

Optically active single-walled carbon nanotubes

XIAOBIN PENG^{1,2†}, NAOKI KOMATSU^{1*†}, SUMANTA BHATTACHARYA^{1‡},
TAKANORI SHIMAWAKI^{1,3}, SHUJI AONUMA³, TAKAHIDE KIMURA¹ AND
ATSUHIRO OSUKA⁴

¹Department of Chemistry, Shiga University of Medical Science, Seta, Otsu 520-2192,
Japan.

²International Innovation Organization, Kyoto University, Nishikyo-ku, Kyoto 615-8520,
Japan.

³Department of Materials Science, Osaka Electro-Communication University, Neyagawa,
Osaka 572-8530, Japan.

⁴Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku,
Kyoto 606-8502, Japan

[‡]Present address: Department of Chemistry, Indian Institute of Technology Guwahati,
Guwahati 781 039, India

[†]These authors contributed equally to this work

*e-mail: nkomatsu@belle.shiga-med.ac.jp

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The optical, electrical and mechanical properties of single-walled carbon nanotubes (SWNTs) are largely determined by their structures, and the bulk availability of uniform materials is vital for extending their technological applications¹. Since they were first prepared^{2,3}, much effort has been directed toward selective synthesis and separation of SWNTs with specific structures. As prepared samples of chiral SWNTs contain equal amounts of left- and right-handed helical structures⁴, but little attention has been paid to the separation of these non-superimposable mirror image forms—known as optical isomers. Here, we show for the first time, that optically active SWNT samples can be obtained by preferentially extracting either right- or left-handed SWNTs from a commercial sample. Chiral ‘gable-type’ diporphyrin molecules bind with different affinities to the left- and right-handed helical nanotube isomers to form complexes with unequal stabilities that can be readily separated. Significantly, the diporphyrins can be liberated from the complexes afterwards, to provide optically enriched SWNTs.

It is well-known that the physical properties of SWNTs are closely correlated to their structures. SWNTs with controlled structures are, therefore, in great demand both for fundamental studies and technological applications¹. So far, however, the range of their electric and optical applications has remained rather limited, because as-prepared SWNTs comprise different structures which vary in length, diameter and chiral index.

Extensive investigations have been made in pursuit of selective synthesis and separation of SWNTs with specific structural properties. As for the synthesis, limited chiralities of SWNTs have been selectively prepared, using a silica-supported Co-Mo catalyst (CoMoCAT)⁵. Enrichment and separation of metallic and semiconducting SWNTs have been achieved by drawing on the differences in their electric or electronic properties⁶⁻¹².

Separation based on length, diameter and/or chirality of SWNTs have been conducted by using chromatography¹³⁻¹⁸.

Little attention, however, has been paid to another important feature concerning the structures of carbon nanotubes, namely the optical isomers that arise from the spiral alignment (either left- or right-handed) of the hexagonal carbon rings along the nanotube axis in chiral SWNTs. Most SWNTs are intrinsically chiral, and their helical structures have been atomically observed by scanning probe microscopy^{19,20} and transmission electron microscopy²¹⁻²³. Although their optical properties have been predicted theoretically²⁴⁻²⁷, optical activity—the ability to rotate the plane of plane-polarized light—originating solely from carbon nanotubes has not been reported so far. This is because as-prepared samples contain equal amounts of left- and right-handed helical forms, which cancel each other out in terms of rotating plane-polarized light.

Quite recently, SWNTs wrapped with DNA—which is chiral—were reported to be circular dichroism (CD)-active (CD is a technique that measures the differential absorption of left- and right-handed circularly polarized light as a function of its wavelength and CD-activity indicates a chiral structure), but become CD-inactive upon the replacement of DNA with sodium dodecylbenzenesulfonate (SDBS)—an achiral surfactant⁴.

Here, we report the preparation of optically active SWNTs that show a pair of opposite and symmetrical CD spectra, which is intrinsic to the SWNTs. In this process, ‘chiral nano-tweezers’ comprising *meta*-phenylene-bridged zinc(II) diporphyrins (Fig. 1) are used to extract and enrich nanotubes of a single mirror image form for each chiral index. A remarkable advantage of the present method is the easy and complete removal of the tweezers from the complexes, enabling recovery of pristine SWNTs free from the

dispersing material. Other methods that use molecules such as DNA or other surfactants tend to have difficulties in this removal phase⁴.

