J = 7.5 Hz). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 137.58 (C_{ar}), 137.41 (C_{ar}), 137.13 (CH_{vi}), 134.11 (CH_{ar}), 125.00 (CH_{ar}), 113.59 (CH_{2 vi}), 58.30 (N-CH₂-CH₂), 23.43 (N-CH₂-CH₂), 19.50 (N-CH₂-CH₂-CH₂-CH₃), 13.75 (N-CH₂-CH₂-CH₂-CH₃). ¹⁹F NMR (380 MHz, CDCl₃, δ, ppm): -25.17. ²⁹Si NMR (80 MHz, CDCl₃, δ, ppm): -81.50 (d, J = 2.5 Hz). IR (ν, cm⁻¹): 1628 (C=C), 1600 (C-C ring), 1079 (Si-O-Si).

MALDI-MS: m/z: calculated for C₉₆H₈₄O₁₈Si₁₂F (M+Na+H): 1283.2; found: 1283.2 (NB: During acquisition of the MALDI-MS spectrum, a cation exchange process occurs, resulting in substitution of the TBA ion by a sodium ion. The observed m/z is thus characteristic of (M+Na+H) rather than the expected (M+TBA+H)).

Characterisation methods

FTIR spectra were recorded from 650 to 4000 cm⁻¹ using a PerkinElmer Spectrum 100 equipped with a Gladia-ATR accessory. MALDI-MS spectra were acquired using a Bruker Rapiflex spectrometer with either dithranol/sodium trifluoroacetate or dithranol as desorption matrix.

Liquid ¹H, ¹³C, ¹⁹F and ²⁹Si NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in CDCl₃ at room temperature and at concentrations of around 10 mg/mL. All spectra were proton decoupled and chemical shifts (δ) were calibrated against the signal of tetramethylsilane as internal standard. Decoupling and variable temperature studies were performed using a Bruker TBO triple resonance probe. In the latter case, the temperature was varied from -55 °C to 115 °C, in 10 °C increments, with deuterated dimethyl formamide (DMF-d₇) as solvent. ¹³C and ²⁹Si solid state NMR spectra were obtained with a Varian VNMRS 300 MHz spectrometer while the ¹⁹F NMR spectra were measured using a Varian VNMRS 600 MHz spectrometer.

Single crystal X-ray diffraction data were acquired at 175 K on a Rigaku Oxford Diffraction Gemini-S diffractometer with sealed-tube Mo-Kα radiation using the CrysAlis Pro program (Rigaku Oxford

Diffraction, 2017). Integration of the data frames was also done using CrysAlis, with default parameters being employed. Lorentz and polarisation effects were corrected, and empirical absorption corrections were undertaken using spherical harmonics employing symmetry-equivalent and redundant data.

The crystal structure was solved by employing the ab-initio iterative charge flipping method using the Superflip program ^{1, 2}, with parameters described by Van der Lee ³. Structural models were refined against $|F|$ using full-matrix non-linear least-squares procedures as implemented in CRYSTALS ² on all independent reflections with $I > 2\sigma(I)$. Data were collected up to 1 Å resolution, with data beyond that resolution typically being below the $2\sigma(I)$ threshold.

When the vinyl groups on the cluster surface of the T₈-F compound were poorly identified in the electron density map, the fragments were modelled with soft distance restraints on the double and single bonds. The values employed for this modelling were taken from the mean distances found for 15 styryl entries in the Cambridge Structural Database ⁴ (with data collection temperatures between 160 and 190 K, R-factor below 0.07, and containing no elements heavier than Cl). Thermal similarity restraints were also applied to the carbon atoms in the vinyl groups for modelling.

