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A new light on molecule-nanotube hybrids

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Abstract:

Optoelectronics is benefitting from outstanding new nanomaterials providing emission/detection in the whole visible and near infra-red range, photoswitches, two level systems for single photon emission etc. Among these, carbon nanotubes have first been envisioned as game changers while the difficult handling and control over chirality burden their use. However recent breakthroughs on hybrid carbon nanotubes establish nanotubes as pioneers for a new family of building blocks for optics and quantum optics. Functionalization of carbon nanotubes with molecules or polymers not only preserves the nanotube properties from the environment, but also provides new performance to the resulting hybrids. Photoluminescence and Raman signals are enhanced in the hybrids which questions the nature of the electronic coupling between nanotube and molecules. Furthermore, coupling to optical cavities enhances dramatically single photon emission which operates up to room temperature. This new light on nanotube hybrids shows their potential to push optoelectronics a step forward.

1. Introduction

Optoelectronics and quantum optics rely heavily on particular properties, such as strong exciton binding energy, electrically driven emission, tunable emitted wavelength, single photon source, which carbon nanotubes (CNTs) are known to exhibit.^[1] However, their use has been hindered since the chirality of CNTs has the most impact on their optical and electronic properties and their photoluminescence (PL) quantum yield is poor, which renders them less competitive. Still, efforts have been successfully pursued in order to manage chirality sorting and recent breakthroughs in selective growth^[2] and post-growth sorting^[3] open the possibility to select a desired chirality with given properties. Meanwhile, huge advances have been realized in the physico-chemical engineering of carbon nanotubes^[4] in order to isolate them from the detrimental influence of their local environment, or to expand their properties, by adding functional groups. Indeed, small molecules are known to provide a large range of optical properties in a reproducible manner, while being extremely difficult to address electrically. The point in realizing hybrids is then to impart a dominant, stable and reproducible property to the nanotubes. In this Report, the most recent breakthroughs performed with hybrid nanotubes will highlight the fact that hybrids are more than the sum of its parts. The focus is not here on the practical realization of the hybrids but on the advances in fundamental optics they provide.

CNT-molecule hybrids can be realized either by encapsulating molecules inside carbon nanotubes (endohedral functionalization) or by anchoring functional groups on carbon

nanotube side walls (exohedral functionalization). Photo-induced processes have been observed in both endohedral^[5,6] and exohedral^[7,8,9,10] functionalized carbon nanotubes. The techniques used to perform these different functionalizations are beyond the scope of this article and the reader can find more information in this review^[4] and references therein. The obtained hybrids undergo energy and/or charge transfer between their constituents, resulting in changes in the optical, electrical and vibrational properties of both molecules and carbon nanotubes. As reported in the early literature^[4], both non-covalent and covalent methods can be applied to exohedral functionalization with their respective own advantages and drawbacks. In the process of covalent functionalization, bond breaking leads to the disruption of the sp^2 network of nanotubes and affects the electrical and optical properties of the hybrids as compared to the pristine ones. In contrast, while noncovalent methods do not destroy the nanotube honeycomb structure, the interaction between the molecule and the carbon tube is weak, resulting in instability or poor performances. Recent works have made breakthroughs in both non-covalent and covalent functionalizations. These advances allow formation of stable functional nanotube hybrids and enhanced optical signal of the overall hybrid systems.

First section details the coupling mechanisms unveiled within non-covalent hybrids (both exo- and endohedral) and the consequent impact on the exaltation of optical and vibrational signals. Second section is devoted to the rise of covalently-bound hybrid nanotubes for quantum

optics. Last, new concepts of hybrids beyond the 1D-0D case will be reviewed for future prospects.

2. Dramatic modifications of the optical spectral response of nanotube-hybrids revealed with non-covalent functionalization

Studying the energy/charge transfer mechanisms is very important for designing new functional hybrid devices for optics and optoelectronics. In this section, we will mainly discuss the enhancement of optical signals related to energy and charge transfer within the hybrids.

In order to investigate these mechanisms, CNT-molecule hybrids should be individual to avoid fluorescence quenching caused by exciton energy transfer between different CNTs.^[11] The functional process and measurements of optical properties are carried out on networks or dispersions of individual nanotube hybrids^[5,9,12,13,14,15], or performed at the individual hybrids level.^[16] The first part of this section is devoted to photo-induced energy transfer which has been recently mainly focused on two kinds of non-covalent exohedral CNT-dye complexes: one was created through micelle swelling, the other through direct incorporation of chromophoric units into the surfactant/solvent. The second part of this section shows that charge transfer is also to be considered in both exohedral and endohedral non covalent hybrids, which, as shown in the third part, can also exhibit dramatic enhancement of their Raman responses.

2.1. Evidence of energy transfer in nanotube-molecule hybrids

Multiple optical studies focus on hybrids with molecules chosen according to their ability to perform π -stacking onto CNTs like TPPs^[8], perylene derivatives^[17] etc. Π -stacked molecules modify the nanotubes' optical transitions without preventing photoluminescence to take place, which turns out to be a precious probe for the nanotube-molecule interaction. The obtained hybrid system exhibits both signatures of nanotube and molecule as expected from preserved systems. Roquelet *et al.*^[8] reported a micelle assisted method to functionalize SWNTs non-covalently with Tetraphenylporphyrine (TPP) molecules.^[18] **(Figure 1a)** shows the absorption spectra of SWNTs (black) and SWNT/TPP hybrids (red). After the functionalization with TPPs, absorption peaks of SWNTs are slightly shifted and Soret band of TPP (2.82 eV) can be observed simultaneously. It means that the electronic properties of SWNTs and TPPs are indeed preserved. The coupling between SWNTs and porphyrins is strong enough to observe the shift of the peaks although it only has non-covalent binding in the system. The luminescence of SWNTs is strongly enhanced when the excitation energy is close to the absorption band of TPPs due to efficient energy transfer from TPPs to SWNTs, which can be seen in the PL map presented in Figure 1c.^[8,19] The fast excitation energy transfer occurs within a time scale of less than 100 fs^[20] determined through transient optical spectroscopy. Most of the theoretical^[21] and experimental works^[22,23] on nanotubes and graphene attribute this enhancement to an efficient energy transfer through a Förster process when absorption bands of the molecule are matching

