Supporting Information

# Polaritonic Enhancement of Near-field Scattering of Small MoleculesEncapsulated in Boron Nitride Nanotubes

Dániel Datz*†‡, Gergely Németh†¶, Kate E. Walker§, Graham A. Rance‖, Áron Pekker*†, Andrei N. Khlobystov§ and Katalin Kamarás†

†Wigner Research Centre for Physics, Konkoly Thege Miklós út 29-33., Budapest, Hungary
‡Eötvös Loránd University, Pázmány Péter sétány 1/A, Budapest, Hungary.
¶Budapest University of Technology and Economics, Műegyetem rkp.3., Budapest, Hungary.
§University of Nottingham, School of Chemistry, University Park, Nottingham, NG7 2RD,United Kingdom
‖Nanoscale & Microscale Research Centre, Cripps South, University of Nottingham,University Park, Nottingham NG7 2RD, United Kingdom

Corresponding authors' email address: datz.daniel@wigner.hu, pekker.aron@wigner.hu

## 1. Experimental Details

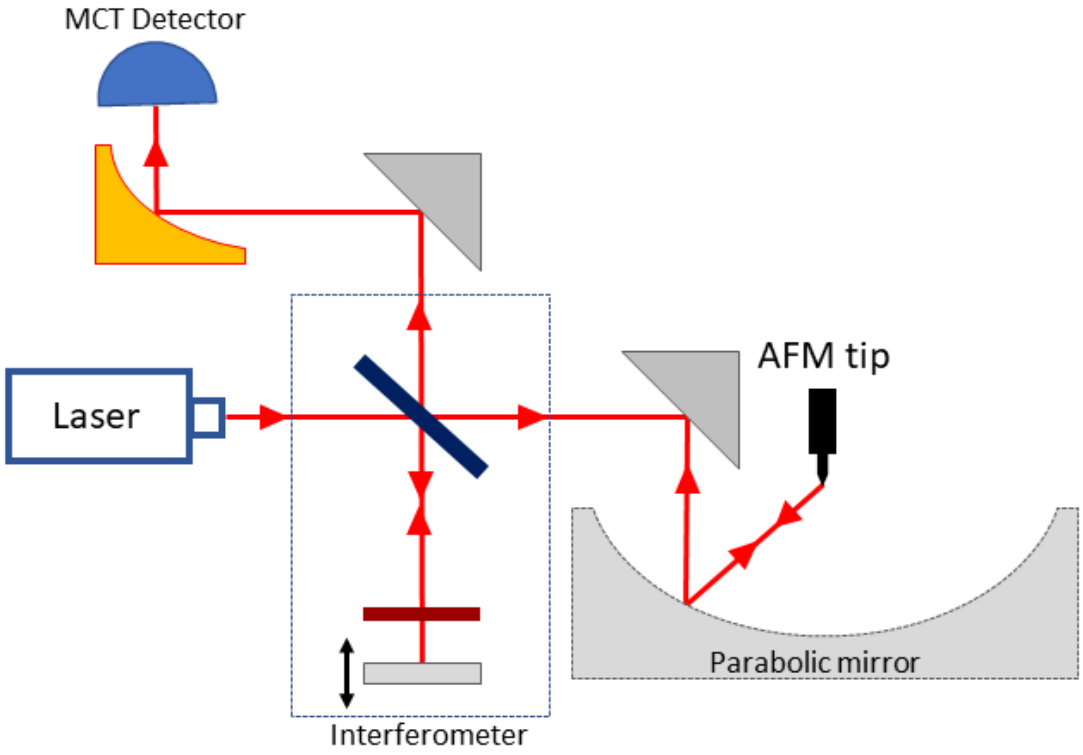
Nanotubes were purchased commercially (BNNT LLC) and filled with $C_{60}$ using the sublimation method.[1] Initially BNNTs were sonicated in 10% ammonia solution for four hours. The precipitate was filtered through a polytetrafluoroethylene (PTFE) membrane (0.2µm) and annealed at 800°C for an hour in air to oxidize the excess boron content. The resulting boron oxide is water soluble and was dissolved in hot water using a vacuum filtration method. The purified BNNTs were mixed with $C_{60}$ powder in a 1:1 mass ratio, then sealed in a quartz tube at $10^{-5}$mbar. The sealed tube was annealed at 600°C for 20 hrs. The resulting powder was thoroughly washed with toluene until $C_{60}$ was undetectable in the UV-Vis spectrum of the filtrate. The filled tubes were dispersed in isopropanol by prolonged, gentle stirring as sonication can force the fullerene molecules out of the nanotubes. Samples were prepared by spin coating the dispersion on a silicon surface (native oxide layer on top). The s-SNOM device (NeaSNOM, NeaspecGmbH) uses a metallic tip (Arrow-NCPt, Nanoworld) in intermittent contact mode. Infrared excitation is provided by a quantum cascade laser, tunable in the range of 1330-1450 $cm^{-1}$. The scattered light is detected by a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. For the photopolymerization, we focused a 532 nm laser beam to the near-field measurement spot by using the parabolic mirror of the infrared laser.