The Squeeze procedure ⁵ was used to model the contributions of the solvent electron density to the total scattering, with atoms of the remaining solvent molecules being refined using isotropic atomic displacement parameters. Many of the H atoms were located in a difference map but were repositioned geometrically. The H atoms were initially refined with soft restraints on their bond lengths and angles to regularise their geometry (with C--H in the range 0.93-0.98 Å) and $U_{iso}(H)$ (in the range 1.2 to 1.5 times the value of U_{eq} for the parent atom). The positions were then refined with riding constraints ⁶ and other hydrogen atoms were positioned geometrically. CCDC 2018516 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Results and Discussion

Table S1. Detailed crystallographic parameters for styryl-functionalised T₈-F.

formula	C ₂₂₄ H ₂₄₀ F ₃ N ₂ O ₃₆ Si ₂₄ [+solvent]
moiety	3(C ₆₄ H ₅₆ O ₁₂ Si ₈), 2(C ₁₆ H ₃₆ N),3(F) [+solvent]
<i>T</i> (K)	175
Space group	<i>P</i> -1
crystal system	triclinic
<i>a</i> (Å)	13.6092(7)
<i>b</i> (Å)	13.6117(7)
<i>c</i> (Å)	39.217(2)
α (°)	80.895(5)
β (°)	81.259(5)
γ (°)	81.193(4)
<i>V</i> (Å ³)	7027.7(4)
<i>Z</i>	1
ρ (g.cm ⁻³)	1.008
<i>M_r</i> (g.mol ⁻¹)	4267.35
μ (mm ⁻¹)	0.164
<i>R</i> _{int}	0.065
θ _{max} (°)	20.831
resolution (Å)	1.19
<i>N</i> _{tot} (measured)	14685
<i>N</i> _{ref} (unique)	14685
<i>N</i> _{ref} (<i>I</i> > 2σ(<i>I</i>))	10540
<i>N</i> _{ref} (least-squares)	10540
<i>N</i> _{par}	1303
<σ(<i>I</i>)/ <i>I</i> >	0.1539
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.1284
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.1402
<i>R</i> ₁ (all)	0.1525
<i>wR</i> ₂ (all)	0.1641
GOF	1.1278
$\Delta\rho$ (eÅ ⁻³)	-0.84/0.69
crystal size (mm ³)	0.10x0.18x0.35

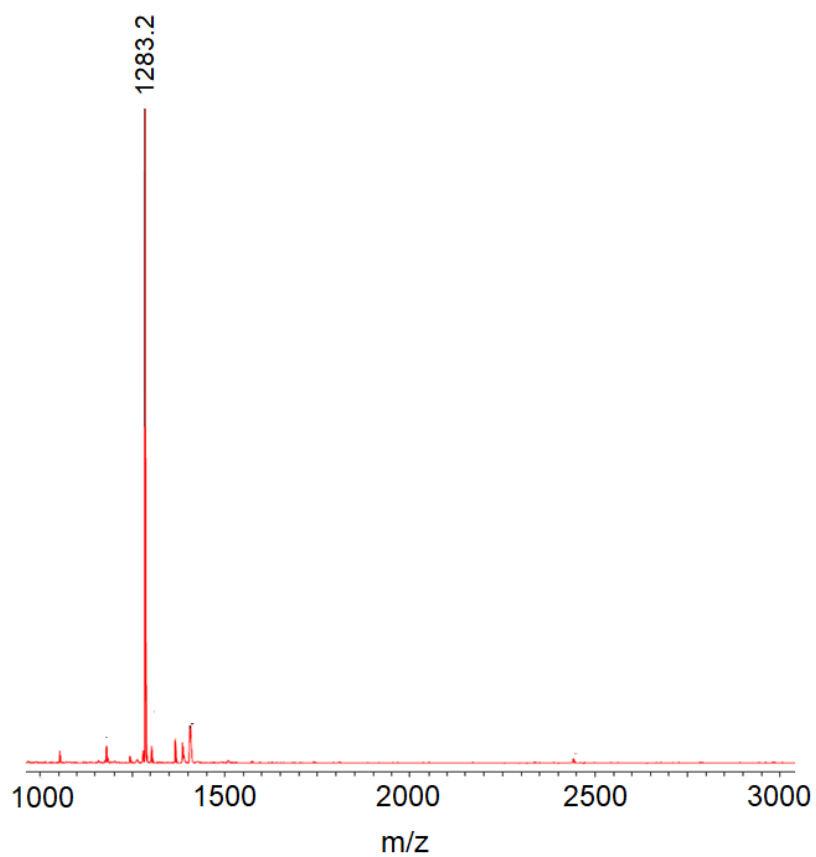


Fig. S1. MALDI-TOF mass spectrum of styryl-functionalised T_8 -F.

