The Binding of Single-Stranded DNA and PNA to Single-Walled Carbon Nanotubes Probed by Flow Linear Dichroism

Jascindra Rajendra and Alison Rodger*[a]

Abstract: The binding of single-stranded DNAs and a neutral DNA analogue (peptide nucleic acid, PNA) to single-walled carbon nanotubes in solution phase has been probed by absorbance spectroscopy and linear dichroism. The nanotubes are solubilised by aqueous sodium dodecyl sulfate, in which the nucleic acids also dissolve. The linear dichroism (LD) of the nanotubes, when subtracted from that due to the nanotubes/nucleic acid samples, gives the LD of the bound nucleic acid. The binding of the single-stranded DNA to the single-walled nanotubes is quite different from that previously observed for double-stranded DNA. It is likely that the nucleic acid bases lie flat on the nanotube surface with the backbone wrapping round the nanotube at an oblique angle in the region of 45°. The net effect is like beads on a string. The base orientation with the single-stranded PNA is inverted with respect to that of the single-stranded DNA, as shown by their oppositely signed LD signals.

Keywords: carbon · DNA · linear dichroism · nanotubes · PNA

Introduction

Carbon nanotubes, a comparatively recently recognised allotrope of carbon,[1–3] are remarkable materials that are presently being widely studied because of their electronic properties and range of potential applications as semiconductors, catalysts, optical devices and so forth.[4,5] Nanotubes are well-ordered hollow graphitic nanomaterials that vary in length from several hundred nanometers to several micrometers and have diameters of 0.4 to 2 nm, for single-walled carbon nanotubes (SWNT), and 2 to 100 nm, for coaxial multiple-walled carbon nanotubes (MWNT), depending on the number of concentric tubes.[6] A SWNT can be described as a single graphene sheet rolled into a tube, whereas a MWNT contains overlapping cylindrical tubes, like a coaxial cable. These tubes are proposed to be either metallic or semiconducting, depending on how the sheet is rolled up and its diameter. One of the attractions of SWNTs is that if they are fabricated with biomacromolecules (proteins, carbohydrates and nucleic acids)[7,6] attached to their surface, they have the potential of being used in antigen recognition, enzyme-catalysed reactions[8] and a wide range of DNA-hybridisation applications.[9]

The literature reports a range of molecules binding to SWNTs,[1–9] but as yet methods for characterizing the interaction, particularly in solution, are lacking. Most of the available literature data on DNA/SWNT systems studied by a wide range of techniques does not refer to the solution phase. A recent report of DNA solubilizing nanotubes described the use of AFM and absorbance spectroscopy to prove they were in solution; however, there was no attempt to characterise the interaction.[10] We have recently shown[11] that Couette flow linear dichroism (LD), the differential absorbance of light polarised parallel and perpendicular to a sample orientation direction, could be used to probe the binding of small aromatic molecules and double-stranded (ds) DNA to SWNTs. Interpretation of the flow LD data ideally requires the spectroscopy of the species being studied to be understood, and in particular their transition moments to be known. In the case of nanotubes, there is very little information in the literature about their spectroscopy in the near and far UV regions. In fact, it is usually assumed that there is none, as this region is dominated by light-scattering artifacts in most spectrometers. We showed[11] that the sample of CNTs (SWNTs formed by arc discharge and purified by refluxing with nitric acid) used in our work has an unstructured UV absorbance spectrum that gives rise to a large negative LD signal with maximum at 225 nm. The sign of this signal means that the dominant transition polarisa-

[a] J. Rajendra, Dr. A. Rodger
Department of Chemistry, University of Warwick
Coventry, CV4 7AL (UK)
Fax: (+44) 24-765-24112
E-mail: a.rodger@warwick.ac.uk

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tion of these SWNTs lies at more than 54.7° from the nanotube long axis, since the reduced LD (LD^r) may be expressed as Equation (1)[12], in which α is the angle between the orientation axis and the transition moment of interest, S is the orientation parameter (1 for perfect orientation and 0 for an unoriented sample) and A is the sample's isotropic absorbance.

$$LD^r = \frac{LD}{A} = \frac{3}{2}S(3\cos^2\alpha - 1) \quad (1)$$

Assuming the SWNT has cylindrical symmetry about its long axis, ligand-binding geometry is best defined in terms of the normal to the cylinder surface. So, in principle the LD could yield the orientation of ligands on the SWNT by using Equation (2)[11,13,14] in which β is the angle the transition moment of interest makes with the normal to the nanotube surface.

