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## Synthesis, properties and water permeability of SWNT buckypapers

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## Synthesis, properties and water permeability of SWNT buckypapers

### Abstract

The ability of macrocyclic ligands to facilitate formation of dispersions of single-walled carbon nanotubes (SWNTs) was investigated using a combination of absorption spectrophotometry and optical microscopy. Vacuum filtration of aqueous dispersions containing SWNTs and various macrocyclic ligands (derivatised porphyrin, phthalocyanine, cyclodextrin and calixarene) afforded self-supporting membranes known as buckypapers. Microanalytical data and energy dispersive X-ray spectra were obtained for these buckypapers and provided evidence for retention of the macrocyclic ligands within the structure of the membranes. The electrical conductivities of the membranes varied between  $30 \pm 20$  and  $220 \pm 60$  S  $\text{cm}^{-1}$ , while contact angle analysis revealed they all possessed hydrophilic surfaces. The mechanical properties of buckypapers prepared using macrocyclic ligands as dispersants were shown to be comparable to that of a benchmark material prepared using the surfactant Triton X-100 (Trix). Incorporation of the macrocyclic ligands into SWNT buckypapers was found to increase their permeability up to ten-fold compared to buckypapers prepared using Trix. No correlation was observed between the water permeability of the membranes and the average size of either their surface or internal pores. However, the water permeability of the membranes was found to be inversely dependent on their surface area.

### Keywords

swnt, buckypapers, permeability, synthesis, water, properties

### Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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## Synthesis, properties and water permeability of SWNT buckypapers†

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The ability of macrocyclic ligands to facilitate formation of dispersions of single-walled carbon nanotubes (SWNTs) was investigated using a combination of absorption spectrophotometry and optical microscopy. Vacuum filtration of aqueous dispersions containing SWNTs and various macrocyclic ligands (derivatised porphyrin, phthalocyanine, cyclodextrin and calixarene) afforded self-supporting membranes known as buckypapers. Microanalytical data and energy dispersive X-ray spectra were obtained for these buckypapers and provided evidence for retention of the macrocyclic ligands within the structure of the membranes. The electrical conductivities of the membranes varied between  $30 \pm 20$  and  $220 \pm 60$  S cm<sup>-1</sup>, while contact angle analysis revealed they all possessed hydrophilic surfaces. The mechanical properties of buckypapers prepared using macrocyclic ligands as dispersants were shown to be comparable to that of a benchmark material prepared using the surfactant Triton X-100 (Trix). Incorporation of the macrocyclic ligands into SWNT buckypapers was found to increase their permeability up to ten-fold compared to buckypapers prepared using Trix. No correlation was observed between the water permeability of the membranes and the average size of either their surface or internal pores. However, the water permeability of the membranes was found to be inversely dependent on their surface area.

## Introduction

Membrane-based methods have become an integral feature of the industrial separations sector. This is due to their low cost compared to other techniques, ease of scale-up, low impact on the environment, and flexibility.<sup>1,2</sup> Despite these advantages, there is still a need to find new membrane materials which can overcome technical problems associated with fouling, short service lifetimes and low chemical selectivity.<sup>3</sup> One such material is carbon nanotubes (CNTs), which have exceptional mechanical, electrical and thermal properties.<sup>4</sup> Theoretical studies of CNTs, using molecular dynamics simulation, have revealed that they are exceptionally permeable to gases and liquids.<sup>5,6</sup> Several research groups have also shown that membranes composed of

aligned CNTs, prepared by a chemical vapour deposition process, can selectively filter dissolved molecules and colloidal particles on the basis of differences in their sizes. For example, Holt and co-workers showed that aligned multi-walled carbon nanotube (MWNT) membranes allowed the passage of [Ru(bipy)<sub>3</sub>]<sup>2+</sup> and gold nanoparticles with diameters of 2–5 nm, but not nanoparticles >10 nm.<sup>6</sup> Other workers showed aligned CNT membranes can separate the components of a hydrocarbon mixture, and remove microorganisms such as *E. coli* from aqueous solution.<sup>7</sup>

An alternative method for preparing CNT membranes is by filtration of dispersions obtained by applying ultrasonic energy to samples containing CNTs and a suitable dispersant.<sup>8</sup> While the resulting buckypapers have a broader distribution of larger pores than those in aligned membranes, this approach offers several advantages. These include greater ease of preparation and avoiding harsh chemicals required to remove the supporting substrates that are generally used to grow aligned membranes on. Previous studies have shown that buckypaper membranes can remove bacteria and viruses from water supplies,<sup>9</sup> separate mixtures of gases,<sup>10</sup> and be used for desalination.<sup>11</sup> While the permeabilities of buckypapers composed of MWNTs and single-walled carbon nanotubes (SWNTs) towards water has been reported previously,<sup>9,12</sup> the materials examined were prepared using very small quantities of CNTs and without a dispersant. Furthermore the buckypapers examined were not removed from the underlying polyvinylidene (PVDF) support membrane that the initial CNT dispersions were filtered through. It is very likely

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† Electronic supplementary information (ESI) available: UV-vis spectra of SWNTs and dispersant molecules, EDX spectra of buckypapers, water permeability plots for buckypapers, TGA of buckypapers and graphs showing the effect of applied pressure on the flux of water across buckypapers. See DOI: 10.1039/c2jm31382k

that the results obtained using these composite CNT–PVDF membranes would have been significantly influenced by the presence of the substrate, and of only a very thin overlying buckypaper film. In the current study, we address this issue by measuring the water permeability of mechanically robust free-standing SWNT buckypaper membranes (*i.e.* without the underlying PVDF supporting layer).

Most studies on buckypapers have focused on materials made from dispersions prepared using either a surfactant or a polymer, as the latter classes of molecules have been shown to be very effective for stabilizing solutions of nanotubes through non-covalent interactions.<sup>13–17</sup> In contrast, there have been limited studies into the suitability of different classes of other small molecules for dispersing CNTs. Our goal is to produce new membrane materials that are highly permeable to water, and able to discriminate between different dissolved solutes. Therefore we were particularly interested in determining whether different classes of macrocyclic ligands could be employed as dispersants for CNTs, and are retained in the final material when the resulting solutions are filtered to prepare buckypapers. Ultimately we wish to explore whether retention of molecules such as calixarenes and cyclodextrins in buckypapers might provide materials that combine the host–guest recognition properties of the macrocyclic ligands, with the strength and permeability towards water displayed by various classes of CNT membranes. Such materials may exhibit selective permeability owing to their capacity to discriminate between potential analytes through both a size exclusion mechanism, and on the basis of differences in the strength and type of interactions between the embedded molecules and dissolved analytes.

This paper describes the results of investigations into the ability of a calixarene, cyclodextrin, porphyrin and phthalocyanine to produce stable dispersions of SWNTs, as well as the electrical, mechanical and morphological properties of buckypapers produced from those dispersions. In addition, the effect of varying the dispersant present in a SWNT buckypaper on its permeability towards water, as determined using a dead-end filtration apparatus, was examined in a series of experiments designed to test the suitability of these materials for membrane filtration applications.