## 2. s-SNOM setup and data acquisition

The s-SNOM method measures the amplitude and phase of the scattered light using the interferometric pseudo-heterodyne method. The detected signal is demodulated at frequencies (nΩ + mM), where Ω is the frequency of the tip vibration, and M is the frequency of the vibrating mirror in the interferometer arm. In this paper, we used the third harmonic signals (n = 3, m=1,2) for the characterization of the samples. The near-field absorption is defined as the imaginary value of the detected near-field signal at the given harmonic, that is

$$Abs_3 = A_3 \sin \phi_3$$

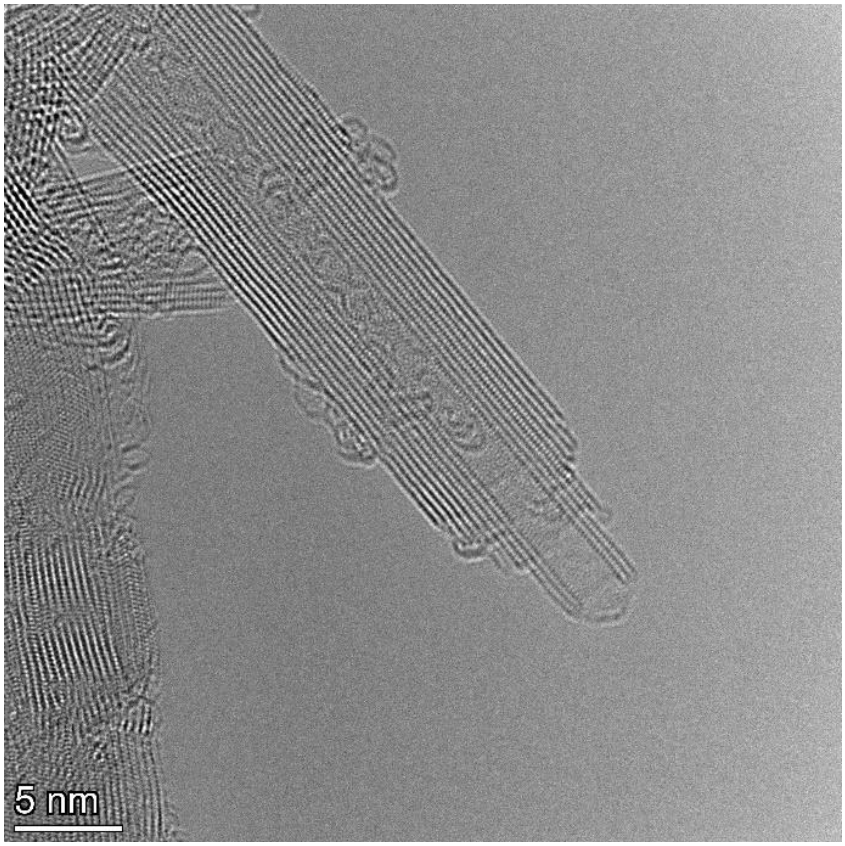
where $Abs_3$ is the near-field absorption at the third harmonic, while $A_3$ and $\phi_3$ are the third harmonic amplitude and phase, respectively.



