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Complete structural characterization of single carbon nanotubes by Rayleigh scattering circular dichroism

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The accurate characterization of the chiral indices (n,m) of carbon nanotubes has greatly facilitated fundamental investigations and practical applications ranging from electronic circuits and quantum emission to biological detection¹⁻⁴. To meet the growing miniaturization-driven demand, handedness, the key structural quantity associated with mirror symmetry breaking, needs to be identified both accurately and efficiently⁵⁻⁷. To date, optical spectroscopic techniques with unprecedented high-throughput and noninvasive characteristics have achieved great success in identifying chiral indices even at the single-tube level⁸⁻¹³. However, none of these optical methods are capable of handedness characterization for single nanotubes due to their extremely weak chiroptical signals ($\sim 10^{-7}$) compared to the excitation light^{14,15}. Here, we demonstrate the complete structure identification of single nanotubes in terms of both chiral indices and handedness by Rayleigh scattering circular dichroism. The success originates from the background-free feature of Rayleigh scattering collected at an oblique angle, which enhances the chiroptical signal from nanotubes by three to four orders of magnitude compared to that using conventional absorption circular dichroism. We measured a total of 30 single-walled carbon nanotubes (including both semiconducting and metallic nanotubes) and found that their absolute chiroptical signals show an obvious structure dependence, which can be qualitatively understood through tight-binding calculations. Our strategy not only opens up exciting opportunities for unlocking the sophisticated functionality of nanotubes but also provides a new platform for chiral discrimination and chiral device exploration at the level of individual nanomaterials.

Chiral effects exist in a variety of natural phenomena and are of fundamental importance in science, ranging from particle physics to artificial metamaterials^{16,17}. Chiral materials with left-handed and right-handed counterparts linked by mirror symmetry are useful for advanced applications in polarization optics, spintronics and stereochemistry⁷. Recently, research into chiral materials has gradually focused on chiral nanostructures. Carbon nanotubes, the prototypical one-dimensional material^{5,6}, are generally chiral except for zigzag and armchair nanotubes (Fig. 1a and Supplementary Fig. 1). Two nanotube enantiomers, left- (L) and right-handed (R), can show different interactions with circularly polarized light (Fig. 1b). From a fundamental point of view, when excited by an external field $\mathbf{E}$, both the electric moment $\boldsymbol{\mu}$ and the magnetic moment $\mathbf{m}$ exist in chiral nanotubes (in achiral nanotubes, $\mathbf{m} = 0$). Quantitatively, $\mathbf{m}$ is defined as $i\mathbf{G}\mathbf{E}$, where $\mathbf{G}$ is the complex electric-magnetic coupled susceptibility and its imaginary part (G_2) is related to the chiral asymmetry of the material^{18,19}. Since the orientation of $\mathbf{m}$ (determined by the sign of G_2) varies with the nanotube handedness, in principle, it is possible to identify the nanotube handedness through circular dichroic spectroscopic techniques²⁰⁻²⁴.

Handedness discrimination, which can be traced back to the initial studies of natural products with chiral structures in the early 1800s²⁵, is now an important quantum concept at the heart of nanoscience and technology²⁶⁻³¹. To date, standard circular dichroism spectroscopic techniques based on linear and nonlinear chiroptical effects have been successfully developed³²⁻³⁵, and significant progress has been achieved in measuring the chiral optical response of single chiral entities, such as plasmonic nanostructures and nanoparticles³⁶⁻³⁸. However, for a single carbon nanotube, handedness discrimination is extremely challenging due to its much smaller size (~ 1 nm) and the complex structures formed with hundreds of chiral indices. In addition, the chiroptical signal from individual nanotubes is extremely weak ($\sim 10^{-7}$) compared to the excitation light¹⁵ and easily overwhelmed with either the distortion of circularly polarized light³⁹, the chiral experimental arrangements^{40,41} or the interference of the sample substrate⁴². Currently, only non-optical techniques, such as scanning tunnelling microscopy and transmission electron microscopy, can

provide high-resolution images for handedness identification of individual carbon nanotubes^{43,44}, whereas they have proven to be unsuitable for scalable and routine characterization due to their limited accessibility and low efficiency. Till now, the handedness of single nanotubes remains the only structural degree of freedom to be determined by optical means, and the development of sophisticated handedness-related applications of single nanotubes has been greatly hindered⁴⁵⁻⁴⁷.