the nanotube ones. In ref. ^[20], the authors discuss the limits of this Förster model for interpreting the experimental observation of energy transfer from TPP to nanotube with a rate close to 1. Indeed, the authors propose a generalized Förster model to take into account the excitonic nature of the light induced excitations (see Figure 1d). Furthermore, they point out that the observed enhancement is not chirality dependent as for an overlap of the molecule Soret band with the nanotube one. Moreover, the nanotube-molecule distance in the case of π -stacking is less than one nanometer which is more compatible with a Dexter-type energy transfer. This is in contrast with results obtained by integrating the functional molecule (perylene in this case) directly into the surfactant (Figure 1b).^[31] The energy transfer follows the Förster like transfer mechanism while the nanotube-compound distance is well below the Förster radius. In the above examples, carbon nanotubes were functionalized non-covalently but the coupling between nanotube and functional groups is still efficient enough to induce the energy transfer and enhance the optical signals. All these experimental findings point out the need for a model of energy transfer including specificity of 1D hybrids and in particular the specific role of phonons and excitons. Still, not only energy transfer between moieties needs to be accounted for in order to fully understand the properties of the hybrids. One also needs to consider the role of charge transfer in hybrid nanotubes, which will be detailed in the next section.

2.2. Role of charge transfer in electrical and vibrational response of the hybrids

In CNT-molecule hybrids, CNTs can either be charge donors or acceptors depending on the electronic properties of the two parties in the hybrids. Since ambipolar, semiconducting CNTs can accept electrons or holes tunneling from a molecular counterpart (chemical doping). It is therefore a good system to probe small molecules which are otherwise difficult to connect electrically.^[24] In general, charge transfer leads to the change of carrier density of CNTs and can be detected through transfer characteristics of transistors by shifts of the threshold voltage. An example is given in **Figure 2a**, which shows the drain-source current versus gate voltage ($I_{DS}(V_G)$) curves of CNT field effect transistors (CNFET) before and after on-chip π -stacking of porphyrins.^[25] The addition of porphyrin introduces a shift in the threshold voltage towards negative gate voltages meaning that electrons transfer from porphyrin molecules to CNTs, resulting in lifting of CNTs' Fermi level (Figure 2e). Recently, similar TPP-CNFETs were investigated in the low temperature regime (10K).^[10] At this temperature the FET still exhibits classical transfer characteristics. Thermal energy exceeds the charging energy of the micron-long nanotube conductor which accounts for Coulomb repulsion of charges and prevents Coulomb blockade to set in the transistor. However, the hybrid FETs exhibit step like features at regularly spaced gate voltages (Figure 2b) which are reminiscent of nanotube FETs decorated with single nanocrystals.^[26] These features are signatures of single charge trapping in nanoscale traps capacitively coupled to the nanotube FET: tunneling is activated by the gate-tuned electric

field since electric field lines are concentrating at the nanotube surface. In the case of TPP-nanotube FETs, the study was conducted under light illumination at different wavelengths. At low temperature, the shift of the transfer characteristics is still clear according to p-doping induced by the excitation of the TPP molecules. Again, the signature of single charge tunneling is modified only for a wavelength matching an absorption peak from the molecule, meaning the dynamics of single charge tunneling between the molecular trap and the nanotube depends on the molecule excitation by means of the modification of the TPP-nanotube capacitive coupling. Therefore, this hybrid FET can realize a light-tunable tunneling junction for specific wavelengths determined by the choice of the porphyrin molecule.

Besides the gate transfer characteristics method, charge transfer can also be investigated by spectroscopic methods, including PL, transient absorption and Raman spectroscopy. Thanks to the unique and rich vibration properties of carbon nanotubes, Raman spectroscopy has been used extensively to investigate CNTs. Doping nanotubes and graphene is known to shift the position and to change the width of the Raman G mode.^[27,28] In the case of hybrid nanotubes^[29] or graphene^[30], a charge transfer from the molecules to the CNTs will be visible as a shift of the Raman G mode of nanotubes. Moreover, in metallic CNTs, electron-phonon coupling strength can be modified by charge transfer, which is observed and quantified experimentally through the G mode width.^[28] Figure 2c shows the comparison of CNT Raman spectra before and after grafting TPPZn molecules.^[10] The spectra are taken at 532 nm excitation wavelength

at which, normally, Raman signature is hidden by luminescence in the molecule powder. But when deposited onto CNTs, TPPZn luminescence is quenched by the nanotube and its Raman fingerprint can be observed superimposed onto the nanotube one. The nanotubes modes are also enhanced by a factor four to seven in intensity and their frequency are downshifted by 3 cm^{-1} for the G mode. The luminescence quenching and shift of nanotube modes are strong signatures of charge transfer. In the other example, the authors inserted dimethylquaterthiophenes (4T) (Figure 2d) into SWNTs.^[9] Charge transfer was also observed through shift of SWNTs' G modes when 4T molecules were inserted and in particular when the excitation laser is close to an absorption band of the oligomer.