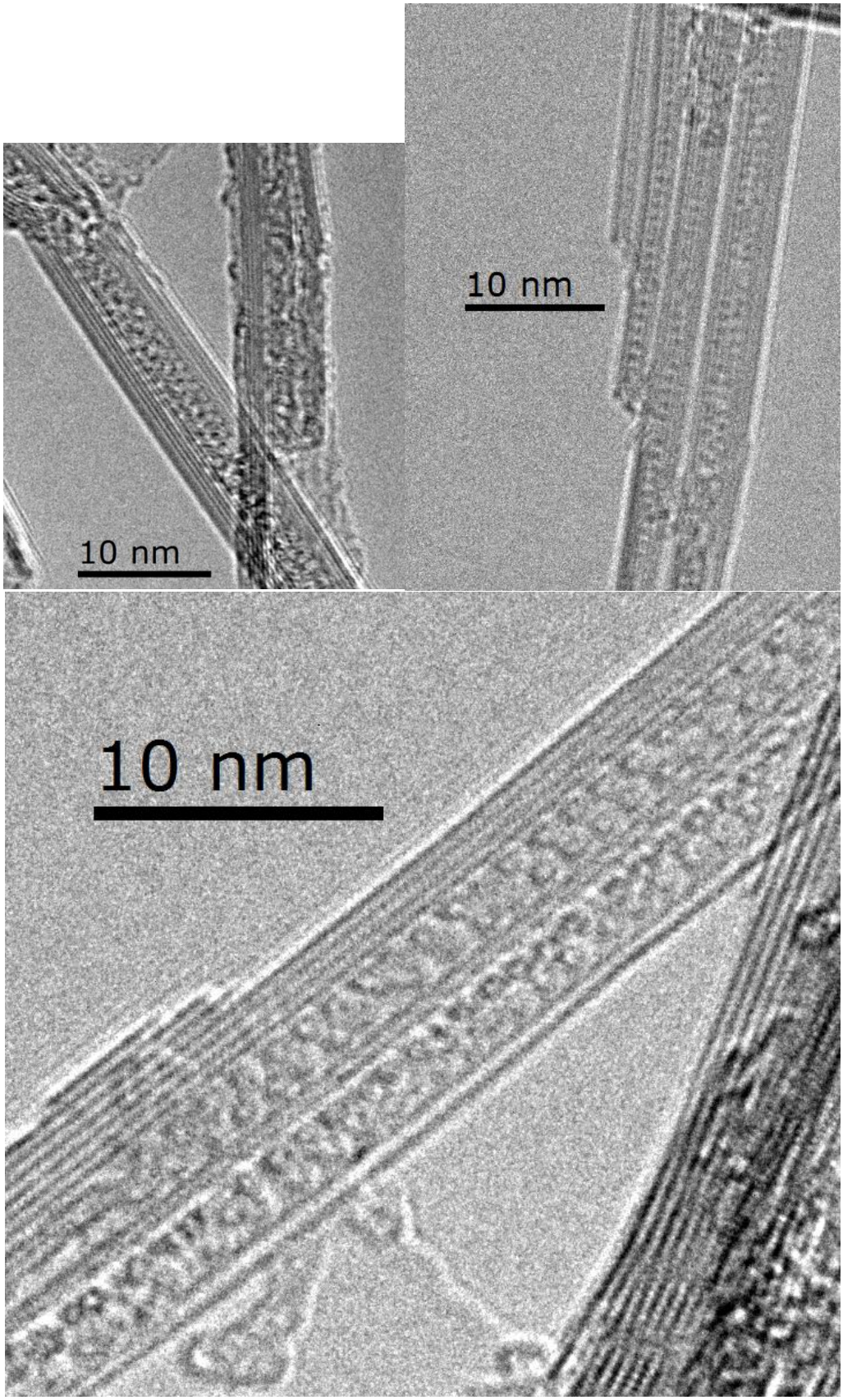

*S1. The schematic s-SNOM setup*

## 3. TEM images of C60@BNNT

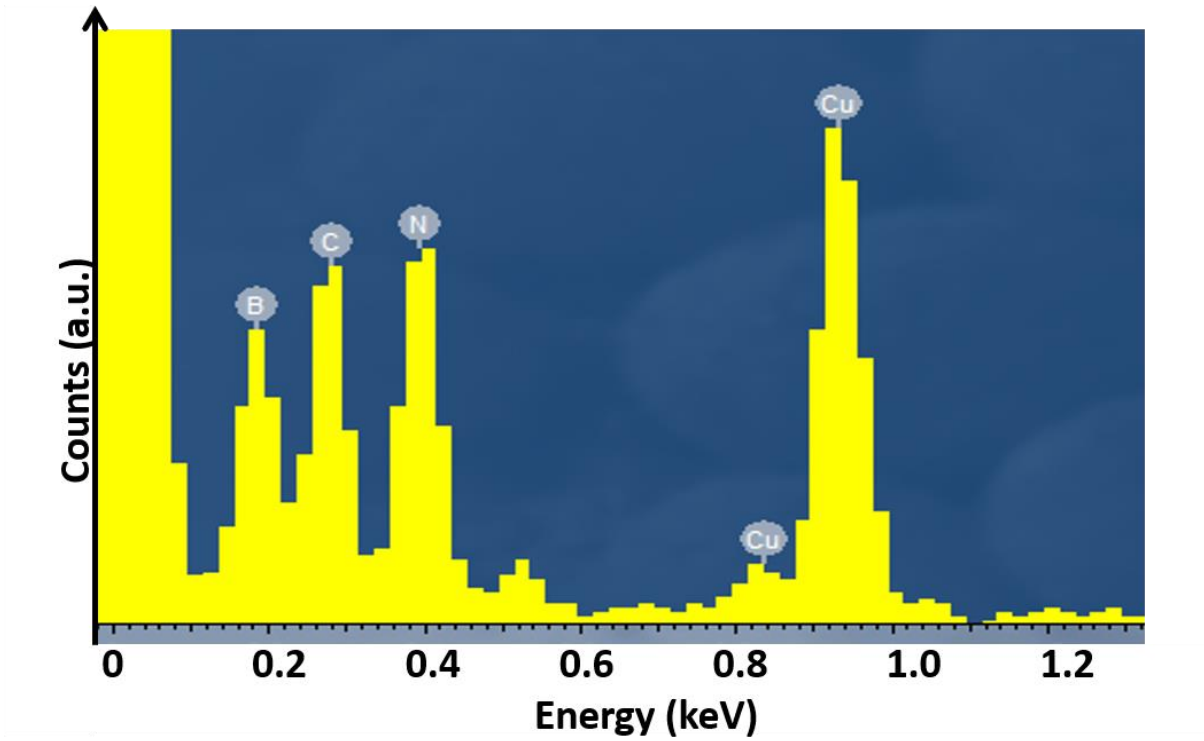
TEM images were taken by a Thermo Fisher Scientific FEI Thems 200 instrument at 100 kV at room temperature. High-resolution TEM imaging was performed using a JEOL 2100F TEM (field emission gun source, information limit <0.19 nm) at 100 kV at room temperature. EDX spectra were recorded using an Oxford Instruments 30 mm2 Si(Li) detector or an Oxford Instruments x-Max 80 SDD running on an INCA microanalysis system. Samples for TEM and EDX were prepared by casting several drops of a suspension of nanotubes onto copper-grid mounted "lacey" carbon films.