In this work, we experimentally develop a high-sensitivity Rayleigh scattering circular dichroism (Ray-CD) spectroscopic technique, which is demonstrated to determine the complete structure of individual carbon nanotubes for the first time. In our setup, Rayleigh scattering of an individual suspended carbon nanotube is collected by an oblique objective. Compared to absorption measurements under a large background of excitation light, Rayleigh scattering in our configuration is free from the interference of the transmitted light. Therefore, the dichroic signal measured in Rayleigh scattering can be three to four orders of magnitude larger than that measured using an absorption circular dichroism setup (Supplementary Note 1), enabling the detection of an extremely weak chiroptical signal from a single nanotube.

Based on our design, we built an experimental setup with microscopic imaging and spectroscopic collecting abilities. As shown in Fig. 1c, a supercontinuum laser coupled with a tuneable filter provides broadband excitation light with a tuneable wavelength λ , a polarizer and photoelastic modulator (PEM) are utilized to generate alternating left- and right-handed circularly polarized light with a frequency of 50 kHz, a polarization-maintaining objective serves to focus the modulated light onto nanotubes and an obliquely placed objective is used to collect the nanotube-scattering light. Since the intensity of the nanotube scattering varies with the polarization of the incident light, the detected intensity includes a time-varying signal (I_{AC}) at the alternating frequency (f) of the circularly polarized light and an average signal (I_{DC}) (Fig. 1d and Supplementary Note 2). Experimentally, the time-varying value is recorded by a lock-in amplifier, and the average Rayleigh scattering intensity is read from a photomultiplier tube simultaneously (see Methods for more details). The Ray-CD intensity at a wavelength (λ) can be finally obtained as

$$I_{\text{RCD}}(\lambda) = \frac{(I_{\text{L}} - I_{\text{R}})}{(I_{\text{L}} + I_{\text{R}})} = \frac{I_{\text{AC}}}{I_{\text{DC}}} \cdot A,$$

where I_{L} (I_{R}) represents the Rayleigh scattering intensity excited by left- (right-) circularly polarized light and A is an experimental constant (Supplementary Note 2). As the laser wavelength is swept from 450 nm to 700 nm, the Rayleigh scattering and Ray-CD spectra can be obtained simultaneously. In our measurement, to obtain a high purity for the light polarization, the PEM has been precisely calibrated (Supplementary Fig. 2 and Supplementary Note 3), and optical components with minimized residual birefringence have been carefully selected by monitoring the destruction of the extinction ratio when placing them between two crossed polarizers. Meanwhile, we used a spatial filter unit to obtain a focused Gaussian beam (Supplementary Fig. 3) and guaranteed that the light passed perpendicularly through the centre of the optical components, which is critically required to realize the Ray-CD measurements.

We first applied this technique to an isolated semiconducting single-walled carbon nanotube (SWNT) bridged over an open slit (Fig. 2a). The scattering light of the nanotube can be focused and seen in the Rayleigh image (the bright spot in the slit centre), by which the spatial position of the nanotube relative to the laser focus can be monitored in real time (Fig. 2b). The chiral index of the nanotube was unambiguously determined as (18,10) from its electron diffraction pattern (Fig. 2c) and the two prominent optical resonances in its absorption (Fig. 2d, top panel) or Rayleigh spectrum¹¹ (Fig. 2d, middle panel). According to the type definition of carbon nanotubes (for type I, $|n - m| \text{ MOD } 3 = 2$; for type II, $|n - m| \text{ MOD } 3 = 1$), we can determine that this nanotube belongs to type I. In addition, according to the established atlas for SWNT optical transitions¹¹, the two resonance peaks at approximately 565 nm and 635 nm were assigned to the S_{44} and S_{33} optical transitions of the nanotube (18,10), respectively. In contrast to the absorption spectrum, the Rayleigh peaks show different line shapes and a slight redshift due to the influence of the real part of the complex optical susceptibility, which is consistent with the previous report⁹. In particular, the acquired Ray-CD spectrum (Fig. 2d, bottom panel) also possesses two appreciable peaks at positions similar to those observed in the absorption and Rayleigh spectrum but with opposite signs, which