Non-superimposable mirror image forms (enantiomers) of the nano-tweezers (*R*)- and (*S*)-**1** were synthesized separately using the same procedures, and full details can be found in the Supplementary Information (Methods and Fig. S1). The extraction of SWNTs with either (*R*)- or (*S*)-**1** was carried out according to the schematic representation in Fig. 2. Commercial SWNTs (CoMoCAT), used for the extraction, are reported to include several kinds of chiral indices such as (6,5), (7,5), (7,6), (8,4) and (8,3)⁵, with equal amounts of both helical isomers for each chiral index⁴. After the suspension of SWNTs and chiral diporphyrin in methanol was bath-sonicated and centrifuged, the resulting supernatant liquid containing soluble porphyrin:SWNT complexes was analyzed with absorption and CD spectroscopies (Fig. 3). The same spectroscopic analysis was also carried out for the extracted SWNTs after thorough removal of the diporphyrin tweezers, followed by solubilisation in D₂O with SDBS (Fig. 4)²⁸.

(*R*)- and (*S*)-**1** display symmetrical bisignate Cotton effects²⁹ (sequential CD with alternate signs, characteristic of the chiral compounds having two adjacent chromophores) at 411 and 422 nm in their CD spectra (Fig. 3a, light blue and yellow traces, respectively) that correspond to the split Soret absorption band (absorbance around 400 nm characteristic of porphyrin compounds) of **1** (Fig. 3a, green trace). After the SWNTs were extracted with either (*R*)- or (*S*)-**1**, the extracts exhibit a similar red-shifted split Soret band at 415 and 430 nm, as well as a new broad absorption band around 450 nm (Fig. 3a, dark green trace). Much enhanced, red-shifted and symmetrical CD signals are also observed at 433 and 448 nm in the extracts (Fig. 3a, blue and red traces, respectively).

The signs (+ or –) of the strong bisignate Cotton effects of the complexes SWNTs:(*R*)-**1** and SWNTs:(*S*)-**1** remain the same as those of (*R*)-**1** and (*S*)-**1**, respectively. The red-shift of the Soret band in the extracts is probably caused by electronic interactions of the diporphyrins with the SWNTs, indicating that the diporphyrins form complexes with SWNTs²¹ such as those shown in Fig. 2b, namely left-handed (*LH*)-SWNTs:(*S*)-**1** and right-handed (*RH*)-SWNTs:(*S*)-**1**. The enhanced CD signals are considered to be attributed to conformational fixation of the two porphyrin planes by complexation²⁹. CD signals are also observed for the Q-band (absorbance around 500 – 700 nm characteristic of porphyrin compounds) at 562 and 596 nm (Fig. 3b) and for the E_{11}^S (the first optical transition energy of semiconducting SWNTs) absorption band at 986 and 1002 nm (Fig. 3c), all of which are symmetrical in the SWNTs:(*R*)-**1** and SWNTs:(*S*)-**1** complexes.

After removal of the chiral nano-tweezers (see Methods), the resulting diporphyrin-free SWNTs were well-dispersed with the aid of SDBS in D₂O²⁸ and the resulting supernatants were analyzed by UV-VIS-NIR spectroscopy in addition to CD and photoluminescence measurements. The samples extracted with mirror image nano-tweezers (either (*R*)-**1** or (*S*)-**1**) give symmetric and opposite CD signals in the ranges of 300-700 and 900-1050 nm as shown in Figs. 4a and b. The signals arising from semiconducting SWNTs are assigned to the chiral indices, (6,5), (8,4), (7,5), (8,3) and (7,6), on the basis of the present and reported UV-VIS-NIR (Fig. 4) and photoluminescence spectra (Supplementary Information, Fig. S2)^{5,30}.

The (6,5) index exhibits three CD signals at 980, 562 and 344 nm that correspond to the E_{11}^S , E_{22}^S and E_{33}^S transitions, respectively. The signs of the three signals are alternate, negative-positive-negative for SWNTs extracted with (*R*)-**1** and positive-negative-positive for those extracted with (*S*)-**1**, and the intensity becomes larger as the wavelength

is shorter. Similar characteristics, such as the alternate signs and larger intensity for shorter wavelength, are also found for the (8,4) index. All of these features are consistent with the theoretical prediction²⁴. Symmetrical CD signals are also observed in the region of E^M_{22} transition, though they are not fully identified.

