## Brightening of carbon nanotube photoluminescence through the incorporation of $sp^3$ defects

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### 1.    Introduction

#### 1.1.    Photoluminescence in Semiconducting Single-Walled Carbon Nanotubes

Semiconducting single-walled carbon nanotubes (SWCNTs)

➢ Characteristic near-infrared photoluminescence

Problem: Low photoluminescence quantum yield $\Phi$ $(< 1\%)$

#### 1.2.    Energy States of Semiconducting SWCNTs

Previous reports revealed the existence of 'bright' and 'dark' excitons (*Figure 1*).[1]

• Non-radiative 'dark' excitons reside below and above the optically allowed 'bright' excitons.

Relaxation of excitons to this low-lying dark state results in high population of dark excitons, and low photoluminescence $\Phi$ of SWCNTs.

• Harnessing these inaccessible dark excitons is challenging.



*Figure 1*. **Energy states of semiconducting SWCNTs.** The 'dark' excitons reside above and below the 'bright' excitons ($E_{11}$). Because the dark excitons have lower energy than bright ones, large number of excitons will relax to dark state. This results in a weak intensity of photoluminescence, and low $\Phi$. In this work, by adding $sp^3$ defects, the harnessing of these excitons was achieved.

#### 1.3.    This Work

SWCNT photoluminescence was brightened by covalent sidewall functionalization.

• Inducing $sp^3$ defects in the carbon $sp^2$ lattice is known to quench the photoluminescence drastically.[2]

• Careful control of the reaction conditions revealed that small window of reaction conditions can brighten the photoluminescence.

• Control of the photoluminescent properties by the substituents was also available.
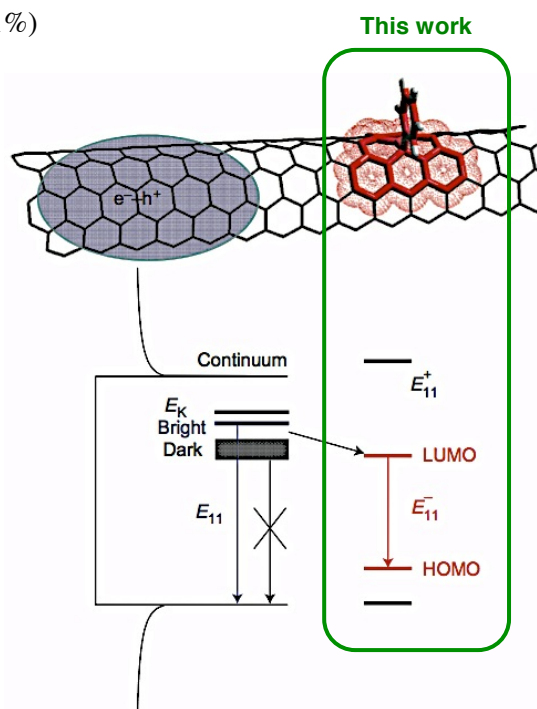
### 2.    Results and Discussion

#### 2.1.    Photoluminescence of Functionalized SWCNTs

(6,5)-SWCNTs were functionalized covalently with aryl diazonium salt $p$-$(NO_2)C_6H_4N_2^+ BF_4^-$.
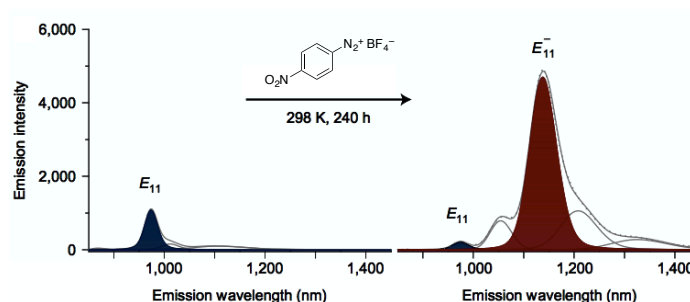


*Figure 2*. **Photoluminescence before and after functionalization of (6,5)-SWCNTs.** After functionalization, new peak red-shifted by 162 nm was observed. This namely $E_{11}^-$ emission was 8.4 times brighter than the original $E_{11}$ emission.

Photoluminescence of the SWCNTs before and after the functionalization were measured (*Figure 2*).

- A red-shifted, brighter peak, namely $E_{11}^{-}$ peak appeared.

The new photoluminescence feature is sensitive to reaction conditions or chirality of nanotubes.

