Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Sugar-derived organogels as templates for structured, photoluminescent conjugated polymer-inorganic hybrid materials.

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1. Experimental Details

1.1 Materials

The sugar-based organogelator 5-di-*O*-methanesulfonyl-1,4:3,6 dianhydro-D-sorbitol (OG) was prepared at QUB using published procedures.[1] TEOS (98% reagent grade, CAS Number 78-10-4) and poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) (**PFO**, M_n =15,834 g mol^{-1}, PDI = 3.7, CAS Number 19456-48-5) were purchased from Sigma Aldrich and were used as received. All other reagents (ethanol, benzylamine) were commercially available and used as received.

1.2 Synthesis

1.2.1 Synthesis of an organogel using OG and Ethanol

Organogelator 1 (OG – see manuscript) is known to make a gel stable to inversion with ethanol using the following preparation.[1] In a typical synthesis organogelator 1 (0.2 g, 0.66 mmol) in ethanol (15.3 g, 365 mmol) (~0.5 wt%) was heated in a sample vial at ~60 ˚C until dissolved. The solution temperature was maintained for a further 10 minutes before being allowed to cool to room temperature. On cooling a gel is formed which is stable to inversion. This gel is thermoreversible. This preparation was modified to include the conjugated polymer PFO into the gel to produce PFO-OG as described below.

1.2.2 Synthesis of an organogel using OG and ethanol doped with PFO to prepare PFO-OG

In a typical synthesis of a PFO-organogel (PFO-OG), organogelator 1[1] (0.2 g, 0.66 mmol) in ethanol (15.3 g, 365 mmol) (~0.5 wt%) was heated in a sample vial at 60 ˚C until dissolved, before 200 µL of a PFO/chloroform solution (1 mg mL^{-1}) was added. The solution was heated for a further 10 minutes before being allowed to cool to room temperature. On cooling an orange gel is formed, which is stable to inversion. This gel is thermoreversible.

1.2.3 Transcription of organogel synthesised from OG and ethanol with TEOS to form SiO_2 coated tubes OG-Si

Transcribed organogel (OG-Si) was prepared by addition of TEOS (0.95 g, 4.56×10^{-3} mol) and benzylamine as the sol-gel catalyst (0.0400 g, 0.373 mmol) to the OG-Ethanol mixture. Subsequent cooling to ambient temperature resulted in the formation of the silica-transcribed organogel. The samples were heated to reflux in ethanol, filtered by gravity, washed with ethanol and air-dried resulting in a powdery white solid.

1.2.4 Transcription of PFO-OG with TEOS to form SiO_2 coated tubes PFO-OG-Si

Transcribed PFO-organogel (PFO-OG-Si) was prepared by addition of TEOS (0.95 g, 4.56×10^{-3} mol) and benzylamine as the sol-gel catalyst (0.0400 g, 0.373 mmol) to the OG-Ethanol mixture. Subsequent cooling to ambient temperature resulted in the formation of the silica-transcribed organogel. Subsequent cooling to ambient temperature resulted in the formation of the silica-transcribed PFO-containing organogel. The samples were heated in warm (40 °C) ethanol, filtered by gravity, washed with ethanol and air-dried resulting in a powdery pale orange solid.

1.3 Key to Samples

Sample	Description
OG	Organogelator **1** (see manuscript)[1]
OG-Si	Organogel made from OG-Ethanol, transcribed with silica using TEOS *via* the sol gel route (results in the formation of hard blank silica tubes).
PFO-OG	Organogel made from PFO-OG-Ethanol (results in the formation of soft, thermoreversible gels containing PFO).
PFO-OG-Si	Organogel made from PFO-OG-Ethanol, transcribed with silica using TEOS *via* the sol gel route (results in formation of hard silica tubes containing PFO).

