

Chirality Dependence of the Absorption Cross Section of Carbon Nanotubes

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The variation of the optical absorption of carbon nanotubes with their geometry has been a long-standing question at the heart of both metrological and applicative issues, in particular because optical spectroscopy is one of the primary tools for the assessment of the chiral species abundance of samples. Here, we tackle the chirality dependence of the optical absorption with an original method involving ultraefficient energy transfer in porphyrin-nanotube compounds that allows uniform photoexcitation of all chiral species. We measure the absolute absorption cross section of a wide range of semiconducting nanotubes at their S_{22} transition and show that it varies by up to a factor of 2.2 with the chiral angle, with type I nanotubes showing a larger absorption. In contrast, the luminescence quantum yield remains almost constant.

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The versatility of the physical properties of single-wall carbon nanotubes (SWNTs) with respect to their geometry [the so-called (n, m) chiral species] is very attractive for applications [1–4], but, on the other hand, the uncontrolled mixtures of species produced by regular synthesis methods blur out their specific properties. Postgrowth sorting methods now allow to enrich samples in some specific species [5], but they also miss a tool for the quantitative assessment of their outcome. Optical techniques such as absorption, photoluminescence (PL) or resonant Raman spectroscopies are the primary tools to this end. However, these techniques can neither give a quantitative estimate of the species concentration nor their relative abundance to date because they miss the knowledge of the (n, m) dependence of the optical cross section at the nanotubes' resonances (S_{11} and S_{22}). Although several studies revealed that the optical properties of carbon nanotubes depend on their chiral angle, they all actually dealt with a combination of physical parameters (such as the absorption cross section, Raman scattering cross section, or PL quantum efficiency). As a result, the literature gives quite contradictory or inconclusive results, some of them pointing to a larger abundance of near armchair nanotubes (interpreted as energetically favored in the growth process), whereas other studies concluded for a larger optical cross section for large chiral angles [6–10].

Here, we propose an original method for assessing the chirality dependence of the absorption cross section of semiconducting carbon nanotubes, by means of noncovalent functionalization with tetraphenyl porphyrin (TPP) molecules (inset of Fig. 1). This functionalization gives rise to an extremely efficient energy transfer [11] that allows us to excite uniformly the whole set of carbon nanotubes regardless of their chirality. By comparison with the PL signal obtained in the regular excitation

scheme (on the intrinsic S_{22} transition of the SWNTs) of the same sample, we can single out the contribution of the absorption cross section in the chirality dependence of the PL intensity. We show that the main variation of this absorption cross section comes from the chiral angle θ [12] and fits well to the inverse of the geometrical parameter $q \cos(3\theta)$, where $q = n - m \pmod{3}$ stands for the family type: $q = +1$ ($q = -1$) for the so-called type II (type I) nanotubes. In contrast, we show that the PL quantum yield hardly depends on the chiral species. This opens the way to the quantitative analysis of the chiral species content of samples by means of optical tools.

The (n, m) dependence of the optical cross section of carbon nanotubes has been investigated theoretically by several teams. Computations by Reich *et al.* [14], Oyama *et al.* [15], and Malic *et al.* [16] suggest with different physical arguments that the S_{22} absorption of the chiral species with small chiral angles and $q = +1$ is intrinsically weaker. From an experimental point of view, several studies combining PL and Raman spectroscopies [9] or PL and TEM [8] concluded for a sizable (n, m) dependence of the optical signals. However, the specific (n, m) dependence of the absorption cross section σ could not be singled out. As a work around, Tsybolski *et al.* [17] proposed to use empirical factors to estimate the abundance of each chirality based on the so-called action cross section A that combines the absorption cross section at the S_{22} transition ($\sigma_{S_{22}}$) and the photoluminescence quantum yield (ϕ_{PL}) of the nanotubes. In total, a thorough experimental investigation of the chiral angle dependence of the absorption of SWNTs is still lacking despite the important metrological and applicative issues at stake.