*Table 1. $E_{11}^{-}$ luminescence dependence on (n,m) chirality.* In smaller diameter nanotubes, significant increase of $\Phi$ was observed.

| | Pristine | Covalently functionalized | | $E_{11}^{-} - E_{11}$ | $\Phi(E_{11}^{-})$ |
|---|---|---|---|---|---|
| *(n,m)* | $E_{11}$ (nm) | $E_{11}$ (nm) | $E_{11}^{-}$ (nm) | (meV) | /$\Phi(E_{11})$ |
| (7,6) | 1113 | 113 | 1263 | −132 | 0.5 |
| (8,4) | 1109 | 1109 | 1263 | −136 | 1.0 |
| (9.2) | 1133 | 1134 | 1300 | −140 | |
| (7,5) | 1015 | 1015 | 1179 | −170 | |
| (6,5) | 972 | 975 | 1137 | −181 | 8.4 |
| (8,3) | 942 | 942 | 1154 | −241 | |
| (6,4) | 870 | 869 | 1058 | −254 | 28.6 |

- (*Table 1*) The increase of $\Phi$ is significant in smaller diameter nanotubes, (6,4) or (6,5).
- (*Figure 3*) While $E_{11}$ emission drops to noise level immediately, $E_{11}^{-}$ peak grows as the reaction proceeds over a period of ~200 h.
- (*Figure 4*) $E_{11}^{-}$ emission is observable only around 0.33 mol% diazonium salt is used, beyond which it is completely lost.
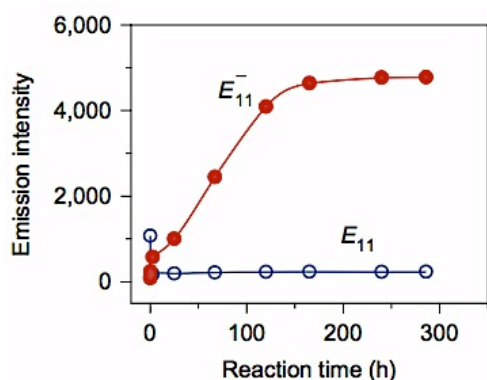


*Figure 3.* **Emission intensity dependence on reaction time.** $E_{11}^{-}$ emission growed over a period of 200 h. Obtained at a diazonium salt to carbon molar of 1:300.
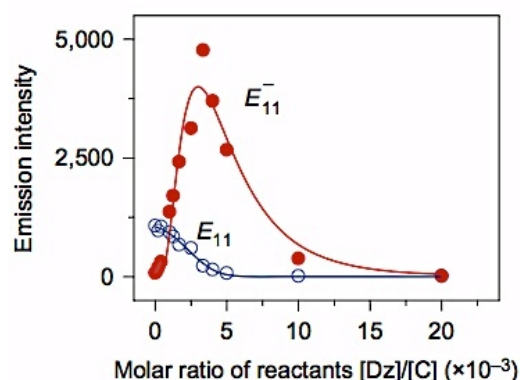


*Figure 4.* **Emission intensity dependence on relative concentration of diazonium salts.** [Dz]/[C] = diazonium salt/carbon concentration ratio. The $E_{11}^{-}$ emission is only observable in a narrow window of molar ratio.

The surface density of functional groups was quantified by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

- In Raman spectra, disorder (D) peak at 1,300 cm$^{-1}$ grew as the ratio of salts increases (*Figure 5*). Non-covalent physical adsorptions of diazonium salts, dimers or polymerized byproducts do not give this peak.[3]
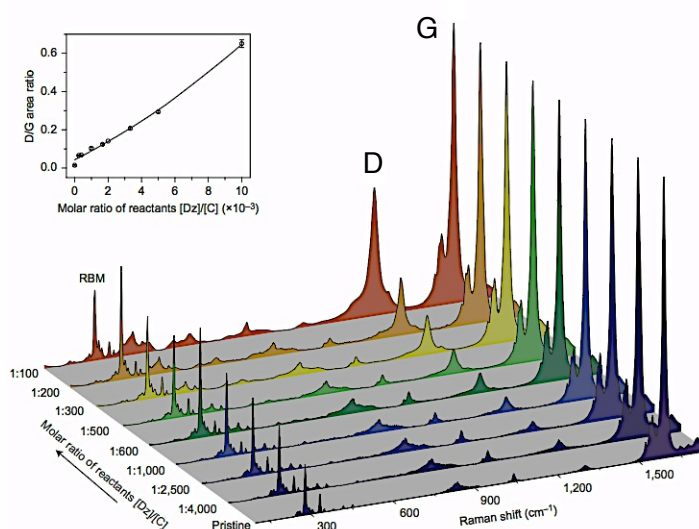  - Covalent bonding of the aryl groups were confirmed.



*Figure 5.* **Raman spectra of (6,5)-SWCNTs.** As the molar ratio of diazonium salt increased, the disorder (D) peak growed, while the $sp^2$ stretching G band was proportional.

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- From XPS data, $0.06 \pm 0.01\%$ of the C atoms were bonded with an aryl group. This corresponds to one functional group per 20 nm length of (6,5)-SWCNT.
  - ➢ Low concentration of functional groups gives little change in the optical properties from the pristine nanotube.
  - ➢ As the functional density increases, the $sp^3$ defects also increases, results in quenching of the photoluminescence of both $E_{11}$ and $E_{11}^-$.
- ✓ Careful control of the diazonium chemistry allowed the access to this new photoluminescence.

## 2.2. Origin of the Dark-Exciton Brightening

Electronic structure of an aryl-functionalized 4 nm long (6,5)-SWCNT was calculated.

- Compared to pristine SWCNT, the split of HOMO and LUMO was found (*Figure 6*).
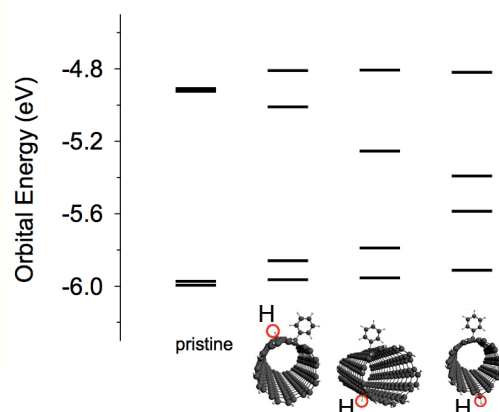- The split is regardless of where the pairing H is attached.

*Figure 6*. **Energy level split of (6,5)-SWCNTs.** The attached pairing H atom are highlighted.

As more aryl functional groups are attached covalently to the nanotube sidewall, the red-shifted absorption has increased (*Figure 7*).

- $E_{11}$ has splitted to $E_{11}^-$ (181 meV below $E_{11}$) and $E_{11}^+$ (225 meV above $E_{11}$).
- $E_{11}^-$ absorption occurs at exactly the $E_{11}^-$ photoluminescence energy.
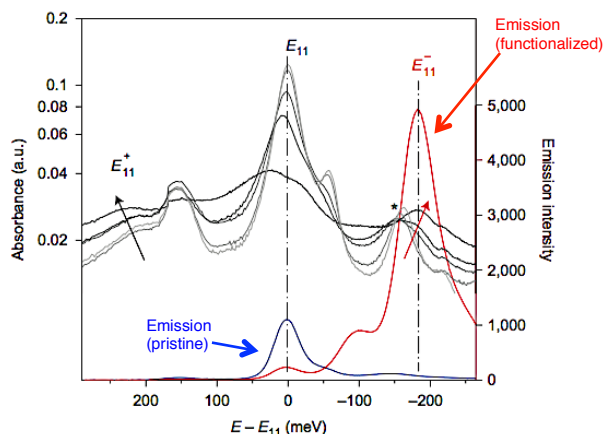
*Figure 7*. **Absorption and emission spectra of (6,5)-SWCNTs.** The arrows highlights increase of $E_{11}^+$ and $E_{11}^-$ absorption as the degree of functionalization increases.

The red-shift of $E_{11}^-$ from $E_{11}$ shows a 1/(nanotube diameter)$^2$ dependence (*Figure 8*).

- Low-lying dark excitons are predicted to have similar diameter dependence.[4]
- For (6,5)-SWCNT, the energy difference between $E_{11}^-$ and predicted dark exciton matches to the energy of the observed D phonon (1301 cm$^{-1}$ = 161 meV).
  - ➢ Vibronic coupling between $E_{11}^-$ and low-lying dark exciton can take place.
- In larger diameter nanotubes, $E_{11}^-$ state is higher, thus couples to less-populated $K$-momentum dark excitons rather than low-lying 'dark' excitons.
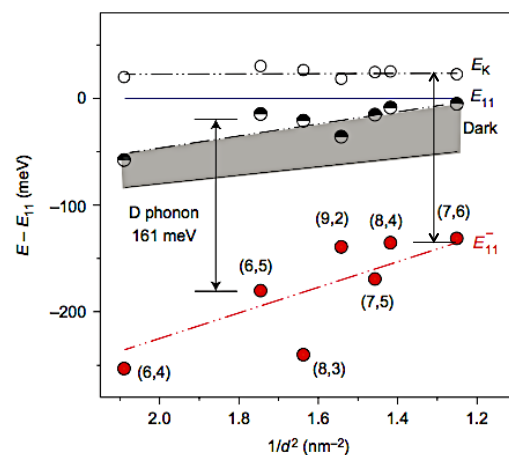
*Figure 8*. **Energy levels of each states.** The red-shift of $E_{11}^-$ from $E_{11}$ shows a dependency on nanotube diameter. This results in a different coupling of $E_{11}^-$ states.

From these energy relationships,

- Bright emissions in (6,4) and (6,5) nanotubes come from the relaxation of the low-lying dark excitons to the emissive $E_{11}^-$ state, because of the increased $sp^3$ defects.

- Coupling to the low-lying dark excitons was possible because of the lower energy level of $E_{11}^-$ state.

- Larger diameter nanotubes, such as (7,6) or (8,4), have higher energy level, so that the $E_{11}^-$ state couples to less-populated $K$-momentum dark excitons. This results in negligible brightening of the nanotubes.

## 2.3. Control of the Optical Properties by the Aryl Functional Groups

Instead of $NO_2$ group, several electron withdrawing or donating groups were introduced (*Figure 9, 10*).

- $E_{11}^-$ emission energy and $\Phi$ can be controlled by substituents.

- The photoluminescence peak can be correlated with the Hammett constant $\sigma_p$.
  - ➢ This trend of frontier orbital energy level changes is consistent with those observed in conjugated polymers.
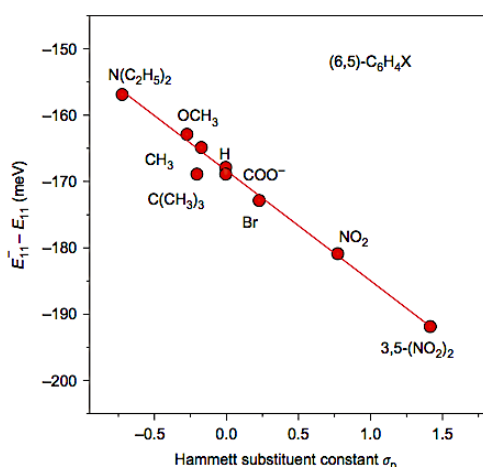
*Figure 9.* **Red-shifted energy dependence on Hammett constant $\sigma_p$.** (6,5)-SWCNTs were used.
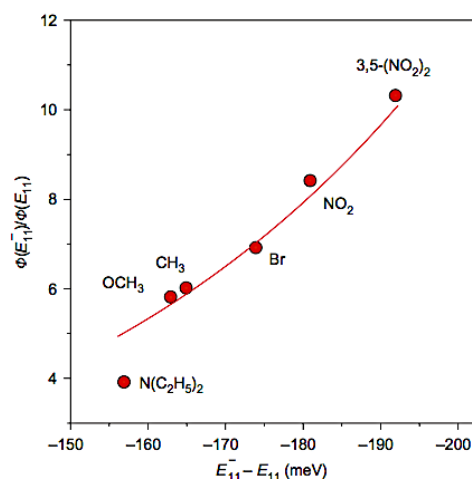
*Figure 10.* **Photoluminescence brightening dependence on red-shifted energy.** (6,5)-SWCNTs were used.

## 3. Conclusions

- It was found that covalent functionalization of semiconducting SWCNTs gives a brighter photoluminescence than the original SWCNT with a controlled number of aryl functional groups.

- The emission energy and the photoluminescence quantum yield are tunable by the substituents on the aryl functional group.

- These phenomena can be understood by enhanced exciton-phonon coupling induced by controlled number of $sp^3$ defects.

## 4. References

(1) Spataru, C.; Ismail-Beigi, S.; Capaz, R.; Louie, S. *Phys. Rev. Lett.* **2005**, *95*, 247402.
(2) Karousis, N.; Tagmatarchis, N.; Tasis, D. *Chem. Rev.* **2010**, *110*, 5366–5397.
(3) Usrey, M. L.; Lippmann, E. S.; Strano, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 16129–16135.
(4) Capaz, R.; Spataru, C.; Ismail-Beigi, S.; Louie, S. *Phys. Rev. B* **2006**, *74*, 121401.