1.4 Instrumentation

Fourier Transform Infrared (FTIR) spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer at room temperature between 4000-400 cm^{-1} with a resolution of 1 cm^{-1}. To obtain a reasonable signal to noise ratio the average of 64 scans was taken. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris 1 TGA thermogravimetric analyser in the range 30-900 °C in an air atmosphere using a heating rate of 10 °C/min. SEM was obtained at QUB on a Jeol 6500 FEG Scanning Electron Microscope. Solution phase photoluminescence spectra were measured on a Varian-Cary Eclipse fluorimeter. Solid-state photoluminescence spectra were recorded on a Horiba-Jobin-Yvon Fluorolog-3 spectrometer using a Horiba-Jobin-Yvon integrating sphere. Emission and excitation spectra were corrected for the wavelength response of the system using correction factors supplied by the manufacturer. Appropriate excitation and emission wavelengths were selected for each system and the excitation and emission slit widths were both typically 1.0 nm. Solid-state nuclear magnetic resonance (NMR) spectroscopy was conducted by the EPSRC service at the University of Durham. ^{29}Si were obtained using a Varian Unity Inova spectrometer operating at 59.56 MHz. BET surface area measurements were performed using a NOVA 4200 from Quatacrome Instruments, the samples were outgassed at 200^{o}C for 6 hours prior to testing.

2. Figures

Figure S1 shows the observed photoluminescence from PFO-OG and PFO-OG-Si under UV excitation (366 nm). **Figure S2** is an SEM image of a PFO-OG-Si sample illustrating the hollow nature of the microstructures, thus confirming the formation of tubes. **Figure S3** and **Figure S4** show representative SEM images of OG-Si and PFO-OG-Si microtubes, respectively, for samples prepared from different synthesis batches. **Figure S5** shows the ^{29}Si MAS-NMR of PFO-OG-Si and **Figure S6** shows TGA thermograms of analysis (TGA) of OG-

Si, OG and PFO-OG-Si. **Figure S7** shows the FTIR spectra of OG, OG-Si, PFO-OG and PFO-OG-Si. **Figure S8** is a fluorescence microscopy image of PFO-OG. **Figure S9** provides a schematic representation of transcription of an organogel with silica.

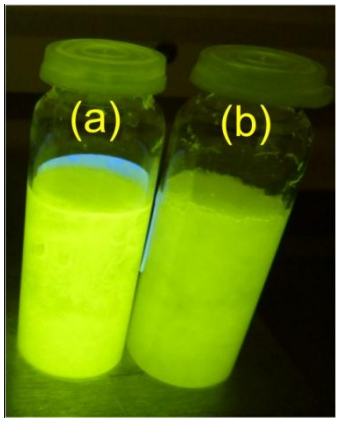

Figure S1. Observed photoluminescence from (a) PFO-OG and (b) PFO-OG-Si under UV excitation (366 nm).

