Supplementary Material (ESI) for Chemical Communications

Hydrogen Adsorption in Microporous Organic Framework Polymers

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Supporting Information:

Schemes 1-3

Figures 1-11

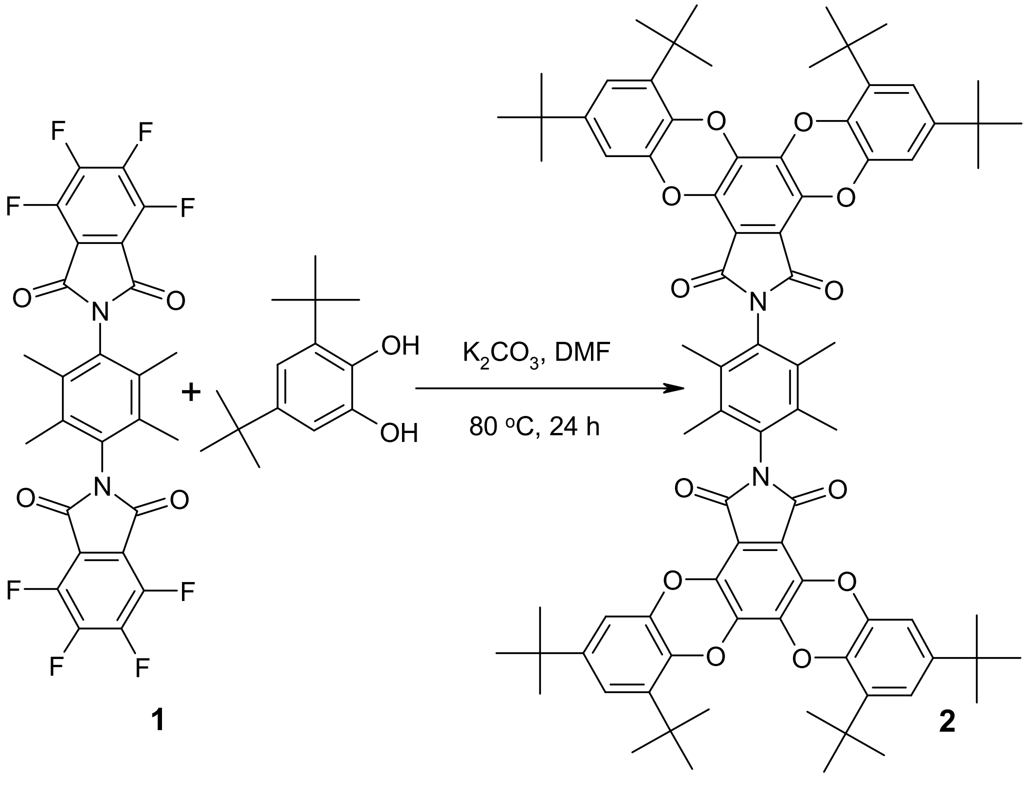
Materials and methods

All the chemicals were of reagent grade purity and used without further purification. The dry solvent Dimethylformamide (DMF) and was purchased from Aldrich Co. The finely grounded anhydrous potassium carbonate was used after drying at 200 °C. ^{1}H NMR spectra (400 MHz) were recorded using Bruker DPX 400. FTIR spectra were recorded on a Perkin Elmer System 2000 FTIR. Elemental analyses were carried out using LECO Elemental Analyzer CHNS 932. Mass analyses were done on a VG Autospec-Q. Solid state NMR measurements were carried out on a Bruker Avance 300 spectrometer equipped with a cross polarization magic angle spinning (CP/MAS) probe and a fully automated pneumatic unit for sample spinning. X-ray photoelectron spectroscopy (XPS) measurement was carried out in a VG ESCALAB 200 instrument. High resolution transmission electron Microscopy (HRTEM: JEOL Model JEM- 3010 [300 KV]). TGA and DSC analyses were carried out on Shimadzu TGA-50 and Shimadzu DSC-50. Molecular structures were created using the Spartan programme and the Semiempercal molecular orbital methods (PM3 and MNDO) were used to simulate molecular structure. Surface area analysis was carried out using ASAP 2010 Micromeritics Sorptometer. Hydrogen sorption measurements were done using the Micromeritics ASAP 2020.

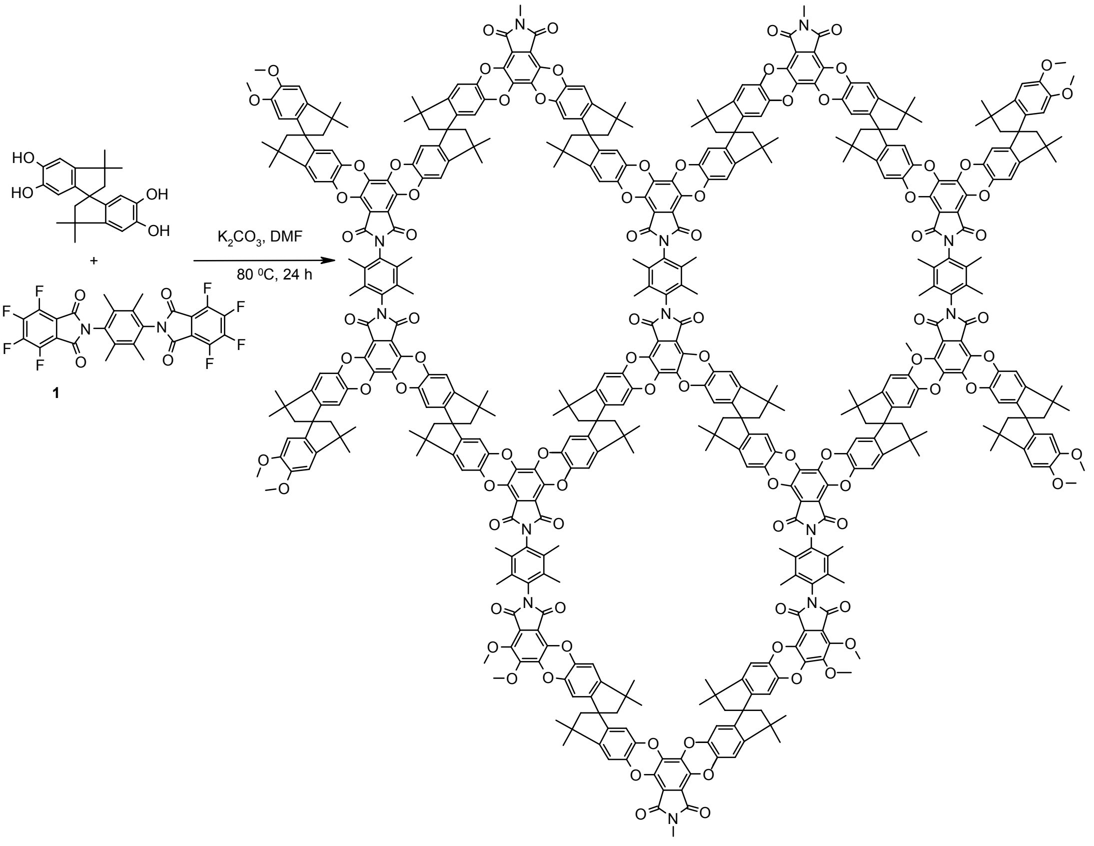
The precursor tetraflurophthalic anhydride was synthesized from the commercially available tetraflurophthalic acid by refluxing in xylene.

