Organic Molecular Tuning of Many-Body Interaction Energies in Air-Suspended Carbon Nanotubes

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ABSTRACT: We investigate adsorption effects of copper phthalocyanine molecules on excitons and trions in air-suspended carbon nanotubes. Using photoluminescence excitation spectroscopy, we observe that exciton energy red-shifts gradually with the molecular deposition thickness. The trion emission is also observed at large deposition amounts, which indicates charge transfer between the phthalocyanine molecules and carbon nanotubes. Analysis of the spectra for individual tubes reveals a correlation between the exciton–trion energy separation and the exciton emission energy, showing that the many-body interaction energies scale similarly with the molecular dielectric screening.

INTRODUCTION

Single-walled carbon nanotubes (CNTs) have attracted considerable attention due to their remarkable physical and electronic properties, and much effort has been devoted to functionalize CNTs for expanding their capabilities.1–4 In particular, noncovalent functionalization with organic molecules is a powerful strategy for developing CNT-based devices such as photovoltaics and photodetectors.5–10 The interactions between the organic molecules and CNTs are considered to be less perturbative compared to covalent modification, and therefore the outstanding properties of CNTs can be preserved. Organic molecules such as porphyrin and phthalocyanine couple to nanotubes through π–π interactions to modify the charge density of CNTs, while the emission energy is reduced due to the molecular screening.11–16 Furthermore, there are unique exciton dynamics at the organic molecule/CNT interface including energy and charge transfer.14,17–22

In the measurements performed for nanotubes in solutions, however, the existence of solvent molecules inevitably complicate the interpretation by influencing the interactions. Additionally, the solvents themselves provide molecular screening, reducing the dielectric effects of the organic molecules. Investigation of molecular adsorption on air-suspended nanotubes would provide invaluable information toward fundamental understanding of the adsorption effects, as thermal evaporation techniques23,24 allow for molecular deposition without introducing other molecules. The use of pristine tubes should further enable drastic dielectric modification for developing noncovalently functionalized CNT devices.

Here, we demonstrate control over many-body interaction energies in air-suspended CNTs by copper phthalocyanine (CuPc) molecule adsorption. The molecules are deposited on chirality-assigned CNTs by thermal evaporation, and we perform photoluminescence (PL) spectroscopy of the CuPc/CNT hybrid. From the averaged PL and PL excitation (PLE) spectra for various chiralities, we find that the $E_{11}$ and $E_{22}$ resonances red-shift with increasing deposition thickness. Furthermore, a new emission peak is observed at an energy below the $E_{11}$ peak, which is attributed to trion emission. Data from individual tubes reveal a good correlation between exciton–trion energy separation and the exciton emission energy, suggesting the existence of a universal relationship. We consider a model assuming power law scaling of the interaction energies with dielectric constant to explain the observed correlation.

EXPERIMENTAL SECTION

Air-Suspended CNTs. Our suspended CNTs are grown over trenches on bare Si substrates (Figure 1a). We perform electron beam lithography and dry etching to form the trenches, and another electron beam lithography step defines catalyst areas near the trenches. Fe(III) acetylacetonate and fumed silica dispersed in ethanol are spin-coated as catalyst for
peak is observed in the emission spectrum and whether the measurements are performed. We check whether only a single CNTs are located by line scans along the trenches, and PLE characterize the suspended nanotubes before the deposition. The laser polarization is parallel to the tube axis for the sample. The linear polarization of the excitation laser is 0.8 and a working distance of 3.4 mm focuses the laser onto a power continuous-wave Ti:sapphire laser is used for excitation with a home-built confocal microspectroscopy system. 25,26 A μW, and (f) PLE map, PL image, and laser polarization angle dependence, respectively, for the same (d,e), the PL intensity is obtained by integrating PL over a 10 meV wide spectral window centered at 0.91 eV. (f–h) PLE map, PL image, and laser polarization angle dependence, respectively, for the same tube after the deposition. For (g,h), the PL intensity is obtained by integrating PL over a 10 meV wide spectral window centered at 0.91 eV. (b,d,g) Scale bars are 1 μm. Panels (c–e) are taken with P = 5 μW, and (f–h) are taken with P = 300 μW.