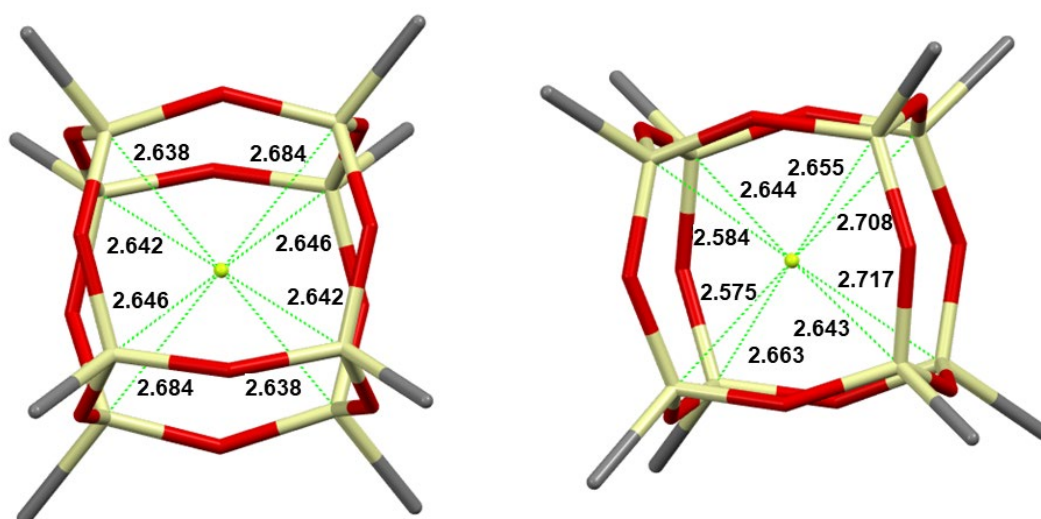


Fig. S2. Silicon-fluorine distances for non-equivalent T_8 -F cages in which the fluoride is located at the centre-of-symmetry (left) and off-centre (right).