This observation of enhancement in specific resonant conditions will be discussed in more details in the next part. Similar charge transfer peaks have been predicted for endohedral indigo@CNT hybrids in the visible and NIR range.^[31] In this article, Joshi *et al.* have demonstrated that as the nanotube diameter governs the coupling to the encapsulated species, the charge carriers mobility decreases as the diameter increases for the hybrid system. This is also corroborated by experimental studies of hydrogenated graphene ribbons inside nanotubes: specific nanotube diameters lead to a dramatic quench of the ribbon luminescence.^[32] It was argued, in the case of phtalocyanine-decorated nanotubes, that charge transfer induces changes in the energy level of the nanotube, and lowers the trion level even below the exciton one, as visible with photoluminescence.^[33]

Therefore, charge transfer between the species is clearly observed through changes in the electronic, excitonic levels, and also in the vibrational response thanks to electron-phonon coupling. There are indeed strong signatures of charge transfer, even in the case of weak interaction through non-covalent functionalization (both exo- and endohedral), which cannot be neglected. Furthermore, these are resonant processes that give rise to peculiar enhancement detailed in the following section.

2.3. Raman exaltation arising from the nanotube-molecule coupling

As we have seen before, nanotube hybrids allow coupling nanotube opto-electronic properties with molecular ones through energy and charge transfer. In this section, recent results highlight the fact that the resulting hybrid systems exhibit non-conventional features, in particular strong enhancement of the optical signatures.

This is particularly striking in the case of endohedral nanotube since 1D confinement is a new parameter determining the hybrids' properties. Endohedral filling method is a common strategy to make functional carbon nanotube hybrids. In the early works, fullerenes,^[34] metals,^[35] sulfur chain,^[36] and proteins^[37] have been inserted into carbon nanotubes using thermal and chemical methods. As we have seen in the previous section, endohedral filling leads to hybrid systems with resonant features which are strongly dependent on the nanotube-filler coupling. Recent progress has been made showing outstanding enhancement of the optical

signals of molecules or CNTs after endohedral filling, especially with dye molecules,^[38,6] perylene and carbon atoms.

Gaufrès *et al.* obtained a record enhancement of Raman signal for rod-like dyes encapsulated into SWNTs, such as α -sexithiophene and β -carotene.^[38] Due to the confinement in the nanotube hollow core, these molecules assemble inside SWNTs as highly polarizable J-aggregates. In addition to the quench of molecular luminescence by the nanotube, a giant Raman enhancement of the molecules up to 10^4 is measured (**Figure 3d**) from both resonant effect and polarizability of J-aggregated dye which allows detecting individual aggregates in the limits of optical resolution. Such hybrids are therefore promising as Raman labels for biological imaging.

Regarding non-linear optical signature of dyes, Cambré *et al.* inserted an elongated dipolar dye (p,p'-dimethylaminonitrostilbene, DANS) into SWNTs (Figure 3a,b).^[6] This molecule is known to have a strong non-linear optical (NLO) response. The optical signal of both DANS and SWNTs were influenced dramatically by the encapsulation. In accordance with the works of^[9,38], the electronic transitions of both DANS and SWNTs are modified and nearly complete quenching of the DANS molecules fluorescence is observed. Most importantly, the hybrids show an enhanced NLO response, which was proven by measuring the NLO polarizability by second harmonic light scattering: the signal of DANS inside SWNTs is enhanced by a factor of 54 to 69 compared to free DANS in chloroform solution. Actually, DANS molecules commonly

organize in an antiparallel configuration due to dipole-dipole interaction which kills the NLO signal. On the contrary, confinement in nanotubes forces a head-to tail alignment of DANS molecules which ensures the dipolar fields of each molecule add up coherently. More generally, confinement in the nanotube promotes certain molecular configurations with strong alignment: for DANS, it favours hyperpolarizability and therefore strong NLO response. Recently, Koyama *et al.* reported different molecular arrangement of perylene according to the electronic nature of nanotubes.^[15] Perylene molecules in semiconducting tubes are one dimensionally head-to-tail stacked, while they formed H-type molecular dimers in metallic SWNTs. This has strong consequences on the PL spectra of the hybrids. Indeed, PL spectra of exohedral perylene show both features of solubilized and bulk perylene, while perylene in semiconducting nanotubes have spectra similar to solubilized molecules and perylene in metallic nanotubes resemble the bulk perylene one. Conformation and chirality of the nanotubes are therefore two major ingredients to control optical response of the hybrids. Intensity of the peaks are modified, and furthermore, new features appear as demonstrated in NIR spectroscopy (Figure 3f). The exaltation of the infrared absorption response of SWNTs was found in 4T@SWNT hybrids.^[39] Encapsulation of the dye leads to a change in the IR selection rules. With DFT calculations, the enhanced IR band at 786 cm^{-1} was assigned to a “radial-like” mode of the hybrid SWNTs. Still, enhanced optical response is not limited to endohedral nanotubes. Indeed, enhancement of the Raman response was measured for a nanotube decorated with π -stacked porphyrins.^[10]

In this configuration, the enhancement (approx. one order of magnitude) occurs when the porphyrin is exposed to a light wavelength matching one of its absorption bands (Figure 3e). The difference here compared to Alvarez *et al.*^[9] is that this enhancement is not accompanied by signature of charge transfer. It is more likely associated to an alignment between an excitonic level of the system with an electronic one. Therefore, a complete picture involving both energy and charge transfer, along with alignment between electronic and excitonic levels need to be included in a general model.

Hybrid nanotubes allow addressing small light-sensitive molecules in order to obtain tailored light emission and/or charge transfer which are useful for optoelectronic applications. This has been demonstrated with non-covalent coupling between nanotubes and dyes. However, covalent grafting has also opened unexpected and very promising routes towards optoelectronics.

3. Ultimate control over the hybrids towards single photon regime

This section deals with recent breakthroughs allowing carbon nanotubes to be implemented as efficient single photon sources. The first part presents the impact of a new covalent grafting process preserving photoluminescence of nanotubes, while the second part discusses the efficiency of hybrid single photon sources up to room temperature. Last, single photon emission can be further tuned and optimized thanks to the use of optical cavities.