†Model compound

To a stirred solution of 2,5-di-tertiarybutylcatechol (1g, 4.5 mmol) and 1,4-Bis(4,5,6,7-tetrafluorophthalimido)-2,3,5,6-tetramethylbenzene (**1**) (0.57 g, 1mmol) in dry DMF (100 ml), K_2CO_3 (1.86 g, 13.5 mmol) was added. The reaction mixture was heated at 80 °C for 24 hrs under nitrogen. On cooling, the reaction mixture was poured into 200 ml of distilled water and neutralized with hydrochloric acid. The collected precipitate was washed with deionised water, and then recrystallised from methanol. The resulting material was dried under vacuum to give yellow fluorescent powder (yield >90%). mp > 300°C; ^{1}HNMR ($CDCl_3$, 400 MHz, δ ppm): 7.05 (s, 4H), 6.99 (s, 4H), 2.12 (s, 12H) 1.50 (s, 36H), 1.32 (s, 36H). IR (KBr) /cm^{-1}: υ = 1773 and 1725 (imide), 1467 (C=C). Elemental analysis calcd (%) for $C_{82}H_{92}N_2O_{12}$ (1297.65) requires C, 75.90; H, 7.19; N, 2.16%; Found C, 75.78; H, 7.10; N, 2.34%; MS (EI): *m/z* (%) 1296.9 (M$^{+\cdot}$,100).



Scheme 1. Synthesis of model compound.



Scheme 2. Synthesis of OFP-3

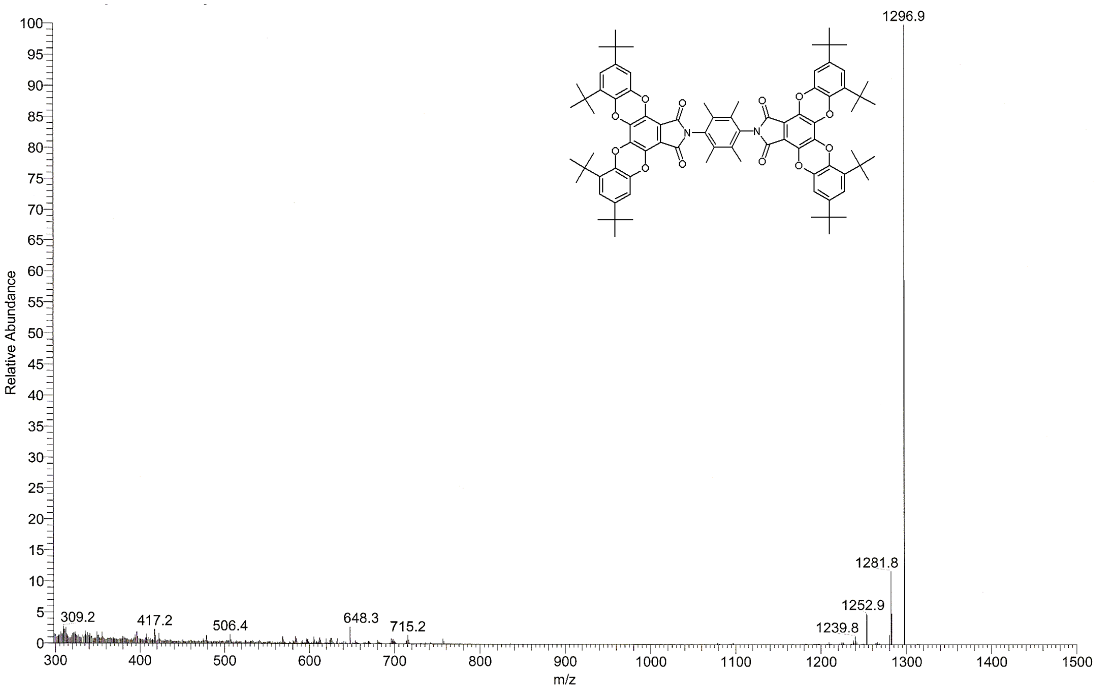


Figure 1. Mass spectrum of the model compound (**2**).

FT-IR spectra

Assignments and analysis of infrared bands of starting materials, model compound, and OFP-3 were presented in this section. Discussion pertaining to the IR spectral relationships between these compounds offers a good support for the proposed structure of OFP-3.