Since tetrahydrofuran dispersions of porphyrin-free SWNTs gave almost the same CD spectra as those of D₂O dispersions in the presence of SDBS (Figs. 4a and c), we tracked the change in optical activity of the SWNTs during the centrifugation (2.5 and 5 h). After 2.5 h of centrifugation, mirror-image CDs are observed in SWNTs extracted with (*R*)- and (*S*)-**1**, and the signs in the spectra are the same as those after 5 h centrifugation. However, the intensity of CD signals increased remarkably when the samples were centrifuged for a longer time. In each case, the less stable complex is more prone to precipitate, increasing the optical activity of SWNTs remaining in the solvent extracts after longer duration of centrifugation. On the basis of the CD observations of chiral diporphyrin-free SWNTs mentioned so far, it is concluded that optically active SWNTs were obtained by the extraction with chiral zinc(II) diporphyrins and subsequent liberation of the diporphyrins.

The complex structures of (*S*)-**1** with *LH* and *RH* (6,5)-SWNTs²¹ were calculated theoretically to give their energy-minimised molecular mechanics models as shown in Fig. 2. The shape of the diporphyrin fits nicely to the curvature of SWNT by bending the porphyrin rings, stabilising the complex structures. In addition, three phenyl rings in (*S*)-**1** come close to the SWNT surface at a distance of 0.34 nm, indicating that there are stabilizing π - π interactions between them. Moreover, a C-H/ π interaction is also observed between the nanotube and a hydrogen atom on the benzene ring that bridges the two porphyrins in (*S*)-**1**, at the distance of 0.28 nm from the SWNT. The multi-point

interactions are considered to stabilise the complexes in solution to improve the solubility and enable the chiral nano-tweezers to discriminate the helical structures of SWNTs.

The enthalpy of the association of *LH* and *RH* helicities of (6,5)-SWNT with one (*S*)-diporphyrin molecule are calculated to be -56.04 and -56.36 kcal/mol, respectively. The energy gap between these two different complexes, *LH:(S)-1* and *RH:(S)-1*, should grow as the number of the diporphyrin molecules bound to the SWNT increases, making *RH:(S)-1* even more stable and, as a result, more soluble than *LH:(S)-1*. The results of this calculation indicate that right-handed (6,5)-SWNTs are preferentially extracted with (*S*)-**1**. As expected, the opposite result was obtained in calculations concerning the mirror image nano-tweezers (*R*)-**1**, indicating that left-handed (6,5)-SWNTs form more stable complexes (i.e., *LH:(R)-1* is more stable than *RH:(R)-1*) with this compound, than right-handed SWNTs, which reinforces the validity of the calculation. In this case, therefore, (*R*)-**1** selectively extracts and enriches left-handed nanotubes (Supplementary Information, Fig. S3).

In order to eliminate the possibility of CD activity induced by residual porphyrin molecules, thorough liberation of chiral nano-tweezers from the SWNT complexes was directly confirmed by disappearance of the Soret absorption band (Fig. 3a) both in the last washing (Supplementary Information, Fig. S4) and in the D₂O suspension of the washed SWNTs (Fig. 4a). In the CD spectra, the signs were observed to invert at 430, 600 and 1000 nm after liberation of chiral diporphyrin, i.e., ($-$, $+$, $+$) signals of SWNTs:(*R*)-**1** and ($+$, $-$, $-$) signals of SWNTs:(*S*)-**1** in Fig. 3 turned into ($+$, $-$, $-$) and ($-$, $+$, $+$) in Figs. 4a and b by the removal of (*R*)-**1** and (*S*)-**1**, respectively.

The signal inversions at 430 and 600 nm suggest that the CD activity inherent to porphyrin-free SWNTs become dominant in Fig. 4a after removal of the strong CD

influence of chiral diporphyrins shown in Figs. 3a and b. Around 1000 nm, where the diporphyrins have no CD activity, the CDs originating from SWNTs are opposite in Figs. 3c and 4b, apparently indicating that the CD in Fig. 3c is induced by the chiral diporphyrins and that the one in Fig. 4b is intrinsic to SWNTs. Even if a small amount of diporphyrin still remains bound to the nanotubes, it should be replaced by a large excess of SDBS⁴, one of the most powerful solubilising agent, on the solubilisation of SWNTs. We conclude from the above discussion that there is no chance of induced CD in Fig. 4 and, therefore, that optically active SWNTs are obtained for the first time.

METHODS

SYNTHESIS OF NANO-TWEEZERS

(*R*)- and (*S*)-Diporphyrins (Fig. 1) were prepared in the same procedure via double Suzuki-Miyaura coupling reaction of the corresponding chiral monoporphyrins (see Supplementary Information, Methods and Fig. S1).