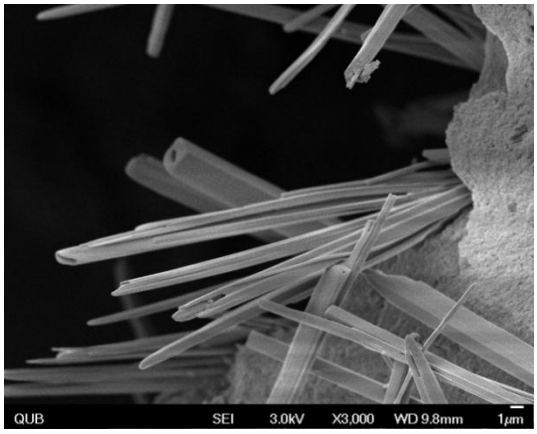

Figure S2. Representative SEM image of PF-OG-Si microtubes**.**

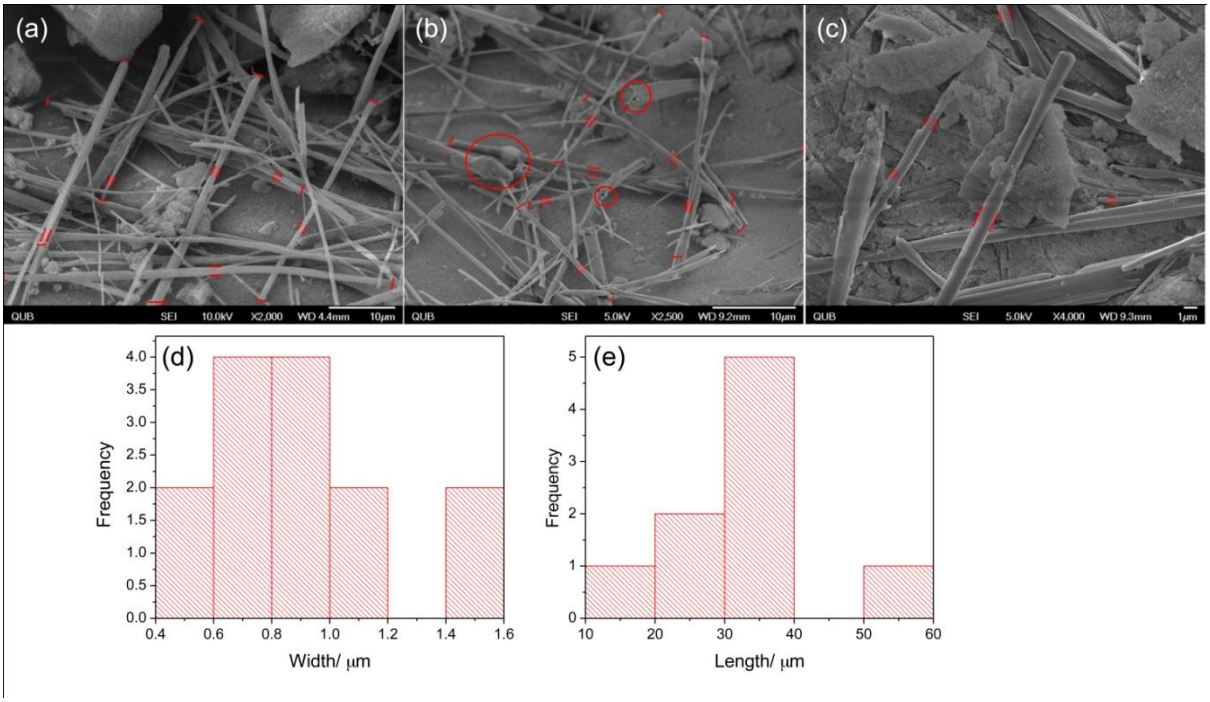

Figure S3. (a-c) Representative SEM images of OG-Si microtubes (sorbitol gelator transcribed with silica) prepared from different synthesis batches. Samples aged for 14 weeks. (d) and (e) show the corresponding width and length distributions of OG-Si microtubes across all batches.