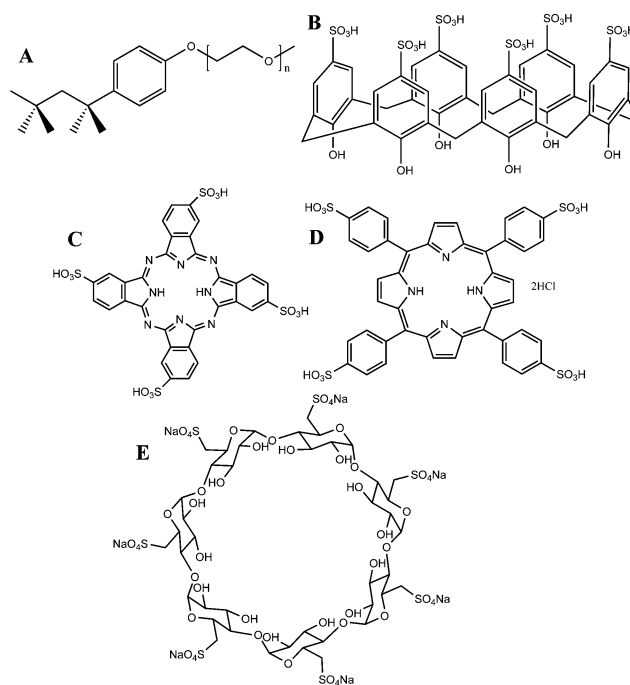
## Experimental

### Reagents

HiPco SWNTs produced by chemical vapour deposition were used in this study and were obtained from Unidym™ (Lot no. P0348) and used without further purification. The dispersants used were Triton X-100 (Trix; Sigma-Aldrich),  $\beta$ -cyclodextrin sulfated, sodium salt ( $\beta$ -CD; Sigma-Aldrich), 4-sulfonic calix[6]arene hydrate (C6S; Alfa Aesar), *meso*-tetra(4-sulfonatophenyl)porphyrin dihydrogen chloride (TSP; Frontier Scientific) and phthalocyanine tetrasulfonic acid (PTS; Frontier Scientific). The structures of the dispersants are shown in Fig. 1.

### Preparation of dispersions

All dispersions were prepared in Milli-Q water (18 M $\Omega$  cm) using a SWNT concentration of 0.1% (w/v). The concentration of Trix,  $\beta$ -CD or C6S in solutions to be sonicated was always 1% (w/v),



**Fig. 1** Molecular structures of: (a) Triton X-100 (Trix) where  $n = 9–10$ , (b) 4-sulfonic calix[6]arene hydrate (C6S), (c) phthalocyanine tetrasulfonic acid (PTS), (d) *meso*-tetra(4-sulfonatophenyl)porphyrin dihydrogen chloride (TSP), and (e)  $\beta$ -cyclodextrin sulfated, sodium salt ( $\beta$ -CD).

while for solutions containing PTS or TSP the concentration of dispersant was 0.1% (w/v). In a typical experiment, 15 mg of SWNTs were dispersed in 15 mL of dispersant solution by using a Branson 450 (400 W, Ultrasonics Corp.) digital sonicator horn with a probe diameter of 10 mm to apply ultrasonic energy for 30 min. The conditions used were an amplitude of 30%, pulse duration of 0.5 s and pulse delay of 0.5 s. During sonication, the sample vial was placed inside an ice/water bath to minimize increases in temperature.

### Preparation of buckypapers

In order to produce a small circular buckypaper, two of the above dispersions were prepared and added to a further 50 mL of dispersant solution (1% (w/v) Trix,  $\beta$ -CD or C6S or 0.1% (w/v) PTS or TSP) before being subjected to further treatment in an ultrasonic bath (Unisonics, 50 Hz, 150 W) for 3 min. The resulting homogeneous 80 mL dispersions containing 0.038% (w/v) of SWNTs were then diluted to a final volume of 250 mL with Milli-Q water, prior to processing into buckypapers. Larger, rectangular buckypapers were prepared by first combining six of the above dispersions, and then adding a further 50 mL of dispersant solution, after which the resulting mixture was subjected to further treatment in an ultrasonic bath (Unisonics, 50 Hz, 150 W) for 3 min. The resulting homogeneous 140 mL dispersions containing 0.064% (w/v) of SWNTs were then diluted to a final volume of 1 L with Milli-Q water, prior to processing into buckypapers.

Small, circular buckypapers measuring approximately 35 mm in diameter were prepared by vacuum filtration of dispersions through a polytetrafluoroethylene (PTFE) membrane filter (5  $\mu$ m

pore size; Millipore) housed in an Aldrich glass filtration unit, and using a Vacuubrand CVC2 pump that typically operated between 30 and 50 mbar. The tops of the filtration units were covered with plastic film to prevent evaporative losses during the filtration process, which typically took approximately 1 day.

Larger, rectangular buckypapers were prepared in a similar fashion by filtering dispersions using a custom-made filtration unit with a sintered glass frit measuring 5.5 cm × 8.0 cm onto a piece of commercial PVDF membrane (0.22 μm pore size; Millipore). After the dispersions were filtered, the resulting buckypapers were washed with 250 mL of Milli-Q water followed by 10 mL of methanol (99.8%, Merck) whilst still in the filtration unit. After washing, the damp buckypaper was placed between absorbent paper sheets and allowed to dry further overnight. The dry buckypaper was then carefully peeled away from the underlying commercial membrane filter.

### Characterization techniques

Absorption spectra (400–1000 nm) of all dispersions were obtained using a Cary 500 UV-vis-NIR spectrophotometer and quartz cuvettes. The dispersions were first diluted with Milli-Q water to ensure that the measured absorbances were within the optimal range of the instrument.

A Leica Z16 APO LED1000 microscope equipped with a digital camera was used to perform preliminary assessments of the effectiveness of different macrocyclic ligands to produce stable dispersions of SWNTs. The surface morphology of buckypapers was examined using a JEOL JSM-7500FA FESEM. Samples were cut into small strips and mounted onto a small conductive stub using carbon tape or by wedging the sample between a screw mount on the stub itself. All samples had sufficient electrical conductivity to be imaged without prior sputter coating. Images obtained by scanning electron microscopy were analysed using Image Pro Plus software to obtain quantitative information about the size of surface pores. Energy Dispersive X-Ray (EDX) spectroscopy was performed in conjunction with imaging using the SEM to provide information on the identity of elements present on the surface of buckypaper samples.

The contact angles of buckypapers were determined using the sessile drop method and a Data Physics SCA20 goniometer fitted with a digital camera. The contact angles of 2 μL Milli-Q water droplets on the surfaces of the buckypapers were calculated using the accompanying Data Physics software (SCA20.1). The mean contact angle was calculated using measurements performed on at least five water droplets.

The electrical conductivity of buckypaper samples was determined using a standard two-point probe method.<sup>18</sup> Initially buckypapers were cut into rectangular strips approximately 3 mm wide and 3–5 cm long, which were then fixed using high purity silver paint (SPI) onto a small piece of copper tape (3M) adhered to a glass slide. Another glass microscope slide was clamped onto the initial glass slide containing the buckypaper strip using bulldog clips to ensure the sample was secure, and apply a constant force. Electrical leads were used to connect the copper tape overhanging the glass slide to a digital multimeter (Agilent 34410A), while a waveform generator (Agilent 33220A) was used to apply a triangular waveform (potential

limits –0.05 V and 0.05 V; frequency = 5 mHz) to the buckypaper sample, and measure the resulting current output. The data obtained was used to construct a current–voltage ( $I$ – $V$ ) plot, which was then used to determine the sample resistance for the specific length of buckypaper used under the conditions employed (measurements performed in air; 21 °C; 45% relative humidity). The above approach was repeated for different lengths of buckypaper, which were obtained by cutting the end off the sample strip, and then reconnecting it to pieces of copper tape on the microscope slide using silver paint.

The mechanical integrity of samples was determined using a Shimadzu EZ-S universal testing device and buckypaper samples cut into small rectangular strips measuring 15 mm × 3 mm and mounted into a small paper frame. The length of the sample between the top and bottom clamps was kept constant at 10 mm. The paper frame was cut between the clamps prior to testing, and the mounted samples were then stretched using a 10 N load cell, at a strain rate of 1 mm min<sup>–1</sup> until failure. The tensile strength of each sample was determined as the maximum stress measured, while the ductility was the percentage elongation at breaking point. The Young's modulus and sample toughness were also determined.