Figure 1. (a) Schematic image of our sample. (b) Scanning electron microscope image of a CuPc/CNT hybrid. (c–e) PLE map, PL image, and laser polarization angle dependence, respectively, for a (9,7) nanotube in the 26 nm sample before CuPc deposition. For (d,e), the PL intensity is obtained by integrating PL over a 10 meV wide spectral window centered at 0.96 eV. (f–h) PLE map, PL image, and laser polarization angle dependence, respectively, for the same tube after the deposition. For (g,h), the PL intensity is obtained by integrating PL over a 10 meV wide spectral window centered at 0.91 eV. (b,d,g) Scale bars are 1 μm. Panels (c–e) are taken with P = 5 μW, and (f–h) are taken with P = 300 μW.

CNT growth. CNTs are synthesized by alcohol chemical vapor deposition at 800 °C for 1 min. 25

PL Microscopy. The PL measurements are carried out with a home-built confocal microspectroscopy system. 25,26 A continuous-wave Ti:sapphire laser is used for excitation with a power P, and an objective lens with a numerical aperture of 0.8 and a working distance of 3.4 mm focuses the laser onto the sample. The linear polarization of the excitation laser is rotated using a half-wave plate and PL from the sample is detected by an InGaAs photodiode array detector attached to a spectrometer. The laser polarization is parallel to the tube axis for measuring PLE maps and PL images. All measurements are conducted at room temperature in dry nitrogen.

Sample Characterization before CuPc Deposition. We characterize the suspended nanotubes before the deposition. CNTs are located by line scans along the trenches, and PLE measurements are performed. We check whether only a single peak is observed in the emission spectrum and whether the E11 and E22 resonance energies match tabulated data for air-suspended nanotubes. 25 If a nanotube satisfies these conditions, the position and the chirality of the nanotube are recorded into a list for the measurements after the deposition.

CuPc Deposition on Nanotubes. After the characterization, the sample is placed in a vacuum chamber for evaporation of CuPc (Sigma-Aldrich) and is kept at about 80 °C for 10 min to remove air molecules before the evaporation. CuPc molecules are deposited on suspended CNTs in the chamber at room temperature using an evaporator heated to 480–520 °C under a vacuum of less than 10−4 Pa. A glass slide is also placed in the chamber to quantify the deposition thickness from absorbance of CuPc peak at 2.0 eV. 27 Calibration is performed by measuring the actual thickness by a surface profiler for two CuPc films with 80 and 167 nm. Four samples with different deposition amounts are prepared by changing the evaporation time, with nominal thickness on the substrate of 3, 7, 16, and 26 nm.

RESULTS AND DISCUSSION

CuPc Adsorption Effects. In order to investigate the molecular adsorption effects, we compare the nanotubes before and after molecular deposition. A scanning electron microscopy image of a typical CNT after the evaporation is shown in Figure 1b. Bright spots are observed sparsely on the suspended CNTs, indicating inhomogeneous adsorption of CuPc. Figure 1c–h shows PL spectra, PL images, and polarization dependence for a suspended CNT before and after CuPc deposition for the 26 nm sample. We note that the data before deposition have been taken prior to heating and therefore air molecules are adsorbed. In the PLE map before the deposition (Figure 1c), the emission occurs at the E11 energy and the E22 transition can be observed as a resonance in the excitation energy. The values for the E11 and E22 resonances are consistent with those for a (9,7) air-suspended nanotube, 25 indicating that air-molecules such as water are adsorbed.