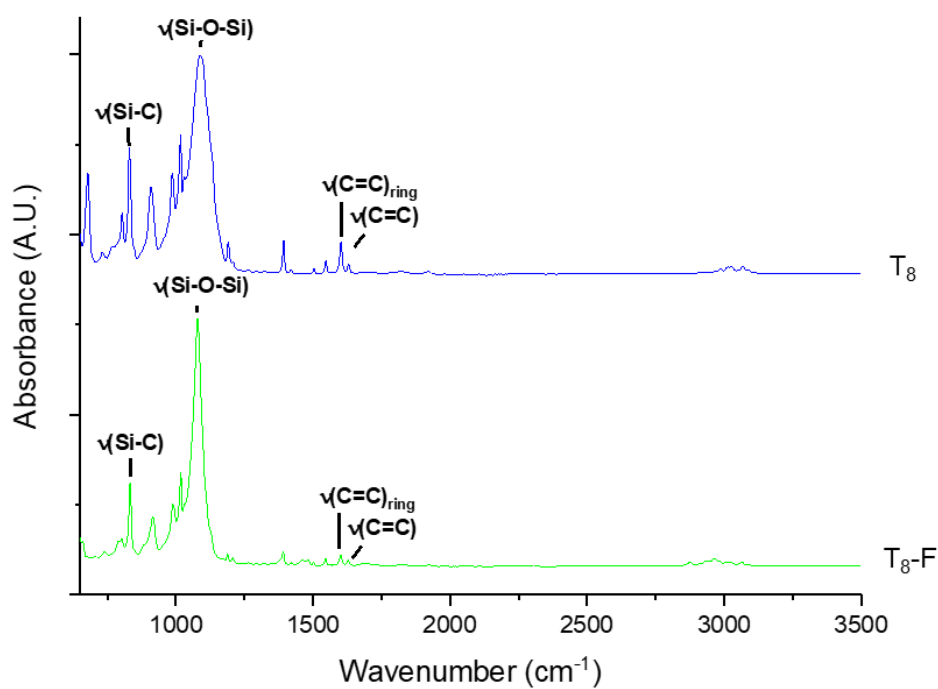


Fig. S3. IR spectra of styryl-functionalised T₈-F and T₈ cage silsesquioxanes.

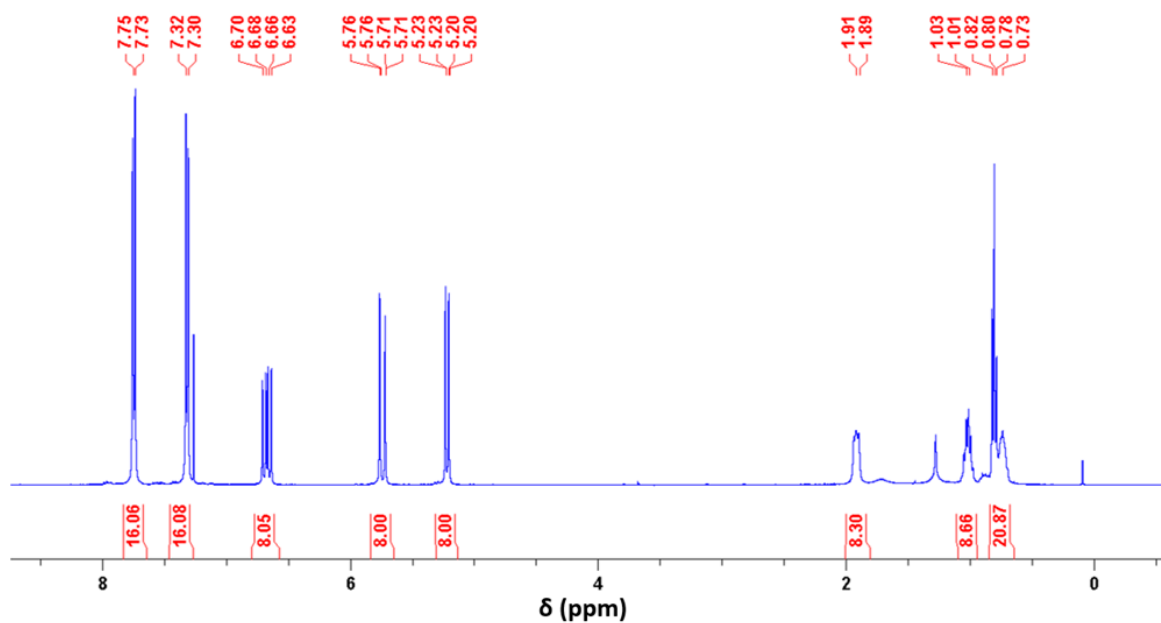


Fig. S4. Solution ¹H NMR spectrum of styryl-functionalised T₈-F.