The thermal stability of buckypaper samples was examined by thermogravimetry (TGA) using a TA instruments, Q500 thermogravimetric analyser. Samples were tested in air, and were examined over the temperature range 20–1000 °C at a heating rate of 10 °C min<sup>–1</sup>.

Nitrogen adsorption/desorption isotherms were obtained using a surface area analyser (ASAP 2010 or ASAP 2400, Micromeritics®) operating at 77 K. Prior to analysis, residual gas trapped within samples was removed under vacuum at 200 °C. The resulting isotherms were analysed using the Horvath–Kawazoe (HK) and Barrett, Joyner and Halenda (BJH) methods to determine the distribution of small and large pores, respectively.<sup>19,20</sup> In addition, multipoint Brunauer, Emmett, and Teller (BET) analysis of the isotherms was used to calculate the specific surface areas of the samples.<sup>21</sup>

The permeability of buckypapers towards water was measured using a custom-made dead-end filtration cell setup, which used compressed air to force a feed solution consisting of Milli-Q water across the membranes. Initially, a pressure of 0.069 bar was applied to induce water transport across the buckypaper. The volume of water passing across the membrane was monitored for 10 min using an analytical balance connected to a personal computer, and then the pressure was incrementally increased and the process repeated. The obtained data were used to calculate the membrane flux.

## Results and discussion

### Preparation and properties of SWNT dispersions containing macrocyclic ligands

Sonication using an ultrasonic horn is a common method used to facilitate the dispersion of CNTs into solution. However, excess sonication can lead to the introduction of structural defects and shortening of nanotubes, as well as adversely affecting their electronic properties.<sup>22,23</sup> Consequently, it is important to ensure that the duration of sonication is kept as brief as possible. We

previously examined the effect of increasing sonication time on the UV-visible absorption spectra of samples containing 0.1% (w/v) SWNTs and 1% (w/v) Trix.<sup>24</sup> Increasing the amount of sonication resulted in SWNT dispersions that gave absorption spectra displaying bands arising from the van Hove singularities. The absorbance arising from these electronic transitions increased dramatically during the first 5–10 min of sonication, after which the absorbance continued to increase more gradually.<sup>24</sup>

In the current study, we carried out a similar investigation using samples containing 0.1% (w/v) SWNTs and either 0.1% (w/v) or 1% (w/v) of different macrocyclic ligands. Most of the latter molecules proved effective at dispersing the nanotubes. For example, Fig. 2a shows a representative series of absorption spectra obtained by sonicating a sample containing SWNTs and C6S for different periods of time. Although the spectra of this and other dispersions containing macrocyclic dispersants did not display bands arising from the van Hove singularities that were as sharply resolved as those seen previously in the spectra of SWNT/Trix dispersions,<sup>24</sup> in each case absorbance increased in a regular fashion at all wavelengths with increasing sonication time. This is illustrated by Fig. 2b, which shows how the absorbance at a specific wavelength (810 nm) increased as a function of sonication time for all dispersions produced using macrocyclic dispersants, as well as that made using Trix. In each of the graphs shown in Fig. 2b, absorbance has either reached or is nearing a plateau region after approximately 30 min. Similar results were obtained when the absorbance at other wavelengths (*e.g.* 660 nm) was plotted as a function of sonication time (Fig. S1a†). However, in the case of dispersions produced using PTS and TSP, absorbance data in the vicinity of this wavelength could not

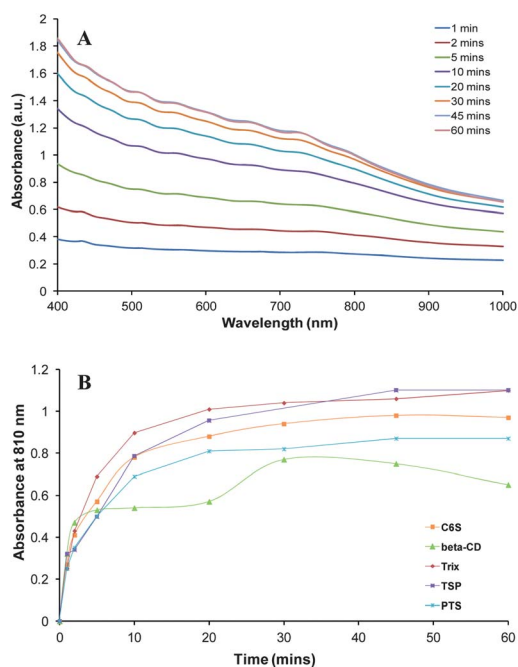
be used owing to strong absorbance by these macrocyclic ligands in this region of the spectrum (Fig. S1b†).

The results presented in Fig. 2b show that subjecting the samples to sonication times greater than 30 min did not result in a significant increase in exfoliation (degree of dispersion) of the SWNTs. Hence a 30 min sonication time was considered optimal for dispersing the SWNTs, and was used for the preparation of all dispersions used to make buckypapers. The dispersions were found to be stable for periods longer than that required to complete the vacuum filtration procedure used to prepare the buckypapers. A similar series of results was obtained in our previous study involving SWNT dispersions prepared using various biopolymer dispersants.<sup>24</sup> On that occasion we monitored the absorbance of the dispersions at 660 nm as a function of sonication time.

The physical appearance of SWNT dispersions prepared using the different macrocyclic ligands was examined immediately after their preparation using optical microscopy. Dispersions produced using Trix, C6S, PTS and TSP all appeared homogeneous, with no solid aggregates of non-stabilized carbonaceous material apparent. In contrast, the dispersion produced using  $\beta$ -CD showed evidence of significant aggregation (data not shown). This confirms that this particular macrocyclic ligand was not as effective as most of the others or Trix at exfoliating the SWNTs.

### Preparation of SWNT buckypapers containing macrocyclic ligands

The results presented in the previous section demonstrate that it is possible to produce dispersions containing SWNTs using a diverse range of macrocyclic ligands. This enabled the preparation of free-standing buckypapers by vacuum filtration of the dispersions onto either PTFE or PVDF support membranes. As one of the aims of this work was to produce buckypapers with varying permeability characteristics owing to the incorporation of different macrocyclic dispersants, it was important to obtain evidence that indicated the latter molecules had been retained in these membranes. Table 1 compares the microanalytical data obtained for buckypapers composed of SWNT/Trix, SWNT/C6S, SWNT/ $\beta$ -CD, SWNT/PTS and SWNT/TSP, with that of the initial SWNT starting material from which they were prepared. Microanalysis of the latter showed that it contained a very small amount of nitrogen and essentially no sulfur. In contrast, each of the buckypapers produced using the macrocyclic ligand dispersants contained significant amounts of sulfur. This is consistent with retention of dispersant molecules, each of



**Fig. 2** (a) UV-vis spectra of a SWNT/C6S dispersion as a function of sonication time. (b) Effect of increasing sonication time on the absorbance at 810 nm of SWNT dispersions containing different macrocyclic ligands.

**Table 1** Microanalytical data for SWNT buckypapers and SWNT starting material. The error in each case is  $\pm 0.1\%$

Samples	Elemental composition (%)			
	C	H	N	S
P0348 SWNTs	85.1	0.7	0.1	0.0
SWNT/Trix	78.3	0.8	0.5	0.0
SWNT/C6S	76.9	1.0	0.4	1.0
SWNT/ $\beta$ -CD	79.1	0.9	0.3	0.5
SWNT/PTS	64.5	0.4	4.7	3.5
SWNT/TSP	68.9	1.7	1.3	2.0

which contained either sulfate or sulfonate groups, in the membranes. Both the SWNT/C6S and SWNT/ $\beta$ -CD buckypapers gave nitrogen analyses which were only slightly greater than that of the SWNT starting material, as expected owing to the lack of this particular atom in these dispersants. However, the SWNT/TSP and SWNT/PTS buckypapers gave nitrogen analysis results of 1.28% and 4.73%, respectively. This provides further proof that these dispersants had been retained to some extent in the membranes.