provides handedness information for this nanotube. Such opposite signs of neighbouring transitions can be understood in the cutting-line concept of nanotube optical transitions. For neighbouring transitions, their corresponding cutting lines are located on the opposite side of the K point of the Brillouin zone in a zone-folding scheme (Supplementary Fig. 4), thus resulting in the opposite wave vectors ($\mathbf{k}$) of the electron and magnetic dipole moments of the transition⁴⁸. In such cases, alternating signs for the neighbouring Ray-CD signal at van Hove singular energies (E_{ii} , $i = 1, 2, 3, 4, 5, \dots$) are expected. In addition, owing to the difference in the cutting lines between semiconducting type I and type II nanotubes, the given transition for type I and type II nanotubes will have opposite signs (Supplementary Fig. 4). As a result, for L-handed type I nanotubes (type II nanotubes), odd (even) transitions should have positive signs, while the opposite is true for the case of R-handed nanotubes^{5,6,14}. Accordingly, the nanotube (18,10) measured here was identified as L-handed based on the positive Ray-CD sign of the S_{33} transitions and its type I category.

In addition to the sign information, one can clearly see that the magnitude of the Ray-CD peak signal is as large as 10^{-3} , which is approximately four orders of magnitude larger than that in the absorption circular dichroism (predicted as $\sim 10^{-7}$)¹⁴, illustrating the high sensitivity of our technique. In contrast, the signal is nearly zero when the nanotube is moved out of the laser spot, confirming that there is little spurious signal in the Rayleigh measurement (Supplementary Fig. 5). Furthermore, we proved that the obtained Ray-CD signal indeed originates from the nanotube itself by changing the polarization of the excitation light. According to calculations (Supplementary Note 4), when reducing the angle (α) between the optical axis of the photoelastic modulator and polarizer (Fig. 2e), the excitation light can be modulated between left- and right-handed elliptically polarized light instead of circularly polarized light; thus, the modulated signal (I_{AC}/I_{DC}) of the one-dimensional nanotube should decrease with α . As expected, a declining trend was observed experimentally as α changed from 45° to 25° (Fig. 2f).

To further investigate the chiral behaviour of SWNTs, we performed measurements for different semiconducting and metallic nanotubes, three of which were displayed representatively.

Their chiral indices were first determined by the resonance peaks in the absorption (Supplementary Fig. 6) or Rayleigh spectra (Fig. 3a-c, upper panels), and their handedness was subsequently identified by the corresponding signs of the Ray-CD signals (Fig. 3a-c, lower panels). Distinct from the type I nanotube (18,10), although both signs for the Ray-CD signals for the S_{44} and S_{33} transitions (Fig. 3a) are the same as those shown in Fig. 2d, the handedness of this type II nanotube (19,6) was identified as right rather than left. In addition, an example of a chiral metallic nanotube (23,11) is displayed in Fig. 3b, where M_{22}^{+} and M_{22}^{-} transitions split by the trigonal warping effect and the corresponding Ray-CD signals with opposite signs can be observed, in line with previous theoretical expectations⁶. Similar to semiconducting nanotubes, the M_{ii}^{-} transitions should have positive (negative) signs for R-handed (L-handed) metallic nanotubes⁶; hence, this metallic nanotube was determined to be L-handed based on the experimental Ray-CD spectrum. Besides, for the armchair nanotube (19,19), only a small Ray-CD signal ($\sim 10^{-4}$) at the resonance wavelength (595 nm) can be detected (Fig. 3c, lower panel) due to its mirror symmetry, which is approximately one order of magnitude smaller than the Ray-CD intensities ($\sim 10^{-3}$) obtained for other chiral nanotubes, proving that the introduced noise is relatively low in our experiment.