Figure 1f shows a PLE map of the same tube after the deposition, and we find differences in the peak energy, the line width, and the intensity. Both of the E11 and E22 resonances show red-shift as well as broadening, and the PL intensity decreases significantly with the molecular adsorption. Additionally, a new emission band appears in an energy region below the E11 emission. The PL image of the molecular adsorbed nanotube is slightly smaller compared to that before the evaporation (Figure 1g,d), which is likely due to the inhomogeneous adsorption as observed in Figure 1b. In comparison, the laser polarization dependence does not change before and after the deposition (Figure 1e,h).

E11 and E22 Resonance Energy Shifts. The PLE maps of the nanotubes for the four samples are measured to examine the deposition amount dependence of the adsorption effects. We integrate the PLE maps for each nanotube along the excitation and emission energy axes to obtain PL and PLE spectra, respectively, and the spectra for nanotubes with the same chiralities are averaged within each sample. The ensemble averaged PL and PLE spectra for (9,7) tubes are shown in Figure 2a,b, respectively. In the PL spectra (Figure 2a), the intensity decreases and the E11 resonance energy red-shifts with the increase of the deposition thickness. Two peaks are observed for the 3 nm sample, corresponding to emission from regions of nanotubes with and without the CuPc molecule adsorption. In contrast, the E11 emission shows only one peak in the PL spectrum for the 7 nm sample, suggesting that the nanotube surface is fully covered with the molecules. For samples thicker than 7 nm, the new emission band is observed as in Figure 1f, and we will refer to this peak as the T emission. While the relative intensity of the T emission becomes higher compared to the E11 emission as the deposition amount increases, the absolute intensity does not seem to depend much on the amount of CuPc molecules.

In the PLE spectra (Figure 2b), the E22 resonance also red-shifts with increasing deposition thickness, and the simultaneous red shifts for the E11 and E22 resonances can be
explained by the molecular dielectric screening. For the 26 nm sample, the $E_{22}$ resonance peak is on top of a broad background slope, which may be attributed to the tail of the CuPc absorption peak at 2.0 eV. Exciton transfer from CuPc aggregates to CNTs would be consistent with the appearance of the absorption tail in the PLE spectra. It has been suggested that the exciton transfer time is less than 100 fs in noncovalently bound nanotube/porphyrin hybrids, and therefore the exciton transfer from the CuPc molecules to the nanotubes could occur before the intersystem crossing. The peaks before and after the deposition are measured with $P = 100 \mu W$ and $P = 300 \mu W$, respectively. The peak shift and peak area obtained from the fitting are shown in (c,d), respectively. The $E_{11}$ and $E_{22}$ peak shifts are compared to the peak energies before the deposition, and the $E_{11}$ and $E_{22}$ peak areas are normalized by those before the deposition. The peak shift for the $T$ emission is compared to the peak energy for the 7 nm sample, and the peak area for the $T$ emission is normalized by that for the $E_{11}$ resonance before the deposition. The error bars are smaller than the symbols.

chirality measured, consistent with the dielectric screening effects due to the adsorbed molecules. The molecule-induced shifts of the $E_{11}$ and $E_{22}$ resonances for the 26 nm sample are plotted as a function of nanotube diameter in Figure 3b. Although we expect that the shifts become gradually smaller as the diameter increases, there is no clear dependence. The scatter of the data points is likely caused by large tube-to-tube deviations of adsorption amounts. Averaging the shifts of the $E_{11}$ and $E_{22}$ resonances for all chiralities, we obtain values of $-58$ and $-67$ meV, respectively. Comparable emission energy shifts have been observed for nanotubes under dielectric screening by solvents, explaining why the shifts due to organic molecule adsorption in solutions are suppressed.