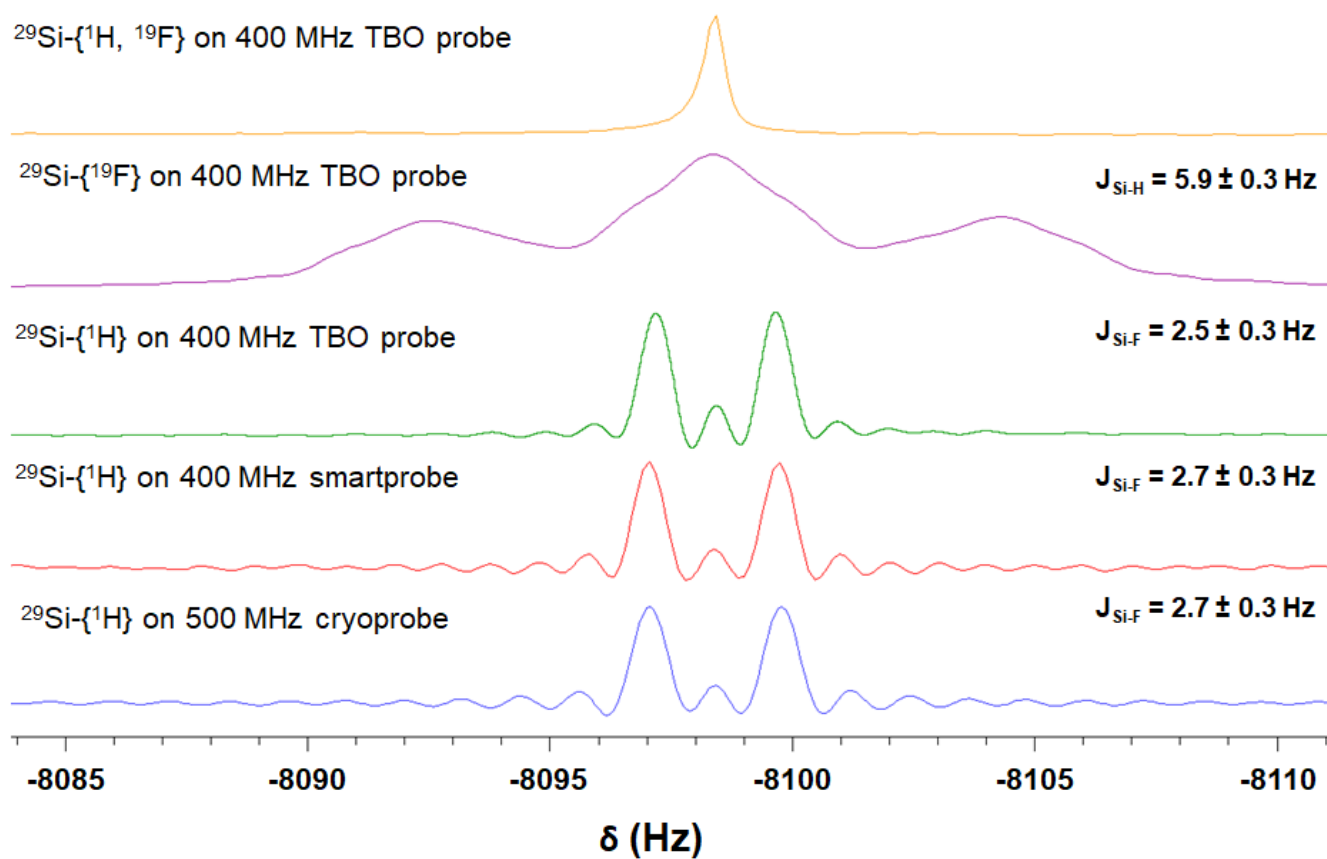


Fig. S5. Solution ^{29}Si NMR spectra in CDCl_3 of styryl-functionalised $\text{T}_8\text{-F}$ using different magnetic field strengths and decoupling sequences.