*S2. Image taken with Thermo Fisher Scientific FEI Thems 200*




*S3. Images taken with JEOL 2100F*




*S4. Energy dispersive X-ray spectrum taken in TEM for $C_{60}$@BNNT showing the presence of all major elements in the material (Cu peaks are due to the TEM sample holder)*

## 4. Approximate number of $C_{60}$ molecules

The approximate number of $C_{60}$ molecules detected in the experiments described in the article:

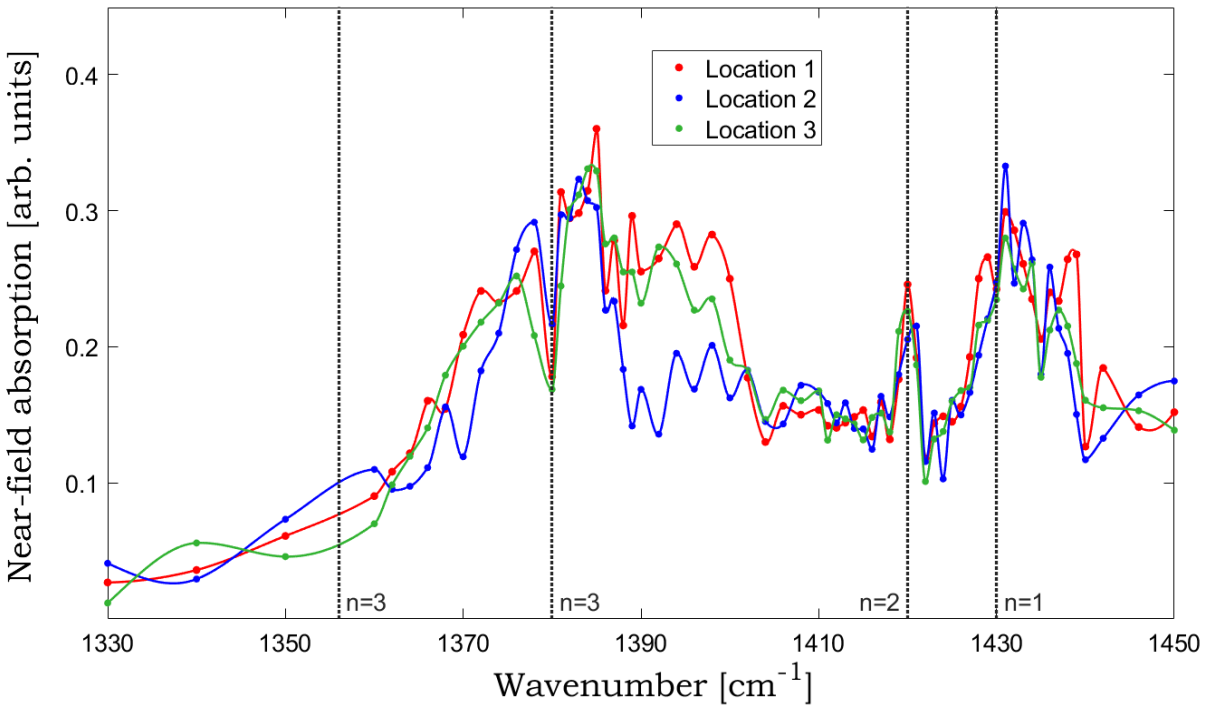
$$N_{C_{60}} = \frac{\pi r_{nanotube}^2 L_{detection}}{V_{C_{60}}} \eta = 157.38 \approx 160$$