$$LD^r = \frac{3S}{4}(1 - 3\cos^2\beta) \quad (2)$$

In practice, at this stage, we are not able to measure the degree of orientation of the SWNT, so our geometric conclusions are qualitative rather than quantitative. An additional application of the LD data was suggested by the fact that spectra of both anthracene and naphthalene were significantly perturbed by the SWNT, and the intensity of the SWNT's signal was also changed. This suggests that LD may also be a means of probing the type of interaction anchoring a ligand onto the SWNT. Before this is really feasible, we need to understand more about the interaction of ligands with SWNTs. In this paper, we use LD to investigate the interaction of a range of different single-stranded (ss) nucleic acids binding to sodium dodecyl sulfate solubilised SWNTs. Literature reports suggest that ss DNA binds better to nanotubes than does ds DNA[15] (ds = double-stranded). A recent report has concluded from surface-enhanced infrared absorption (SEIRA) studies that ss DNA wraps SWNT more efficiently than ds DNA,[16] and the proposed binding geometry may be the reason for this. So, we anticipated that LD could be used to probe the role played by the structure of the ss DNA upon interaction with SWNTs.

Results and Discussion

The DNA absorption spectrum is the net effect of overlapping $\pi \rightarrow \pi^*$ transitions of the purine and pyrimidine bases. These transitions are polarised in the plane of the bases, and when polymeric ds DNA is flow-oriented, their polarisations are all approximately perpendicular to the DNA helix axis.[12] This results in ds DNA having a negative LD signal under its absorbance bands. We showed previously that extensively sonicated double-stranded calf thymus (ct) DNA has no detectable intrinsic LD signal, though it does acquire a small negative LD signal at ~260 nm (the absorbance maximum) when in the presence of SWNTs.[11] To our surprise we found that all the supposedly single-stranded DNAs used in this work have intrinsic LD signals. By way of contrast, duplex DNAs of 250 base pairs scarcely orient.[17] In each case, the ss DNA LD maximum was negative and at the same wavelength as the absorbance maximum. This means that the ss DNAs form long structures in solution.

Preparing solutions of SWNTs in the presence of DNA proved not to be straightforward. When ds DNA was melted in the presence of SWNTs, the sample came out of solution. When sonicated, pre-melted and cooled ds DNA (which should be ss DNA) was added to a solution of SWNTs, everything remained in solution. However, as noted above, the isolated DNA has an intrinsic LD signal (of $\sim 10^{-4}$) even though it had no detectable signal before melting. The effect was much the same whether the DNA was fast cooled (by putting it onto ice) or slow cooled (leaving it to cool at 1 °C min^{-1} in a spectrometer). Single-stranded ct-DNA obtained from Sigma had the same feature. Despite these issues, we believe we are seeing the LD of single-stranded DNA bound to SWNTs in Figure 1c, as the LD difference spectra obtained from subtracting the SWNT LD spectrum from DNA/SWNT LD spectra (Figure 1) has a negative peak at ~275 nm and a positive peak at ~230 nm, rather than a single negative peak at the absorbance maximum near 260 nm.

To understand why the bisignate LD spectrum arises, it is necessary to consider the spectra of the DNA bases, of which each has more than one transition in the region of interest (Figure 2a, b). The fact that the 230 nm region of the spectrum gives a positive LD signal means [following Eq. (2)] that β (the angle between the normal to the nanotube and the transition moment) for these transitions is greater than 55°. In other words, on average the transitions are within 35° of the nanotube long axis. Figure 2c is a schematic diagram indicating the orientations of the base transitions when the bases are linked to a simple backbone and the backbone is wrapped round the nanotube at an inclination angle of ~45°. The 230 nm region transitions of C[18] and A[24] are within 10° of the nanotube axis; this orientation would give a positive LD signal. The 244 and 200 nm transitions of G,[19] which will have some intensity at 230 nm, would also contribute a small positive signal, as oriented in Figure 2c. The T's contribution would be small and negative.[20] The Figure 2c geometry would also result in all bases giving a negative contribution in the ~270 nm region. Although this analysis is by no means definitive, it suggests an orientation that is consistent with the data. The analysis would be improved if it were possible to calculate the LD^r for the spectrum. This is currently hindered by the quality of the absorbance data and the significant contribution made by scattering (which does not follow a simple wavelength–power law).[21,22] It should be noted, however, that the situation in reality is almost certainly a mixture of binding modes. Something like the one proposed may be the dominant one. To avoid the complications introduced by having the transitions of four bases being represented in the spec-

