Supporting Information

Tunable Dielectric Nanoarchitectonics in Carbon Nanotubes via DNA-Directed Pd(II) Nanoarrays

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Experimental Details

Oxidation of CNT via $KMnO_4$ treatment

A typical oxidizing treatment based on $KMnO_4$ was employed on CNT to functionalize them with carboxyl groups (-COOH).

Carbon nanotubes (1 g) were dispersed in 0.05 M $H_2SO_{4(aq)}$ (200 mL) by sonicating for 30 minutes, followed by heating at 150 °C. Subsequently, a $KMnO_4$ solution (2 g solved in 200 mL of 0.05 M $H_2SO_{4(aq)}$) was added dropwise, and the final mixture was refluxed at 150 °C for 5 hours. After reaching room temperature, 37 % HCl (10 mL) was added to dissolve the MnO_2 formed as a byproduct. The solid was vacuum-filtered and washed with ultrapure water using a Soxhlet assembly, dried in an oven at 100 °C, resulting in the CNT-COOH sample.

Figures

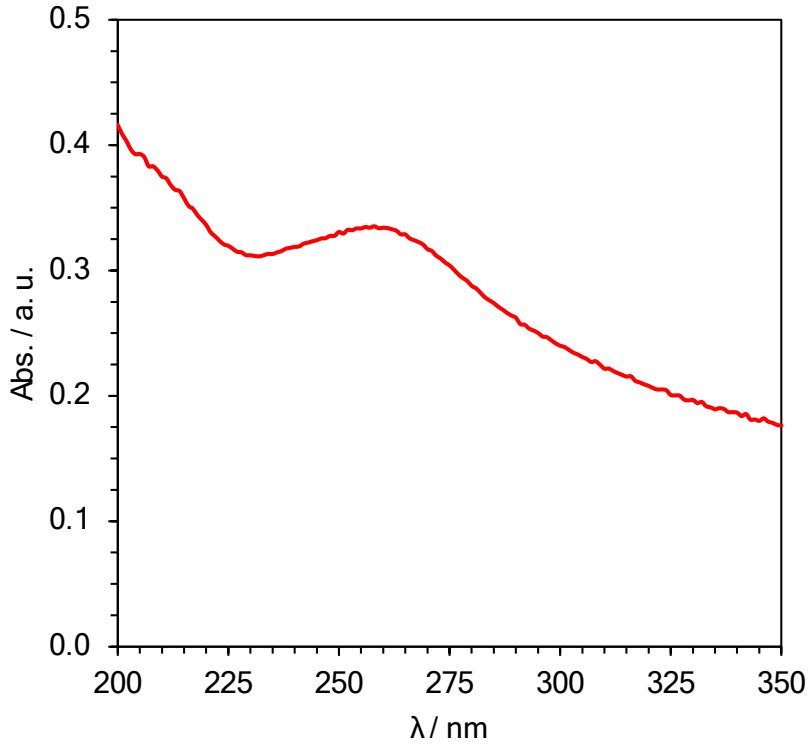


Figure S1 UV-vis spectrum of the solubilized **CNT-dA$_{15}$** dispersion showing the characteristic absorption band of **dA$_{15}$** (ca. 0.8 µM.) The concentration of **dA$_{15}$** (≈ 0.8 µM) as estimated from the difference in absorbance between 300 nm and 260 nm (ΔAbs = 0.11), since the CNT exhibits inherent absorption in the 200–350 nm region. The extinction coefficient used for adenine at 260 nm was 9.4 $mM^{-1}{\cdot}cm^{-1}$. Preparation details: **CNT-dA$_{15}$** solid immersed in 1 mL of 1 mM MOPS buffer (pH = 6.8), sonicated (30 s), stirred (2 h, 50 °C), centrifuged (14000 rpm, 10 min), and supernatant studied via UV-vis spectroscopy.