The results presented in Table 1 also show that all buckypaper samples contained significantly lower amounts of carbon compared to the SWNT starting material. This is also attributable to incorporation of the dispersant molecules, which contained a lower percentage of carbon, and a higher percentage of other elements, than what is found in the starting material. Taken together, the microanalytical results strongly suggest the presence of dispersant molecules within SWNT buckypaper samples, thereby raising the prospect of having access to materials with a range of molecular recognition properties for nanofiltration and other applications. Combining the data provided in Table 1 for each buckypaper reveals that the total elemental compositions do not equate to 100%. This is largely because the buckypapers were not analysed for oxygen, which would have been present owing to the presence of many oxygen atoms in the structures of the dispersants. In addition, the SWNT starting material is likely to have contained some iron impurity, resulting from the catalyst used in the HiPco process.

The buckypapers were also analysed using energy dispersive X-ray spectroscopy (EDX) to obtain further evidence for the presence of elements that could only be attributed to the presence of dispersant molecules. The EDX spectrum of the SWNT starting material showed peaks corresponding to the elements chlorine and iron, in addition to that arising from carbon. The presence of iron is not surprising as iron catalysts are used during synthesis of SWNTs *via* the HiPco process. Chlorine may have been introduced into the original sample of SWNTs as a result of the purification process used, in which catalytic iron particles are typically removed by treatment with an acid such as HCl. Not surprisingly, EDX spectra of all buckypaper samples showed an identical series of peaks indicating the presence of carbon, iron and chlorine from the SWNT starting material. Furthermore, a peak due to the presence of titanium was also identified in the

EDX spectrum of many buckypaper samples. This was attributed to degradation of the titanium sonicator tip used to prepare the initial dispersions from which the buckypapers were produced. It is important to note that the EDX spectra of both the SWNT starting material and SWNT/Trix buckypaper (Fig. 3a) did not contain a signal attributable to the presence of sulfur in these samples. In contrast, the EDX spectrum of a SWNT/ $\beta$ -CD buckypaper (Fig. 3b) showed a peak at  $\sim 2.3$  keV attributable to this element. This peak was also present in the EDX spectra of the SWNT/PTS and SWNT/TSP buckypapers, providing further support for the inclusion of these sulfur-containing dispersants in the buckypapers (Fig. S2†).

### Physical properties

Mechanical strength is an important property that a membrane must exhibit if it is to be used for separation applications. This is because the membrane must be able to survive the application of a range of pressure and flow rates for an extended period, and possibly high working temperatures as well. An investigation of the mechanical properties of the buckypapers was therefore undertaken using the tensile test method, with representative results obtained shown in Fig. 4. All plots show an initial linear stress–strain relationship indicative of elastic deformation. However, small deviations from these linear relationships were observed at higher strains, suggesting the materials have a highly brittle failure mechanism. Fracture was observed at very low strains of approximately 1–3% in all cases. The mechanical properties determined from the stress–strain curves were the Young's modulus, tensile strength, breaking extension or ductility, and toughness. The values obtained for the buckypapers are summarised in Table 2.

The values obtained for each of the four measured parameters fall within relatively narrow ranges, and are generally comparable to those obtained previously for buckypapers. For example, buckypapers obtained from dispersions containing SWNTs and surfactants exhibited Young's moduli that fall between 0.5 and 2.3 GPa, tensile strengths within the range 4.7–33 MPa, and ductility ranging from 1–2.5%.<sup>8,25–27</sup> The similarity between the mechanical properties of the buckypapers examined here may be due to the similar size of the dispersants present in the membrane. Consistent with this hypothesis are the results of a recent study that showed that the tensile strength of buckypapers made from SWNTs was significantly improved only when

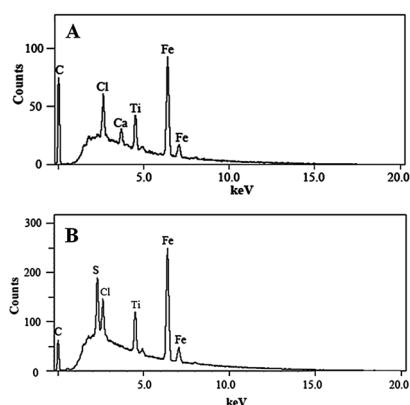


Fig. 3 EDX spectra of: (a) SWNT/Trix and (b) SWNT/ $\beta$ -CD buckypapers.

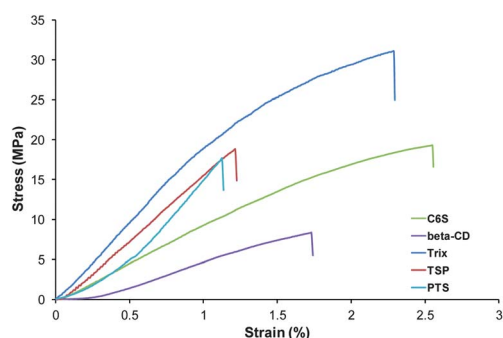


Fig. 4 Representative stress–strain curves for SWNT buckypapers.

**Table 2** Physical properties of buckypapers. Values shown are the average of at least 3 samples, with the errors reported determined from the standard deviation obtained from all measurements

Sample	Young's modulus (GPa)	Tensile strength (MPa)	Ductility (%)	Toughness (J g <sup>-1</sup> )	Electrical conductivity (S cm <sup>-1</sup> )	Contact angle (°)
SWNT/Trix	1.7 ± 0.3	20 ± 10	3.2 ± 0.5	0.3 ± 0.2	85 ± 2	54 ± 4
SWNT/ $\beta$ -CD	0.6 ± 0.1	6 ± 3	1.7 ± 0.7	0.06 ± 0.04	170 ± 20	49 ± 7
SWNT/C6S	0.98 ± 0.04	18 ± 4	2.4 ± 0.8	0.3 ± 0.2	48 ± 10	89 ± 8
SWNT/PTS	2.0 ± 0.3	15 ± 6	1.3 ± 0.3	0.05 ± 0.03	220 ± 60	56 ± 4
SWNT/TSP	1.3 ± 0.6	13 ± 9	1.1 ± 0.3	0.07 ± 0.05	30 ± 20	28 ± 7

high molecular mass dispersants, such as proteins or polysaccharides, were incorporated into the membranes.<sup>24</sup>

The thermal stability of the buckypapers was explored using thermogravimetric analysis. Representative TGA curves are presented for two buckypapers in Fig. 5. In all cases a small loss of mass was observed when the sample was heated to 100 °C, which can be attributed to evaporation of residual water trapped within the material. The mass of the samples remained relatively constant until temperatures between 200 and 300 °C were reached. At this point there was then a sharp decrease in mass of the samples that continued until the temperature reached approximately 600 °C. This loss of mass is attributable to decomposition of the dispersant molecules, followed by the SWNTs themselves. There was no further significant decrease in mass for any of the buckypaper samples between 600 and 1000 °C.