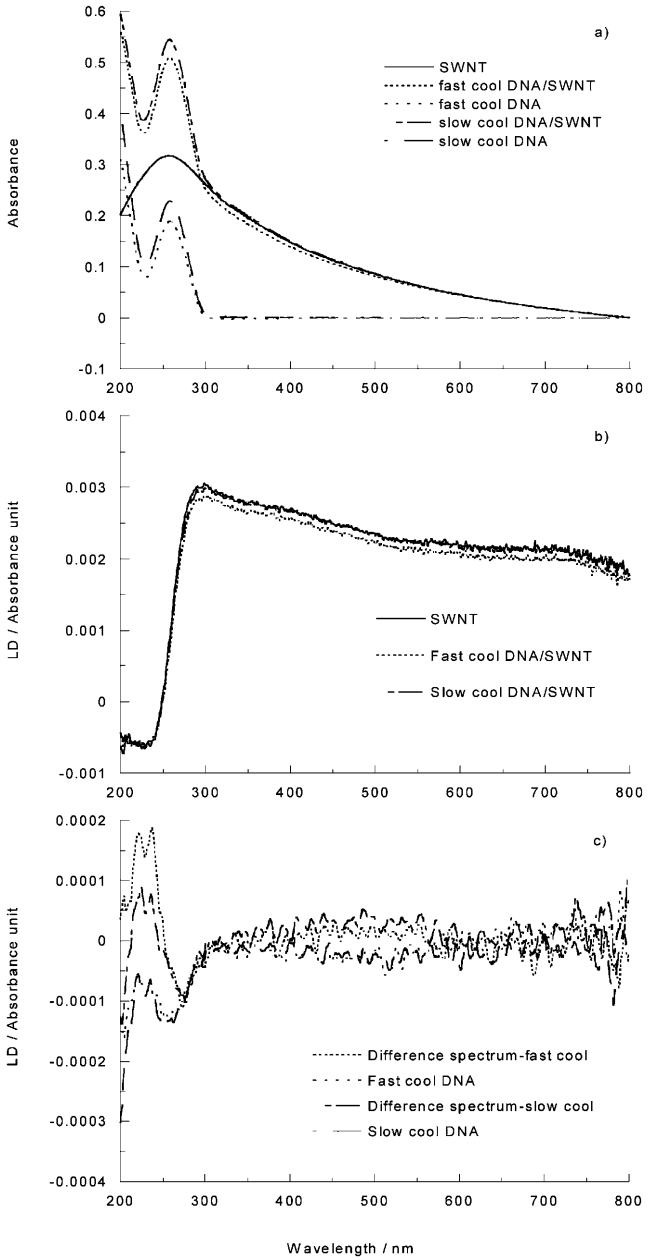

Figure 1. a) Absorbance spectra of SWNT (0.1 mg mL^{-1}), fast-cooled ds DNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex, fast-cooled ds DNA, slow cooled ds DNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex in SDS (9 mM) and slow cooled ds DNA. b) LD spectra of SWNT (0.1 mg mL^{-1}), fast-cooled DNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex and slow-cooled DNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex in SDS (9 mM). c) LD spectra of fast-cooled and slow-cooled DNA in SDS (9 mM) and difference LD spectra of fast-cooled DNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) minus SWNT (0.1 mg mL^{-1}) and slow-cooled DNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) minus SWNT (0.1 mg mL^{-1}) complex, all in (9 mM) SDS. All spectra have SDS (9 mM) baselines subtracted.