Nonpurified HiPCO and CoMoCat nanotubes were functionalized with free-base tetraphenyl porphyrin (TPP) in aqueous solution by means of the micelle swelling

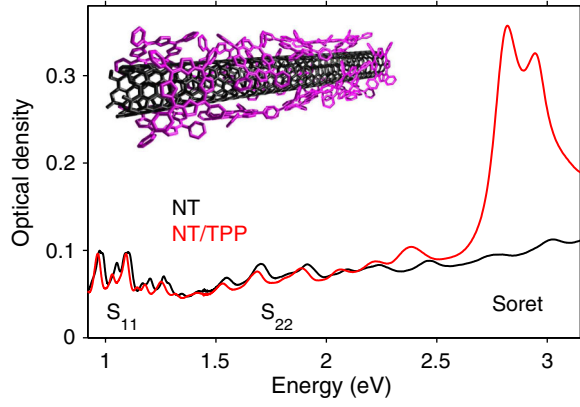


FIG. 1 (color online). Optical absorption spectra of HiPCO SWNTs (black) and SWNT/TPP compounds (red) in micellar solutions. Inset: Schematic view of the noncovalent SWNT/TPP compound.

method (see Ref. [18] for details). The optical absorption spectrum of the HiPCO nanotube-porphyrin compounds is shown in Fig. 1.

The resonance at 2.82 eV corresponds to the so-called Soret band of the TPP molecules stacked on the nanotube walls. The shoulder at 2.95 eV is the contribution of residual free porphyrins. The absorption bands in the 0.9–1.35 eV range correspond to the S_{11} transitions of the various chiral species of nanotubes.

PL maps were recorded using an InGaAs detector and using the output of a monochromator illuminated by a UV-vis Xe lamp for the excitation (5 nm excitation steps). The PL intensity is normalized by the incoming photon flux at each excitation wavelength. The lower part of the PL map (Fig. 2) displays several bright spots that correspond to the emission of carbon nanotubes at their S_{11} transition upon excitation on their S_{22} transition. Each spot can be assigned to a specific chiral species following the procedure proposed by Bachilo *et al.* [6]. An additional set of resonances can be seen at the same emission energies for an excitation at 2.82 eV. This energy corresponds to the absorption of the porphyrin molecules stacked on the nanotube. We assign these spots to the resonant excitation of the Soret transition of porphyrin followed by energy transfer to the nanotube and by the regular S_{11} emission of the nanotubes [11,19–21]. In other words, the emission of the nanotubes is enhanced when the excitation is tuned in resonance with the porphyrin molecules. As can be seen qualitatively in the figure, this resonance appears for all chiral species. Therefore, this energy transfer resonance provides a new handle to achieve uniform photoexcitation of the whole set of chiral species.

This PL map allows us to compare the optical properties of the different chiral species of nanotubes and infer their intrinsic absorption cross sections. Let us define, for each (n, m) species, the ratio R between the PL intensities recorded for an excitation on the Soret resonance (I_{Soret}^{NT})

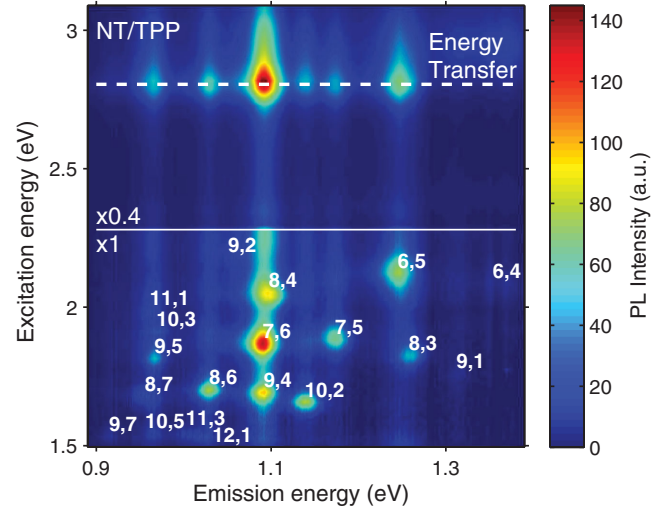


FIG. 2 (color). PL map of the HiPCO SWNT/TPP compounds suspension. The dashed white line at 2.82 eV is a guide to the eye showing the energy transfer resonance upon excitation of the TPP molecules. The spectra are normalized to a constant incoming photon flux. The upper part intensities are reduced by a factor 0.4 for the sake of clarity.

or for an excitation on the intrinsic S_{22} resonance ($I_{S_{22}}^{NT}$) [22]. Provided that all spectra are normalized to the incoming photon flux, R reads

$$R = \frac{I_{\text{Soret}}^{NT}}{I_{S_{22}}^{NT}} = \frac{\sigma_{\text{TPP}} N \eta_T C_{n,m} \phi_{\text{PL}}}{\sigma_{S_{22}} C_{n,m} \phi_{\text{PL}}} = \frac{\sigma_{\text{TPP}} N \eta_T}{\sigma_{S_{22}}} \quad (1)$$