3.1. Covalent preservation of sp^2 delocalized electrons

At first, covalent grafting on nanotubes has been ruled-out since it is too invasive for a one-atom-thick system with poor screening. Indeed, covalent grafting of molecules requires to disrupt the sp^2 lattice of the nanotubes and the created sp^3 defects turn as scatterers for electron transport. A very versatile technique to covalently graft molecules onto nanotubes is to use diazonium salts as the anchoring groups.^[40] This reaction is however detrimental to the nanotube conductivity, yet partly reversible by thermal defunctionalization of the diazonium groups.^[41] However, new covalent strategies are now growing fast and provide very promising routes. They consist in minimizing the impact of functionalization on the sp^2 character of the conjugated carbon nanotubes by grafting divalent adducts (methylene groups) without any conductivity loss of the hybrids,^[42] or by using [2+1] cycloaddition reaction (**Figure 4a**) based on electron-poor aromatic nitrenes without any change of the PL signature (Figure 4b).^[43]

With these grafting approaches, it is now possible to use the robustness of the covalent bond to anchor a large range of moieties onto nanotubes. The control over the density of the grafted groups will allow to obtain blinking rates of the photoswitchable hybrids which are compatible with super-resolution NIR imaging for application in biology.^[44] It is also an efficient way to induce strong luminescence from trions and access spin related phenomena.^[45] From these advances, the path is now open to get full advantage of a wide range of hybrid nanotubes' optical and electronic properties in the near future.

3.2. Covalent hybrid nanotubes as single photon emitters

Early works have soon emphasized the potential of carbon nanotubes as single photon emitters. The first demonstration was obtained with individual nanotubes directly deposited onto a lens. Single-photon emission is characterized by a low probability for simultaneous photon emission, the so-called photon-antibunching: it is quantified by the zero-delay second-order correlation function of the light detection noise $g^2(0)$ which is close to zero for a pure single photon source. Single photon emission was observed at low temperature with a two photon emission probability as low as 15% even at 25K and of only 3% up to 10K.^[46] This is quite high compared to less than 1% for quantum dots^[47] but the possibility to increase the single photon emission up to high temperature was already promising. Decoupling nanotubes from the substrate by suspending them then allowed to measure long lived excitons up to nanoseconds, with dephasing time in the picosecond range.^[48] A 50-fold enhancement of the emission was later observed for nanotubes embedded in a polymer (to decouple them from glass) and integrated into an optical cavity.^[49] Recently, significant advances detailed below have been further obtained,^[50] and in particular by using nanotube-molecules hybrids based on covalent addition of a functional group.

First measurements of photon antibunching up to room temperature (on suspended and on DOC-wrapped-nanotubes) exhibited zero-delay second-order correlation function $g^2(0)$ below 0.5.^[51] In suspended nanotubes, antibunching was attributed to exciton localization

induced by potential barriers from uncontrolled amorphous carbon on the nanotube-wall.^[52] A breakthrough was performed by coupling nanotubes to solitary oxygen dopants.^[53] The localized dopants allow first, PL to be free of fluctuations both in intensity and spectral position, and second, single photon emission to reach a lifetime of 120 ps at room temperature (to compare to the nanosecond range for quantum dots)^[47]. Control over the dopant formation can be obtained by following the strategy of the group in Maryland who manages enhanced PL emission from sp^3 defects obtained through aryl-diazonium covalent functionalization.^[54] PL measurements reveal the existence of a new redshifted state, which emission rate is increasing exponentially with the energy redshift. Unexpected PL enhancement is attributed to a resonant defect-enhanced exciton-phonon coupling.^[53,55] For antibunching experiments, chirality-enriched nanotubes are encapsulated in sodium deoxycholate (DOC) surfactant or by polyfluorene (PFO-bpy) polymer. Encapsulation ensures the decoupling of the sp^3 -decorated nanotubes from their environment. The measured photon antibunching (**Figure 5**) shows single photon emission at room temperature with a purity of 99% and in the range of telecom wavelengths.^[56] Experiments and theory point to the fact that a finite number of optical transition energies and intensities can occur in the hybrid system.^[57] Indeed, the location of the sp^3 defects onto the carbon ring determines the emission properties of the single photon source, more than the functional group itself or the dielectric environment. The main role of the solitary defect is to localize the exciton and prevent its diffusion towards a non-radiative scatterer as

demonstrated with PL imaging^[57]. Furthermore the lifetime of the excitons can reach hundreds of picoseconds.^[53] Similar isolated hybrid nanotubes have been mapped by super-resolution imaging (based on Gaussian fitting of differential PL images) which directly reveals exciton trapping at the defect sites with a subwavelength resolution.^[58] However, the barriers associated with these sp^3 traps are fluctuating in energy, therefore modifying the trapping efficiency. This has been proposed to be the origin of fluctuations in the intensity of the PL emission which can be significantly larger than the shot noise.^[59]

Nanotubes as single photon sources are a major step since they are the first sources to operate at room temperature. Moreover the sp^3 defects and environment of the nanotube provide tunability of the emission over a broad range including the telecom one (as visible on (Figure 5)), which can be controlled through aryl-functionalization chemistry to get narrow band emission as proposed theoretically.^[60] This inspired a recent work on graphene quantum dots which also exhibit room temperature single photon emission at a wavelength that can be modified according to the grafting of groups at the graphene edges.^[61] These new emitters open the way to room temperature quantum optics.