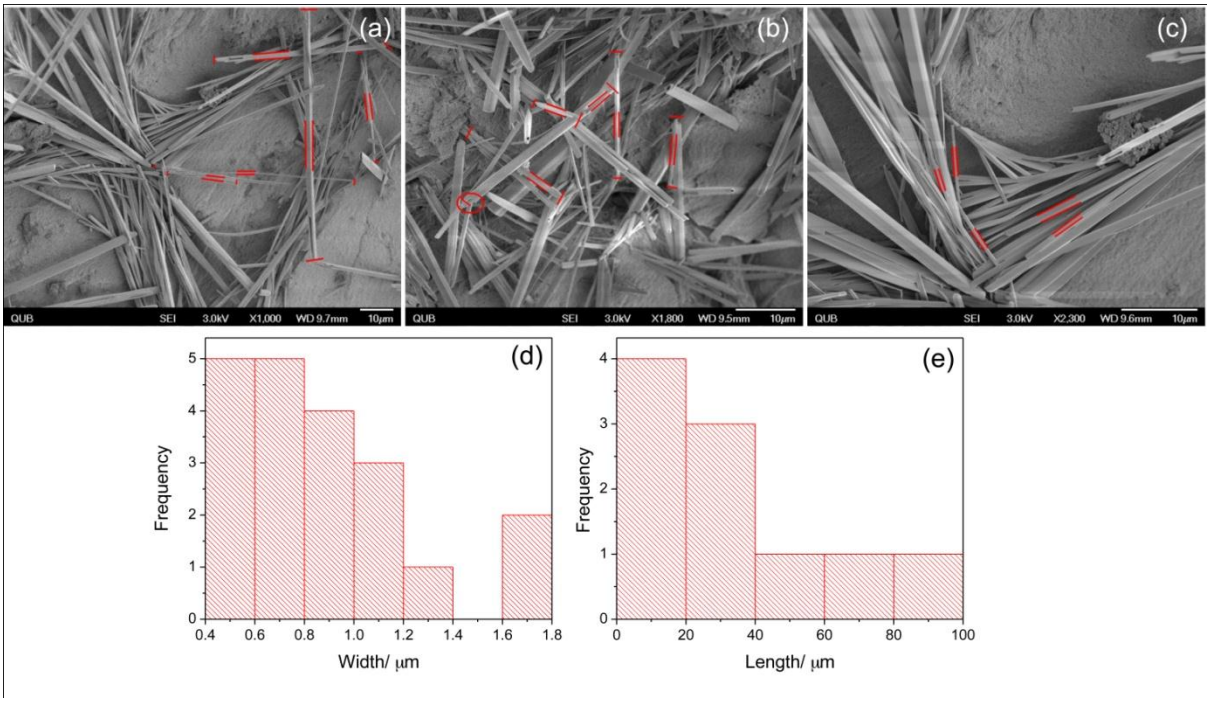

Figure S4. (a-c) Representative SEM images of PFO-OG-Si microtubes (PFO/sorbitol gelator transcribed with silica) prepared from different synthesis batches. Samples aged for 14 weeks. (d) and (e) show the corresponding width and length distributions of PFO-OG-Si microtubes across all batches.

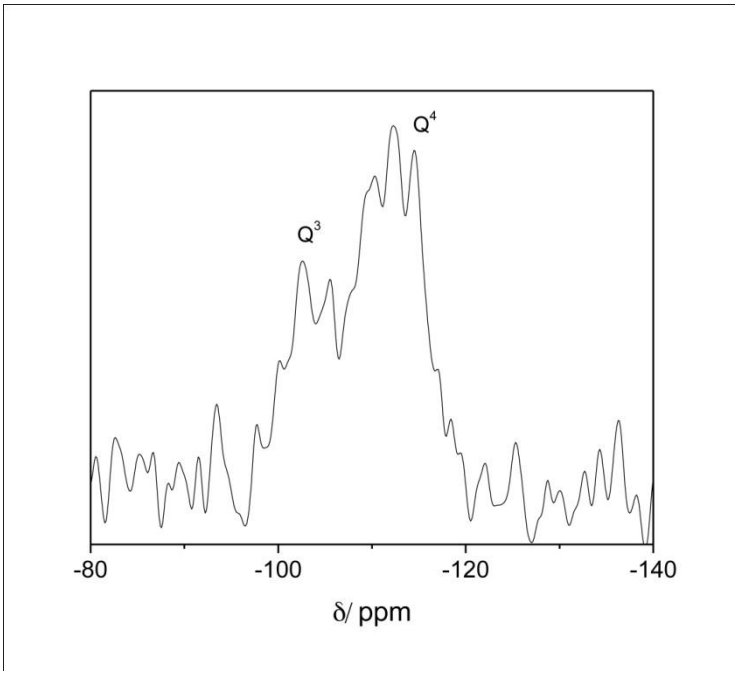

Figure S5. ^{29}Si MAS-NMR of PFO-OG-Si.