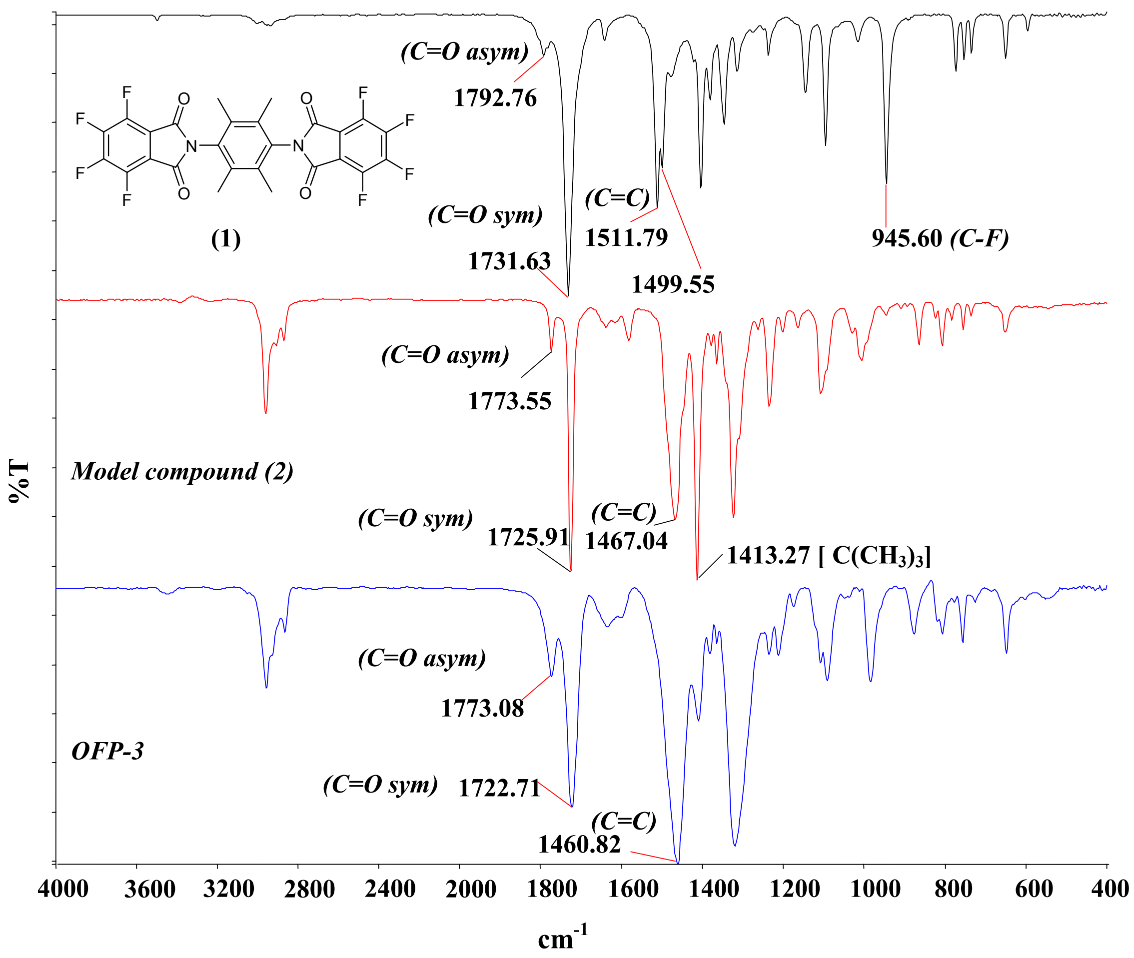


Figure 2. FTIR spectra of monomer (**1**), the model compound and the OFP-3.

As shown in figure 2, the characteristic bands related to the imide stretching (C=O symmetric and asymmetric bands in the range of 1722-1792) found in the spectrum of all the three materials. However the bands slightly shifted to lower wave number in the case of both **2** and **OFP-3** in comparison to the monomer **1,** which can be attributed to the inductive effect of fluorine atoms. More over both spectra are quite similar and can be superimposed nicely excluding the bands related to the tert-butyl groups at 1413 cm^{-1}. Another feature of monomer **1** is the presence of strong bands observed at 1499 & 1511, which are characteristic of the ***fluorine-containing C=C***. This is also identified in other fluoro compounds (figure 3). In the case of **2** and OFP-3 the bands due to C=C appeared as a single broad band and shifted to low wave number, which is a clear indication of change in the C=C environment (1458 & 1467) through the dibenzodioxane link formation. The assignment for the aromatic F-containing C=C and C-F stretching spectral data was made on the basis of some known aromatic fluoro-compounds and the precursor molecules. A strong band at 945 is present in the monomer **1** which is absent in the case of model compound and OFP-3 (figure 2). The comparison spectra of the monomer **1** with other fluoro-compounds clearly give comparable values for fluorine-containing C=C and C-F bonds (figure 3).