I_{Soret}^{NT} is proportional to σ_{TPP} (absorption cross section of the TPP molecule), N (number of molecules stacked on a nanotube per unit length), η_T (energy transfer quantum yield), $C_{n,m}$ (species concentration), and ϕ_{PL} (PL quantum yield of nanotubes). $I_{S_{22}}^{NT}$ is proportional to $\sigma_{S_{22}}$ (absorption cross section of the nanotube at the S_{22} transition per unit length), $C_{n,m}$ and ϕ_{PL} [11].

The important point here is that R is the ratio of two PL intensities measured on the same transition (S_{11}) for the same chiral species and for the same sample. Thus, this ratio allows us to eliminate the contribution of the unknown PL quantum yield ϕ_{PL} and the contribution of the unknown species concentration $C_{n,m}$. This point is crucial since these two parameters are very difficult to measure, which is the main reason that has hampered the determination of $\sigma_{S_{22}}$ in previous studies. Finally, we have shown recently that both the direct and transfer excitation mechanisms share the same polarization diagram due to the reshaping of the electric field in the close vicinity of the nanotube [23]. As a consequence, polarization dependences are also eliminated in R provided that polarized cross sections are used in the calculation. Namely, we obtain $\sigma_{S_{22}}^{\prime\prime} \approx 3\langle\sigma_{S_{22}}\rangle_{\text{or}}$ by using $\sigma_{\text{TPP}}^{\prime\prime} \approx 3/2\langle\sigma_{\text{TPP}}\rangle_{\text{or}}$ in (1), where $\langle\ \rangle_{\text{or}}$ stands for the average over random orientations (see Supplemental Material [24]).

R can bring an original insight into the (n, m) dependence of $\sigma_{S_{22}}$ provided that both the coverage N and the transfer yield η_T do not depend on the chiral species (see Eq. (1)). To assess the coverage N , we performed in a previous study a systematic analysis of the functionalization degree as a function of the amount of TPP molecules ([18] and [24]). We found that all the spectroscopic signatures of functionalization reach a plateau above a critical TPP concentration while those of free TPP grow linearly. This is interpreted as the completion of a full single layer of TPP molecules on the nanotube. Molecular simulations show that the TPP/SWNT distance is 0.32 nm and that the average distance between TPP molecules is $L_{\text{TPP}} \approx 1.6$ nm [25]. Therefore, only 3 TPP molecules can fit on the circumference of a nanotube for any of the species investigated in this study. Thus, we assume $N = 3/L_{\text{TPP}}$, with no (n, m) dependence [26].

The transfer quantum yield η_T was assessed in a former study and turned out to be of the order of 99.9% on average in a sample enriched in the (6,5) species [11]. One of the methods used for this estimate relies on the average quenching of the Q bands luminescence of TPP molecules stacked on the nanotubes, which is greater than 10^3 . We observe the same quenching for unsorted nanotubes. Clearly, this would not be possible if the transfer yield was to be significantly lower for some chiral species. Therefore, we can safely assume that the energy transfer occurs with an almost 100% efficiency for all chiral species observed in this sample. Note also that the time-resolved measurements reported in Ref. [27] support the same conclusion and give similar results for unsorted nanotubes.

We end up with the important result that R is simply proportional to $1/\sigma_{S_{22}}$, the proportionality coefficient being the same for all chiral species. R is thus a direct image of the relative variations of $\sigma_{S_{22}}$ with the chiral species.

Practically, R is estimated from a global fitting of the lines of the PL map (Fig. 2, see [24] for details). We were able to measure R for 13 chiral species spanning a wide range of chiral angles and the 0.68–1.1 nm diameter range.

We find that R , and hence $\sigma_{S_{22}}$, shows no clear dependence with respect to the nanotube diameter (see Supplemental Material [24]). In contrast, Fig. 3 shows a linear relationship between R and the geometrical parameter $q \cos(3\theta)$. R , and hence $\sigma_{S_{22}}$, strongly depend on the chiral angle regardless of the diameter and vary by up to a factor 2.2 for zigzag nanotubes of opposite families. Generally speaking, type I SWNTs show a larger absorption than their type II counterparts.