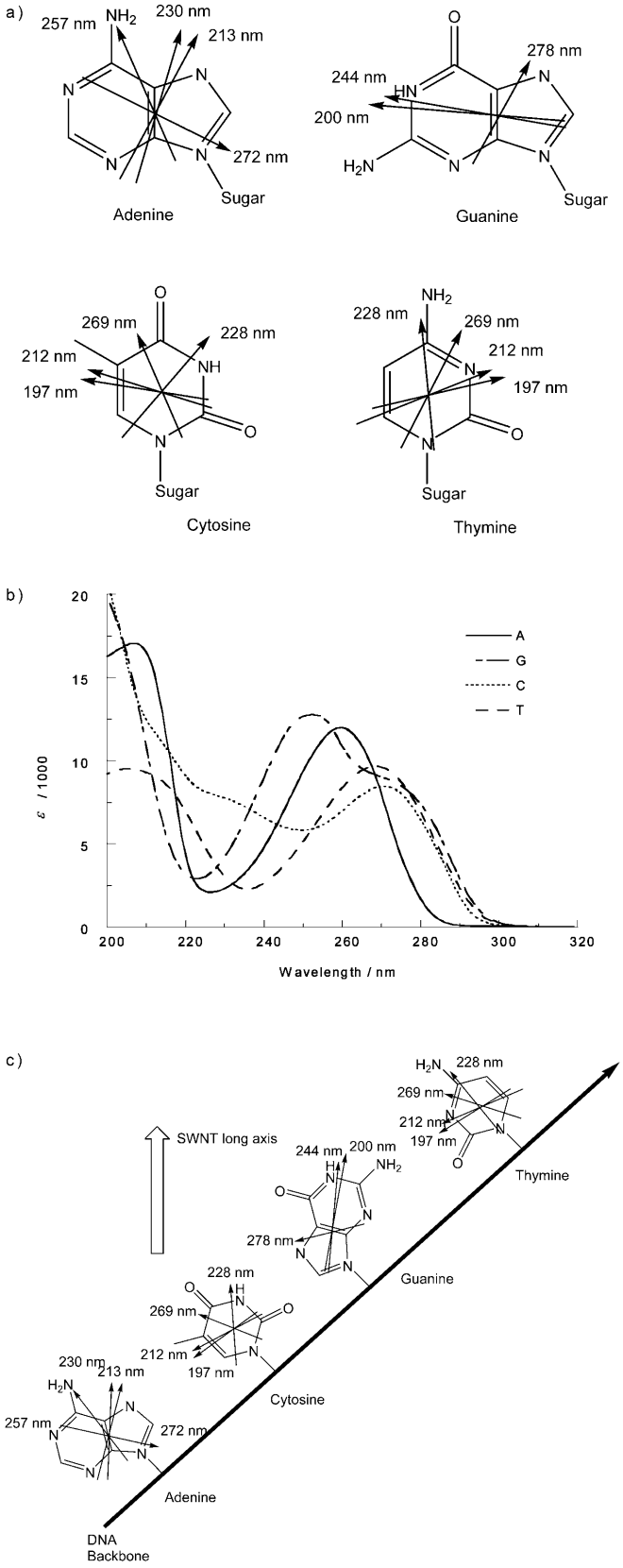

Figure 2. a) Probable transition polarisations for UV transitions of adenine, guanine, cytosine and thymine. b) UV spectra of the DNA nucleotides. c) Schematic diagram of orientation of DNA bases on a SWNT consistent with the observed LD spectra. For PNA the SWNT is rotated 90°.

trum, we also considered synthetic DNAs of well-defined sequence, as discussed below.

From Figure 1a it is apparent that the fast-cooled (though not slow-cooled) DNA assists the solubility of SWNT in

sodium dodecyl sulfate (SDS), as the light scattering of the spectra reduced when fast-cooled DNA is added to the SWNT solution. This DNA also gives a larger low-wavelength DNA LD signal, suggesting its bases prefer lying flat on the SWNT following the above analysis. The fast-cooled DNA absorbance is smaller than that of the same concentration of slow-cooled DNA, suggesting it has more π–π stacking. Rather than implying the fast-cooled DNA has more ds DNA (the usual interpretation of such a hypochromic effect), it may be that the fast-cooled sample is less tangled and so better stacked within its strands. This would also make it more available than the slow-cooled DNA for binding in the flat-on-surface mode. Molecular modelling has suggested that ss DNA can adopt many different modes of binding to SWNTs, including helical wrapping with different pitches,[23] but it is not possible to differentiate them with LD at this stage. The spectra for the Sigma ss DNA (data not shown) are very similar to those for the fast-cooled DNA.

Poly(deoxyadenylate): Poly(dA) is the single nucleotide ss DNA least likely to form hydrogen bonds, though as is evident from Figure 3c it still has an intrinsic LD signal with a negative maximum at 255 nm. When it is in solution with SWNT, this shifts to 260 nm. The DNA–SWNT complex also has a small positive signal at ~225 nm (Figure 3c). Adenine has strong transitions centred at 257 and 213 nm and two weaker transitions at 230 and 272 nm (Figure 2).[24] The SWNT binding geometry proposed for ss DNA in Figure 2c would give rise to the observed LD spectrum. As is the case with ss ct-DNA (both melted and from Sigma), the light scattering is reduced in the poly(dA)/SWNT complex spectra when compared to SWNT spectra (Figure 3). This indicates that the poly(dA) facilitates the solubility of SWNT in SDS.