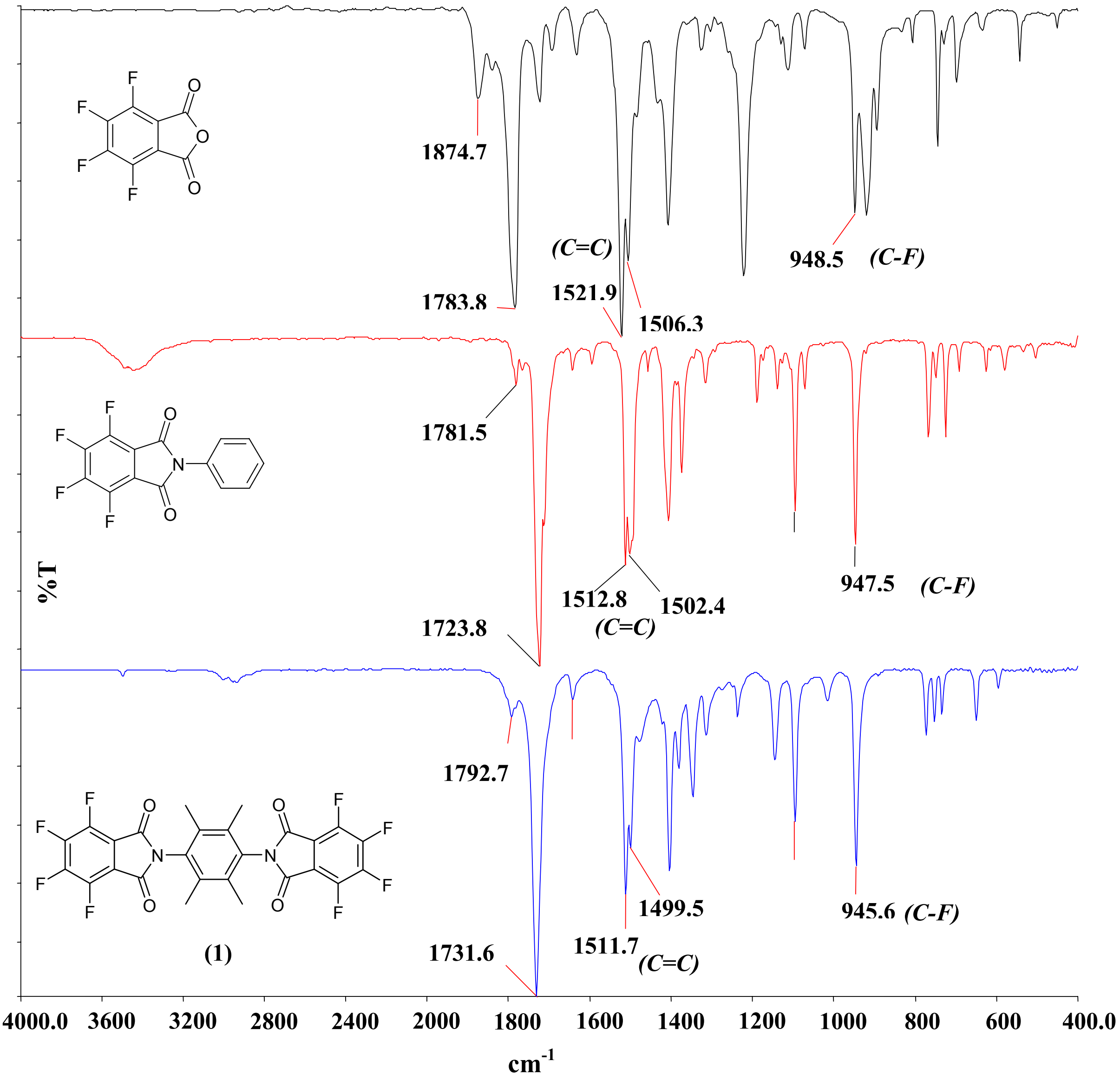


Figure 3. Comparison of FTIR spectrum of 1,4-Bis(4,5,6,7-tetrafluorophthalimido)-2,3,5,6-tetramethylbenzene (**1**) with tetrafluorophthalic anhydride and tetrafluorophenyl phthalimide.

Solid-state ^{13}C NMR

Solid-state ^{13}C NMR measurements were carried out on a Bruker Avance 300 spectrometer (7.0463 T) equipped with a cross polarisation magic angle spinning (CP/MAS) probe and a fully automated pneumatic unit for spinning. Single pulse excitation (SPE) was applied using a 4 mm multinuclear CP/MAS probe. 13 kHz MAS was chosen to reduce the spinning side bands to approximately 3 % of the centre signal and to move them to margins of spectral range. The recycling delay was 60s. All spectra were measured with a sweep width of 55 kHz, and the FID was sampled with 4 k data points.