R can be compared for each chiral species to the PL action cross section A reported in the literature [17]. This quantity is the product of the absorption cross section $\sigma_{S_{22}}$ with the PL quantum yield ϕ_{PL} . The inverse of the action cross section experimentally evaluated for individual pristine nanotubes by Tsyboulski *et al.* is reported in Fig. 3,

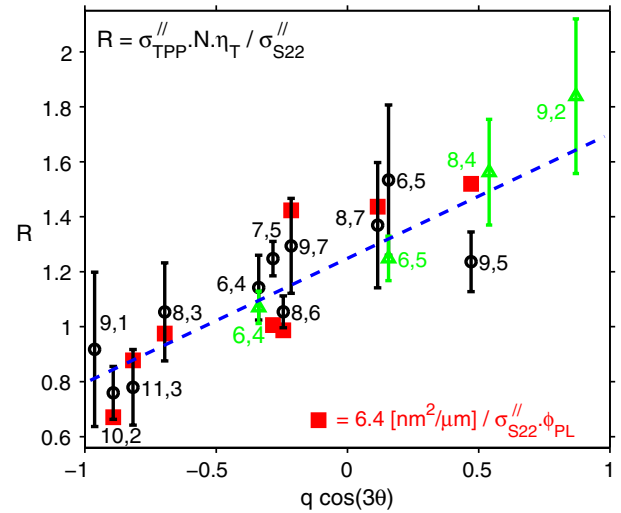


FIG. 3 (color online). Black circles: R ratio between the PL intensity excited on the Soret resonance and the PL intensity excited on the intrinsic S_{22} resonance in the HiPCO based SWNT/TPP compounds as a function of $q \cos(3\theta)$. Green triangles: same ratio R evaluated for a sample made from CoMoCat material. Blue line: linear fit of R . Red squares: Inverse of the action cross section A of pristine nanotubes (from Ref. [17]) scaled with a simple proportionality factor.

simply scaled by an arbitrary factor. Obviously, R and $1/A$ share the same variations with $q \cos(3\theta)$. This excellent agreement between the two sets of data is particularly remarkable for they stem from different types of samples and were obtained with different setups and methods. This strongly supports our conclusion that R reflects intrinsic properties of the nanotubes, independently of the excitation scheme through the porphyrins.

This new insight into the chiral dependence of the absorption cross section is extremely valuable for assessing the relative abundance of chiral species in a sample and can be used to revisit the previous chiral species abundance assessment deduced from absorption or PL measurements [6]. The absorption corrected data lead to much more symmetrical chiral angle distributions, with no preferential type (I or II) of nanotubes (see Supplemental Material [24]). Retrospectively, the limited number of type II nanotubes observed in this study may be understood as a consequence of their lower absorption and thus reduced PL signal rather than weaker abundance. We note that even after correction near zigzag nanotubes are found to be less abundant, raising questions about the underlying growth mechanism.

The (n, m) dependence of the absorption of carbon nanotubes can be compared to theoretical models available in the literature. Especially, Oyama *et al.* computed explicitly the absorption cross section on the S_{22} transition for all the chiral species observed in this study [15]. We report their data, simply scaled by an arbitrary factor, in Fig. 4 together with the experimental absorption cross sections evaluated

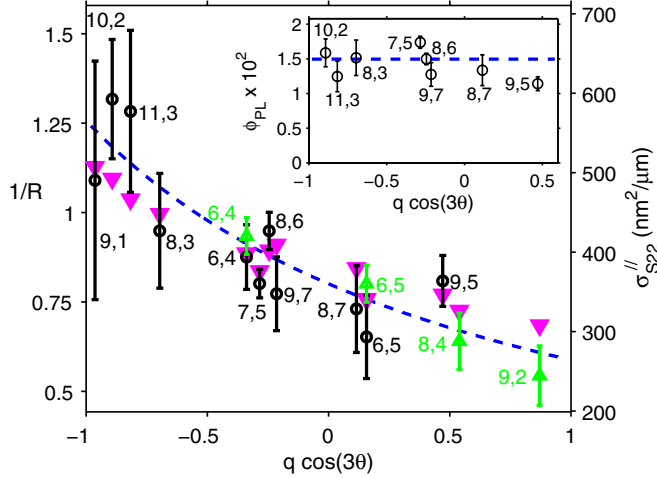


FIG. 4 (color online). Inverse of the R ratio (which is directly proportional to the absorption cross section), as a function of $q \cos(3\theta)$ for HiPCO (black dots) and CoMoCat nanotubes (green triangles). Purple down triangles: Theoretically calculated absorption probability (arb. units, from Ref. [15]). Blue line: fit to the data leading to the empirical formula (2). Inset: PL quantum yield as a function of $q \cos(3\theta)$ deduced from the action cross section measured in Ref. [17] and from the absorption cross section presented in the main figure.

