

Supporting Information

Real Time Hyperspectroscopy for Dynamical Study of Carbon Nanotubes

Jacques Lefebvre*

National Research Council, 1200 Montreal Rd, Ottawa, Ontario, K1A 0R6, Canada

1. Hyperspectroscopy setup

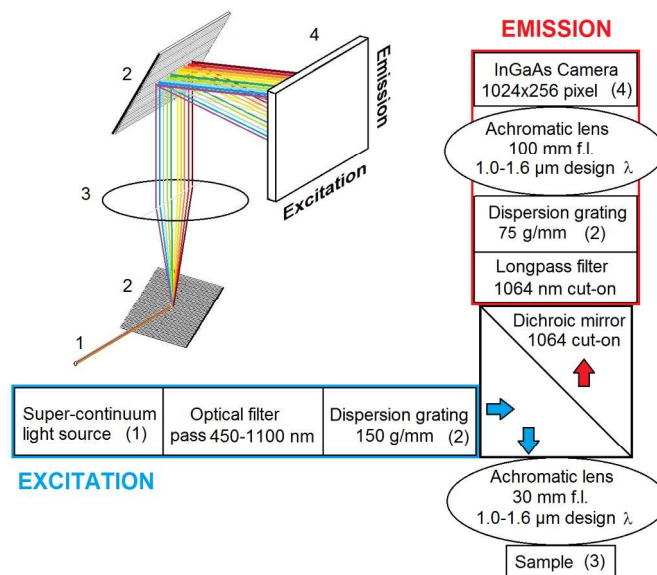


Figure S1: Schematic of the method. Note: An alternative to the 3D illustration is to use a dichroic mirror so both excitation and emission occur from the same side, the actual configuration for the present experiments. Both configurations are possible and have been tested.

Figure 1 of the main text has been supplemented with Figure S1. As presented in the main text, the core of the setup is a supercontinuum (SC) source (NKT Photonics). It produces $>1\text{mW/nm}$ throughout its emission range, from 450-2100 nm. Although this represents a reasonable amount of power for PL excitation between 450-1000 nm, the challenge is to efficiently remove the long wavelength portion of the SC. The adopted solution was to set up a pair of high reflectors

(Newport BB.HR2) to obtain multiple reflections of the beam. Upon each reflection, most of the infrared is transmitted through the mirror and becomes insignificant after 16 reflections or so. Since the cutoff of the mirrors is 1100 nm, an additional short pass filter (Edmund Optics, Techspec OD4 high performance filter) is added before the dispersion grating. The filtered beam is directed to a 150 *g/mm* diffraction grating blazed at 500 nm (Newport 10RG150-500-1). Figure S2 shows the spatial extent of the excitation source at the sample location: It is of order of 1 *mm*. Although excitation can be done through a separate lens from the collection, the present experiment uses a dichroic mirror (Semrock Di02-R1064) with a cutoff at 1064 nm. The focusing lens on the sample and imaging lens on the detector are both achromats (Thorlabs AC254-030-C and AC508-100-C). On the collection side, the excitation source is filtered using a combination of longpass filters before reaching the dispersion grating (75 *g/mm* blazed at 1.7 μm , Richardson Gratings 53-*-756R). The current setup does not use a grating spectrometer but simply relies on the fact that sufficient spectral resolution can be obtained by direct imaging of the illumination slit (at the low magnification provided by the optics). A spectrometer can be used but it is possible that vignetting occurs, limiting the span of excitation wavelength measured. For compactness of the design, the imaging lens was positioned after the dispersion grating. The detector is an InGaAs camera (MOSIR from Intevac) with 256x1024 pixels. Although this camera offers excellent sensitivity, the readout electronics is slow compared to other cameras in the lab (Xenics InGaAs 320x256 array). The detector size, however, is an advantage since the zeroth order reflection of the grating can readily be seen. At the modest spectral resolution in this work, only a fraction of the detector, 220x220 pixels, produces PLE data. The camera is interfaced with LabView (National Instruments) and several peaks can be tracked in real-time or images can be saved and analyzed later.