3.3. Hybrid nanotubes for cavity quantum electrodynamics

An efficient manner to enhance the quantum emission rate from a nanotube is to couple it to an optical cavity. This was performed as early as 2014 by using suspended carbon nanotubes (in order to prevent quenching from the substrate) which exhibited emission rates up to 10^3 photons per second.^[62] However, coupling a suspended nanotube to a cavity remains delicate and hybrid nanotubes wrapped in polymers (polyfluorene, polystyrene or even a layer of Al_2O_3) offer an easier way to isolate the nanotube from the substrate and obtain emission rates as high as $10^5 \cdot \text{s}^{-1}$.^[63,64,65,56] Once coupled to the cavity mode, the nanotube emission can be optimized and provides a narrow band along with increased intensity using the so-called cavity feeding. Another striking feature arises from tuning the cavity length which results in changing the emission wavelength over 15meV while keeping the spectral width narrow (300 μeV)^[62] with a record linewidth $< 20\mu\text{eV}$ ever measured for SWNTs^[65], which reaches the lifetime-limit, as for arsenide quantum dots.^[47]

Considering new quantum emitters discussed in the previous section, it clearly appears that nanotube hybrids coupled to optical cavities are promising systems both for understanding quantum emission properties of these new emitters and for application to quantum information. This has been recently performed by coupling a nanotube with aryl sp^3 defects as emitting sites and individualized in sodium deoxycholate with a silicon photonic crystal microcavity.^[66]

Coupling the single photon source to the mode of the silicon microcavity leads to an emission rate enhancement of two orders of magnitude (1.7×10^7 photons per second).^[66]

These recent results represent a breakthrough as hybrid nanotubes can be used as high emission, room temperature stable single photon sources which can be tuned when coupled to the mode of an optical cavity. This opens up new possibilities for quantum optics and cryptography. Next section presents perspectives on hybrid materials beyond carbon nanotube-based hybrids, which enlarge further on the opportunities for optics and optoelectronics.

4. Beyond 0D-1D hybrids

In the previous sections, we have mostly presented exohedral or endohedral carbon nanotubes functionalized with small molecules, or wrapped in polymers. The advantage of small molecules is they are intrinsic quantum dots. However, confinement in 1D opens new possibilities, in the same approach as the works taking advantage of molecular alignment inside the nanotube hollow core.^[38,61] Indeed, the nanotube can be used as a template hosting systems that would otherwise be unstable or defective. It is in that frame valuable to encapsulate long linear chains inside carbon nanotubes (**Figure 6a**), or graphene ribbons.^[36,67] In the case of double wall nanotubes, the presence of the carbon chain enhances the PL intensity of the inner tube (Figure 6b).^[68] Further calculations need to be performed to better understand such enhancement mechanism, still it shows the possibility to selectively enhance (x6, see (Figure

6b)) the PL of the inner wall by charge transfer with the linear chain. Furthermore, the PL from double wall nanotubes inner wall is a long debated issue and this hybrid system shows the possibility to reduce the PL quench from the outer wall related to exciton transfer between the walls^[69] and have, at last, insights into the inner wall PL properties.

Investigating further the interest of 1D hybrids, another class of nanotubes, transition metal dichalcogenide (TMDC) nanotubes, has just been implemented as excitonic light emitters.^[70] The detected PL is similar to the one of the 2D counterpart, still the direct exciton can be dominant in the spectrum. This could be of particular interest considering the new class of 1D van der Waals nanotubes obtained by using carbon nanotubes as a template for growth of boron nitride and TMDCs (Figure 6c).^[71] Nanotubes of up to 5 different walls have been synthesized which allows realizing coaxial heterojunctions at the few-atom-thick limit. As measured with electron energy loss spectroscopy, the inner carbon nanotubes are still intact and present unchanged PL signature when wrapped in h-BN. It would therefore be possible to induce interlayer excitons as realized in 2D^[72] with additional confinement. Managing excitons in these 1D confined van der Waals heterostructures could provide interesting systems for photocurrent and electroluminescence for example.

5. Conclusion

Long sought control over the nanotubes optical properties has now come real through the pursuit of chemical engineering. All methods to functionalize nanotubes (exo/endo-hedral, covalent or not), have made great advances and offer a wide range of possibilities for the moiety to be coupled to nanotubes. This brings nanotubes back as promising candidates for optoelectronic applications such as photodetectors^[72], biological imaging and quantum optics. 1D confinement allows molecule alignment and new 1D linear chains to be stable, which opens new regimes of charge transfer and exciton localization that require more theoretical investigations and open exciting excitonic physics in 1D. Indeed, exaltation processes related to the coupling with excitons, trions and inserted into optical cavities improve the low quantum yield of pristine nanotubes. Regarding nanoelectronics, there is a need for more investigation of transducing effects offered by hybrid nanotubes, such as photoconductivity and electroluminescence so as to provide functional devices. Moreover, nanotubes, as room temperature single photon emitters, open the way to a brand new family of quantum sources, be it based on carbon functionalized with more complex moieties or on semiconducting materials, exactly as graphene started the whole 2D materials and heterostructure domain. Therefore, there is far more to come with carbon nanotubes for 1D optoelectronics.