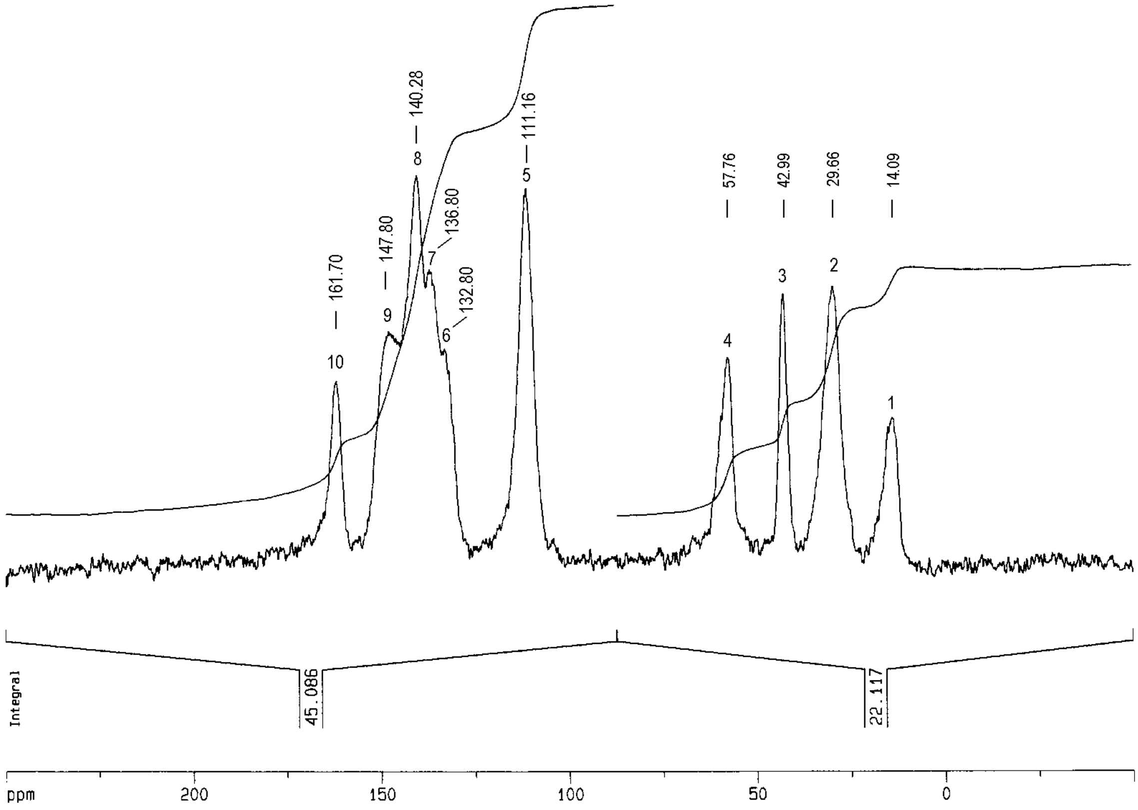
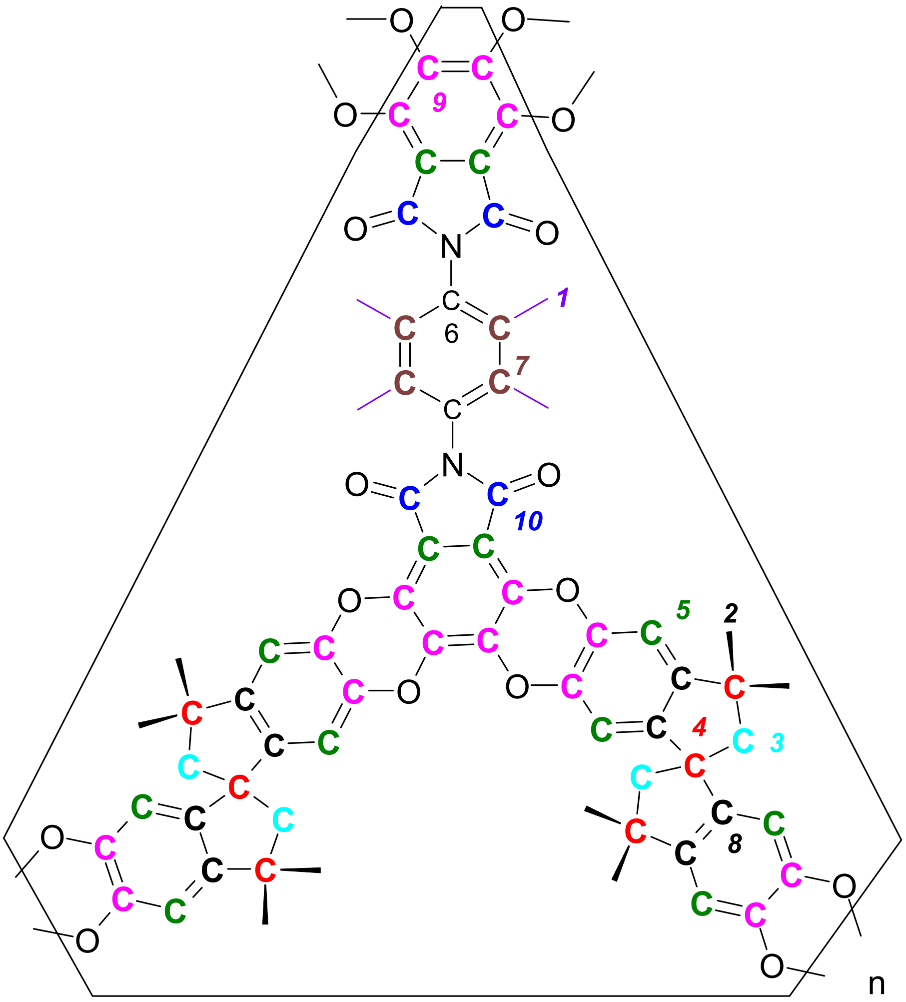


Figure 4. Solid-state ^{13}C NMR spectrum of OFP-3. The signal positions corresponding to aromatic and aliphatic regions clearly marked in the spectrum.

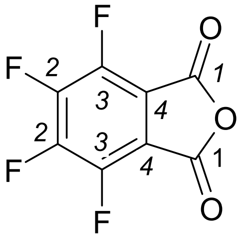
The solid state ^{13}C NMR (75 MHz) spectrum (fig.4) of OFP-3 was examined and the signal positions were located precisely with the help of ^{13}C NMR spectra of monomers and precursor molecules (eg. Tetrafluorophthalic anhydride and 2,3,5,6-tetramethyl-1,4-phenylenediamine). The signals marked as 1 (4 carbons, belongs to monomer **1**) and 2 (8 carbons, belongs to spirobiscatechol unit) represent the methyl groups as depicted in the scheme **3** of the proposed repeat unit. The signal at 42.99 (marked as 3) corresponding to methylene groups of the spirobiscatechol unit, represent a total carbons of four. There are two types of quarternary carbons come under one signal at 57.76 marked as 4 which represent a total of 6 carbons. The signal appeared at 111.16 marked as 5 represents two types of aromatic carbon (4 + 8 carbons). The overlapped signals between 132.8 and 147.8 representing 30 aromatic carbons within the repeat unit. Based on the information retrieved by the ^{13}C NMR spectra of the precursor molecules, the overlapping resonances can be confidently assigned to the four different carbon environments as marked as 6,7,8,9 in the scheme 3. The signal marked as 10 appeared at 161.70 clearly represent the carbonyl carbon (4 carbons).The signal intensities ratio (45.086: 22.117) between the aromatic and aliphatic carbons clearly correlated to the total number of aromatic (46 carbons) and aliphatic (22 carbons). Thus all the signals in the spectrum accounted for the proposed idealised structure of the OFP-3, which further supports the highly efficient poly-condensation process, through the formation of dibenzodioxane links. Moreover it is clear from the spectrum that the base catalysed polymerisation condition does not degrade the imide units as supported by IR and XPS. Additionally, the comparison between the intensity of individual signals supports the proposed repeat unit OFP-3. For example, the ratio between signals 1 and 2 is almost 1/2 and the other signals in the spectrum are also following the ratio which fulfils the proposed structure as shown in figure **2** and scheme **3**.