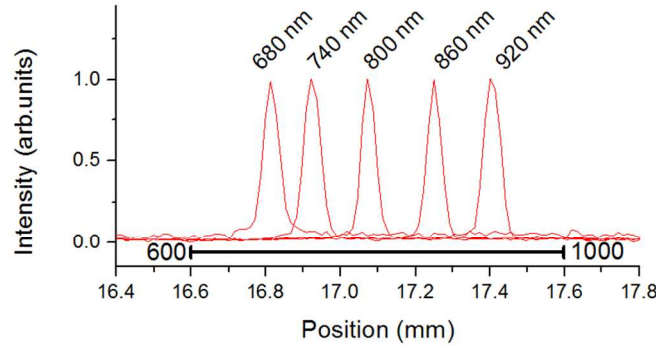


Figure S2: spatial extent of the excitation source at the sample focus. The 600-1000 nm excitation range covers a 1 mm width.

2. SWCNT samples.

The nanotubes in this work are from different sources and the preparation method varies slightly. For toluene dispersions, the concentration is estimated at $2\text{--}5\ \mu\text{g/mL}$. In order of appearance in the manuscript:

Fig.2(a): Nanostructured and Amorphous Materials (product # 1284YJ). Raw material was mixed with toluene and bath sonicated for a few minutes. Drops were evaporated on a cover glass to produce an optically thick layer, with good uniformity. Excitation power was about 10 mW.

Fig.2(b): Nanocyl NC-1100 (Sigma Aldrich product #755710). Preparation was similar to Fig.2(a). Excitation power was about 10 mW.

Fig.2(c): CoMoCAT (NIST standard reference material: SRM 2483). Raw material is mixed with toluene and polyfluorene and tip sonicated for 20 min. The dispersion is left to settle and a clear solution is drawn into a rectangular capillary (Electron Microscopy Sciences, 63842-05) with a $200\ \mu\text{m}$ path length. Excitation power was 0.5 mW.

Fig.2(d): Nanostructured and Amorphous Materials (product # 1284YJ). Preparation was similar to Fig.2(c). Excitation power was 0.2 mW.

Fig.2(e): Nanocyl NC-1100 (Sigma Aldrich product #755710). Preparation was similar to Fig.2(c). Excitation power was 1.5 mW.

Fig.2(f): NRC-Laser (National Research Council standard reference material: SWCNT-1 CRM). Preparation was similar to Fig.2(c). Excitation power was 1.1 mW.

Fig.3: Raymor Nanotechnology (HiPCO: RN-08 and Plasma: RN-020). Preparation was similar to Fig.2(c-f), however, in order to obtain a large number of chiralities, two samples with complementary distributions were mixed together. A PLE map from each material is shown in Figure S3. Excitation power was 0.9 mW during the titration experiment.

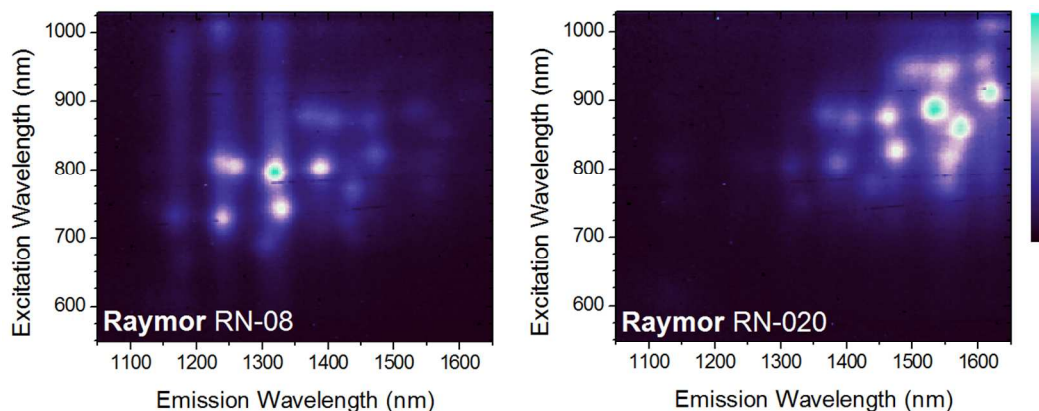


Figure S3: PLE maps from the starting material used in the titration experiment. Both materials were combined to cover a broad range of diameters and chiral angles.