The ^{29}Si MAS-NMR spectrum of PFO-OG-Si exhibits broad signals characteristic of Q^3 $(\equiv SiO)_3SiOH$ (~102 ppm) and Q^4 $(\equiv SiO)_4Si$ (~111 ppm) units, indicating the presence of a silica network composed mainly of cyclic units cross-linked by oxygen bridges.[2] The relative population of each silica species (from Gaussian deconvolution) was used to determine the degree of condensation, *C* , from C (%) = $1/4(\%Q^1 + 2\%Q^2 + 3\%Q^3 + 4\%Q^4)$, which was found to be ~ 92%.

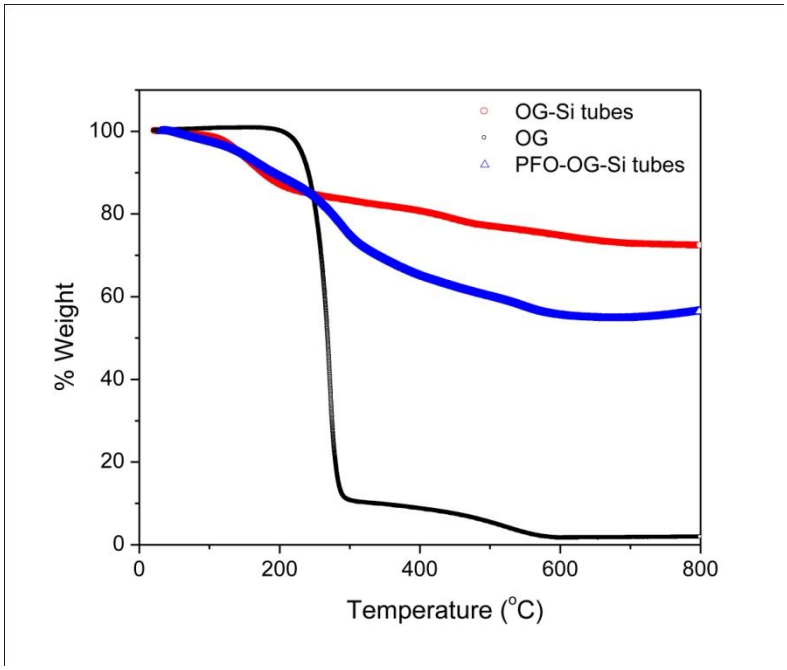

Figure S6. Thermogravimetric analysis (TGA) of (a) OG-Si, (b) OG and (c) PFO-OG-Si. Thermograms were measured in air at a heating rate of 10 °C/min.

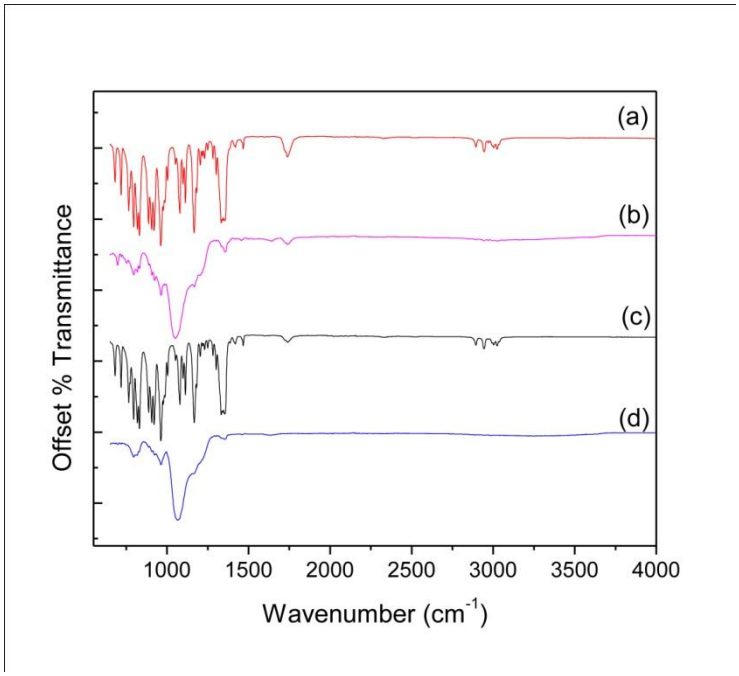

Figure S7. FTIR spectra of (a) OG, (b) OG-Si, (c) PFO-OG and (d) PFO-OG-Si.