Scheme 3. Proposed repeat unit of the idealised structure of OFP-3

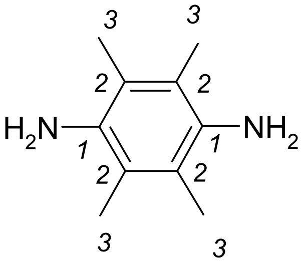
^{13}C NMR spectral data of the precursor molecules and monomers

a) Tetrafluorophthalic anhydride



^{13}C NMR (100MHz) (DMSO-d_6) δ = 162.95 (C1); 144.98 (C2); 141.42 (C3); 118.22 (C4).

b) 2,3,5,6- Tetramethylbenzene-1-4-diamine

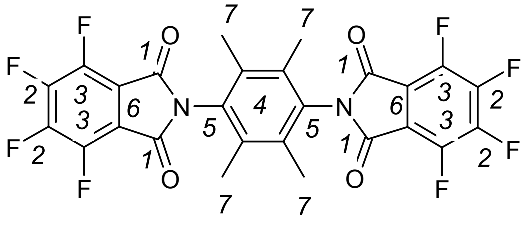


^{13}C NMR (100MHz) (DMSO-d_6) δ = 135.01 (C1); 117.78 (C2); 13.91 (C3)

c) Spirobiscatechol

^{13}C NMR (100MHz) (DMSO-d_6) δ = 144.57; 144.56; 142.11; 140.78; 110.11; 108.27; 59.53; 56.28; 42.32; 31.52; 30.47.

d) 1,4-Bis(4,5,6,7-tetrafluorophthalimido)-2,3,5,6-tetramethylbenzene (1)



^{13}C NMR (100MHz) (DMSO-d_6) δ = 166.22 (C1); 145.90 (C2), 143.24 (C3); 134.25(C4); 130.25 (C5); 113.53 (C6); 15.64 (C7)

XPS Analysis

X-ray photoelectron spectroscopy is an additional technique which was used to detect the presence of fluorine and other elements (Figure 4 and 5). The XPS survey spectra of monomer **1** and **OFP-3** reveals the presence of carbon, nitrogen, oxygen and fluorine. The binding energy of the N1s at 400.2 eV confirms the type of nitrogen bonding to carbon as represented by the structure **1**. However, the polymerisation condition did not affect the type of nitrogen bonding in **OFP-3,** and it therefore appears at the same binding energy. The binding energy of the F1s at 687.97 eV confirms the presence of fluorine in both compound **1** and OFP-3. On the other hand, fluorine analysis of OFP-3 shows only a trace amount (<1 At.%) compared to monomer **1**. This can be considered as a further support that the F atoms have been replaced by the oxygen of the dioxane links and consequently confirm the proposed structure of the OFP-3. Trace amount of fluorine found in OFP-3 could be attributed to the unreacted fluorine containing-end groups and other impurities in terms of entrapped fluorinated by-products from base catalysed reaction.

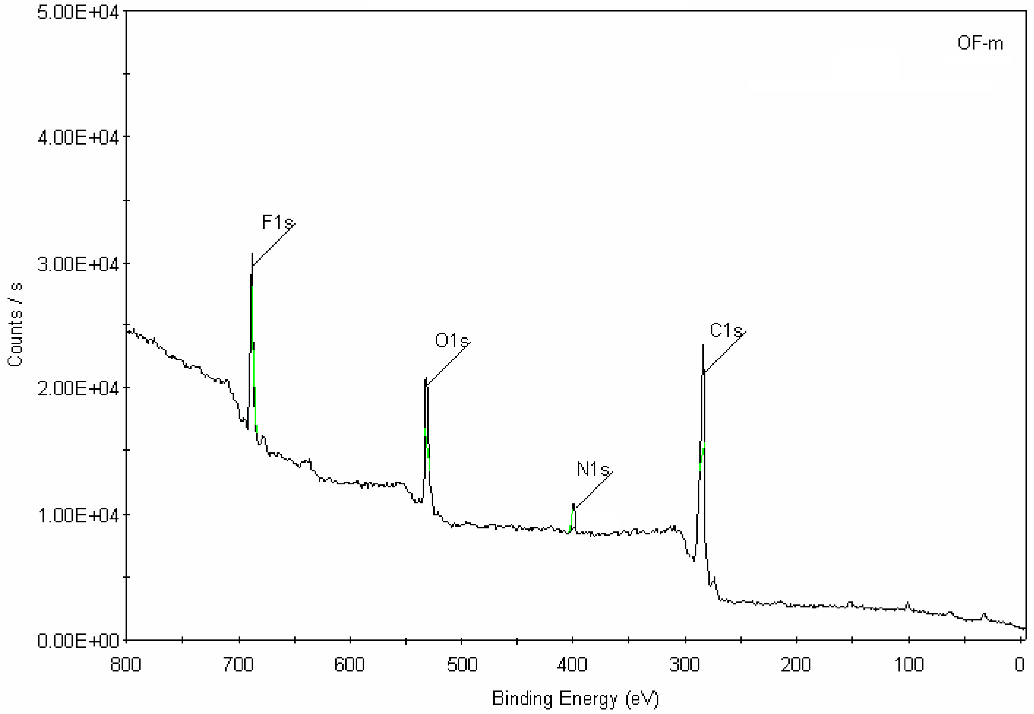


Figure 5. XPS survey spectrum of 1,4-Bis(4,5,6,7-tetrafluorophthalimido)-2,3,5,6-tetramethylbenzene (**1**)