EXTRACTION OF SWNTS

SWNTs (11 mg, CoMoCAT, SouthWest NanoTechnologies, Inc.)⁵ and (*R*)- or (*S*)-**1** (11 mg) in methanol (20 ml) were bath-sonicated at 20 °C for 5 h. After the resulting suspension was centrifuged at 50400 *g* for 5 h, the brownish supernatant was analyzed by UV-VIS-NIR and CD measurements (Fig. 3). After concentration, the residue was washed with THF twice and pyridine five times until the thorough removal of diporphyrins was confirmed by UV-VIS spectra of the washings (Supplementary

Information, Fig. S4). The SWNTs free from the chiral diporphyrin were analyzed with TEM to confirm that metal impurities were mostly removed through the extraction process (Supplementary Information, Fig. S5). Then, the SWNTs were sonicated in D₂O (18.5 ml) with tip-type apparatus in the presence of SDBS (10 mg/ml) for 40 min. After centrifugation of the resulting suspension for 15 min, the upper layer (~75%) of the supernatant was subjected to UV-VIS-NIR and CD spectroscopic analyses (Fig. 4).

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References

1. Baughman, R. H., Zakhidov, A. A. & de Heer, W. A. Carbon Nanotubes-the route toward applications. *Science* **297**, 787-792 (2002).
2. Iijima, S. & Ichihashi, T. Single-shell carbon nanotubes of 1-nm diameter. *Nature* **363**, 603-605 (1993).
3. Bethune, D. S. et al. Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. *Nature* **363**, 605-607 (1993).
4. Dukovic, G. et al. Racemic single-walled carbon nanotubes exhibit circular dichroism when wrapped with DNA. *J. Am. Chem. Soc.* **128**, 9004-9005 (2006).
5. Bachilo, S. M. et al. Narrow (*n,m*)-distribution of single-walled carbon nanotubes grown using a solid supported catalyst. *J. Am. Chem. Soc.* **125**, 11186-11187 (2003).

6. Collins, P. G., Arnold, M. S. & Avouris, P. Engineering carbon nanotubes and nanotube circuits using electrical breakdown. *Science* **292**, 706-709 (2001).
7. Krupke, R., Hennrich, F., Löhneysen, H. v. & Kappes, M. M. Separation of metallic from semiconducting single-walled carbon nanotubes. *Science* **301**, 344-347 (2003).
8. Strano, M. S. et al. Electronic structure control of single-walled carbon nanotube functionalization. *Science* **301**, 1519-1522 (2003).
9. Zheng, M. et al. DNA-assisted dispersion and separation of carbon nanotubes. *Nature Mater.* **2**, 338-342 (2003).
10. Li, H. et al. Selective interactions of porphyrins with semiconducting single-walled carbon nanotubes. *J. Am. Chem. Soc.* **126**, 1014-1015 (2004).
11. Arnold, M. S., Green, A. A., Hulvat, J. F., Stupp, S. I. & Hersam, M. C. Sorting carbon nanotubes by electronic structure using density differentiation. *Nature Nanotechnology* **1**, 60-65 (2006).
12. Maeda, Y. et al. Dispersion and separation of small-diameter single-walled carbon nanotubes. *J. Am. Chem. Soc.* **128**, 12239-12242 (2006).
13. Zheng, M. et al. Structure-based carbon nanotube sorting by sequence-dependent DNA assembly. *Science* **302**, 1545-1548 (2003).
14. Duesberg, G. S., Muster, J., Krstic, V., Burghard, M. & Roth, S. Chromatographic size separation of single-walled carbon nanotubes. *Appl. Phys. A* **67**, 117-119 (1998).

15. Chattopadhyay, D., Lastella, S., Kim, S. & Papadimitrakopoulos, F. Length separation of zwitterion-functionalized single wall carbon nanotubes by GPC. *J. Am. Chem. Soc.* **124**, 728-729 (2002).
16. Duesberg, G. S. et al. Chromatography of carbon nanotubes. *Synth. Metals* **103**, 2484-2485 (1999).
17. Farkas, E., Anderson, M. E., Chen, Z. & Rinzler, A. G. Length sorting cut single wall carbon nanotubes by high performance liquid chromatography. *Chem. Phys. Lett.* **363**, 111-116 (2002).
18. Heller, D. A. et al. Concomitant length and diameter separation of single-walled carbon nanotubes. *J. Am. Chem. Soc.* **126**, 14567-14573 (2004).
19. Wildöer, J. W. G., Venema, L. C., Rinzler, A. G., Smalley, R. E. & Dekker, C. Electronic structure of atomically resolved carbon nanotubes. *Nature* **391**, 59-62 (1998).
20. Odom, T. W., Huang, J.-L., Kim, P. & Lieber, C. M. Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature* **391**, 62-64 (1998).
21. Liu, Z. et al. Determination of optical isomers for left-handed or right-handed chiral double-wall carbon nanotubes. *Phys. Rev. Lett.* **95**, 187406 (2005).
22. Hashimoto, A. et al. Atomic correlation between adjacent graphene layers in double-wall carbon nanotubes. *Phys. Rev. Lett.* **94**, 045504 (2005).
23. Meyer, R. R. et al. A composite method for the determination of the chirality of single walled carbon nanotubes. *J. Microsc.* **212**, 152-157 (2003).