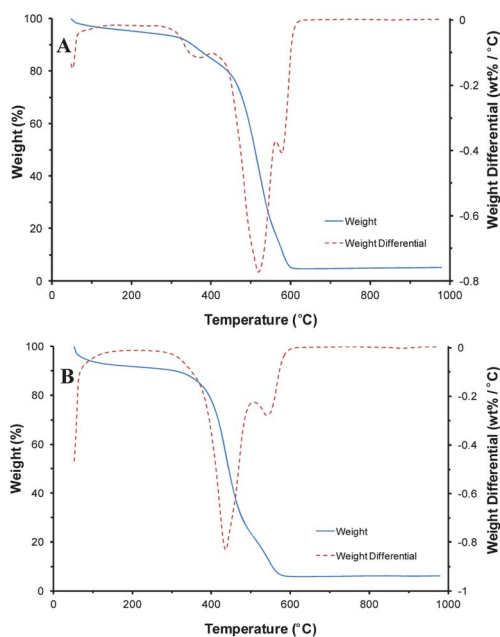
The electrical properties of the buckypapers was investigated, as it has been shown that conductive membranes can prove advantageous for separations applications by providing an additional means to display selectivity towards solutes when subjected to an electric potential.<sup>28,29</sup> In order to determine the conductivity of buckypapers produced in this study, a 2-point probe method was employed.<sup>18,24</sup> The conductivities of the

buckypapers were found to vary significantly in response to changes in the dispersant used during their preparation (Table 2). For example, the conductivity of a SWNT/PTS buckypaper was the highest determined, at 220 ± 60 S cm<sup>-1</sup>, while the value obtained for SWNT/TSP buckypapers, 30 ± 20 S cm<sup>-1</sup>, was the lowest observed. In the case of SWNT/Trix buckypapers, the 2-point probe method gave an electrical conductivity of 85 ± 2 S cm<sup>-1</sup>, in good agreement with our previous investigation.<sup>24</sup>

As part of our evaluation of the potential of buckypapers to act as filtration membranes, an investigation of their wettability was undertaken by measuring the buckypaper-water contact angle. Table 2 shows that all the buckypapers were generally hydrophilic in nature with contact angles varying between 28 ± 7° and 89 ± 8°. It was impossible to determine if a relationship exists between the identity of the dispersant molecules trapped within a buckypaper and its contact angle, owing to the lack of quantitative information concerning the amount of macrocyclic ligand incorporated. However, it is worth noting that incorporation of  $\beta$ -CD, TSP or PTS resulted in a membrane of either comparable or greater hydrophilicity compared to that obtained when Trix was used as the dispersant. This is not surprising in view of the presence of multiple highly polar, charged functional groups, such as sulfonic acid residues, in these dispersants. The one exception to the above general trend was observed when the dispersant used was C6S, which resulted in a SWNT/C6S buckypaper that was less hydrophilic than SWNT/Trix. Therefore with the possible exception of the SWNT/C6S buckypaper, all of the membranes examined would be expected to interact favourably with aqueous solutions, a necessary condition for them to be useful as filtration media.

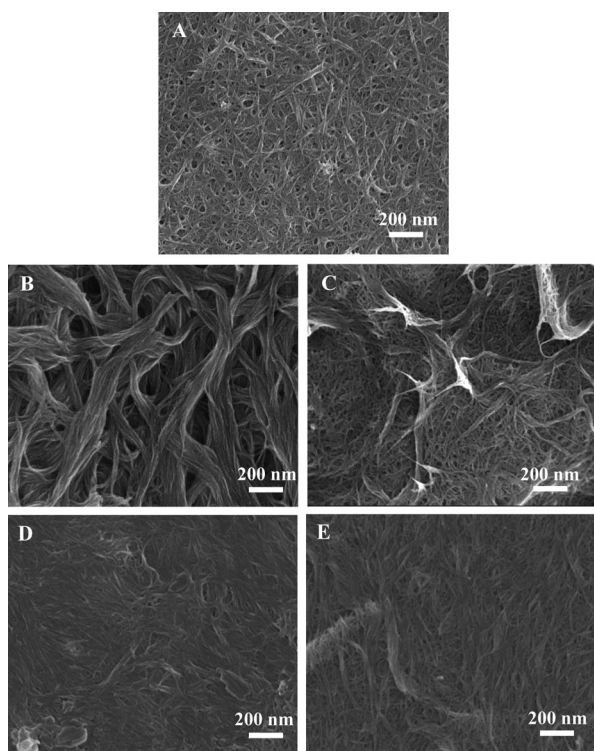
### Surface morphology

The surface morphology of buckypapers was examined using scanning electron microscopy (SEM). Representative images of each of the materials examined are shown in Fig. 6. Each of the buckypaper micrographs show a randomly entangled mat of SWNTs, with the diameter of the pores and other surface features highly dependent on the identity of the dispersant used. Examination of the SEM image of a SWNT/Trix buckypaper (Fig. 6a) revealed a highly porous surface structure, and similar overall morphology to that observed in previous work.<sup>30</sup> It is clear from this figure that the membrane possesses a large number of irregularly sized pores, with image analysis revealing an average surface pore diameter of 23 ± 7 nm (Table 3). This agrees well with previous studies which showed that the surface pore sizes of buckypapers containing SWNTs vary between 10 and 100 nm in diameter.<sup>8,18</sup>



**Fig. 5** TGA curves for: (a) SWNT/PTS and (b) SWNT/TSP buckypapers showing the weight loss and weight differential between room temperature and 1000 °C.





**Fig. 6** Scanning electron microscope images of different buckypapers imaged at 70k magnification: (a) SWNT/Trix, (b) SWNT/ $\beta$ -CD, (c) SWNT/C6S, (d) SWNT/PTS and (e) SWNT/TSP.

The introduction of macrocyclic dispersants into the structure of the buckypapers resulted in significant changes to their surface morphology compared to SWNT/Trix. For example, the SEM micrograph of a SWNT/ $\beta$ -CD membrane (Fig. 6b) revealed a surface morphology consisting of large bundles of nanotubes, with the diameters of the bundles often exceeding 100 nm, and pore sizes considerably larger than those found for the SWNT/Trix membrane. Image analysis of the SWNT/ $\beta$ -CD buckypaper gave an average surface pore diameter of  $49 \pm 38$  nm (Table 3). On the other hand, the SWNT/C6S buckypaper (Fig. 6c) possessed a morphology that showed some similarities to that of the SWNT/Trix buckypaper. Buckypapers prepared from dispersions containing the PTS and TSP dispersants gave surface morphologies which were different to those obtained for the other membranes (Fig. 6d and e). Image analysis of the SWNT/TSP buckypaper gave an average surface pore diameter of only  $7 \pm 3$  nm, which was the smallest obtained for any buckypaper.

**Table 3** Surface morphological and internal pore properties of buckypapers

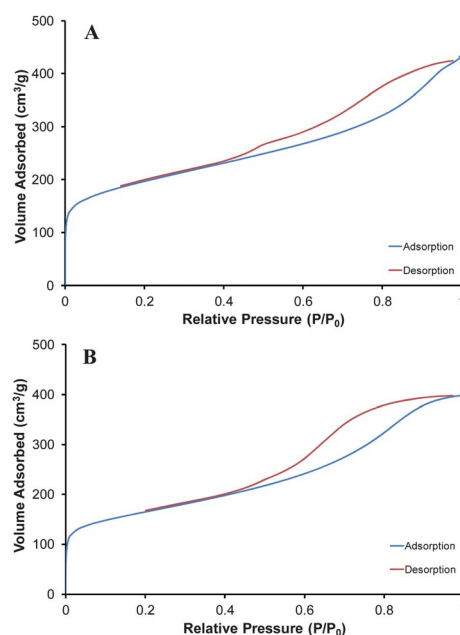
Sample	Average surface pore diameter $D_{SEM}$ (nm) <sup>a</sup>	Surface area derived from BET $A_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	Average internal pore diameter $d_{BET}$ (nm)	Average nanotube bundle diameter $D_{bun}$ (nm)	Interbundle pore volume (%)
SWNT/Trix	$23 \pm 7$	$790 \pm 4$	$4.0 \pm 0.4$	$3.4 \pm 0.1$	$84 \pm 5$
SWNT/ $\beta$ -CD	$49 \pm 38$	$690 \pm 4$	$4.0 \pm 0.4$	$3.9 \pm 0.1$	$93 \pm 6$
SWNT/C6S	$27 \pm 14$	$580 \pm 3$	$4.0 \pm 0.4$	$4.6 \pm 0.1$	$76 \pm 5$
SWNT/PTS	<sup>b</sup> $30 \pm 1$	$30 \pm 1$	$27 \pm 3$	$90 \pm 3$	$78 \pm 5$
SWNT/TSP	$7 \pm 3$	$360 \pm 4$	$2.0 \pm 0.2$	$7.4 \pm 0.1$	<sup>c</sup>

<sup>a</sup> Average surface pore diameter determined by scanning electron microscopy. All other parameters determined through analysis of results obtained from nitrogen adsorption/desorption isotherms. <sup>b</sup>  $< 5$  nm (limit of image analysis resolution). <sup>c</sup> Could not be calculated due to insufficient data points.