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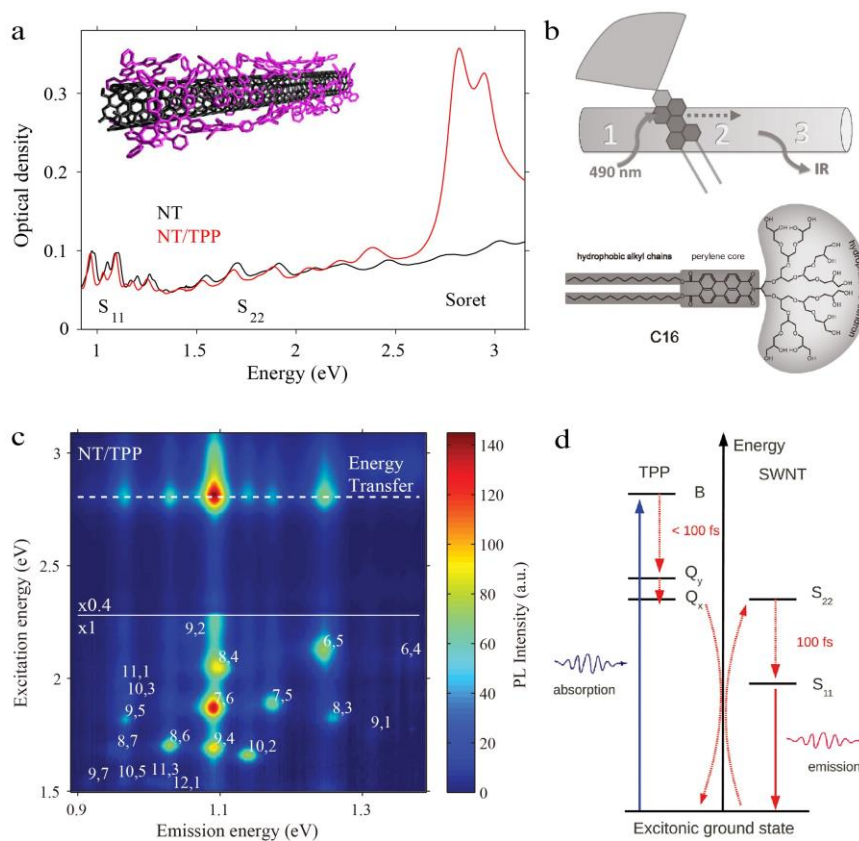


Figure 1. Exohedral non covalent functionalization of SWNTs: a, absorption spectra of SWNTs and SWNT/TPP hybrids in micellar solution, inset: sketch of SWNT/TPP compounds; b, up: schematic depiction of the energy transfer process between perylene, down: chemical structure of the investigated perylene-imido-diester (C16) adsorbate and nanotube. Reproduced with permission.^[17] Copyright 2012, Wiley.; c, PL map of the SWNT/TPP hybrids. The dashed white line at 2.82 eV shows the resonance luminescence signal of SWNTs upon excitation of the TPP molecules, indicating an energy transfer process from TPP to SWNTs; a and c reproduced with permission.^[19] Copyright 2013, American Physical Society. d, schematic model illustrating excitonic energy transfer mechanisms in SWNT/TPP hybrids. Reproduced with permission.^[20] Copyright 2011, ACS Publications.

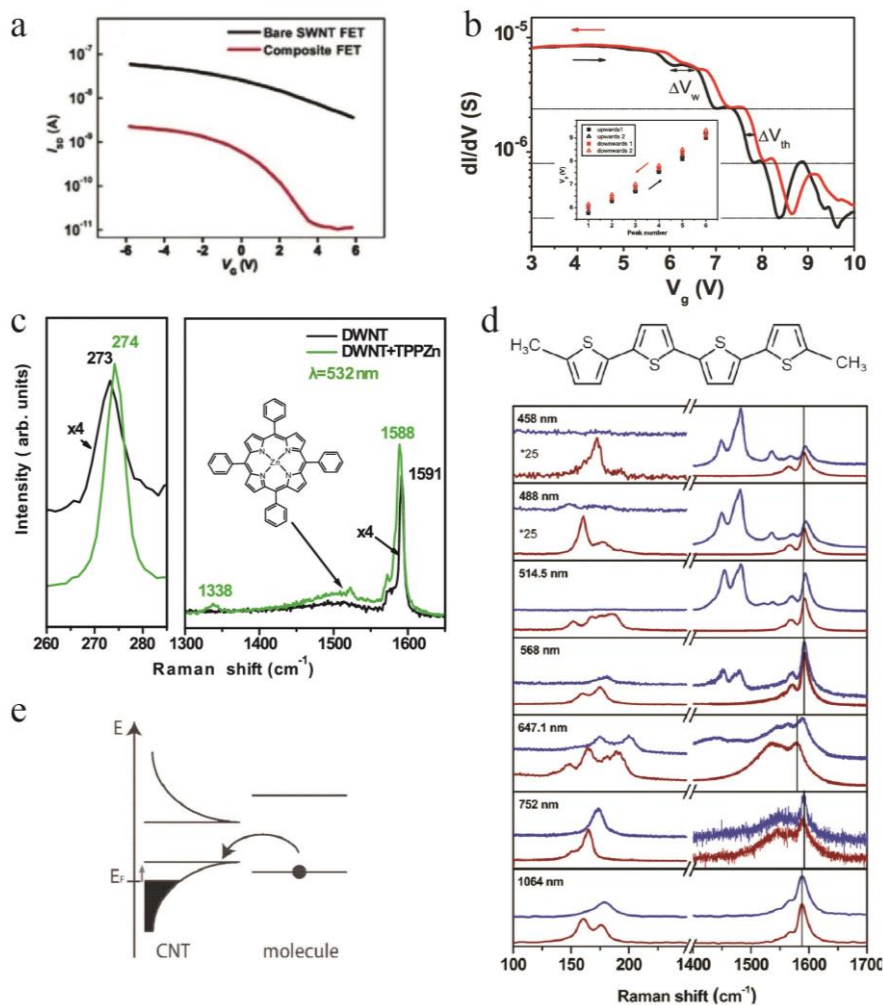


Figure 2. a, Characteristics curve ($I_{SD}(V_G)$) of pristine (black) and porphyrin decorated SWNT-FET ($V_{SD}=15$ mV). Reproduced with permission.^[25] Copyright 2006, American Chemical Society. b, Characteristics curve of a TPPZn CNFET at 10K exhibiting regularly spaced conductance steps (gate position plotted in the inset). c, Raman spectra of isolated pristine (black) and hybrid (green) transistor at 532 nm (inset: chemical structure of the zinc(II) metalloporphyrin derivative (TPPZn)). d, Structure of the 5,5''-dimethyl-2,2':5',2'':5'',2'''-quaterthiophene (4T). Raman spectra of pristine SWNTs (red) and 4T@SWNTs (blue) measured at different excitation wavelengths, with 458 and 488 nm as excitation wavelengths, RBM intensity has been multiplied by 25 for clarity. Reproduced with permission.^[9] Copyright 2011, American Chemical Society. e, Sketch of electron transfer from the molecule to the nanotube inducing an upshift of the Fermi level of the nanotube. b, c, e Reproduced with permission.^[10] Copyright 2017, Wiley.