24. Tasaki, S., Maekawa, K. & Yamabe, T. p-band contribution to the optical properties of carbon nanotubes: effects of chirality. *Phys. Rev. B* **57**, 9301-9318 (1998).
25. Ivchenko, E. L. & Spivak, B. Chirality effects in carbon nanotubes. *Phys. Rev. B* **66**, 155404 (2002).
26. Samsonidze, G. G. et al. Interband optical transitions in left- and right-handed single-walled carbon nanotubes. *Phys. Rev. B* **69**, 205402 (2004).
27. S.-Castillo, A., R.-Velázquez, C. E. & Noguez, C. Optical circular dichroism of single-wall carbon nanotubes. *Phys. Rev. B* **73**, 045401 (2006).
28. Bachilo, S. M. et al. Structure-assigned optical spectra of single-walled carbon nanotubes. *Science* **298**, 2361-2366 (2002).
29. Borovkov, V. V., Hembury, G. A. & Inoue, Y. Origin, control, and application of supramolecular chirogenesis in bisporphyrin-based systems. *Acc. Chem. Res.* **37**, 449-459 (2004).
30. Weisman, R. B. & Bachilo, S. M. Dependence of optical transition energies on structure for single-walled carbon-nanotubes in aqueous suspension: an empirical Kataura plot. *Nano. Lett.* **3**, 1235-1238 (2003).

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Author contributions

X.P., N. K., and A.O. conceived and designed the experiments. T. K. and S. A. provided suggestions on the experiments. X.P. performed most of the experiments and analyses. T. S. contributed to solubilisation of SWNTs. X. P. and S. B. carried out the theoretical calculations. N. K. and A. O. co-wrote the paper.

Competing financial interests

The authors declare no competing financial interests.

Figure captions

Figure 1 Chiral nano-tweezers used to separate left- and right-handed isomers of chiral SWNTs. Two non-superimposable mirror image compounds (*R*)-1 and (*S*)-1 each comprise two large flat porphyrin rings linked through a 1,3-

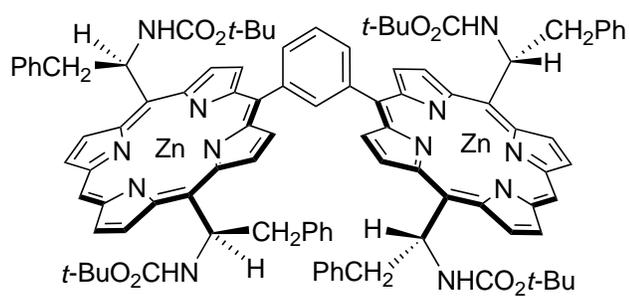
substituted phenyl ring. Since all four stereogenic centres in each molecule have the same configuration, the chiral nano-tweezers are simply designated as (*R*)-1 and (*S*)-1. Phenyl groups are abbreviated as 'Ph' and tertiary-butyl groups as '*t*-Bu'.

Figure 2 Schematic representation of the separation of left-handed (*LH*) and right-handed (*RH*) SWNTs with a chiral diporphyrin, (*S*)-1. **a**, A commercial sample of SWNTs containing left- and right-handed helical isomers is suspended in a methanol solution containing the (*S*)-1 nano-tweezers. **b**, After treatment in an ultrasound bath, some SWNTs are solubilized by forming complexes with multiple copies of the nanotweezers. Energy-minimised structures of the complexes *LH*:(*S*)-1 and *RH*:(*S*)-1, obtained using a comprehensive molecular mechanics (MMMF) calculation indicate that the right-handed nanotubes form stronger complexes and are solubilized in larger amounts than the left-handed ones. **c**, After centrifugation and collection of the supernatant liquid, the samples can be concentrated to give a solid. The nano-tweezers are removed by washing with tetrahydrofuran and pyridine solvents to leave free carbon nanotubes, and there are more right-handed ones than left-handed because of the differential solubilization in the previous step. Although only the most abundant (6,5) SWNTs are shown in this figure, other chiral indices such as (7,5), (7,6), (8,4) and (8,3) are also included in the samples and their mirror-image forms are extracted in a similar manner.