The ability to measure chiroptical signals at the single-tube level allows us to quantify the structure-dependent chiral properties of nanotubes. In this work, we systematically measured a total of 30 single nanotubes and found that their absolute Ray-CD signals at the resonance peaks varied in the range of 1×10^{-3} to 4×10^{-3} . Theoretically, we calculated the Ray-CD peak intensity based on a tight-binding method⁶ and time-dependent perturbation theory^{18,19} (Supplementary Note 5). Ray-CD amplitudes for S_{44} optical transitions were calculated, and the colour maps for semiconducting type I and type II nanotubes with diameters ranging between 1.0 nm and 4.5 nm are plotted in Fig. 4a and Fig. 4b, respectively. The general trend shows that the larger nanotubes have smaller signals. A simple understanding is that the larger nanotubes have less curved surfaces, so the chiral effects are less intense. In the limiting case, when the diameter goes to infinity and recovers the hexagonal graphene sheet, the Ray-CD will be even zero¹⁴. In addition, it is evident that the Ray-CD peak

intensities for the type I and II nanotubes manifest different chiral angle dependences. For nanotubes with large diameters ($d > 2.0$ nm), the Ray-CD intensity of both type I and type II nanotubes is increased when the chiral angle enlarges. However, for nanotubes with relatively small diameters ($d < 2.0$ nm), type II nanotubes exhibit nonmonotonic behaviour with chiral angle. Additionally, such type-dependent asymmetry is reversed for S_{33} optical transitions (Supplementary Fig. 7). All these phenomena can be correlated with the anisotropic energy bands of the nanotubes, whereby equienergy contours in the Brillouin zone of graphene evolve from circles around the K point to triangular shapes around the M point, and the energy dispersion is different on the two sides of the K point⁴⁸. For nanotubes with smaller diameters, their optical transitions have larger energy, and the corresponding cutting lines are far away from the K point; therefore, the Ray-CD patterns show larger asymmetry between type I and type II nanotubes.

Next, we present a comparison between the theoretical prediction (green triangles) and experimental data (orange circles) for nanotubes with approximately the same chiral angle ($\theta \approx 19^\circ$, Fig. 4c,d) and same diameter ($d \approx 2.0$ nm, Fig. 4e,f). The experimental data show the same trend as that for the calculated data, while deviations are observed and might be ascribed to the many-body excitonic effects beyond the tight binding models⁶ (Supplementary Note 5), as well as the higher-order effects of multipole expansion in the time-dependent perturbation theory^{18,19} (Supplementary Note 1). Hence, more precise and in-depth theoretical studies are needed in the future.

Accurate and facile characterization can be an indispensable tool for handedness-controlled growth of carbon nanotubes. Here, we summarize the chiral indices and handedness distributions for the 30 single nanotubes measured (Fig. 3d, Supplementary Tables 1 and 2) and plot a histogram for armchair, left- and right-handed nanotubes (Fig. 3e), whereas no obvious handedness priority was found under our growth conditions with iron catalysts⁴⁹ (see growth details in Methods). This randomness in the handedness may arise from the fact that iron catalysts are in the liquid phase at the growth temperature of approximately 950 °C. In the future, solid catalysts with asymmetric surfaces can be employed to grow nanotubes with preferred or even pure handedness, and our

202 method can provide key feedback. In addition, such chiral-sensitive measurements allow one to
203 explore the influence of handedness on the coupling of double-walled carbon nanotubes or the
204 coupling of other one-dimensional van der Waals heterostructures⁵⁰. This will certainly promote the
205 accurate design and applications of nanotubes in future photonic, optoelectronic, photovoltaic and
206 bioimaging devices. Moreover, this new methodology fills the vacancy of handedness
207 discrimination at the individual nanotube scale, and can be quite universal for characterizing the
208 chiral properties of other single nanomaterials, therefore offering a new platform for the exploration
209 of low-dimensional chiral physics and chiral devices.

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300 **Methods**

301 **Sample preparation.** Suspended single-walled carbon nanotubes were grown across slit structures
302 by the chemical vapour deposition method. The slit structures ($30\text{ }\mu\text{m} \times 1\text{ mm}$) were prepared by
303 standard photolithography and wet etching techniques. A thin iron film (0.2 nm) was deposited as
304 the catalyst at one end of the silicon substrate, which was then loaded into the quartz tube (1 inch)
305 of the CVD furnace. The system was heated to $950\text{ }^{\circ}\text{C}$ in 30 min with 300 sccm Ar and 200 sccm
306 H_2 . When the growth temperature reached, ethanol vapour through a bubbler with 100 sccm Ar was
307 introduced as the carbon precursor for SWNTs growth. Since the growth of SWNTs follows the kite-
308 flying mechanism directed by the gas flow in this condition, long SWNTs could grow across the
309 open slit on the substrates⁴⁹.