We evaluate the change in the exciton resonance energy by considering the reduction of the electronic many-body interactions due to molecular adsorption. The $E_{11}$ exciton energy is determined by $E_{11} = E_{sp} + E_{se} - E_{eh}$, where $E_{sp}$ is the single-particle band gap, $E_{se}$ is the self-energy from repulsive electron interactions, and $E_{eh}$ is the exciton binding energy from the attractive electron–hole interactions. Because the

![Figure 2](image-url) Figure 2. (a,b) Ensemble averaged PL and PLE spectra, respectively, for (9,7) tubes of the samples before deposition (black), 3 nm sample (red), 7 nm sample (green), 16 nm sample (blue), and 26 nm sample (purple). We measure 3–10 nanotubes for each sample and check that the same tube is measured before and after the deposition from the location and the laser polarization dependence. The nanotubes before and after the deposition are measured with $P = 100 \mu W$ and $P = 300 \mu W$, respectively. The peak shift and peak area obtained from the fitting are shown in (c,d), respectively. The $E_{11}$ and $E_{22}$ peak shifts are compared to the peak energies before the deposition, and the $E_{11}$ and $E_{22}$ peak areas are normalized by those before the deposition. The peak shift for the $E_{11}$ resonance band is also fitted by a Lorentz function for the PL spectra of the nanotubes with more than 7 nm thickness. For the 3 nm sample, there is a difficulty for distinguishing the new emission from the background slope, which may be attributed to the tail of the CuPc absorption peak at 2.0 eV. The $E_{11}$ and $E_{22}$ resonances for all chiralities, we obtain values of $-58$ and $-67$ meV, respectively. Comparable emission energy shifts have been observed for nanotubes under dielectric screening by solvents, explaining why the shifts due to organic molecule adsorption in solutions are suppressed.

![Figure 3](image-url) Figure 3. (a) Deposition thickness dependence of the $E_{11}$ and $E_{22}$ resonance energies for various chiralities. The data are obtained by the same procedure as in Figure 2. The excitation energy integration windows are from 1.44 to 1.63 eV for (9,7), (10,5), (11,3), and (12,1) or from 1.35 to 1.50 eV for the others. The $E_{11}$ resonance band is split into two as for the 3 nm sample in Figure 2a, we have obtained a peak area weighted average of the emission energy by fitting the spectrum with two Lorentz functions. The integration window for the emission energy is from 0.77 to 1.09 eV for all chiralities. The filled squares, open squares, filled circles, open circles, and filled triangles correspond to the samples before deposition, 3 nm sample, 7 nm sample, 16 nm sample, and 26 nm sample, respectively. (b) Peak shifts of the $E_{11}$ and $E_{22}$ resonance energies for the 26 nm sample relative to those before the deposition are shown as a function of the diameter. The error bars are smaller than the symbols.
magnitude of the self-energy is larger than that of the exciton binding energy, the $E_{11}$ exciton energy is higher than $E_{ab}$ by the net many-body correlation energy $E_{se}$. Assuming that these interactions scale by the same factor $C_X$, the shift of the $E_{11}$ exciton energy $\Delta E_{11}$ relative to the air-molecule adsorbed state is given by $\Delta E_{11} = (E_{se} - E_{db}) \times (C_X - 1)$. For air-molecule-adsorbed nanotubes with 1 nm diameter, $E_{se}$ and $E_{db}$ have been estimated to be 910 and 660 meV, respectively.29 From the average $\Delta E_{11}$ of $-58$ meV for the 26 nm sample, $C_X$ is calculated to be 0.77, which corresponds to a reduction of the many-body interactions with the molecular adsorption by 23%. Furthermore, $C_X$ values for the 3 nm sample, 7 nm sample, and 16 nm sample are estimated to be 0.94, 0.83, and 0.78, respectively, showing that the many-body interaction energies reduce monotonically with increasing the molecular amounts. The absolute value of the average $\Delta E_{22}$ for the 26 nm sample is slightly larger than that of the average $\Delta E_{11}$, which is reasonable because the net many-body correlation energy for the $E_{22}$ excitons is larger than that for the $E_{11}$ excitons.30,40