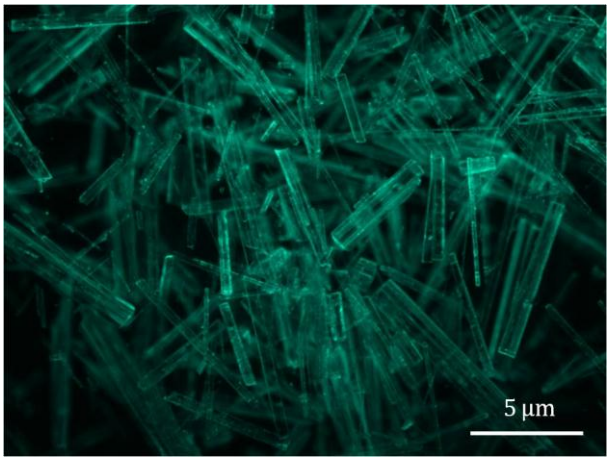

Figure S8. Fluorescence microscopy image of PFO-OG (λ_{ex} = 360-370 nm, 10x magnification)

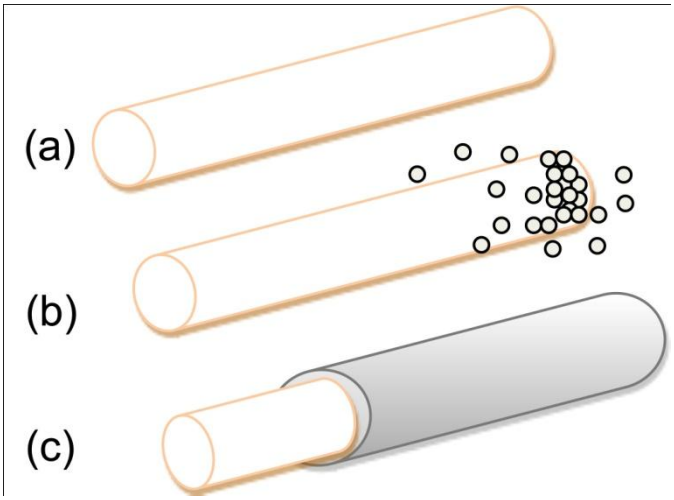

Figure S9. Schematic representation of transcription of an organogel with silica: (a) self-assembled organic fibre; (b) deposition of silica sol from suspension and (c) condensation and structural consolidation of silica around the organic template.