In the case of a SWNT/PTS buckypaper, image analysis could not be used to obtain an estimate of the average surface pore diameter, owing to the very small size of the surface features imaged.

### Surface area

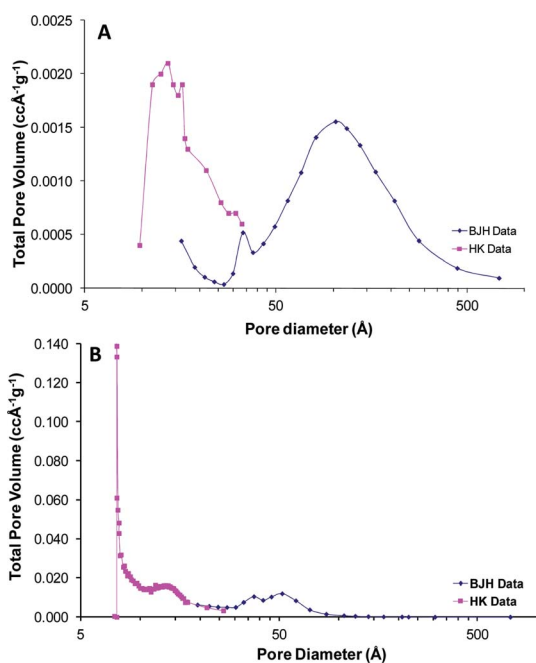
In order to further enhance our understanding of the internal pore structure of the buckypaper samples, nitrogen adsorption/desorption isotherms were obtained and analysed. Prior to analysis, samples were de-gassed under vacuum at 200 °C to remove any loosely adsorbed dispersant molecules, as thermogravimetric analysis confirmed the stability of all samples at this elevated temperature. Fig. 7 shows examples of the typical isotherms obtained. SWNT buckypapers exhibited a general type IV isotherm with hysteresis at higher relative pressures. Hysteresis occurs in porous materials as a result of differences between the rate of filling and removal of the adsorbent, which occurs by a capillary condensation mechanism.<sup>31</sup> The results obtained with all SWNT buckypapers confirmed the presence of a large proportion of mesopores (2–50 nm), consistent with the SEM results.



**Fig. 7** Nitrogen adsorption (blue)/desorption (red) isotherms for: (a) SWNT/ $\beta$ -CD and (b) SWNT/C6S buckypapers.

The changes in  $N_2$  adsorption/desorption at relative pressures ( $P/P_0$ ) below 0.1 can be attributed to the presence of micropores with diameters  $<2$  nm. These are believed to be the interstitial pores, which consist of channels between individual nanotubes within CNT bundles.<sup>32</sup> Barrett, Joyner, and Halenda (BJH) and Horvath–Kawazoe (HK) analysis of the  $N_2$  isotherms was used to calculate the pore size distribution within the BPs.<sup>19,20</sup> HK analysis enabled calculation of the distribution of small pores ( $<2$  nm), while the BJH method allowed estimation of the larger pores. Combining the two sets of results yielded pore size distribution curves such as those shown for SWNT/C6S and SWNT/ $\beta$ -CD buckypapers in Fig. 8. There was good agreement in the crossover region between both analysis methods at approximately 2 nm for all BPs. The distribution of pore sizes reveals a large peak at  $\sim 0.7$  nm, which can be attributed to the interstitial pores. A broad distribution of peaks is also present in both cases between 1 and 100 nm, which is attributed to larger pores whose openings were observable *via* SEM. Numerical integration of the curves in Fig. 8 revealed that these larger interbundle pores are responsible for  $76 \pm 5\%$  of the total free volume of the SWNT/C6S buckypaper, and  $93 \pm 6\%$  for the SWNT/ $\beta$ -CD buckypaper. When this analysis was repeated using data for the other SWNT buckypaper samples, the results presented in Table 3 were obtained. The interbundle pore volumes ranged between 76 and 95% amongst different buckypaper samples. These results are in good agreement with previous reports for SWNT buckypapers made using Trix as the dispersant ( $66 \pm 7\%$ ).<sup>8</sup>

The specific surface area (of the SWNT buckypapers was calculated by the Brunauer, Emmett and Teller (BET) method, and found to vary between 30 and  $800 \text{ m}^2 \text{ g}^{-1}$  (Table 3). The value



**Fig. 8** Pore size distributions of buckypapers derived by applying the HK method (pink line) and BJH method (blue line) to data obtained from nitrogen adsorption/desorption isotherms: (a) SWNT/ $\beta$ -CD and (b) SWNT/C6S.

for SWNT/Trix was in close agreement with those reported previously for other CNT membranes.<sup>8,32</sup> For example, similar SWNT buckypapers prepared using dispersions obtained using Trix and ethanol were shown to possess specific surface areas of  $611 \text{ m}^2 \text{ g}^{-1}$  and  $642 \text{ m}^2 \text{ g}^{-1}$ , respectively.<sup>10,32</sup> Most buckypapers exhibited surface areas ( $A_{\text{BET}}$ )  $> 350 \text{ m}^2 \text{ g}^{-1}$ . The one exception to this general rule was SWNT/PTS, which displayed a much smaller surface area ( $A_{\text{BET}} = 30 \text{ m}^2 \text{ g}^{-1}$ ). Average pore diameters ( $d_{\text{BET}}$ ) calculated using the BET method ranged from 2–27 nm in diameter (Table 3). In general, these values are smaller than those determined by SEM, as secondary and back scattered imaging does not reveal the interstitial pores. By neglecting the contribution due to interstitial pores,  $A_{\text{BET}}$  can also be used to calculate an approximate nanotube bundle diameter ( $D_{\text{bun}}$ ) for each buckypaper, using eqn (1):

$$A_{\text{BET}} = \frac{4}{\rho_{\text{CNT}} D_{\text{bun}}}, \quad (1)$$

and a theoretical CNT bundle density ( $\rho_{\text{CNT}}$ ) of  $1500 \text{ kg m}^{-3}$ .<sup>25</sup> The resulting values range between 3 and 90 nm and are summarised in Table 3. These values are small when compared to what was observed in the SEM images, and should be considered a lower limit.

Reproducible pore structures in membranes are an important feature for industrial filtration applications. To our knowledge, there has been no prior work performed using BET to look at the consistency of the internal pore structure in different samples of the same type of buckypaper. The reproducibility of our buckypaper synthesis was investigated by preparing two SWNT/Trix buckypapers, each measuring  $8 \text{ cm} \times 5 \text{ cm}$ . The average surface areas of the two membranes were  $794 \pm 4$  and  $843 \pm 6 \text{ m}^2 \text{ g}^{-1}$ , while their average internal pore diameters were  $5 \pm 0.5$  and  $4 \pm 0.4$  nm. This is a good indication that the method used for preparing these membranes was reproducible.