DNA oligomers: To our surprise, even a random base hexamer $d(N)_6$ 5′-phosphate gave an intrinsic negative LD signal at ~260 nm of magnitude −0.00025 (data not shown). Therefore, we were forced to conclude that even these small fragments link to form long strands. There was no evidence in the LD spectra (data not shown), however, that this hexamer interacted with the SWNT. By way of contrast, the octamer $(dCdT)_4$ ($T_m = 17\,°C$) gave almost no intrinsic LD signal (Figure 4c), but in the presence of SDS-solubilised SWNTs an LD signal was observed (Figure 4c). The light scattering of this sample is higher (Figure 4a) than that of the SWNT (see below), in contrast to the situation for the polymeric DNAs, in which the SWNT light scattering is reduced upon DNA addition. Despite this, we can clearly see a negative LD band at ~267 nm and a positive band at ~238 nm for the difference spectrum of $(dCdT)_4$/SWNT−SWNT. The LD signs again are consistent with the oligomer wrapping around SWNT in a tilted fashion, as illustrated in Figure 2c. Zheng et al. saw no evidence for this oligomer binding to SWNTs, suggesting that the LD may be a more sensitive test than absorbance spectroscopy.[15,23]

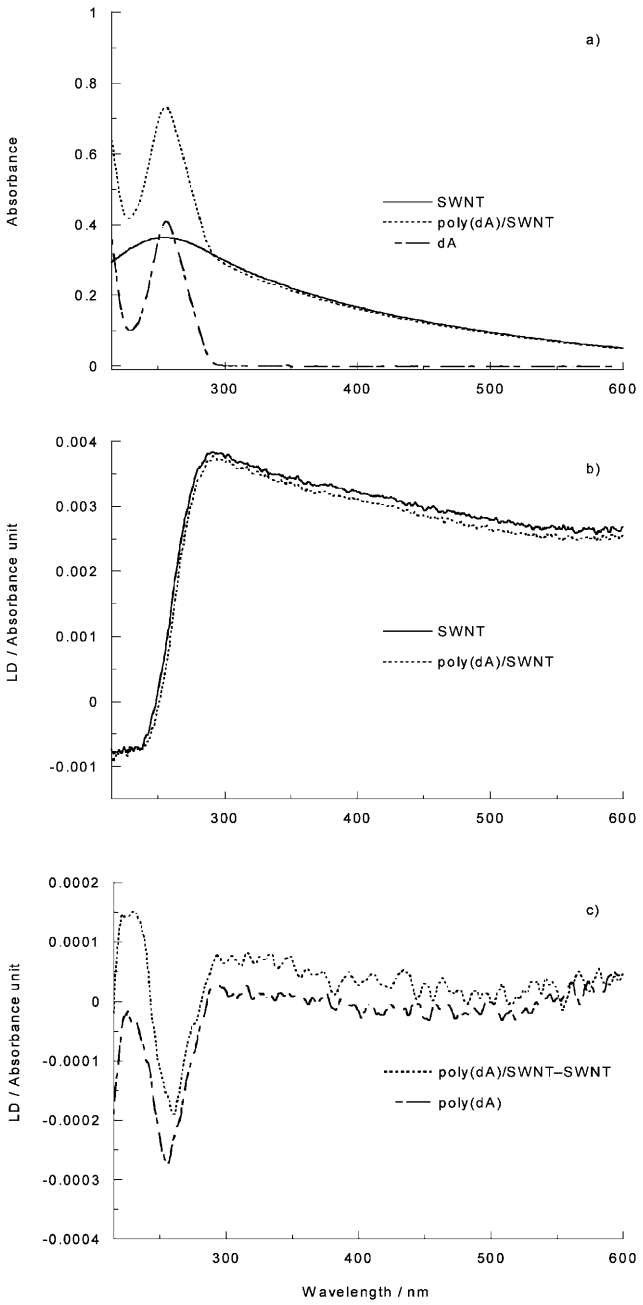

Figure 3. a) Absorbance spectra of SWNT (0.1 mg mL^{-1}), poly(dA) (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex and poly(dA) (0.1 mg mL^{-1}). b) LD spectra of SWNT (0.1 mg mL^{-1}) and poly(dA) (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex in SDS (9 mM). c) LD spectrum of d(A) (0.1 mg mL^{-1}) in SDS (9 mM) and LD difference spectrum of poly(dA) (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) minus SWNT (0.1 mg mL^{-1}). All spectra have SDS (9 mM) baselines subtracted.

Peptide nucleic acid (PNA): We thought that the anionic SDS that seemed to be required to get the SWNTs into solution would hinder the anionic DNA from binding to the nanotubes. Thus, we investigated the interaction between SWNTs and $(CT)_4$ peptide nucleic acid (PNA), which is a neutral DNA analogue with a peptide backbone composed of *N*-(2-aminoethyl)glycine units rather than a sugar phos-