**T Emission.** We now turn our attention to the low energy $T$ emission. Figure 4a is a PLE map for a (9,7) nanotube in the 26 nm sample, and there are two peaks at 0.81 and 0.92 eV corresponding to the $T$ and $E_{11}$ emission, respectively. The absorption resonance energies for both emission are almost the same, and the PL images at the $T$ and $E_{11}$ energies overlap spatially (Figure 4b,c). The spectral and spatial coincidence indicates that the $T$ emission comes from the same tube. We define the energy separation between the $T$ and $E_{11}$ peaks to be $\Delta E_{X-T}$, for example $\Delta E_{X-T} = 0.11$ eV in Figure 4a. The $T$ emission energy for various chiralities is obtained by fitting the ensemble averaged PL spectra with a Lorentz function, and $\Delta E_{X-T}$ is plotted as a function of the diameter in Figure 4d. Because the $K$-momentum exciton emission should appear at 0.13–0.14 eV below the $E_{11}$ emission peak23,34 it cannot explain the $T$ emission with $\Delta E_{X-T} = 0.10–0.12$ eV. In addition, intensity of the $K$-momentum exciton emission is typically 1% of the bright $E_{11}$ exciton emission, but the $T$ emission intensity can be comparable to the $E_{11}$ emission.34 A more plausible interpretation would be emission from trions, as the energy separation can be 0.10–0.14 eV under dielectric screening within the diameter range shown in Figure 4d.41,42 The observed $\Delta E_{X-T}$ tends to become smaller as the diameter increases, consistent with the behavior for the exciton–trion energy separation.28,34 As a trion is a bound state of a carrier and an exciton, we expect trion formation if there is charge transfer between CuPc molecules and CNTs. Such a picture can also explain the $E_{11}$ intensity reduction with the molecular adsorption. The weak dependence of the $T$ emission intensity on deposition thickness is also consistent, as the first layer of CuPc should have formed for thickness larger than 7 nm.

The exciton–trion energy separation for the CuPc adsorbed state is smaller than that for the air molecule adsorbed state by about 70 meV for tubes with diameter $d = 1$ nm, indicating that exciton–carrier interactions are considerably screened by the CuPc molecules. It is known that the exciton–trion energy separation $\Delta E_{X-T}$ follows the relation $\Delta E_{X-T} = E_{ab} + E_{se}$ where $E_{ab} = A/d$ is the trion binding energy and $E_{ab} = B/d^2$ is the singlet-triplet splitting energy while $A$ and $B$ are proportionality constants.43,44 For the air molecule adsorbed state, $A = 105$ meV nm and $B = 70$ meV nm$^{-2}$.43 We fit the data by $\Delta E_{X-T} = (A/d + B/d^2) \times C_T$, under an assumption that both $A$ and $B$ scale by the same factor $C_T$ upon the organic molecule adsorption. The result is shown as a blue line in Figure 4d, giving $C_T = 0.67$, which is comparable to the value of $C_X$.}

**Correlation between $\Delta E_{X-T}$ and $E_{11}$.** So far we have been discussing the ensemble spectra, but data for the individual tubes provide additional insights to molecular screening effects on the many-body interactions. By fitting the PL spectra for each nanotube with the same procedure as the ensemble spectra, we obtain the energies for the $T$ and $E_{11}$ emission in various molecular screening environments. In Figure 5a, $\Delta E_{X-T}$ values for (9,7) individual nanotubes are plotted as a function of the $E_{11}$ exciton emission energy. We find that there is a good correlation between $\Delta E_{X-T}$ and $E_{11}$, where $\Delta E_{X-T}$ becomes smaller as the $E_{11}$ emission energy red shifts. We also plot data points for (9,7) suspended nanotubes with and

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\[\Delta E_{X-T} = E_{ab} + E_{se} \times C_T \]
without air-molecule adsorption from ref 28 as green and blue points, respectively. These data points also follow the trend, suggesting that there is a universal relation applicable to nanotubes under different surface conditions. Similar correlation is observed for (13,2) and (11,3) nanotubes (Figure Sb,c, respectively), as well as for the other chiralities. We note that CuPc adsorption can shift the $E_{11}$ energy by ~100 meV compared to the pristine state, offering flexible tunability over the emission energy.