310 **TEM and SEM characterization.** Electron diffraction patterns were obtained by a transmission
311 electron microscope (JEOL 2100 and ARM 3000) under 80 keV. Both the electron beam and laser
312 beam can go through the open slit with individual carbon nanotubes, which enables direct
313 measurement of diffraction patterns and optical spectra of the same nanotube. SEM images were
314 collected by Hitachi S-4800 field emission at 5 kV.

315 **Ray-CD measurements.** A laser line filter (NKT, LLTF) was used to select monochromatic light
316 from the coupled supercontinuum laser (NKT, WL-SC-400-4) consecutively. A spatial filter unit
317 was utilized to get a good Gaussian beam. At each wavelength, alternating left- and right-handed
318 circularly polarized lights (50 kHz switching frequency) were generated with a polarizer (Thorlabs,
319 GTH10M) and photoelastic modulator (Hinds, PEM100). One objective (Mitutoyo M Plan 50 X,
320 $\text{NA} = 0.25$) was served to focus the light on suspended nanotubes, and another oblique objective
321 (Mitutoyo M Plan 20 X, $\text{NA} = 0.25$) was used to collect the nanotube-scattering signal
322 (Supplementary Fig. 8). A pair of confocal lenses (Thorlabs, AC254-050-A-ML) and a pinhole
323 (Thorlabs, P200D) were used to filter stray scattering before the signal reaching the detector
324 (Thorlabs, PMT2001). To monitor the position of carbon nanotubes, a flip mirror was utilized to
325 switch the scattering light to a CCD camera (PULNIX, TM-7CN) for Rayleigh scattering imaging.

The effective value and sign of the time-varying signal (I_{AC}) changed with the incident circularly light, and was extracted by a lock-in amplifier (Stanford Research, SR-830) referenced to the modulated frequency of photoelastic modulator (Supplementary Fig. 9). At the same time, a high-speed data acquisition card (National Instruments, PCI-6289) connected to a computer was used to record the average scattering signal (I_{DC}). Finally, the Ray-CD signal (I_{RCD}) at the wavelength of λ was obtained as $I_{RCD}(\lambda) = \frac{I_{AC}}{I_{DC}} \cdot A$, where A is an experimental constant. The monochromatic light selection, photoelastic modulator retardance adjustment and data acquisition were controlled by the same computer. As the laser wavelength scanned through the whole spectral range (450 nm to 700 nm, 5 nm increment), both Rayleigh scattering and Ray-CD spectra of a SWNT were obtained after being normalized by the detected profile of the supercontinuum light (Supplementary Fig. 10). In addition, to make the nanotube axis perpendicular to the incident light to avoid spurious signal from the experimental setup, we used a sample holder with 2-axis adjusters (Thorlabs PY003/M) to control the sample tilt within 50 μ rad.

Absorption spectra measurements. The absorption spectra of nanotubes were obtained using the polarization-based transmission microscopy developed previously¹³. In detail, a supercontinuum laser (Fianium SC-400-4) provided a wide-band light source, then the light propagated through polarizer 1 (Thorlabs, GTH10M) and was focused on the sample by objective 1 (Mitutoyo 50 X, NA = 0.25). The transmitted light was collected by another confocal objective 2 (Mitutoyo 50 X, NA = 0.42). Polarizer 2 was placed with a relative angle of $\sim 90^\circ$ with polarizer 1 (with δ deviation), and the nanotubes were placed with their axis 45° to polarizer 1. Two sets of spectra with the nanotube in and out of the beam focus were obtained to generate the contrast signal detected by a spectrometer containing a grating. Based on the extinction signal measured at opposite deviation angles ($\pm \delta$), the absorption spectra for the single carbon nanotube can be further obtained. In addition, this instrument was coupled to the Ray-CD experiment setup, allowing both measurements of absorption and Ray-CD spectra on the same nanotube. All the optical measurements were done in the cleanroom where the temperature was kept constant at $\sim 20^\circ \text{C}$.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper, the Supplementary Information, and the Source Data. Extra data are available from the corresponding author upon request.