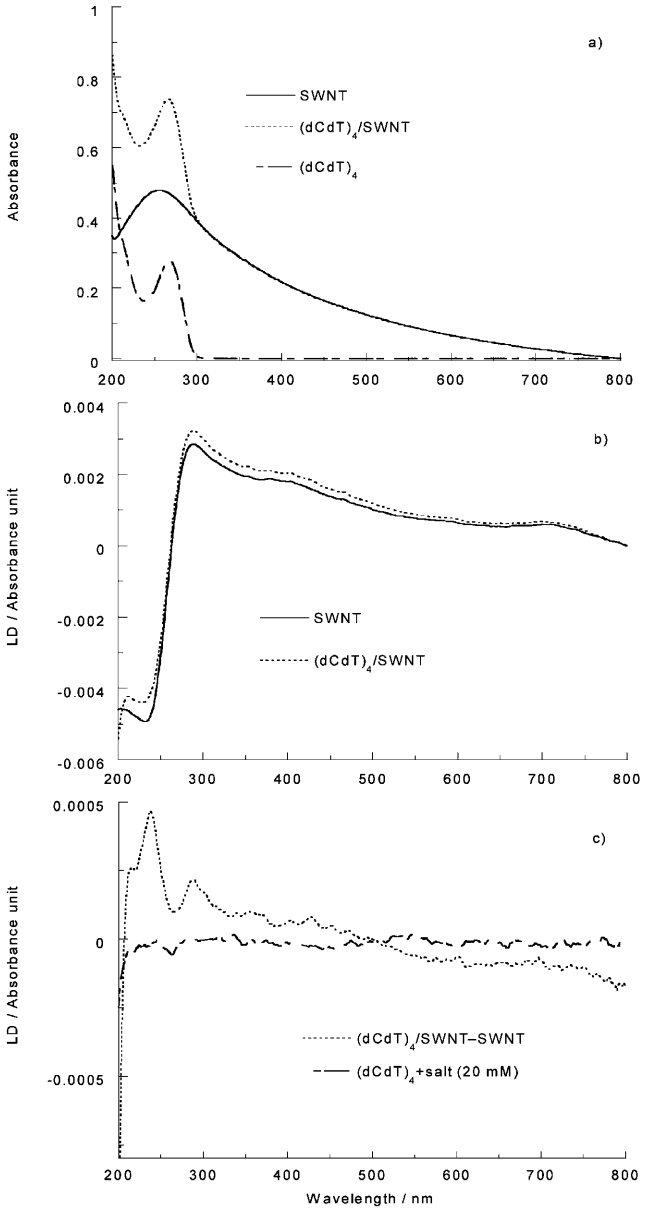

Figure 4. a) Absorbance spectra of SWNT (0.1 mg mL^{-1})/salt (20 mM) in SDS (9 mM), $(dCdT)_4$ (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1})/salt (20 mM) complex in SDS (9 mM) and $(dCdT)_4$/salt absorbance of the same concentration. b) LD spectrum of SWNT (0.1 mg mL^{-1})/salt (20 mM) compared with the $(dCdT)_4$ (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1})/salt (20 mM) spectrum. c) LD spectrum of $(dCdT)_4$ (0.1 mg mL^{-1})/salt (20 mM) spectrum and difference LD spectrum of $(dCdT)_4$ (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1})/salt (20 mM) complex minus SWNT (0.1 mg mL^{-1})/salt (20 mM) zeroed at 500 nm. All spectra had SDS (9 mM) baselines subtracted.

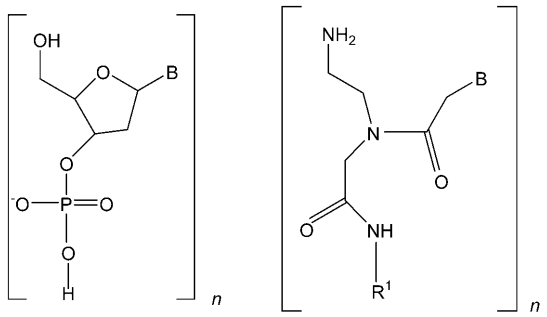

Figure 5. Chemical structures of PNA (left) and DNA (right) backbones. B = base.

phate backbone (Figure 5). PNA is capable of sequence-specific recognition of DNA and RNA obeying the Watson–Crick hydrogen-bonding rules, so it could bind to SWNTs with the same geometry as DNA.[25]