in our study. The general trend is well accounted for by the calculations, with the largest absorption for $q = -1$, near zigzag nanotubes. In this model, this effect is a consequence of the trigonal warping of the band structure of graphene that leads to a chiral dependent matrix element for optical transitions. However, the calculations give an underestimated variation of the absorption cross section with the chiral angle. This may find its origin in many-body effects or $\sigma - \pi$ hybridization effects not included in the model, which can lead to additional (n, m) dependences.

Finally, we can extract absolute estimates for the absorption cross sections by exploiting the knowledge of the absorption of the TPP molecule used as an absorbing unit in the transfer process. Assuming the expressions for N and η_T discussed previously and an absorption cross section $\sigma''_{\text{TPP}} = 2.4 \times 10^{-15} \text{ cm}^2$ (see Supplemental Material [24]), we deduce $\sigma''_{S_{22}}$ for the whole set of species (Fig. 4, right scale and Table in the Supplemental Material [24]). In particular, we can compare our estimate for the very few species for which absorption measurements have been reported in the literature, e.g., for the (6,5) species [28–32]. Using completely different approaches, these studies yielded $\sigma''_{S_{22}}$ ranging from 3 to 300 $\text{nm}^2/\mu\text{m}$, as compared to our own estimate of $\sigma''_{S_{22}}(6, 5) \approx 330 \pm 60 \text{ nm}^2/\mu\text{m}$.

In addition, we can deduce the PL quantum yield ϕ_{PL} of each (n, m) species from the scaling factor between $\sigma''_{S_{22}}$ and the action cross section of Ref. [17] (Fig. 3). We deduce from our absolute estimates of $\sigma''_{S_{22}}$ that ϕ_{PL} is of the order of 1.4% in the sample of Ref. [17] for all chiral

species. The spread of ϕ_{PL} is of the order of $\pm 10\%$ around this mean value (see inset of Fig. 4). This tends to show that the chiral dependence of the PL quantum yield is negligible in agreement with theoretical predictions [15,16] and more generally that most of the (n, m) dependence in the nanotubes PL signal comes from the S_{22} resonant absorption. Assuming that the nonradiative relaxation processes do not strongly depend on the chiral species, we can further infer that the variation of $\sigma''_{S_{11}}$ with the chiral species must be much smaller than that of $\sigma''_{S_{22}}$.

For practical purposes, we deduce from the linear fit to the data in Fig. 3, a simple empirical expression for the absorption cross section $\sigma''_{S_{22}}$ of a (n, m) nanotube:

$$\sigma''_{S_{22}} = \frac{10^3}{q \cos(3\theta) + 2.8}, \quad (2)$$

where σ is in $\text{nm}^2/\mu\text{m}$. This empirical formula provides an estimate with an uncertainty of about $\pm 20\%$ and remains restricted to the case of small diameter ($0.7 \text{ nm} < d_i < 1.1 \text{ nm}$) semiconducting nanotubes. A possible generalization would obviously require an additional diameter dependence to be introduced in the empirical formula. This diameter dependence could not be included properly in this study since the diameter variations ($\pm 20\%$ around the mean value) are of the order of the experimental uncertainties.

In conclusion, we proposed an original method to address a key pending issue in the physics of carbon nanotubes—the chirality dependence of the absorption cross section. We measured the absolute variations of this absorption cross section and proposed an empirical law. In particular, we showed that the type I semiconducting species show a significantly larger absorption than the type II species, whereas their PL quantum yields are almost identical. This study opens the way to quantitative analysis of the chiral species content of samples based on optical measurements. In addition, the tools developed in this study bring a new attractive feature—a uniform photoexcitation of the whole set of chiral species in a sample. This opens an avenue to the investigation of other intrinsic optical properties of SWNTs and to new approaches for using SWNTs in labeling applications.

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