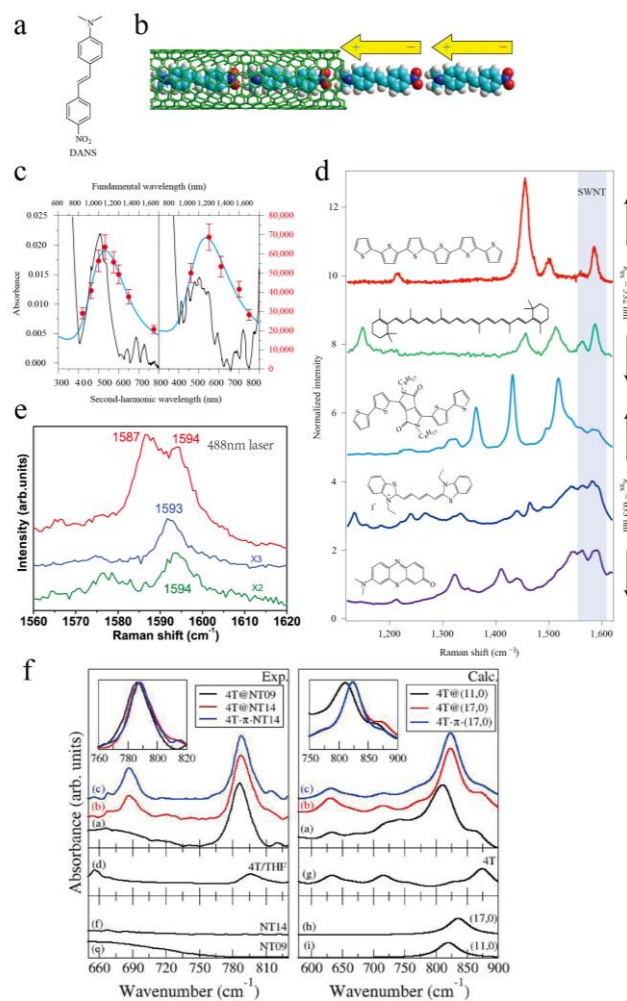


Figure 3. Enhancement of molecule optical signal in Endohedral functionalized SWNT hybrids. a, Chemical structure of p,p'-dimethylaminonitrostilbene (DANS); b, Sketch of DANS molecules in a (9,7) nanotube; c, Spectra of NLO polarizability (red) and of absorption (black) for hybrids made from two different nanotube sources (left and right); a-c Reproduced with permission.^[6] Copyright 2015, Nature Publishing Group. d, Raman spectra of different dyes inside SWNTs (6T, βcar, DPP2, DTDCI and methylene violet B). Reproduced with permission.^[38] Copyright 2014, Nature Publishing Group. e, Raman spectra of a TPPZn decorated nanotube in dark (blue), under white light exposure (red) and after light excitation (green). Reproduced with permission.^[10] Copyright 2017, Wiley. f, Experimental and calculated infrared spectra of (a) 4T@NT09 (4T@(11,0)), (b) 4T@NT14 (4T@(17,0)), and (c) 4T-π-NT14. Reproduced with permission.^[39] Copyright 2016, American Chemical Society.

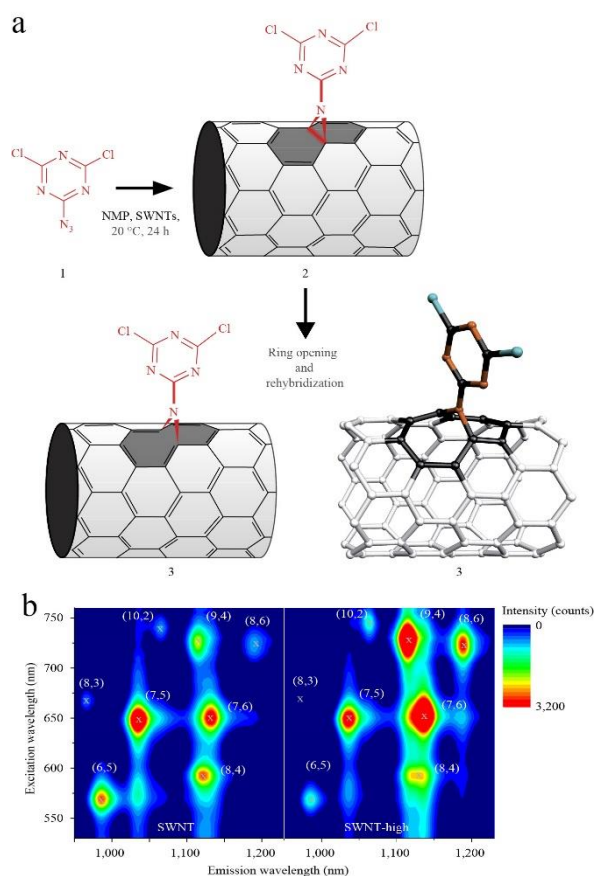


Figure 4. a, One-pot functionalization of carbon nanotubes by heterocyclic [2+1] cycloaddition reaction. b, photoluminescence maps of pristine (left) and hybrid (right) nanotubes. Reproduced with permission.^[43] Copyright 2017, Nature Publishing Group.