The spectra for SWNT and $(CT)_4$ PNA are shown in Figure 6. As with the same sequence DNA oligomer, the light scattering is higher (and somewhat different in shape) for the PNA/SWNT complex than for the SWNT. This contrasts with the situation for the DNA polymers, in which it appeared they helped to solubilise the DNA, reducing the scattering. Whether this difference relates to the way in which the SDS is displaced by the longer and shorter nucleic acids is not clear at this stage. It should be noted that there is a net scattering "baseline" left in the spectra of Figures 4 and 6, due to the different shape of the scattering profiles of the SWNT with and without the oligomers. It may in any case be concluded that PNA is adsorbed on to the SWNT. The PNA itself only has a very small (negative) LD signal at 260 nm. The difference LD spectrum of PNA/SWNT (Figure 6c), like the DNA/SWNT system, has two bands, one at ~290 nm and the other at ~240 nm. These are slightly red-shifted compared with the DNA analogue. More intriguingly, the sign pattern of the PNA system is inverted relative to that of DNA. Thus, whatever the binding mode of DNA on the SWNT, PNA is oriented quite differently. The PNA backbone has even more flexibility than the DNA backbone, and the LD signs would suggest it wraps around the SWNT so that the DNA bases lie approximately perpendicular to those illustrated in Figure 2c. A means of achieving this would be for it to wrap with the opposite sense, which can be visualised by inserting the SWNT with its axis horizontal rather than vertical in Figure 2c Alternatively, each base in Figure 2c can be rotated 180° about the link from the base to the backbone. Although the PNA backbone can be aligned with that of DNA, it is intrinsically flexible and not itself chiral. So the lower energy arrangements for PNA on the SWNT could well be different from those of the DNA.

Conclusions

In this paper, we have established the potential of flow linear dichroism to probe the binding of single-stranded DNAs to SWNTs. DNAs varying in size from a few hundred bases to short oligomers were investigated, and a range of different sequences were found to interact. Although only qualitative analysis of the data is possible at this stage, one could envisage determining the orientation of the DNA

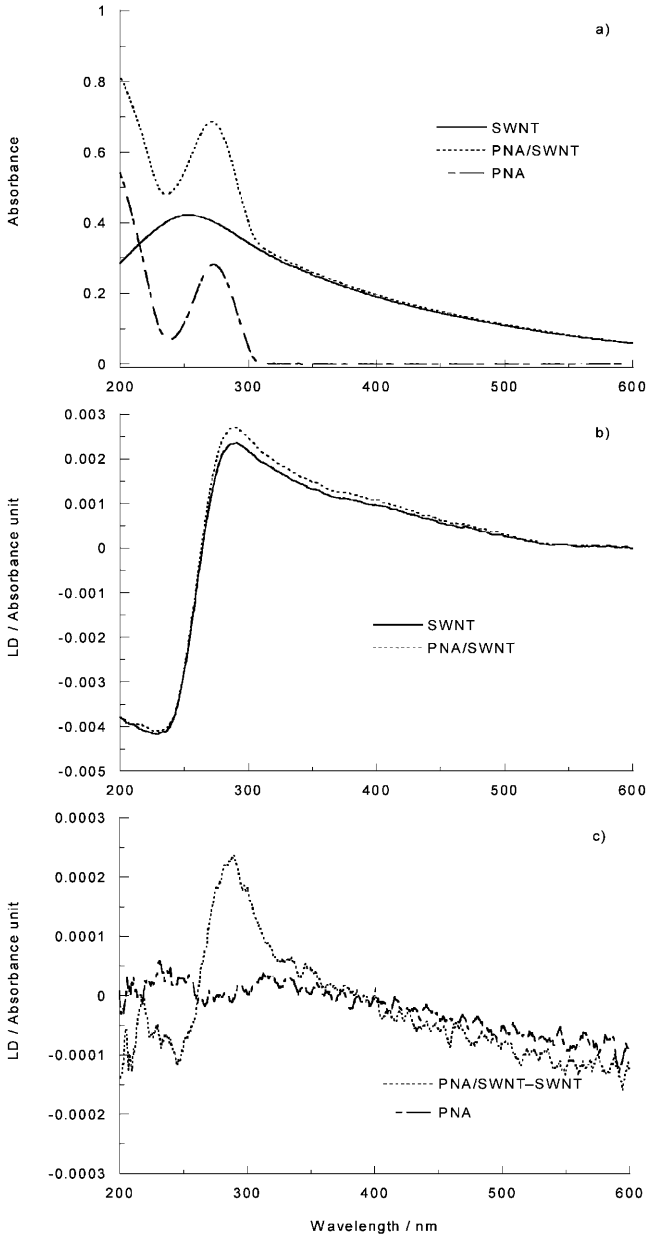

Figure 6. a) Absorbance spectra of SWNT (0.1 mg mL^{-1}) in SDS (9 mM), PNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex in SDS (9 mM) and PNA (0.1 mg mL^{-1}) in SDS (9 mM). b) LD spectra of SWNT (0.1 mg mL^{-1}) in SDS and PNA (0.1 mg mL^{-1})/SWNT (0.1 mg mL^{-1}) complex in SDS (9 mM). c) LD spectrum of PNA (0.1 mg mL^{-1}) in SDS (9 mM) and difference spectrum of PNA/SWNT minus SWNT, zeroed at 400 nm. All spectra have SDS (9 mM) baselines subtracted.

bases on the SWNT by deconvoluting transition polarisations of the bases. A geometry consistent with the observed data is that in which the DNA backbone wraps round the DNA at an oblique angle and the bases lie flat on the nanotube surface. We presume this involves displacing the anionic SDS from the SWNT surface.