Figure 3 CD and VIS-NIR spectra of nano-tweezers ((*R*)- and (*S*)-1) and their complexes with SWNTs (SWNTs:(*R*)-1 and SWNTs:(*S*)-1) in methanol. **a**, 380-500 nm. **b**, 500-700 nm. **c**, 900-1100 nm. The concentration of the diporphyrins is the same in the solutions of (*R*)- and (*S*)-1, and also of

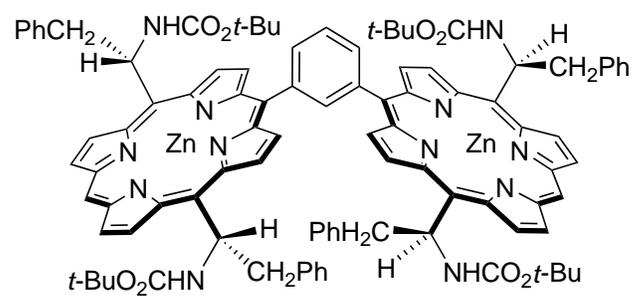
SWNTs:(*R*)-1 and SWNTs:(*S*)-1, which is confirmed by the absorption of the Soret band.

Figure 4 CD and UV-VIS spectra of SWNTs extracted with (*R*)- and (*S*)-1 after removal of the chiral nano-tweezers. a, D₂O / SDBS solution at 300-700 nm. b, D₂O / SDBS solution at 900-1050 nm. c, THF suspension at 300-700 nm. Each CD is assigned to the chiral index shown above by the UV-VIS spectra. The concentration of the SWNTs is the same in the solutions or suspensions of SWNTs extracted with (*R*)- and (*S*)-1.