The correlation can be understood in terms of the molecular dielectric screening (Figure 5d). In general, the many-body interactions determining the $T$ and $E_{11}$ exciton energies are sensitive to environment, which can simply be parameterized as the environmental dielectric constant $\varepsilon$. Assuming that interaction energies scale as $\varepsilon^\alpha$ with $\alpha$ being a constant,25,28 $\Delta E_{X-T} = E_{11}^{\text{pr}} - E_{11}^{\text{ad}}$ and $E_{11} = E_{11}^{\text{pr}} + E_{11}^{\text{at}} - E_{11}^{\text{ad}}$, where $E_{11}^{\text{pr}}$, $E_{11}^{\text{at}}$, $E_{11}^{\text{ad}}$, and $E_{11}^{\text{ad}}$ are the trion binding energy, singlet–triplet splitting energy, self-energy, and exciton binding energy at $\varepsilon = 1$, respectively. The slope for the correlation is then given by $\Delta E_{X-T} = \frac{\Delta E_{X-T}^{\varepsilon=2} - \Delta E_{X-T}^{\varepsilon=1}}{E_{11}^{\text{pr}} - E_{11}^{\text{ad}}}$, indicating a linear relation between $\Delta E_{X-T}$ and $E_{11}$. The experimentally observed correlation therefore implies that the many-body interaction energies scale similarly within the experimental conditions explored, which is reasonable because the scaling factor for the $E_{11}$ exciton $C_X$ is comparable to that for the trion $C_T$.

Using the reported values for pristine suspended nanotubes of $E_{11}^{\text{pr}} = 117$ meV, $E_{11}^{\text{at}} = 78$ meV, $E_{11}^{\text{ad}} = 980$ meV, and $E_{11}^{\text{ad}} = 725$ meV for 1 nm diameter tubes,25,28 the proportionality coefficient is about 0.8. To compare this value with the experimental results, we fit the data points for the organic molecule adsorbed state with a linear function. We impose the line to go through a data point for the air-molecule adsorbed state with a linear function. We impose the $E_{11}$ emission energy from the table in ref 28 and $\Delta E_{X-T}$ is determined from the equation given in ref 34. The obtained coefficients range from 0.8 to 1.2 (Figure 5e), which is a reasonable agreement considering the large uncertainty in the absolute value of $E_{11}^{\text{ad}}$.

## CONCLUSIONS

In summary, we have investigated adsorption effects of CuPc molecules on excitons and trions in air-suspended CNTs by measuring PL spectra of the CuPc/CNT hybrids. By averaging the PLE spectra for tubes with the same chiralities, the red shift of the $E_{11}$ and $E_{22}$ resonances has been observed with increasing deposition thickness due to the molecular screening. The $E_{11}$ energy modification from the pristine state to the CuPc adsorbed state can reach 100 meV, which is significantly larger than the energy shift with organic molecule adsorption in solutions. Furthermore, we find that the trion emission emerges at an energy lower than the $E_{11}$ exciton emission, which is likely due to charge transfer between CuPc molecules and CNTs. The spectra from individual tubes show that there is a good correlation between the exciton–trion energy separation and the exciton emission energy. A model assuming power law scaling of the many-body interactions with dielectric constant can quantitatively explain the observed correlation, which should be able to describe nanotubes with different surface conditions in a universal manner. Our findings show that organic molecule adsorption significantly affects many-body interaction energies of suspended CNTs, which opens up a pathway toCNT devices utilizing noncovalent molecular functionalization.

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