The LD signals for the single-stranded DNAs were not as large as those previously observed[11] for sonicated double-stranded ct-DNA. This might be because of the cooperative effect of a large number of small interactions coupled with the intrinsically greater rigidity of the duplex DNA. In contrast to the situation with ds DNA, in which a single negative band at the absorbance maximum was observed, the spectrum observed in each case for ss DNA is a couplet of bands with a negative one at ~280 nm and a positive one at ~230 nm. The polymeric DNAs also reduced the light scattering observed for the SWNTs, whereas the oligomers increased it, suggesting the latter increase the SWNT size and the former help solubilise it. The neutral DNA analogue, $(CT)_4$ peptide nucleic acid, intriguingly gave the opposite signed spectrum from that of the DNA $(dCdT)_4$, suggesting an orientation of the PNA on SWNTs in which the bases are rotated ~90° with respect to that observed for DNA.

Experimental Section

Materials: SWNTs (synthesised by the catalytic arc discharge method) were obtained from Dynamic Enterprises, were purified by refluxing in 3 M nitric acid at 120 °C for 13.5 h and were then washed with water (18.2 MΩ).[11] Purity was investigated by transmission electron microscopy (TEM) as described previously.[11] In order to overcome problems due to inhomogeneity of the samples, stock solutions of SWNT (0.5 mg mL^{-1}) were prepared. The stock solution of SWNTs was obtained by sonicating the SWNTs for 2 min in aqueous sodium dodecyl sulfate (SDS, Sigma, 9 mM) at a concentration slightly above the critical micelle concentration (which is 8.5 mM) of SDS to give a viscous solution of concentration 0.5 mg SWNT per mL of SDS.[26] The final concentration of SWNT was maintained at no more than 0.1 mg mL^{-1} in all samples in order to avoid excessive absorption. The DNAs were then added to the SWNT SDS solutions as outlined below.

Double- and single-stranded calf thymus DNA (ct-DNA) were obtained from Sigma–Aldrich Chemical Company. Poly(dA) and the random DNA hexamer $(pd(N)_6)$ were obtained from Amersham Biosciences and the DNA and PNA oligomers with the sequence $(CT)_4$ were obtained from Sigma Genosis and Eurogentec, respectively. Stock solutions of the polymeric DNAs were prepared in SDS (9 mM); stock solutions of the oligomers were prepared in water (18.2 MΩ). All spectroscopy experiments were performed with aqueous SDS (9 mM) as the solvent. For the spectroscopy experiments, an aliquot of DNA was added to a SWNT suspension (~0.1 mg mL^{-1}) in SDS to a concentration of 0.1 mg mL^{-1}, though in some cases further dilution (with SDS; 9 mM) was required to avoid excessive absorbance. Short ds ct-DNA of ~200–400 base pairs (as determined by gel electrophoresis[11]) was obtained by sonicating an aqueous SDS solution of ct-DNA for about 2–3 h.[27] All preparations were left overnight to equilibrate before spectroscopic measurements were performed; in fact, the DNA/SWNT samples gave the same results if the spectra were measured immediately upon mixing. Samples left standing for a few days, however, showed some precipitation from solution and gave unsatisfactory spectra. Though SDS was used as baselines for the data presented below, we were also able to use samples without rotation for the LD spectra as they overlaid very well. In fact, this coincidence of the baselines was a good check on system performance.

Spectroscopy

Absorbance: UV-visible absorbance spectra were recorded using a Cary 1E spectrophotometer.

Linear dichroism (LD): LD spectra were recorded using a Jasco J-715 circular dichroism spectropolarimeter with extended sample compartment adapted for LD measurements. In LD spectra the difference in anisotropic absorption of light polarised in planes parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the direction of orientation[12] [Eq. (3)] is measured.

$$LD = A_{\parallel} - A_{\perp} \quad (3)$$

The Couette cell used to flow orient the samples was a small-volume quartz LD cell, the outer quartz cylinder of which had an internal diameter of ~3 mm and rotated, while the inner cylinder was a stationary ~2.5 mm diameter quartz rod.[28] This cell was equipped with focusing lenses before and after the sample; this minimised light scattering. Its demountable sample holding capillary facilitated cleaning. The voltage applied to the cell in all experiments was 3.0 V, which corresponds to a rotation speed of ~1000 rpm.

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