3. Fluidics assembly

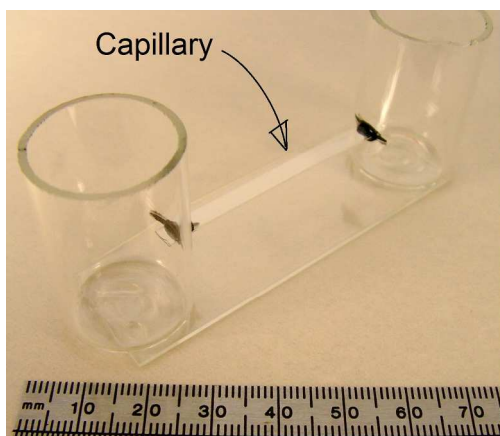


Figure S4: Photograph of the fluidic setup made of two vials connected with a capillary.

A few different fluidic configurations have been tested for the titration experiments. In order to produce a good temporal response, it appeared important to minimize the volume of sample used. In Figure S4, two vials are simply connected with a rectangular capillary ((Electron Microscopy Sciences, 63842-05). A slit opening is made in each vial using a diamond saw and the vials are fixed to a cover glass using a UV curable adhesive. The capillary is then inserted in the slits and sealed with an epoxy (Master Bond EP41S-1HT) selected for its chemical resistance. The flow of toluene in this arrangement is about 0.5 mL/min , and with a capillary volume 0.04 mL , the transit time between the two vials is around 5 s . The excitation spot is positioned near the middle of the capillary so any change in the feed solution should be seen within a few seconds. In order to homogenize the feed solution, a magnetic stirrer (home built using a mini-fan and rod magnets) was mounted underneath the feed vial.

In the titration experiment, the drain vial is initially filled until toluene enters the capillary. The acquisition of PLE maps is then started with initially no signal to be detected. The source vial is then filled with SWCNT solution up to the top, which corresponds to 10 mL , approximately. The PLE signal from sc-SWCNT is readily seen as pure toluene is replaced with the nanotube solution. I then proceeded with the titration experiment.

4. Titration

F4-TCNQ (similarly for TCNQ and TTF) was purchased from Sigma-Aldrich and dissolved in toluene at $18 \mu\text{g/mL}$ concentration. Drops of the solution were delivered to the source vial using a glass pipette with an average drop volume of $15 \mu\text{L}$. The calculated concentration of dopant per drop is $0.03 \mu\text{g/mL}$, considering the source vial contains 10 mL of SWCNT solution.

5. Luminescence recovery

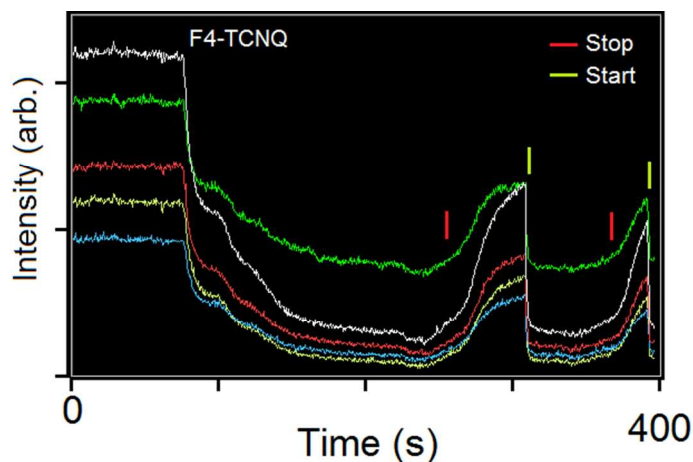


Figure S5: PL time traces tracking five sc-SWCNT chiralities in a doping experiment with F4-TCNQ. The effect of the flow is highlighted with red and green bars.

In the titration experiment with F4-TCNQ, a recovery of the PL intensity is seen at lower doping level. From another experiment, such recovery was seen only if the flow of solution was interrupted. The fluidic system uses a diaphragm pump to circulate the solution at rate up to 20 mL/min and under those conditions, PL dropped steadily without recovery upon doping. Figure S5 shows the PL intensity vs time for five chiralities. At time $< 80\text{ s}$, the solution is in the undoped state (non-intentionally) and at $t > 80\text{ s}$, dopant is added and PL intensity gradually drops. This is done while maintaining a good flow of solution. At $t = 250\text{ s}$ and 360 s , the flow is stopped and PL recovers partially in both cases until the pump is started again at $t = 310\text{ s}$ and 390 s . This result is consistent with the dopant being photo-deactivated. The flow itself is probably too low to have a significant impact on nanotube bundling or other physical properties related to PL.

Corresponding Author

e-mail: jacques.lefebvre@nrc-cnrc.gc.ca