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Author contributions

K.L. and F.Y. conceived the experiments and supervised the project. F.Y., W.Y., C.L. and H.M. conducted the optical experiments, C.L. performed the growth experiments. Y.S., Y.Y., F.Y., W.Y. and H.M. contributed the theoretical calculations. R.Q., P.G. and X.B. conducted the TEM experiments. C.W, C.M., J.Z., Z.S., S.M., F.W., and J.Z. suggested the optical experiments. All of the authors discussed the results and wrote the manuscript.

Competing interests

The authors declare no competing interests.

374 **Additional information**

375 **Supplementary information** is available for this paper at https://doi.org/****

376 **Correspondence and requests for materials** should be addressed to K.L.

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Figure captions

Fig. 1 | Chiroptical signal measurement for single nanotubes. **a**, Schematic geometric structure of carbon nanotubes with different helicities, where zigzag chains are highlighted for clarity. L- (R-) handed represents nanotubes with left- (right-) handedness. **b**, Different optical responses to circularly polarized light of nanotubes with different chiral asymmetries. When excited by an external field E , an electric moment μ is excited both in achiral and chiral nanotubes, whereas a circular current I and magnetic moment m are excited only in chiral nanotubes and their directions are reversed with a change in nanotube handedness, making them distinguishable in chiroptical experiments. **c**, Schematic of the Ray-CD experimental setup, showing the placement of optical components and connection of electronic instruments. LLTF, laser line tuneable optical filter; PEM, photoelastic modulator; SWNT, single-walled carbon nanotube; PMT, photomultiplier tube. **d**, Simplified diagram of the nanotube-scattering intensity over time, containing the average signal (I_{DC}) and signal varying with the alternating circularly polarized incident light (I_{AC}).

Fig. 2 | Rayleigh circular dichroism measurement for a suspended nanotube. **a**, Scanning electron microscopic image of a suspended single-walled nanotube across an open slit. **b**, Rayleigh scattering image of the nanotube (the bright spot in the slit centre). Edges of the slit are marked with white dashed lines. **c**, Transmission electron microscopic diffraction image of the nanotube; based on this image, the nanotube was identified to have a chiral index of (18,10) and to be a semiconducting type I nanotube. **d**, Optical absorption spectrum (top panel), Rayleigh scattering spectrum (middle panel) and Ray-CD spectrum (bottom panel) for the nanotube. Based on the signs of the two optical transitions in the Ray-CD spectrum and its type I category, left-handedness was determined. **e**, Layouts for polarization control and the nanotube. The ellipticity of the excitation light can be modulated by controlling the angle (α) between the polarizer and the optical axis of the photoelastic modulator. **f**, A set of Ray-CD spectra measured at different α values, showing the declining modulated signals for the one-dimensional nanotubes as α decreases from 45° to 25° .

Fig. 3 | Typical Ray-CD results for three representative nanotubes and the statistical handedness results for 30 nanotubes. a-c, Rayleigh scattering (upper panel) and Ray-CD (lower panel) spectra for semiconducting (19,6) (a), chiral metallic (23,11) (b) and armchair (19,19) (c) nanotubes. Optical transitions are marked above each peak, which were used to determine the chiral indices of the nanotubes. Furthermore, the nanotube handedness was identified from the signs of the Ray-CD peaks and their type category. **d,** Detailed chiral index and handedness distribution for 30 measured nanotubes. The nanotubes were grown with iron catalysts. **e,** Histogram for the handedness distribution, showing similar proportions of left- and right-handed nanotubes.

Fig. 4 | Structure-dependent Ray-CD peak intensity. **a,b**, Calculated mapping of the Ray-CD peak intensity as a function of the diameter and chiral angle of the S_{44} transition for semiconducting type I (**a**) and type II (**b**) nanotubes. **c,d**, Calculated (green triangles) versus experimental (orange circles) peak Ray-CD intensities for S_{44} transitions as a function of diameter for the type I (**c**) and type II (**d**) families. The chiral angle of the selected nanotubes is approximately 19° (black lines in the calculated mappings). **e,f**, Calculated (green triangles) versus experimental (orange circles) peak Ray-CD intensities for S_{44} transitions as a function of chiral angle for type I (**e**) and type II (**f**) families. The diameter of the selected nanotubes was approximately 2 nm (white lines in the calculated mappings). Error bars are derived from the absolute values obtained for armchair nanotubes.