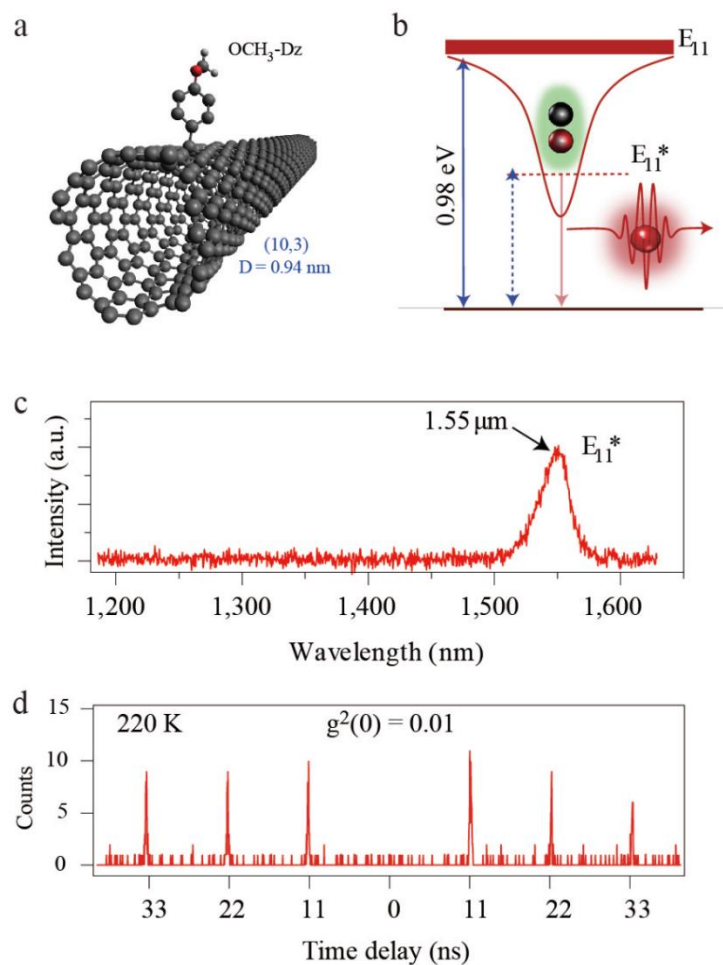


Figure 5. Single photon emission at room temperature from nanotubes with sp^3 defect sites. a, sketch of (10,3) nanotube functionalized with a single covalently bound aryl defect site. b, the sp^3 defects create trapped excitons which relax to ground state and emit a single photon. c, single photon emission in the telecom range. d, second-order photon correlation ($g^2(t)$) plot shows single photon emission at room temperature with a 99% purity. Reproduced with permission.^[56] Copyright 2017, Nature Publishing Group.

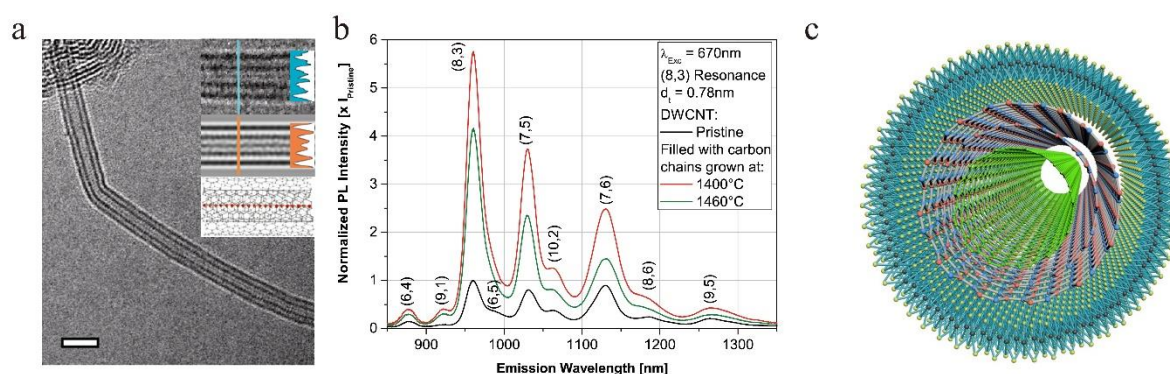


Figure 6. New family of 1D hybrids. a, HRTEM image of an LLCC@DWCNT with bending. Inset: enlarged HRTEM experiment (top) and simulated images and line profiles (middle), molecular model of an LLCC@DWCNT (bottom). Reproduced with permission.^[67] Copyright 2016, Nature Publishing Group. b, Photoluminescence line scans of different inner tube species, excitation wavelength 670 nm (the E₂₂ resonance of (8,3) tubes); Reproduced with permission.^[68] Copyright 2016, Wiley-VCH. c, Atomic model of a CNT@BN@MoS₂ (Courtesy of S. Maruyama).

Yani Chen studied in hybrid group of Néel Institute in Grenoble from 2012 to 2016. She obtained her PhD degree from Université Grenoble Alpes in 2016. Now she works as a post-doc in Shenzhen University, China. Her research interests include physical properties of low dimensional materials, two dimensional charge density wave materials and devices.



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Table of contents entry:

How molecular-nanotube hybrids can bolster optoelectronics and quantum optics is highlighted. These systems reveal new fundamental issues related to confinement of the molecules and excitons. Furthermore, they provide building blocks for efficient emission down to the single photon regime.

Keywords: Carbon nanotubes, molecular hybrids, Optical and Raman spectroscopy, enhancement, exciton

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Title: A new light on molecule-nanotube hybrids

ToC figure:

