

## Supporting Information

### Experimental

#### Materials.

Single wall carbon nanotubes were purchased from Carbon Nanotechnologies Inc., Houston, TX (HiPCo). 2-amino-5-bromo benzophenone[1] and 4-vinylphenylboronic acid was synthesized according to previous reports[2]. 1-Bromo-4-nitrobenzene 99% (Aldrich), 2',3',4',5',6'-Pentafluoro-acetophenone 97% (Aldrich), Copper bromide 99,999% (Aldrich), N,N,N',N',N''-Pentamethyl diethylene triamine 99% (Aldrich), 2-chloropropionyl chloride (Merck) and Isopentyl Nitrite (Fluka). All solvents were used as is unless reported. The filtration of carbon nanotubes were perform in a typical apparatus using filtration papers purchased from Sterlitech Corp., (Nylon 200nm, 47mm).

#### Instruments and Measurements.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Advance DPX 400 and 100 MHz spectrometer, respectively, with  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  as solvents containing TMS internal standard.

Gel permeation chromatography (GPC) measurements were carried out using a polymer lab chromatographer with two Ultra Styragel linear columns ( $10^4$ , 500 A), UV detector polystyrene standards and  $\text{CHCl}_3$  as eluent, at 25 °C with a flow rate of 1 mL/min.

Sonication was done on a Bransonic (Branson), ultrasonic cleaner 2510 model.

The TGA experiments were performed on a TA instrument Q50 series. The functionalization degree of functionalized carbon nanotubes was estimated according to: (% Carbon / atomic

weight of carbon) / (% function group / molecular weight of the function group).

UV-Vis spectra were recorded using a Hewlett Packard 8452A Diode Array. Continuous wave photoluminescence was measured on a Perkin Elmer LS45 spectrofluorometer.

UV-Vis-NIR spectroscopy was conducted on a Perkin Elmer L 900 spectrometer.

Raman measurements were performed with a Renishaw inVia Reflex Raman spectrometer at 785nm (1.58eV) excitation, in the backscattering geometry. The laser power was kept below ~0.8mW, to avoid laser induced local heating on the samples. A 50x objective is used and the spot size is estimated to be ~1x2 $\mu$ m.

The photoemission experiments were carried out in an ultra-high-vacuum system, which consists of a fast entry specimen assembly, a sample preparation and an analysis chamber with a base pressure  $<5 \times 10^{-10}$  mbar. The system is equipped with a hemispherical electron energy analyzer (SPECS LH-10) and a UV lamp for UPS measurements. UPS spectra were obtained using the HeI resonance line ( $h\nu=21.23\text{eV}$ ). The work function ( $e\Phi$ ) was determined for all the surfaces from the UPS spectra by subtracting their width (i.e. the energy difference between the analyzer Fermi level and the high binding energy cutoff), from the HeI excitation energy. For these measurements a bias of  $-12.29$  V was applied to the sample in order to avoid interference of the spectrometer threshold in the UPS spectra. The high and low binding energy and highest occupied molecular orbital (HOMO) cutoff positions were assigned by fitting straight lines on the high and low energy cutoffs of the spectra and determining their intersections with the binding energy axis. The analyzer broadening was defined via UPS, from the width of the Fermi edge of a sputtered clean Au foil and it was found to be  $0.16\text{eV}$ . Since this broadening applies to the entire UV spectrum, the cutoff positions were corrected only by half this value by adding  $0.08\text{eV}$  at the high binding energy cutoff and subtracting the same amount from the low binding

energy cutoff. Regarding measurement errors it should be noted that an error of  $\pm 0.1\text{eV}$  is assigned to the absolute values for ionization energies, work function and other UP-spectra cutoff features where the error margin is significant, due to the process of fitting straight lines. The ionization energy (IP) of the material under investigation, i.e., the distance between the vacuum level and the HOMO cutoff, is calculated by adding the absolute values of the measured work function and the HOMO cutoff. The position of the lowest unoccupied molecular orbital (LUMO) can only be measured directly by using inverse photoemission, or it can be deduced from HOMO–LUMO energy gap measurements. The value of the work function ( $\Phi$ ) of the SWCNTs as measured from the UPS spectrum was  $4.3\pm 0.1\text{eV}$ , in very good agreement with reported values.[3]

Electrochemistry studies were performed using a standard three-electrode cell. Platinum wire was used as counter and platinum disc (1.6mm diameter) as working electrode. Silver/silver nitrate (0.1 M  $\text{AgNO}_3$  in acetonitrile) was used as a reference electrode. Tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ , 98%) was used as electrolyte and was recrystallized three times from acetone and was dried in a vacuum at  $100\text{ }^\circ\text{C}$  before each experiment. Measurements were recorded using an EG&G Princeton Applied Research potentiostat/galvanostat Model 2273 connected to a personal computer running PowerSuite software. All experiments were calibrated, by running Ferrocene before each experimental run.

## Synthetic Procedures and Schemes, Molecular Characteristics of Homopolymers

**Synthesis of bromo phenyl pentafluoro quinoline (Br-5FQ).** A 100ml round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 1.75g (6.34mmol) of 2-amino-5-bromo benzophenone and 20mL acetic acid (AcOH) were added in the flask and the mixture was heated at 110°C. When 2-amino-5-bromo benzophenone was dissolved, 2g (9.52mmol) 2',3',4',5',6'-Pentafluoro-acetophenone and 1 mL of sulfuric acid 95% (H<sub>2</sub>SO<sub>4</sub>) were added. The system was degassed and flushed with argon again and was heated to reflux temperature for 5days. After the solution was cooled it was precipitated in a mixture of 1/1/0.2 water/ice/ammonia. The mixture was filtered and was dried under vacuum at 60°C over night. Then the solid was added in 25mL absolute ethanol and after 1hour was filtered and the purified solid was dried under vacuum at 50°C over night (yield=1.52g, 53%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 8.13 (d, 1H), 8.10 (s, 1H), 8.08 (s, 1H), 7.86 (dd, 1H), 7.6-7.5 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 148.80, 147.36, 136.68, 133.72, 131.84, 129.48, 129.14, 128.98, 128.02, 127.30, 123.70, 122.20. **Figure S1.**

**Synthesis of vinyl monomers (5FQ).** A 100ml round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 2g (4.44mmol) Br-5FQ, 0.86g of 4-vinylphenylboronic (5.78mmol), 1.84g K<sub>2</sub>CO<sub>3</sub> (13.32mmol) in 2M aqueous solution, 0.15g Pd(PPh<sub>3</sub>)<sub>4</sub> (0.13mmol) and 50mL toluene were added and the system was degassed and flushed with argon again. The flask was covered with aluminum foil and the reaction mixture refluxed for 4 days. Then the mixture was filtered from paper filter followed by

the extraction of the organic layer with EtOAc (3x 40mL) and distilled water (3x 40mL). The organic part was stirred with magnesium sulphate ( $\text{MgSO}_4$ ), filtrated and the solvent was rotary evaporated. The solid was dried under vacuum at  $40^\circ\text{C}$  over night and then dispersed in MeOH for further purification. The solid was then filtered and the light yellow solid was vacuum dried over night. Yield 78%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 8.29 (d, 1H), 8.18 (s, 1H), 8.07 (dd, 1H), 7.7-7.5 (m, 10H), 6.79-6.72 (q, 1H), 5.80 (d, 1H), 5.28 (d, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 149.68, 148.20, 140.07, 139.54, 137.37, 137.31, 136.17, 130.64, 129.69, 129.60, 128.90, 128.86, 127.62, 126.85, 126.34, 123.40, 123.30, 114.51 (**Figure S2 a and b**).

**Polymerization (FRP) for P5FQ-i.** A 5ml round bottom flask, equipped with a gas inlet/outlet and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 200mg (0,423mmol) of monomer **M3**, 5mg AIBN and 2mL DMF were added and the system was degassed and filled with argon again. The reaction mixture heated at  $130^\circ\text{C}$  for 4 days. Then the mixture was cooled and was added dropwise in 20mL Methanol (MeOH). After 1 day the mixture was filtered and the solid was dried under vacuum at  $60^\circ\text{C}$  over night. Then the solid was washed with ethyl acetate for 1 day to remove the unreacted monomers and after the filtration the solid was dried under vacuum at  $60^\circ\text{C}$  over night.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 8.4-6.7 (three broad, 13H), 2.2-1.3 (two broad, 3H), **Figure S3**. The molecular characteristics of the synthesized homopolymers **P5FQ** are listed in **Table S1** below, as determined from SEC.

**Table S1.** Molecular Characteristics of homopolymers **P5FQ-i,ii**.

	<b>5FQ/AIBN</b>	<b>Mn</b>	<b>Mw</b>	<b>Mw/Mn</b>
<b>P5FQ-i</b>	14/1	4800	10640	2.20
<b>P5FQ-ii</b>	17/1	3240	4370	1.35
<b>P5FQ-iii</b>	10/1	9000	14400	1.60

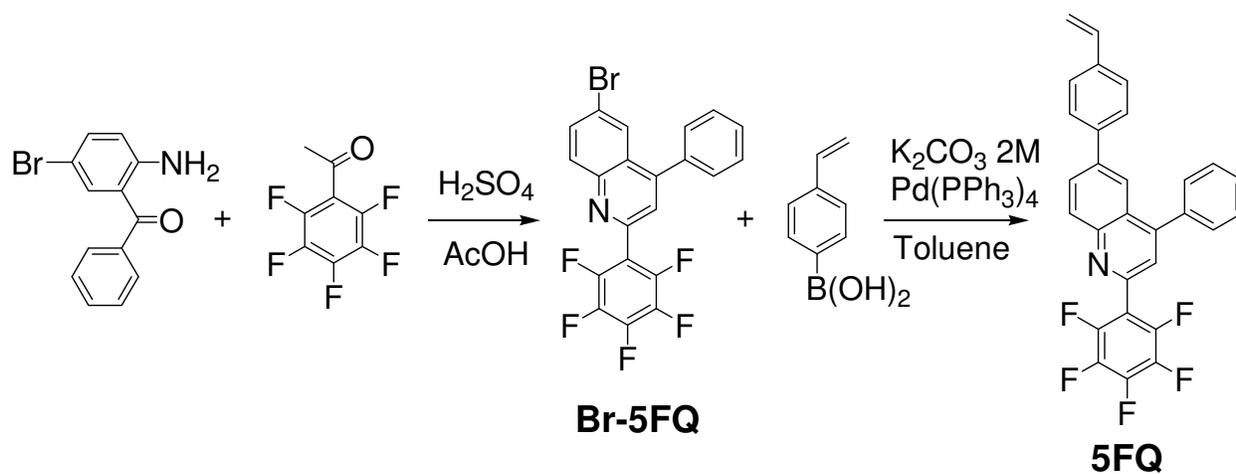
**Functionalization of SWCNT's with OH group (SWCNT-OH).** A 250ml round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 100mg SWNT, 4mL isoamyl nitrite, and 2g 4-aminophenol were added and the system was degassed and filled with argon again. The flask was covered with aluminum foil and the reaction mixture was heated at 65°C for 4 days. After cooling down to room temperature, 15mL of acetone was added to the resulting mixture and then it was vacuum-filtered through Nylon 200nm membrane. The obtained solid was washed with dichloromethane and acetone, and then it was dispersed in DMF for further purification. The mixture was treated in an ultrasonic bath for 1hour and after was vacuum filtered again. The solid was dried under vacuum at 80°C over night.

**Functionalization of SWNT's with the Initiator (SWCNT-Init).** A 100ml round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 100mg of the **SWCNT-OH** and 100ml DMF were added and the mixture was treated in an ultrasonic bath for 20 minutes. The system was degassed and filled with argon again. Then the system was placed in an ice bath and when it was cooled 6mL Et<sub>3</sub>N and 5mL 2-

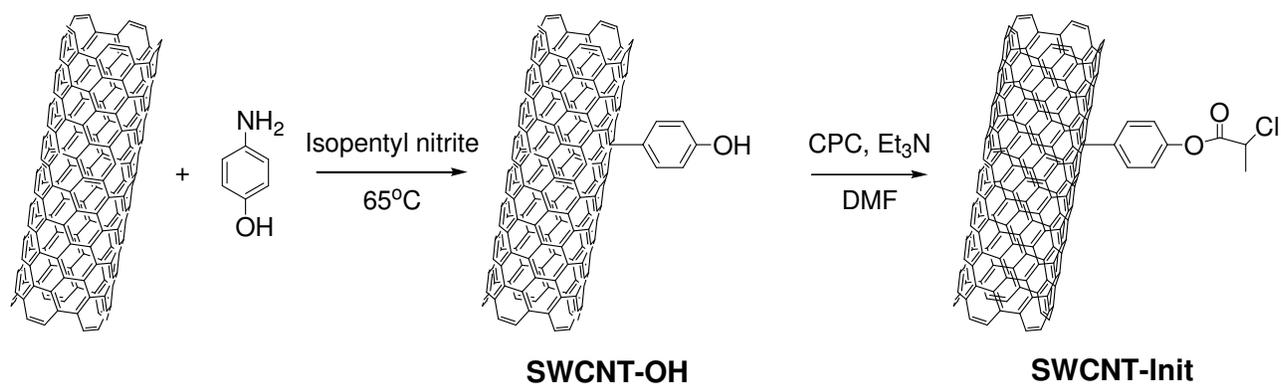
chloropropionyl chloride were added in the flask. The system was stirred in the ice bath for 1 hour and then the reaction mixture was heated at 100°C for 4 days. After cooling down to room temperature, the resulting mixture was vacuum-filtered through Nylon 200nm membrane. The obtained solid was washed with dichloromethane and acetone and then it was dispersed in DMF for further purification. The mixture was treated in an ultrasonic bath for 1 hour and after was vacuum filtered again. The solid was dried under vacuum at 80°C for 2 days.

**Polymerization of M3 onto SWCNT-Init (SWCNT-g-P5FQ).** A 5ml round bottom flask, equipped with a gas inlet/outlet and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. Then 40mg CuBr, 60µL PMDETA, and 1mL DMF were added and the system was degassed under vacuum and filled with argon again. A 10ml round bottom flask, equipped with a gas inlet/outlet and a magnetic stirrer, was degassed (flamed under vacuum) and filled with argon. 25mg **SWCNT-Init**, 1mmol of monomer **5FQ**, and DMF were added the mixture was treated in an ultrasonic bath for 20minutes and the system was degassed under vacuum and filled with argon again. The mixture of the catalytic system from the 5mL round bottom flask was added in the 10mL flask via syringe and the system was degassed and filled with argon again. The reaction mixture was heated at 110°C for 2 days. The obtained solid was washed with chloroform and tetrahydrofuran and then it was dispersed in DMF for further purification. The mixture was treated in an ultrasonic bath for half hour and after was filtered again. The obtained **SWCNT-g-P5FQ** solid was dried under vacuum at 80°C for 2 days.

### Scheme S1



### Scheme S2



# <sup>1</sup>H NMR and TGA characterization.

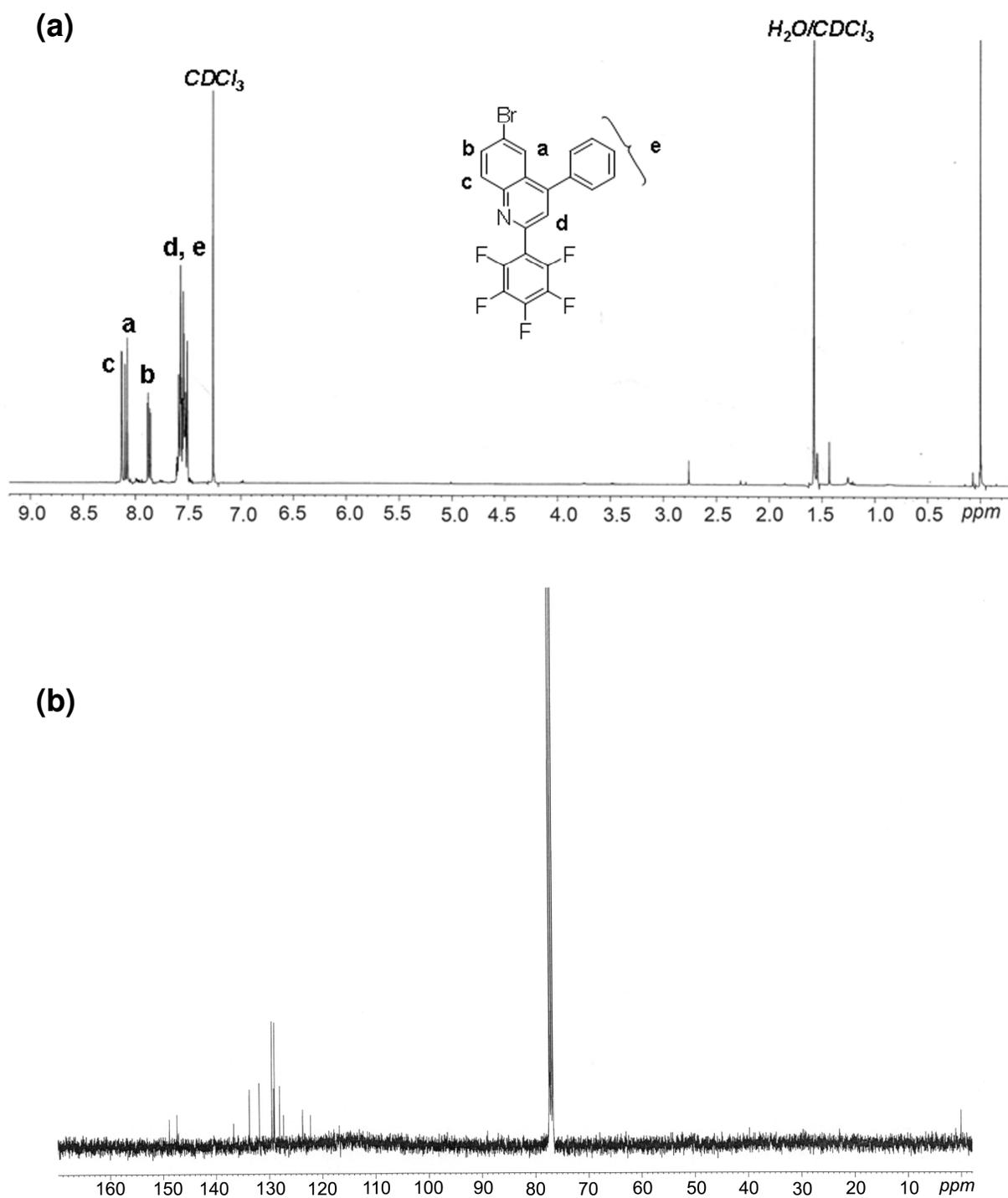
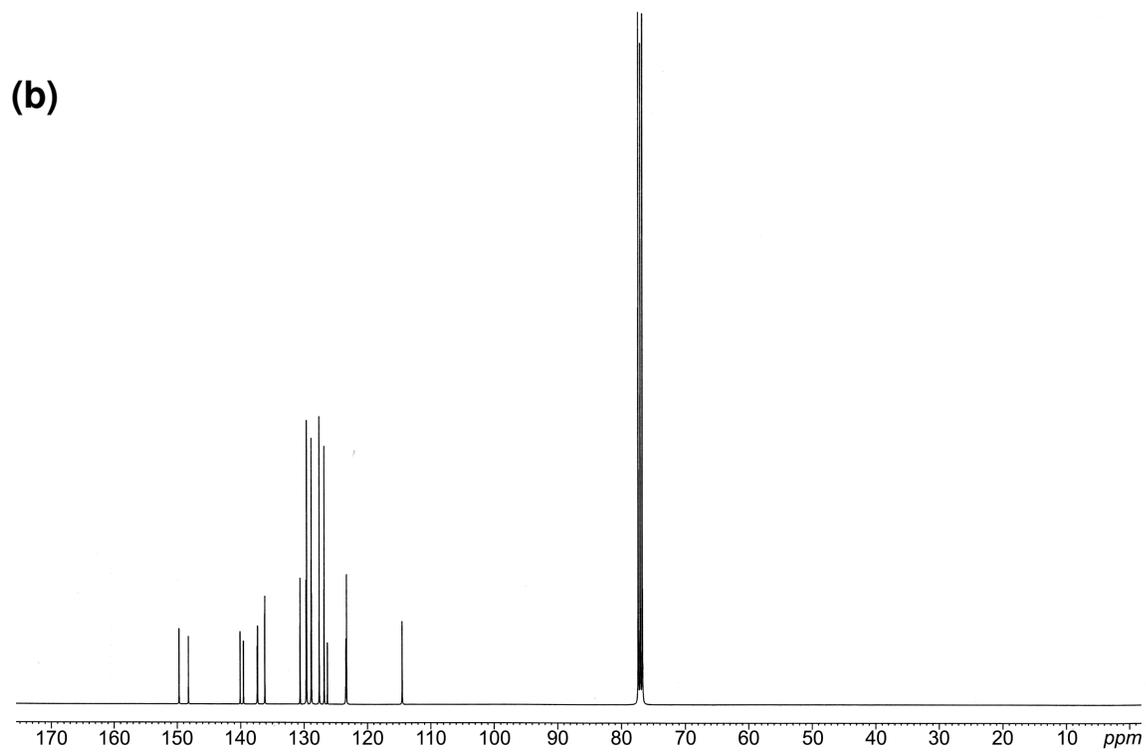
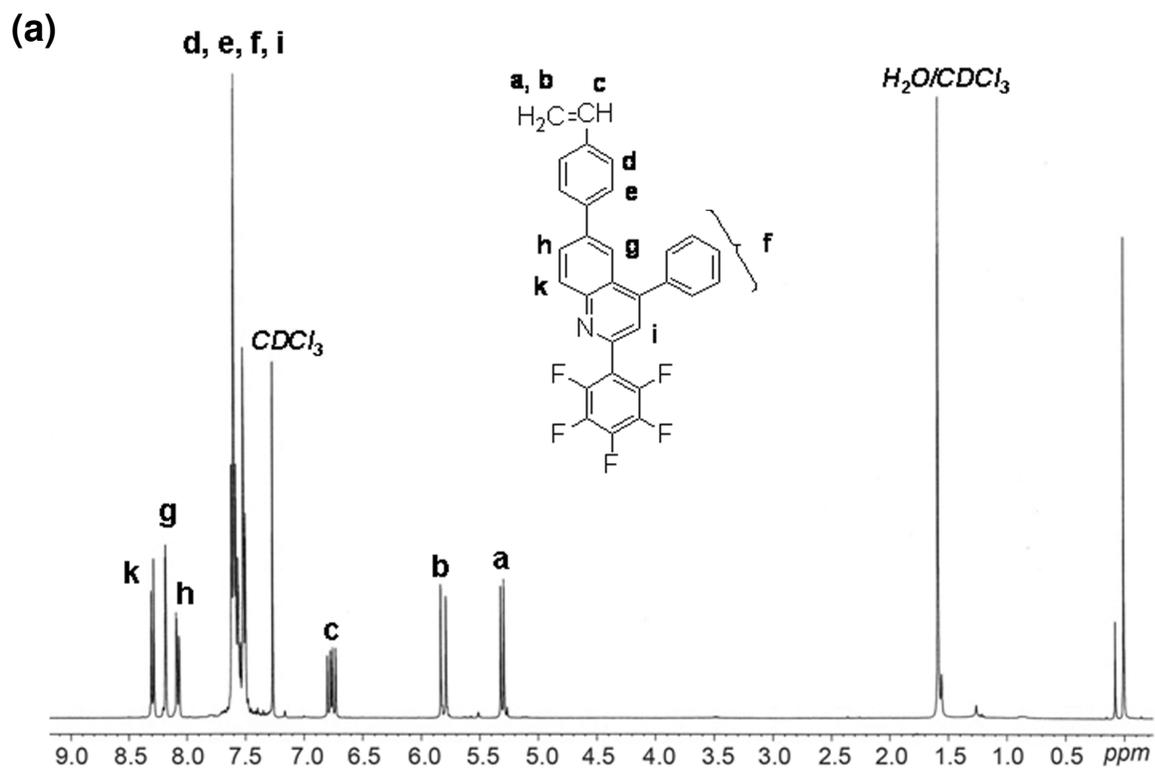
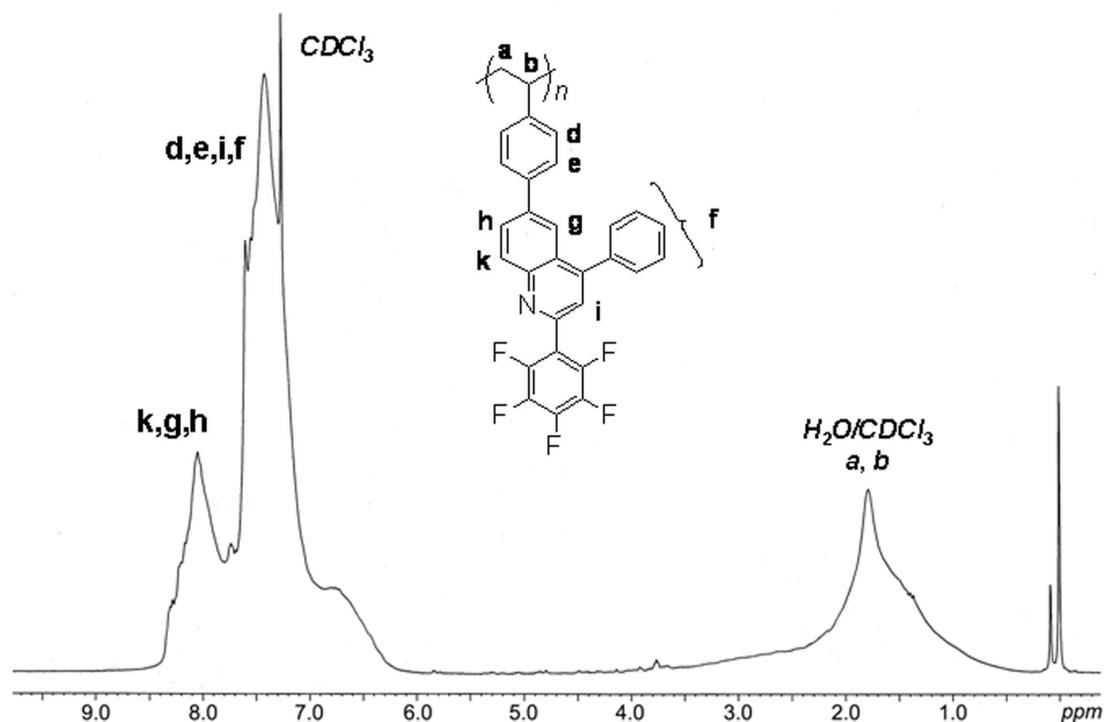


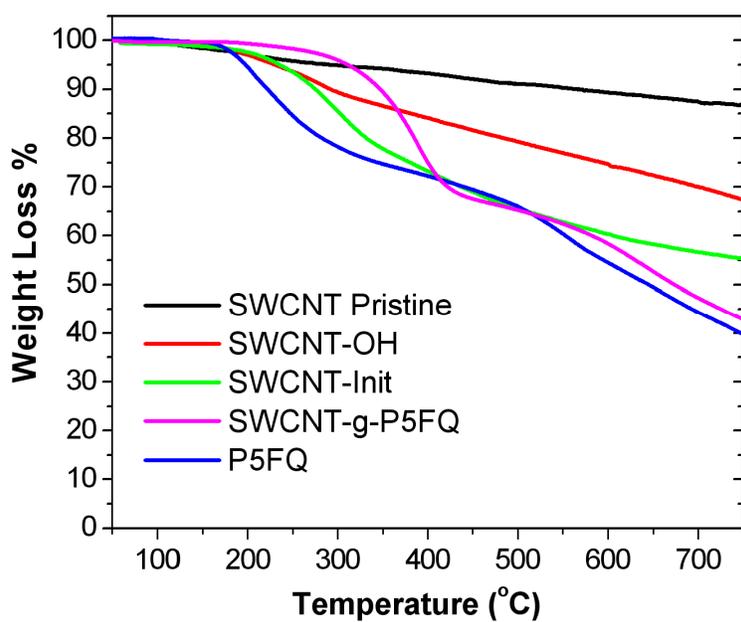
Figure S1. (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR of Br-5FQ in CDCl<sub>3</sub>



**Figure S2.** (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR of **5FQ** in CDCl<sub>3</sub>.

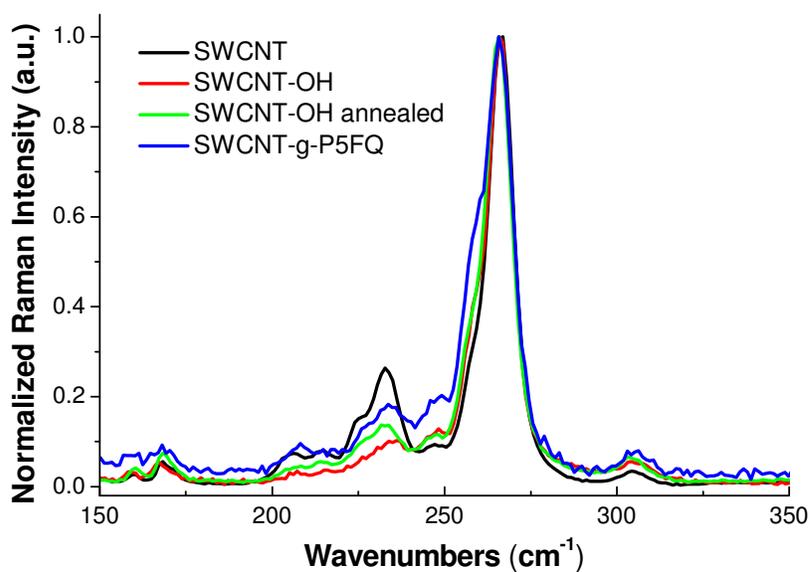


**Figure S3.**  $^1\text{H}$  NMR of **P5FQ** in  $\text{CDCl}_3$ .

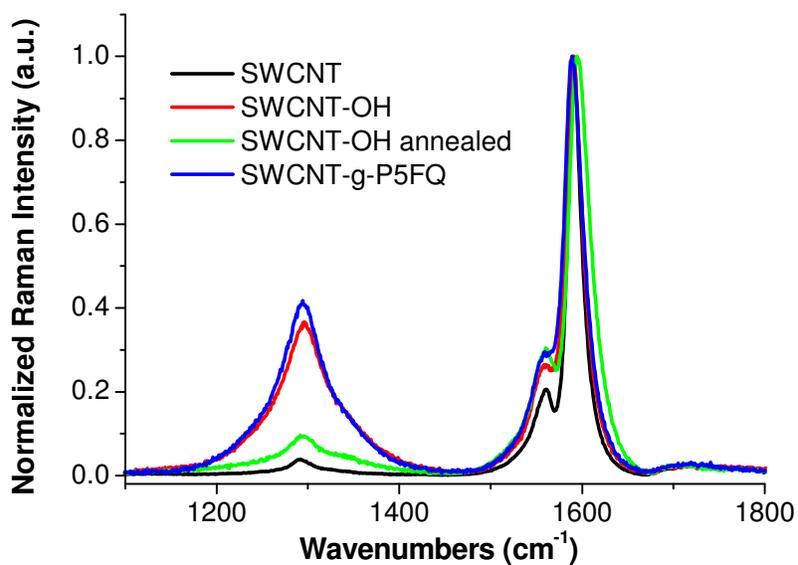


**Figure S4.** Thermogravimetric analysis of pristine, hydroxy (**SWCNT-OH**), ATRP initiator (**SWCNT-Init**) and polymer (**SWCNT-g-P5FQ**) functionalized carbon nanotubes.

## Raman and UV-Vis-NIR Spectroscopies



(a)

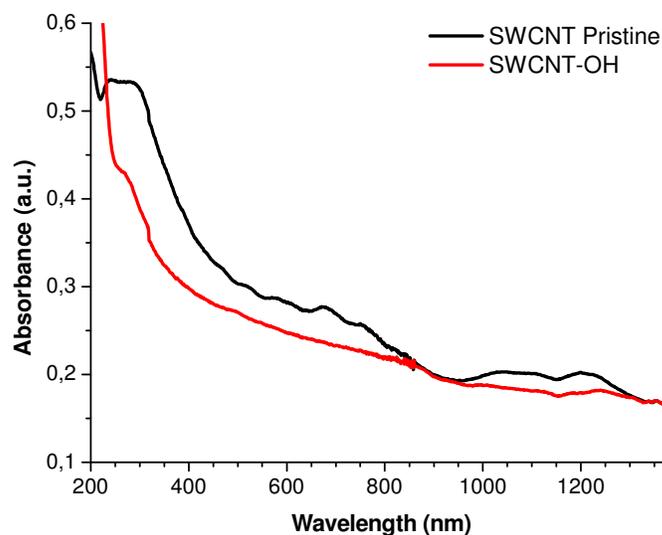


(b)

**Figure S5.** Raman spectroscopic analysis of pristine, hydroxy functionalized carbon nanotubes (SWCNT-OH) before and after annealing at 800°C (SWCNT-OH Annealed) and of polymer functionalized carbon nanotubes SWCNT-g-P5FQ in RBM bands (a) and in D & G bands (b).

**Table S2.** Raman ratio  $I_D/I_G^+$  of the studied samples ( $\lambda=785\text{nm}$ ).

Sample	$I_D/I_G^+$
SWCNT-pristine	0.07
SWCNT-OH	1.17
SWCNT-OH Annealed	0.22
SWCNT-g-P5FQ	1.10



**Figure S6.** UV-Vis-NIR absorption spectroscopy of dispersed pristine and hydroxy functionalized nanotubes (**SWCNT-OH**).

As stated in the main text, it is clear from the ratio  $I_D/I_G^+$  of the pristine SWCNTs and **SWCNT-OH** sample (**Table S2**) that the intensity of the D-band increases considerably upon functionalization (**Figure S5a**). Additional evidence of the  $sp^2$  to  $sp^3$  conversion after the

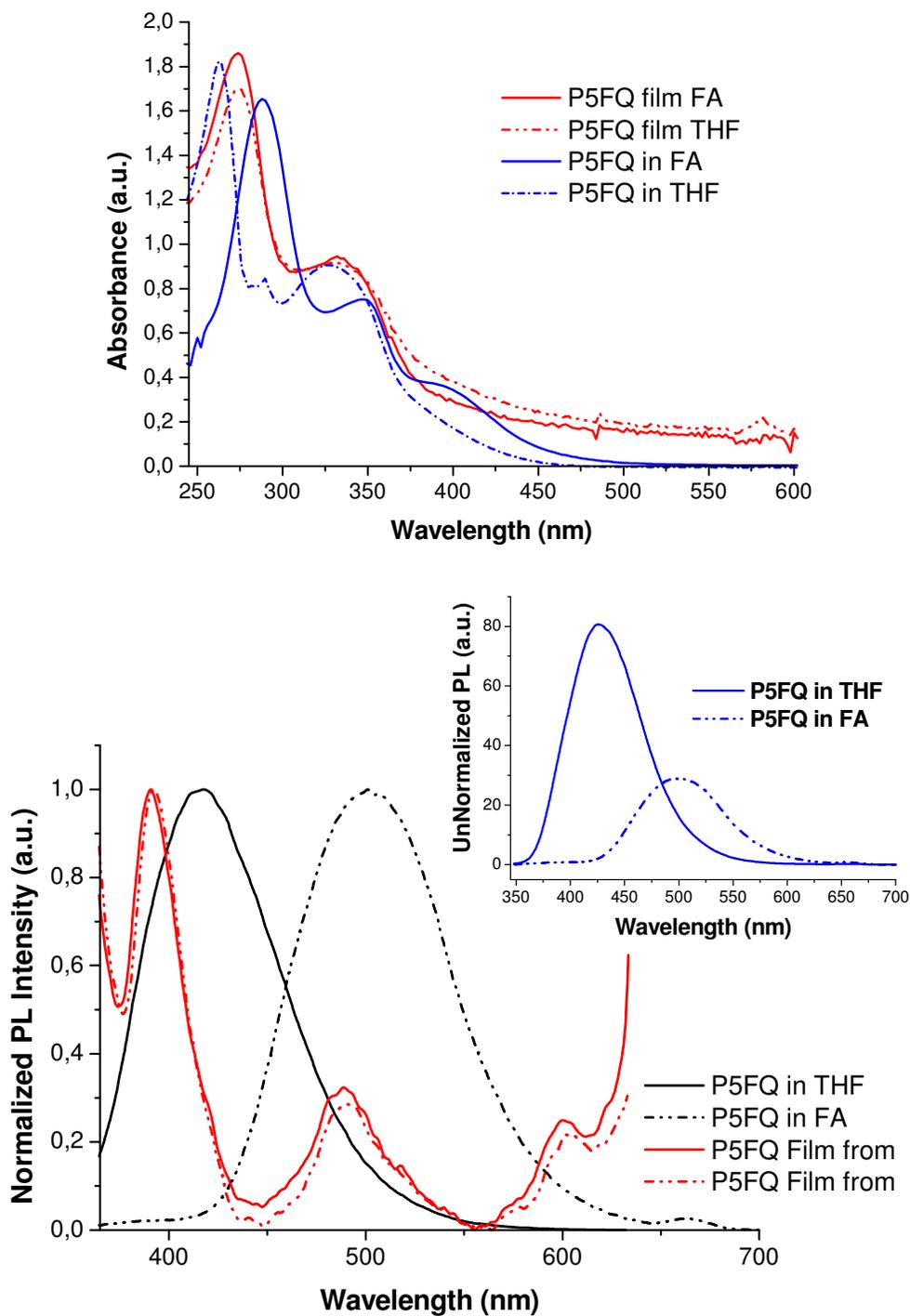
covalent addition of the phenol groups on the SWCNTs, came from UV-Vis-NIR spectroscopy of the pristine and hydroxy functionalized nanotubes, dispersed in water with sodium dodecyl sulfate (SDS) as surfactant. **Figure S6** reveals the successful attachment due to the disappearance of the van Hove's singularities in the spectrum of hydroxy-treated tubes. The decay of the spectral features is driven from the localization of the valence electrons making them no longer free to participate in photoabsorption.[4]

Moreover, to accredit that no critical damage was made on the nanotubes structure due to functionalization, Raman spectroscopy of the annealed **SWCNT-OH (Figure S5a)**, shows that the nanotubes, after the TGA in inert atmosphere, were almost fully restored. This was able to be qualified from the pronounced decreased of the D- relative to the G<sup>+</sup>-band (**Figure S5a** and **Table S2**). Additionally, it should be stressed that compared to the pristine material the **SWCNT-OH annealed** sample shows a blue shift of  $\sim 5 \text{ cm}^{-1}$  for the G<sup>+</sup> band, accompanied by an increase of the full-width at half maximum (FWHM) from  $19 \text{ cm}^{-1}$  (pristine) to  $28 \text{ cm}^{-1}$ . The experimental findings can be attributed to the presence of defect concentration on SWCNTs after the thermal treatment, originated from the removal of the polymer chains attached to the SWCNTs (thermal defunctionalization) and/or the quite mild destruction of the graphitic integrity at high temperature.[5]

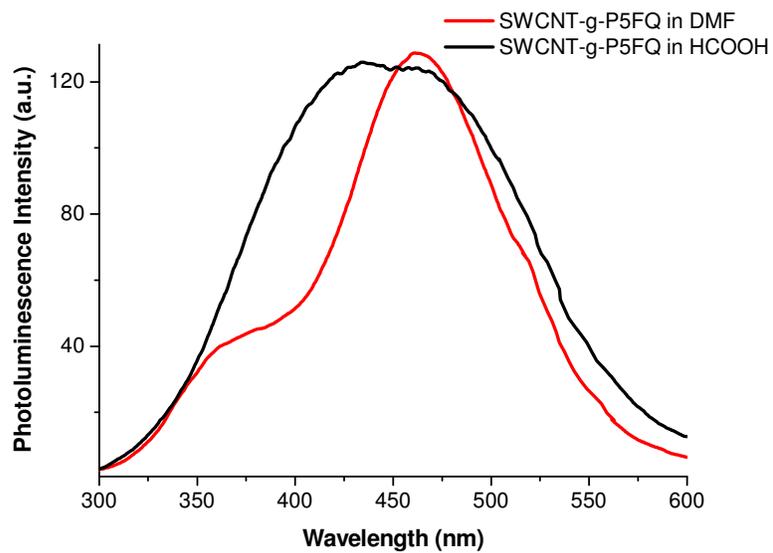
**Figure S5b** shows the Raman spectra of the studied materials in the RBM frequency region, at 785nm excitation. At this laser wavelength the excitation is primary resonant with  $\nu_2 \rightarrow c_2$  transitions of semiconducting nanotubes. The members of two branches namely the (12,1) and the (11,0) contribute to the spectra.[6] The highest intensity RBM feature at  $267 \text{ cm}^{-1}$  corresponds to a diameter of 0.862nm and can be assigned to (10,2) or (11,0) nanotubes of the (11,0) branch. Interestingly, the **SWCNT-OH** modified material shows a significant reduction of the Raman

scattering intensity associated with the (12,1) branch, located at the region between 210-240 $\text{cm}^{-1}$ . The aforementioned intensity suppression is not so pronounced for the **SWCNT-g-P5FQ** sample, while a redistribution of the Raman signal within the (12,1) is clearly observed. However, Raman scattering in carbon nanotubes is a resonant process [7] and the RBM Raman intensity as a function of the laser energy (resonant profiles) must be recorded in order to assess in detailed the effect of chemical modification on SWCNTs. This work is underway.

## Optical Characterization.

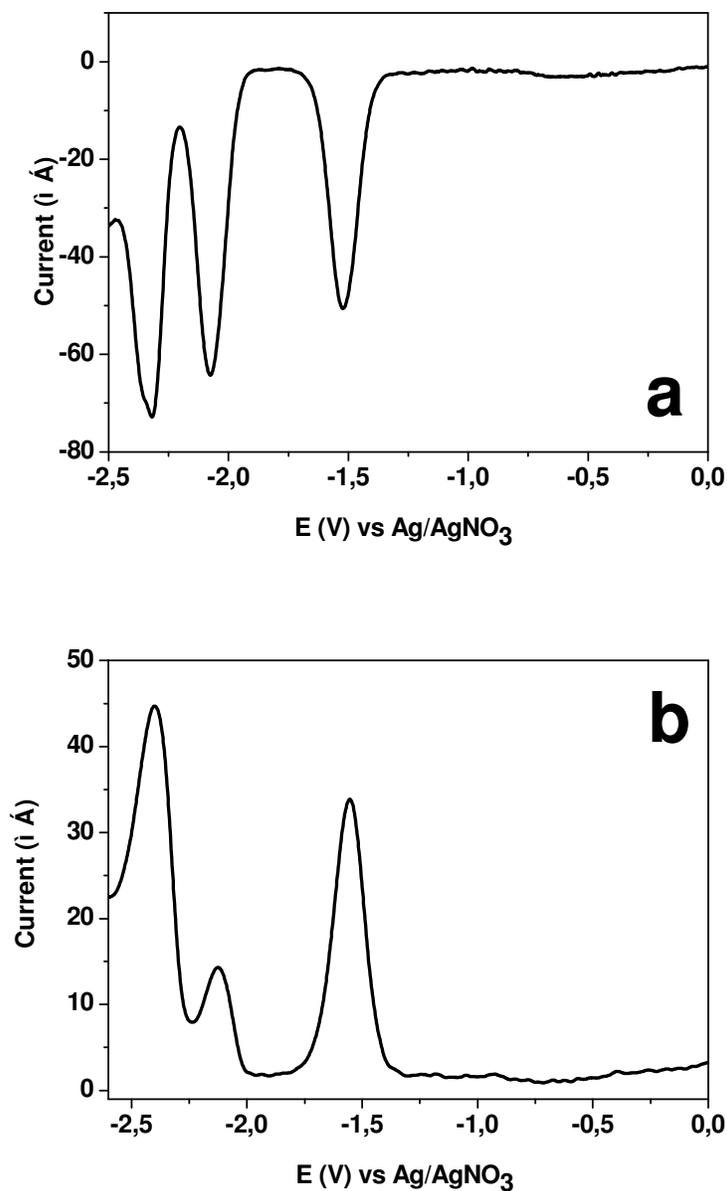


**Figure S7.** UV-Vis (S7a) and PL after excitation in absorption maxima (S7b) spectra of homopolymer **P5FQ** in THF and Formic acid (FA) solutions and film form.



**Figure S8.** Photoluminescence spectroscopy of polymer functionalized nanotube (SWCNT-g-P5FQ) in DMF and formic acid.

## Differential Pulse Voltammetry



**Figure S9.** Differential Pulse Voltammogram of quinoline monomer **5FQ** a) reduction run and b) oxidation run obtained in TBAPF<sub>6</sub> 0.1M in DMF. The three redox processes at  $E_{1/2}$  -1.53V, -2.09V and -2.36V are clearly observed. Experimental details: pulse height 0.0025V, pulse width 50ms, step height 2mV, step time 100ms

## References

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