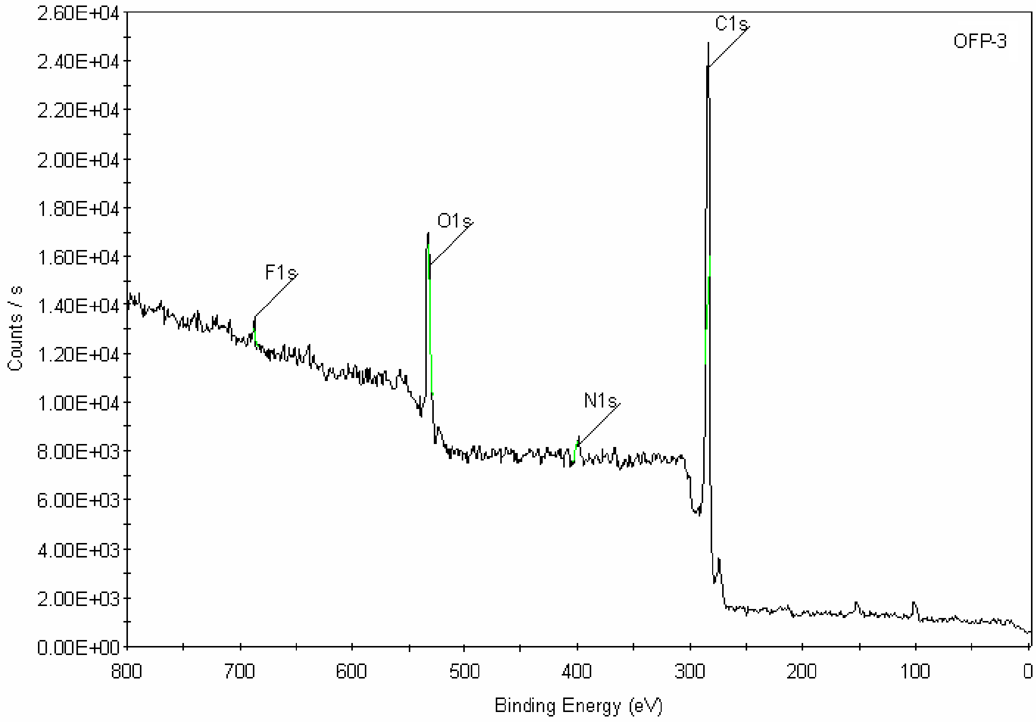


Figure 6. XPS survey spectrum of OFP-3

Figure 7. HRTEM image of OFP-3 illustrates its porosity (Wormhole structure), homogeneity, and structural stability under the experimental condition (300 kV). The pore dimensions in good agreement with the micropore size distribution as calculated by the Horvath-Kawazoe method.

Thermogravimetric Analysis (TGA)

The organic framework polymer (OFP-3) was tested in nitrogen atmosphere with a heating rate of 5 °C/min. The material is stable up to 312 °C, where a 5 % initial loss, corresponding to the evaporation of the residual solvents which has been identified as the entrapped solvents used for washing the sample.