(R)-1

mirror image



(S)-1

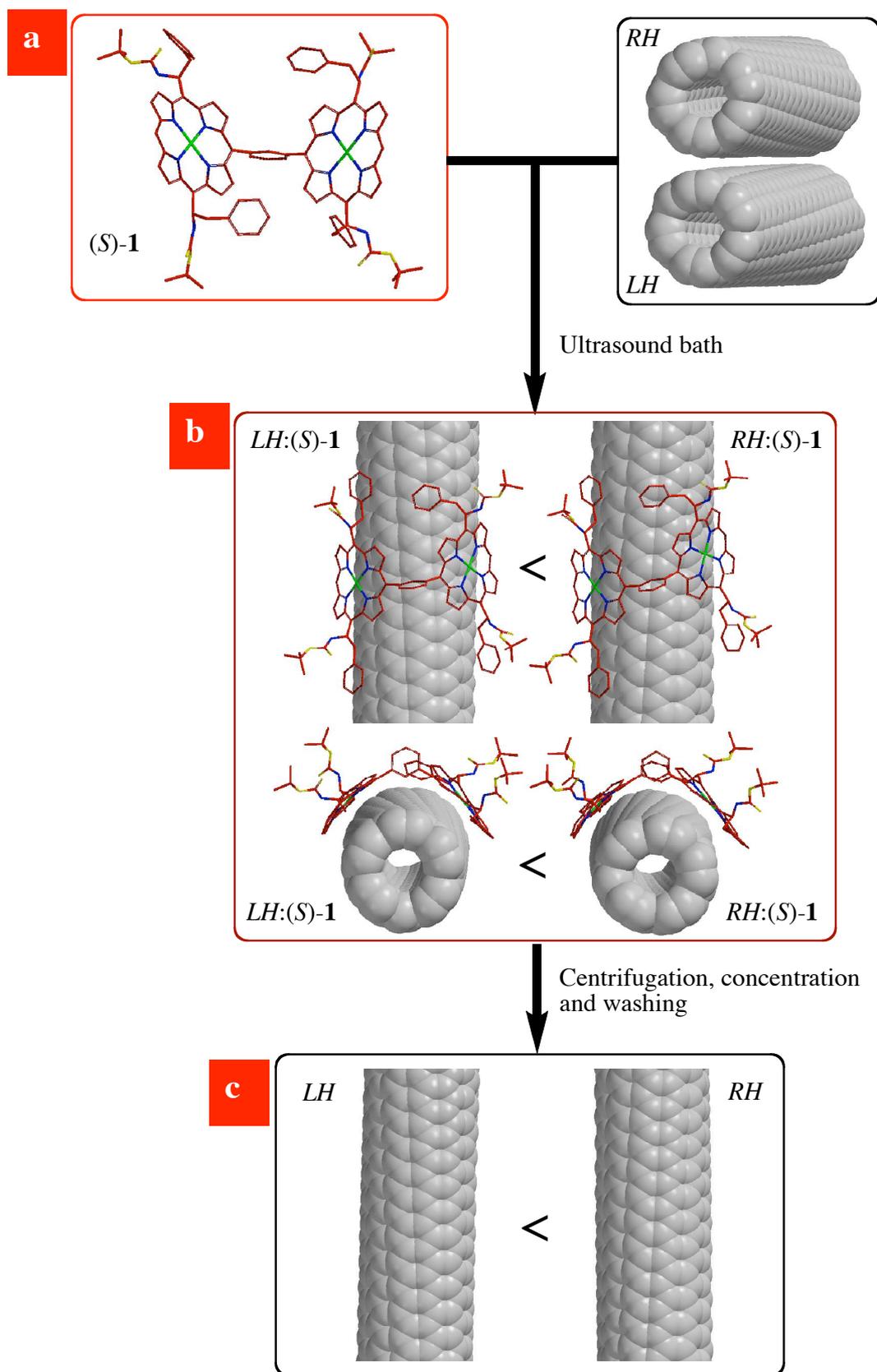


Figure 2