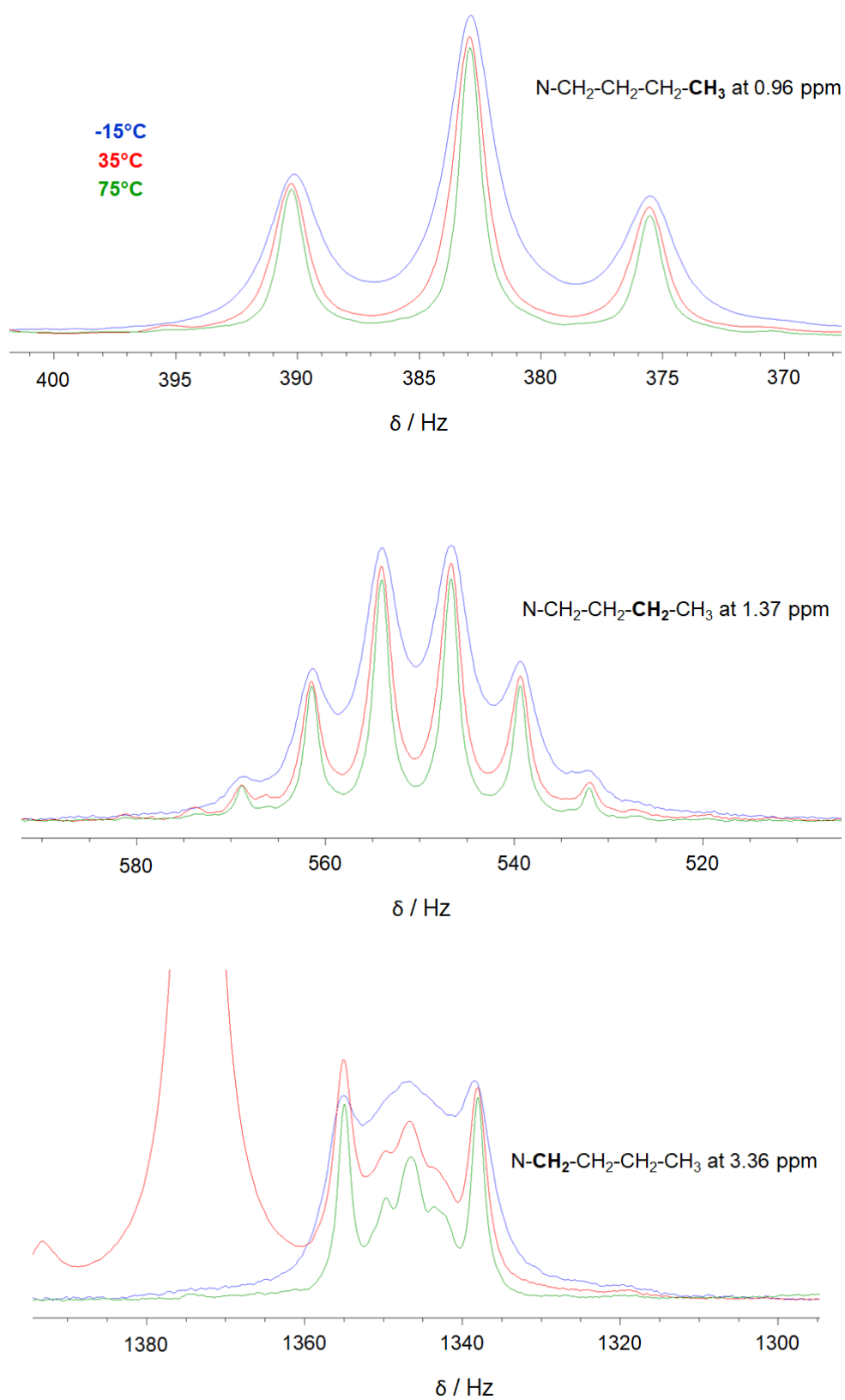


Fig. S6. Variable temperature solution ^1H NMR spectra of styryl-functionalised $\text{T}_8\text{-F}$ in DMF-d_7 .

References

1. L. Palatinus and G. Chapuis, *J. Appl. Crystallog.*, 2007, **40**, 786-790.
2. P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallog.*, 2003, **36**, 1487-1487.
3. A. Van Der Lee, *J. Appl. Crystallog.*, 2013, **46**, 1306-1315.
4. C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr. Sect. B Struct. Sci. Crys. Eng. Mater.*, 2016, **72**, 171-179.
5. A. L. Spek, *Acta crystallogr., C Struct. Chem.*, 2015, **71**, 9-18.
6. R. I. Cooper, A. L. Thompson and D. J. Watkin, *J. Appl. Crystallog.*, 2010, **43**, 1100-1107.