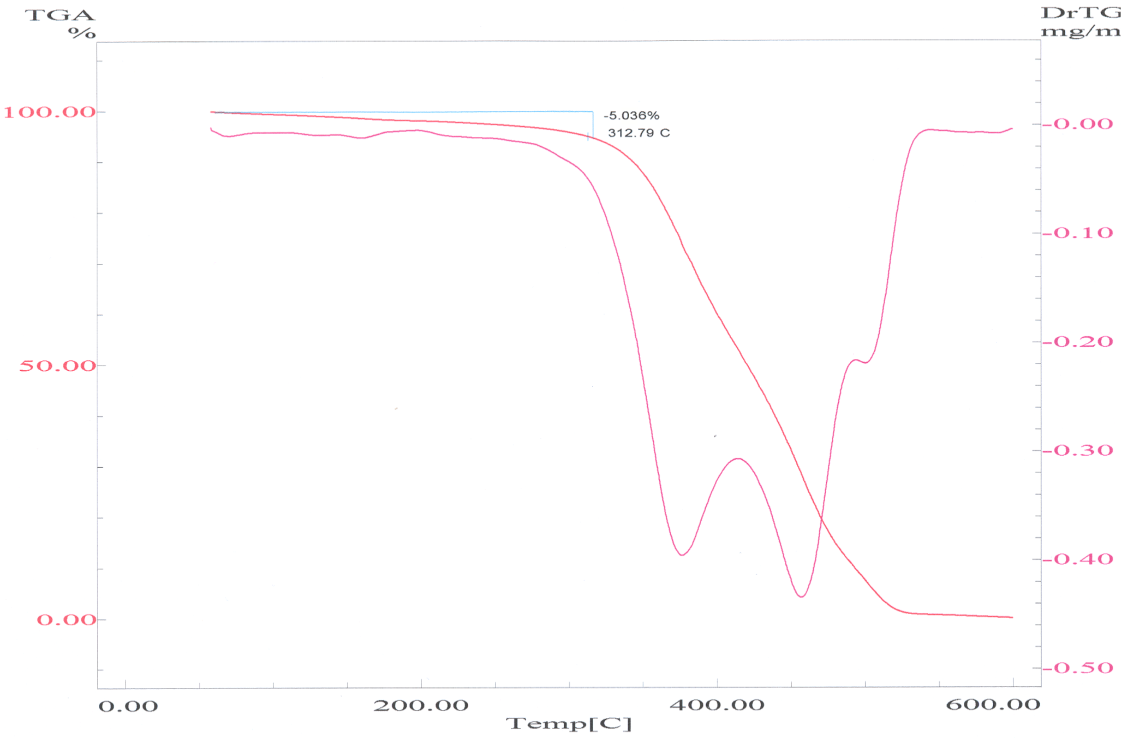


Figure 8. Thermogravimteric analysis of OFP-3

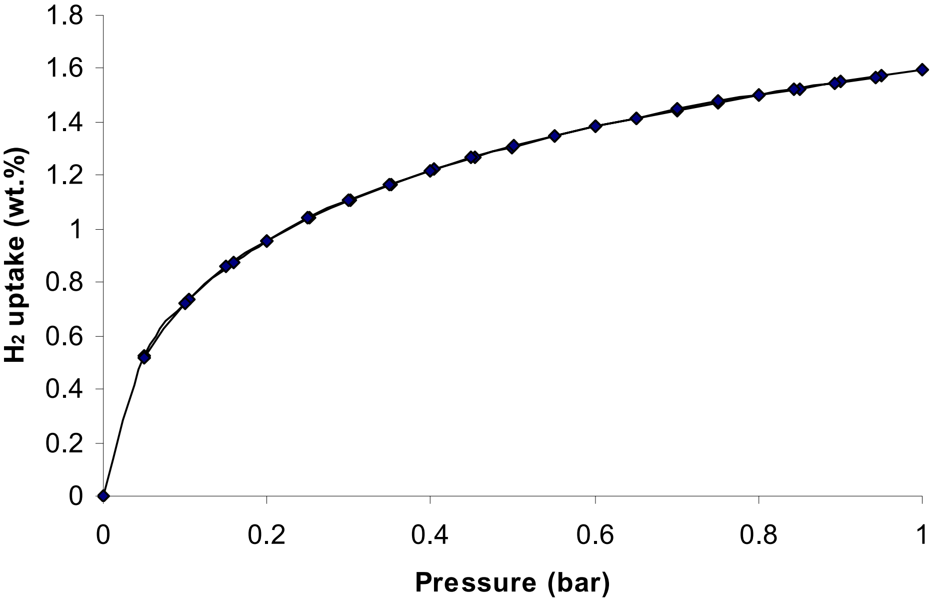


Figure 9. Hydrogen adsorption/desorption isotherm for **OFP-3** at 77 K and 1 bar.

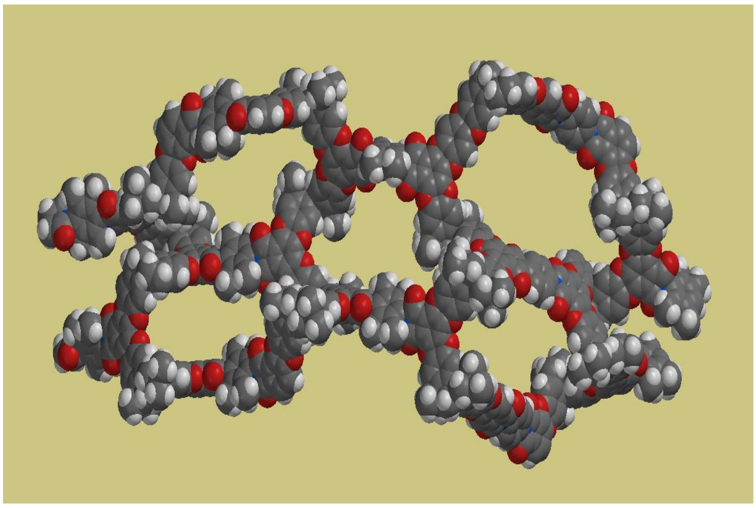


Figure 10. Space filling molecular model of **OFP-3**

Semiemperical molecular orbital methods (**PM3 and MNDO**) were used to simulate idealised frame work structure of OFP-3. The molecular structure was created using the Spartan programme and the semiemperical calculations were performed to optimize the molecular geometry at **PM3 and MNDO** levels and the geometries were re-optimized using G03 programme.

This is a force field semiemperical calculation. These calculations are at a gas phase in which there is no intermolecular forces and no interchain interaction. Although these calculations show some differences from the experimental results (HK analysis and HRTEM) the PM3 calculations gives a reasonable optimized geometry for the OFP-3 as a large molecule comprising of many frame work architectures [I. N. Levine (2000), "Quantum Chemistry", 5th Edition, Prentice Hall, New Jersey]. The differences between the theoretical and experimental pore dimensions mainly due to the calculations based on single molecular framework at MNDO level. On the other hand the calculation on the larger molecule including many frameworks (figure 10) at PM3 level, gives a shorter dimension of 0.92 nm (fig. 11). These computational results suggest that OFP-3 was constructed with nanometer size frame works.

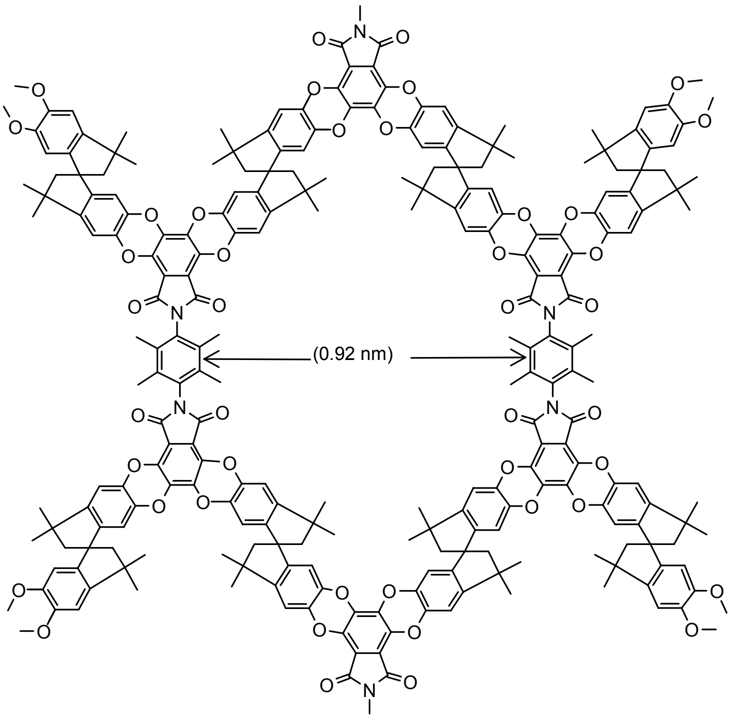


Figure 11. Optimised geometry of the framework structure of **OFP-3**