### Permeability studies of buckypapers

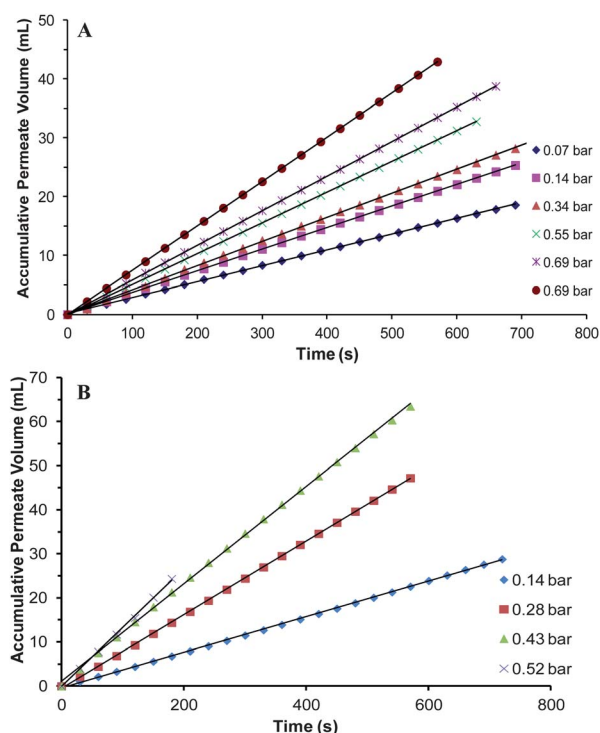
The results presented in the previous section demonstrate that it is possible to incorporate different macrocyclic ligands into SWNT buckypapers, to produce membranes which are mechanically robust and hydrophilic. These properties are ideal for membranes with potential applications in microfiltration or nanofiltration. In order to further investigate the suitability of the buckypapers for these and other applications, their permeability towards water was determined using a custom-made dead end filtration apparatus.

All buckypaper membranes investigated here were permeable to water at less than 1 bar (Table 4). Representative water permeability plots for two buckypapers (SWNT/Trix and SWNT/PTS) are shown in Fig. 9. In all filtration experiments, the accumulative permeate volume increased linearly as a function of time and a stable permeate flux ( $J$ ) could be obtained from the slope at each of the applied pressures. The permeate flux was observed to increase for all buckypapers as a function of applied pressure until membrane rupture occurred. The pressure required to initiate water transport across the membranes varied between 0.07 and 0.8 bar, and membrane rupture occurred between 0.7 and 1.4 bar (Table 4).

**Table 4** Membrane flux ( $f$ ), water transport initiation pressure, membrane rupture pressure and thickness of different buckypapers and commercial membranes<sup>a</sup>

Samples	Membrane flux ( $f$ ) ( $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )	Water transport initiation pressure (bar)	Rupture pressure (bar)	Membrane thickness ( $\mu\text{m}$ )
SWNT/Trix	$83 \pm 5$	$0.07 \pm 0$	$1.2 \pm 0.3$	$36 \pm 4$
SWNT/ $\beta$ -CD	$160 \pm 50$	$0.5 \pm 0.4$	$1.1 \pm 0.5$	$66 \pm 5$
SWNT/C6S	$800^b$	$0.9^b$	$1.4^b$	$44 \pm 4$
SWNT/PTS	$2400 \pm 1300$	$0.4 \pm 0.3$	$1.0 \pm 0.5$	$41 \pm 5$
SWNT/TSP	$1000^b$	$0.2^b$	$0.7^b$	$41 \pm 4$
0.22 $\mu\text{m}$ PTFE	$1900 \pm 300$	$0.07 \pm 0$	$c$	$120 \pm 10$
5.0 $\mu\text{m}$ PTFE	$7000 \pm 1000$	$0.07 \pm 0$	$c$	$129 \pm 10$

<sup>a</sup> Values shown are the average and standard deviation of 2 or 3 samples. <sup>b</sup> Only one membrane sample was measured. <sup>c</sup> Did not rupture over the range of applied pressures investigated.



**Fig. 9** Water permeability plots for selected buckypapers obtained using applied pressures between 0.07 and 1.0 bar: (a) SWNT/Trix and (b) SWNT/PTS.

By plotting the permeate flux rate for each buckypaper as a function of the applied pressure, a series of linear relationships such as those shown in Fig. 10 were obtained. The membrane flux ( $f$ ) was determined using eqn (2):

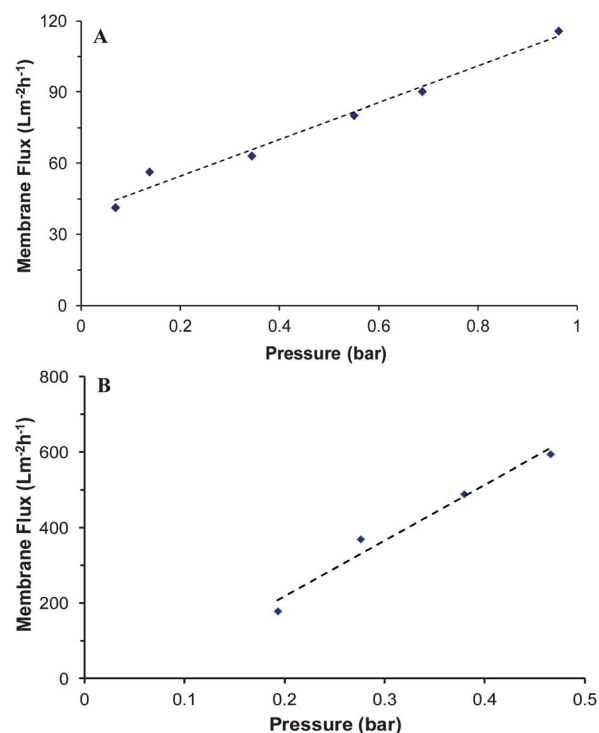
$$f = \frac{J}{A\Delta P}, \quad (2)$$

where  $J$  represents the slopes of the plots shown in Fig. 9 and  $A$  is the effective membrane area exposed to water.

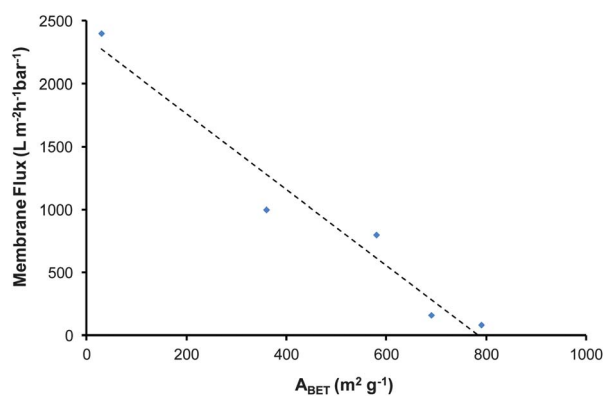
Changing the dispersant present in a SWNT buckypaper from Trix to one of the macrocyclic ligands resulted in significant increases in permeability towards water in all cases. The most dramatic increase in permeability was exhibited by SWNT/PTS buckypapers, which displayed an average membrane flux of  $2400 \pm 1300 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ , which is almost 30 times greater

than the average obtained for the SWNT/Trix buckypapers ( $83 \pm 5 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ ). The membrane flux for the SWNT/PTS buckypapers was even greater than that of commercial 0.22  $\mu\text{m}$  PTFE membranes ( $1900 \pm 300 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ ), but less than that of 5.0  $\mu\text{m}$  PTFE membranes ( $7000 \pm 1000 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ ). Replacement of the surfactant Trix with the PTS dispersant therefore clearly introduces a more water permeable structure into the buckypaper. The exact cause of the variation in permeability of the two SWNT/PTS buckypapers is not clear at this stage. However, it is worth noting that the amount of time taken to filter SWNT/PTS dispersions was typically much longer (>10 hours) than that required to filter SWNT/Trix dispersions (3–4 hours).