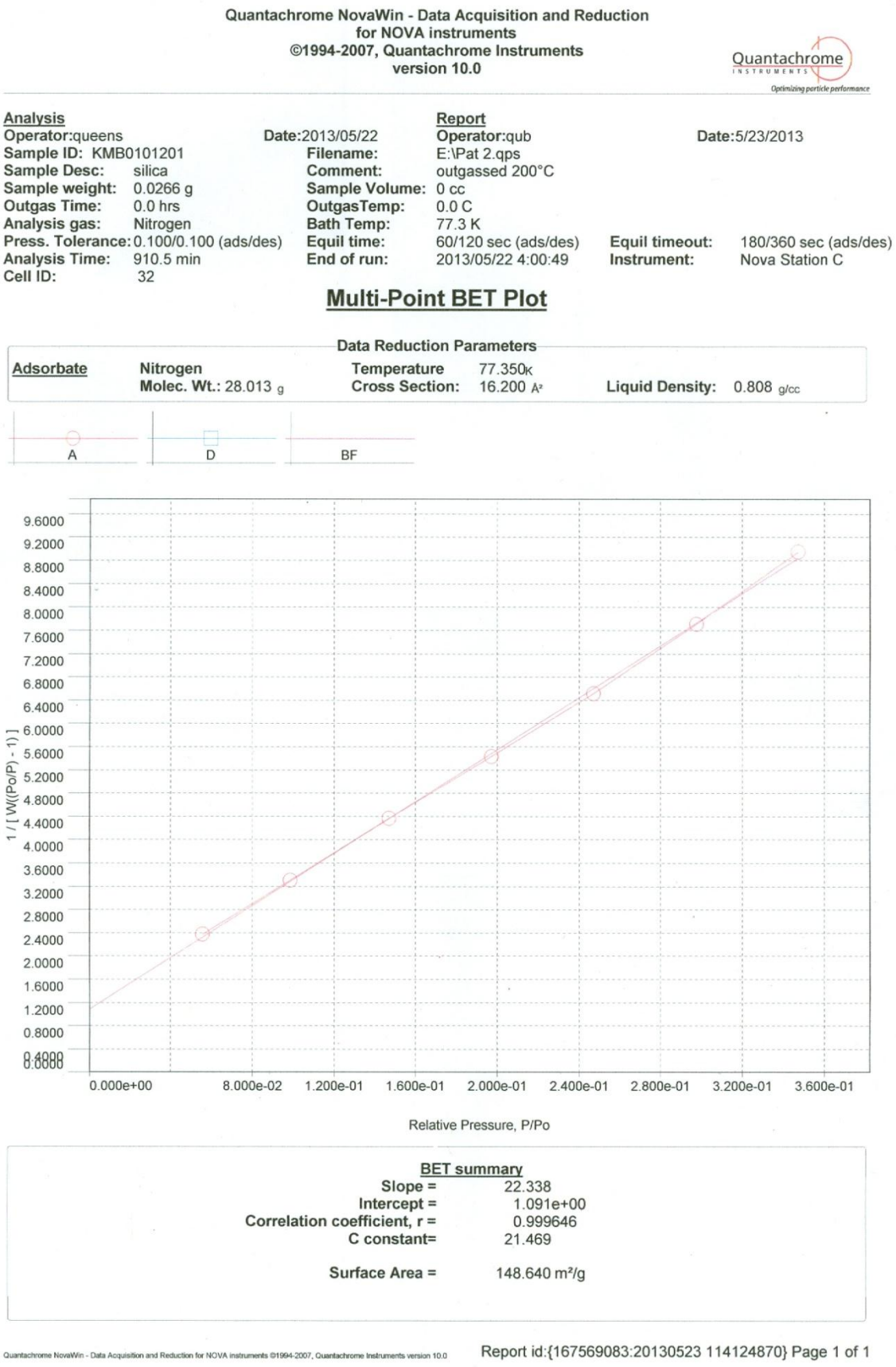

Figure S9. BET surface area measurements OG-Si

PFO-OG was a wet thermoreversible gel (60-70°C) so BET analysis was not practical.

OG-Si Surface area measurement was obtained. In this case the organogel OG and ethanol were removed by heating the sample to reflux in ethanol for 2 hours, filtered and dried in air thus removing the template. The sample was outgassed at 200°C for 6 hours. OG-Si surface area (BET) 148.64m^2/g

BET of PFO-OG-Si was not successfully obtained in this instance. The samples were worked up at 40°C thus the sample retained some of the OG template (The Organogelator does not dissolve in ethanol until above 60°C.). While preparing this sample for BET the sample (outgassed at 200°C for 6 hours). The sample degraded and did not provide useable data. SEM data alluded to the incomplete removal of the organogel template. Therefore a direct comparison between the samples cannot be made at this time.

References

1. S. J. Craythorne, C. L. Pollock, A. J. Blake, M. Nieuwenhuyzen, A.C. Marr and P.C. Marr, *New J. Chem*., 2009, **33**, 479.

2. G. Engelhardt, in *Encyclopedia of Magnetic Resonance*, Wiley Interscience, 2007, New York.