where the nanotube radius is $r_{nanotube} = {}^{3.5\ nm}/_{2} = 1.75\ nm$, the length of the nanotube in the detection volume under the tip is taken as $L_{detection}$ = 20 nm, the volume of a $C_{60}$ molecule is approximated as a sphere of diameter 1.1 nm [1] and the filling factor η takes into account the volume ratio of stacked spheres in cylinders [2], and in this case η = 0.57.

[1] Qiao, Rui, Aaron P. Roberts, Andrew S. Mount, Stephen J. Klaine, and Pu Chun Ke. "Translocation of $C_{60}$ and its derivatives across a lipid bilayer." *Nano Letters* 7, no. 3 (2007): 614-619.

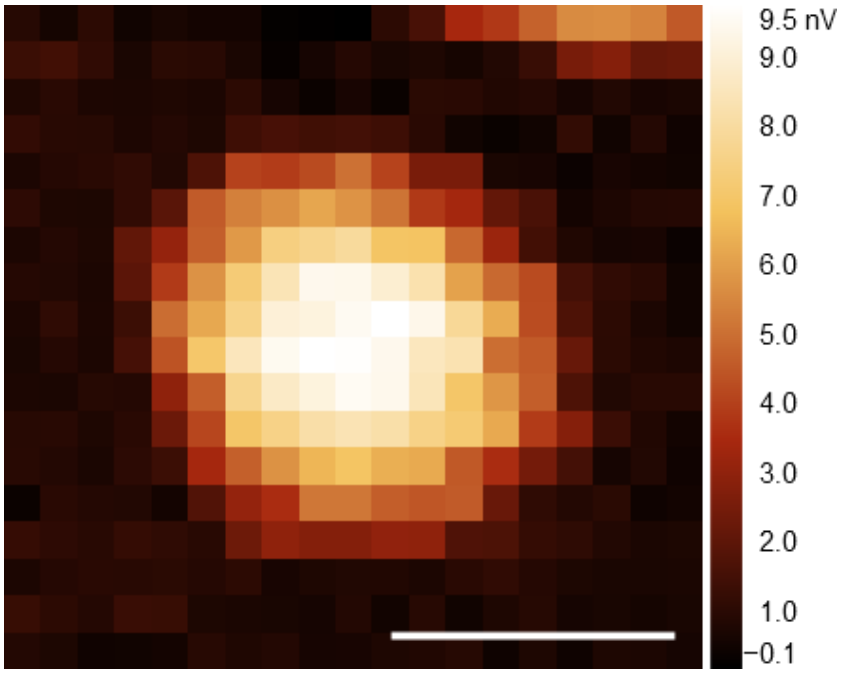
[2] Fu, Lin, William Steinhardt, Hao Zhao, Joshua ES Socolar, and Patrick Charbonneau. "Hard sphere packings within cylinders." *Soft matter* 12, no. 9 (2016): 2505-2514.

5. Spectra on different locations on the filled BNNT after photo-oligomerization




*S5. Spectra on different locations on the filled BNNT after photo-oligomerization*

6. AFM map of $C_{60}$ island used for the reference




*S6. AFM map of $C_{60}$ island. Scale bar is 50 nm*