Further evidence of the impact varying the dispersant can have on the aqueous permeability of buckypapers is provided by inspection of the membranes fluxes for SWNT/TSP, SWNT/ $\beta$ -CD and SWNT/C6S in Table 4. These were  $1000 \pm 500$ ,  $160 \pm 50$



**Fig. 10** Effect of applied pressure on the permeate flux ( $J$ ) of different buckypapers: (a) SWNT/Trix, (b) SWNT/PTS.



**Fig. 11** Effect of membrane surface area ( $A_{\text{BET}}$ ) on permeability towards water displayed by SWNT buckypapers.

and  $800 \pm 100 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , respectively. The smallest increase in permeability (relative to a SWNT/Trix buckypaper) was a factor of two displayed by the SWNT/ $\beta$ -CD buckypaper, whereas the remaining two membranes were at least ten times more permeable than SWNT/Trix. For the SWNT buckypapers prepared using low molecular mass dispersants, there was no discernible correlation between membrane flux and either average surface pore size (determined by SEM) or the BET-derived average internal pore size ( $D_{\text{BET}}$ ). Despite this, it is noteworthy that the most permeable buckypaper (SWNT/PTS) possessed an average nanotube bundle diameter of  $90 \pm 3 \text{ nm}$  which was more than ten times greater than that of any of the other materials examined. Perhaps even more significantly, the average internal pore diameter of the SWNT/PTS buckypaper ( $27 \pm 3 \text{ nm}$ ) was at least five times greater than that of any other SWNT membranes examined in this study. The presence of significantly larger internal pores in the SWNT/PTS buckypapers would be expected to facilitate faster transport of water molecules.

The permeability of the buckypapers towards water was found to increase linearly with decreasing membrane surface area, as determined by BET. The linear fit in Fig. 11 ( $R^2 = 0.956$ ) suggests that the membrane flux is inversely proportional to the surface area according to eqn (3):

$$J = c \frac{1}{A_{\text{BET}}} + J_0, \quad (3)$$

where  $c$  and  $J_0$  are constants. It is likely that  $J_0$  could represent the limiting membrane flux attainable with this type of membrane, which is likely to be highly dependent on the preparation conditions employed to prepare the buckypaper, *i.e.* sonication and filtration conditions. The inverse dependence on  $A_{\text{BET}}$  is consistent with the hypothesis that a membrane with lower surface area will have larger pores on its surface, which would be expected to increase membrane flux. However, further research is necessary to confirm this hypothesis.

## Conclusions

Single-walled carbon nanotube dispersions were successfully obtained using a range of functional dispersant molecules. Buckypapers were produced from the dispersions using vacuum filtration onto a commercial substrate. Although some

dispersions containing macrocyclic dispersants were not as homogeneous as those made using Trix, UV-vis spectroscopy confirmed that all dispersions remained relatively stable throughout the filtration timeframe required to prepare the buckypapers. The retention of dispersant molecules in the buckypapers was confirmed by microanalytical results and EDX spectra, both of which confirmed the presence of elements that could only be attributed to the dispersants. Buckypapers displayed modest conductivity ( $30\text{--}220 \text{ S cm}^{-1}$ ), good mechanical integrity (Young's modulus =  $0.6\text{--}2 \text{ GPa}$ ) and a hydrophilic surface ( $28\text{--}89^\circ$ ), making them ideal candidates as filtration membranes. All buckypapers were shown to be highly porous by SEM and BET analysis, and subsequently were found to be permeable to water at low applied pressures ( $<1 \text{ bar}$ ). The permeability of the membranes towards water was also strongly dependent on the identity of the dispersant incorporated into the membrane, which was found to significantly affect the morphology of the buckypaper. The SWNT/TSP and SWNT/PTS buckypapers showed the highest permeability towards water with membrane fluxes of  $1000$  and  $2400 \pm 1300 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , respectively. Although these values are considerably less than those reported previously for SWNT buckypapers prepared using organic solvents,<sup>9,12</sup> it must be remembered that the latter materials consisted of very thin layers of SWNTs deposited on a highly porous commercial PVDF membrane, which conferred mechanical integrity on the entire composite. The permeabilities reported here therefore represent the first values obtained for mechanically robust, free-standing SWNT membranes.

The production of a material (SWNT/PTS) that displayed a permeability towards water that was at least comparable, if not greater than that of a commercial membrane ( $0.22 \mu\text{m}$  PTFE) was a significant result, as this suggests that some buckypapers might be sufficiently efficacious for commercial membrane applications. It is therefore instructive to analyse the physical and morphological properties of the SWNT/PTS buckypaper in order to determine what characteristics might be most important to modify to obtain membranes that are viable for specific applications. Although the SWNT/PTS buckypaper was three times thinner than the commercial membrane, its average surface pore diameter ( $<5 \text{ nm}$ ) and average internal pore diameter ( $27 \pm 3 \text{ nm}$ ) are significantly smaller. The membrane flux of the SWNT/PTS buckypapers therefore most likely reflects the high intrinsic permeability towards liquids and gases previously reported by other researchers for CNTs in theoretical studies,<sup>5,6</sup> as well as favourable changes to membrane pore structure induced by the presence of the PTS dispersant.

While no clear correlation could be discerned between surface or internal morphological features of the buckypapers and their permeabilities towards water, the data obtained for the SWNT/PTS membranes offers some clues regarding the factors which may determine buckypaper permeability. It may be especially pertinent that of all the SWNT buckypapers examined, SWNT/PTS exhibited the smallest average surface pore diameter and surface area, and the largest average internal pore diameter and average nanotube diameter. This suggests that the surface of the SWNT/PTS buckypapers are covered with very small diameter pores that lead to much larger internal pores whose walls are supported by thick nanotube bundles. Such a structure may encourage rapid movement of water molecules near the

membrane–solvent interface through the narrow surface pore openings into much larger internal pore cavities. It is therefore of interest to explore the effect of varying conditions such as the sonication time used for preparing the dispersions from which the buckypapers were made, on the surface area and pore structure of the latter, as this might lead to some general principles for modifying these properties in a systematic and favourable manner. In a preliminary experiment, we prepared a SWNT/Trix buckypaper under identical conditions to that normally used, with the exception that the sonication time employed was shortened from 30 to 15 min. BET analysis of the nitrogen adsorption/desorption isotherm produced using this new material showed that the surface area had been reduced from  $790 \pm 4$  to  $350 \pm 4 \text{ m}^2 \text{ g}^{-1}$ , while the average internal pore diameter increased from  $4 \pm 0.4$  to  $6 \pm 0.4 \text{ nm}$ . Since a smaller surface area and larger internal pores appear to be contributing factors to the greater permeability of SWNT/PTS buckypapers, this suggests that reducing sonication time might be a viable method for producing more permeable membranes of this type.

It is also worth noting that the microanalysis results showed that the carbon content of the SWNT/PTS buckypaper was lower than that of the other membranes examined, and that its nitrogen and sulfur contents were higher. This suggests that PTS was retained to a greater extent than any of the other dispersants in the SWNT buckypapers studied here, which may have been a significant contributing factor to the different structure of this membrane. This suggests that methods for introducing greater numbers of dispersant molecules, such as the use of a higher concentration of dispersant in the initial solution, or covalent attachment, might result in even higher permeabilities for SWNT/PTS and other buckypapers. Work is currently underway to examine these hypotheses, as well as what effects the presence of dispersant molecules has on the permeability of buckypapers towards dissolved solutes.

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