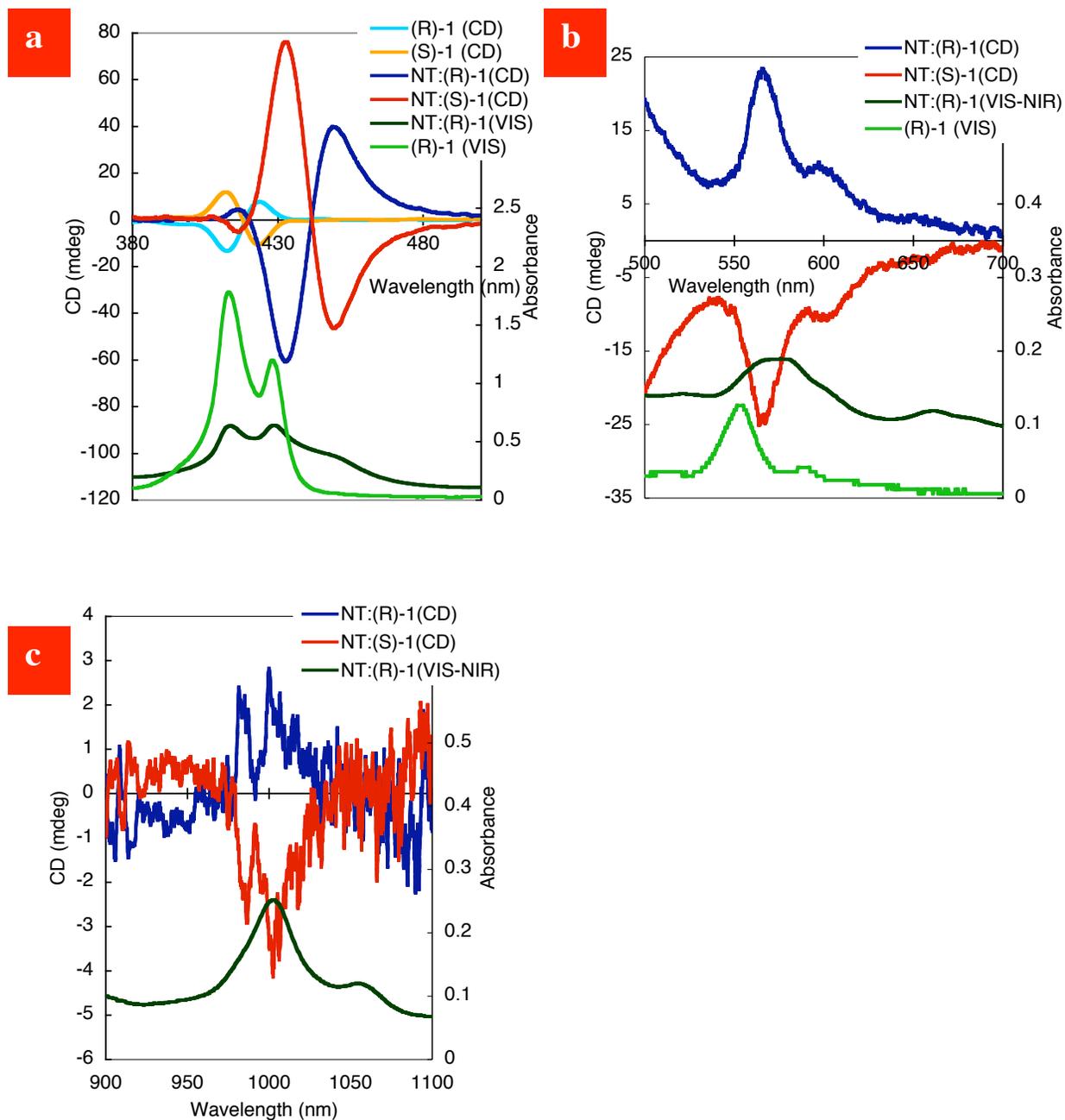


Figure 3

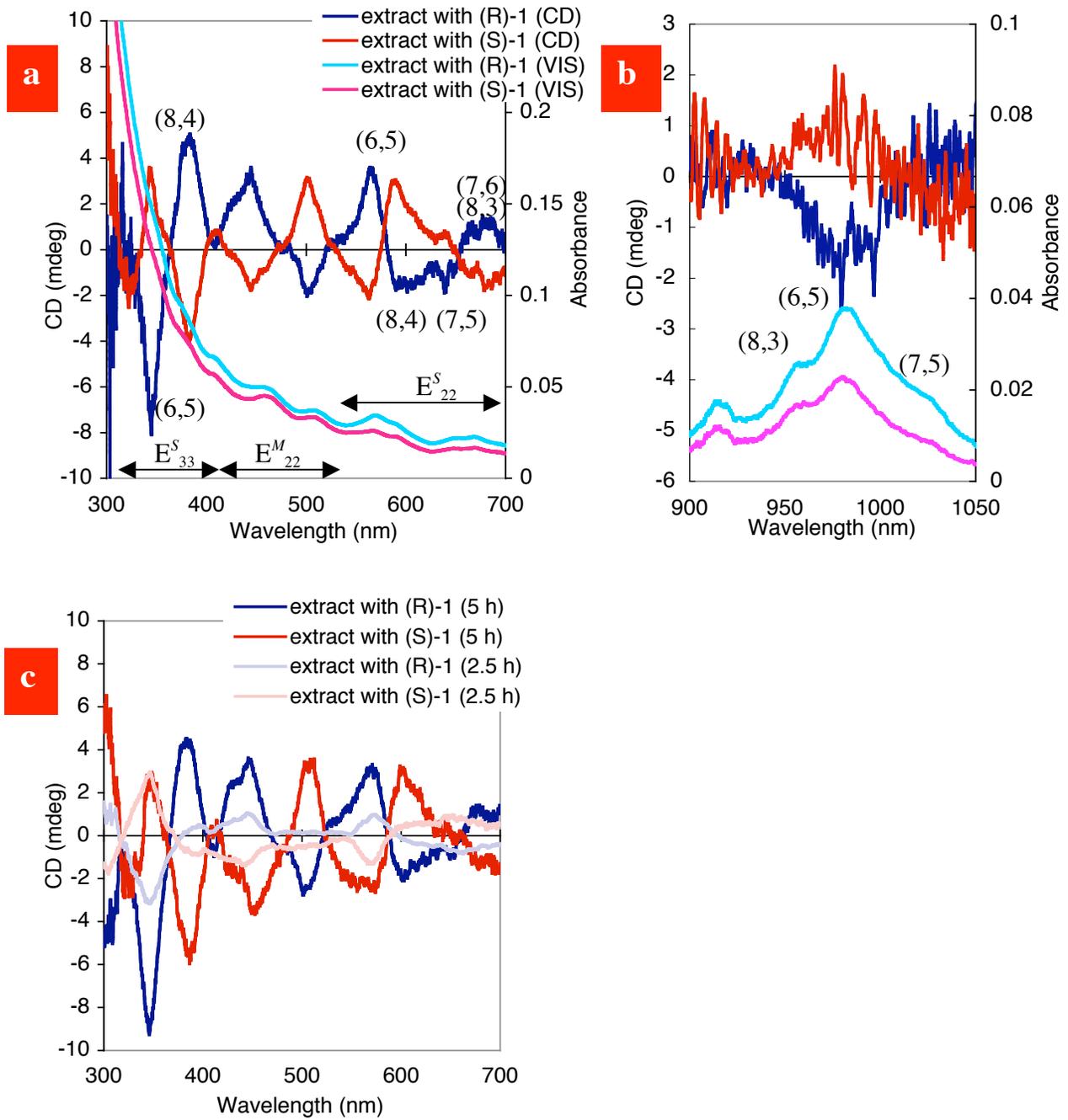


Figure 4