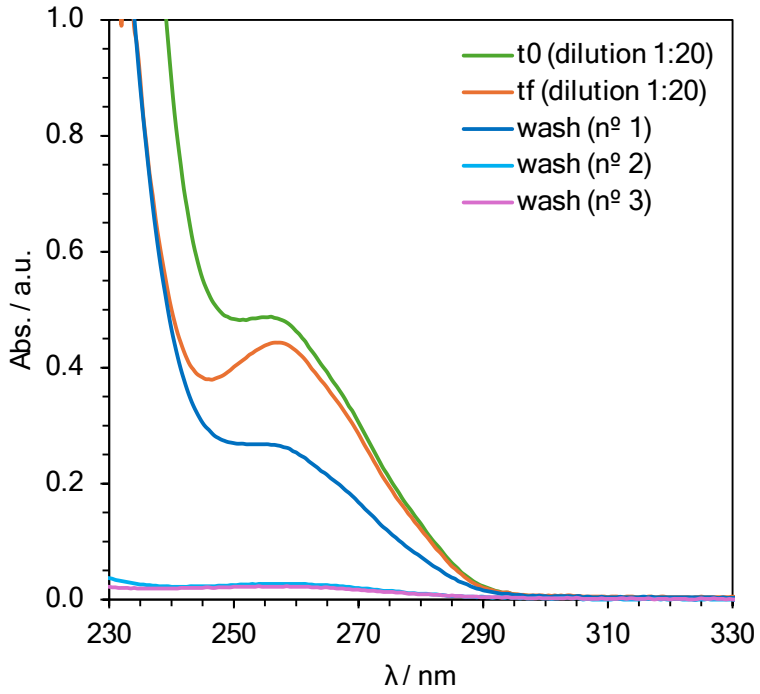


Figure S2 UV-vis spectra of CNT-COOH and **dA$_{15}$** reaction medium at initial and final times, showing the characteristic absorption band of **dA$_{15}$**. UV-vis spectra of the supernatants collected after each wash are shown. Preparation: (1) CNT-COOH (55 µg) was dispersed in 25 mM MOPS buffer (189 µL, pH 6.5) by sonication, then activated with EDC (0.4 M, 11.70 mg) and NHS (0.027 M, 0.58 mg) at an NHS:EDC molar ratio of 1:15 and left to react for 15 min. (2) A 100 µM **dA$_{15}$** solution in 25 mM MOPS buffer (311 µL, pH 6.5) was added to the activated CNT-COOH dispersion and undisturbed at 4 °C overnight without agitation. The mixture was then centrifuged (14000 rpm, 10 min), and the pellet was washed repeatedly with MOPS buffer until no **dA$_{15}$** was detected in the supernatant by UV-vis spectroscopy.

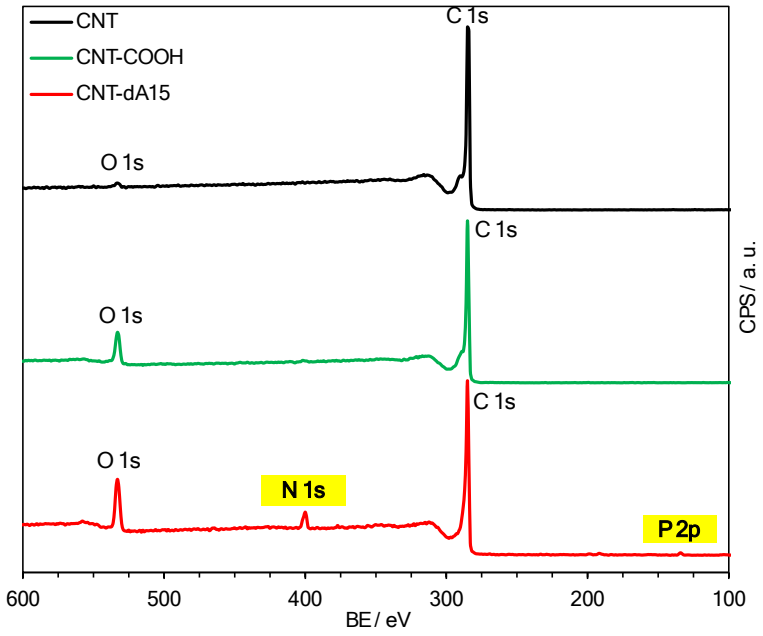


Figure S3 XPS wide spectra of the CNT, **CNT-COOH** and **CNT-dA$_{15}$** samples.

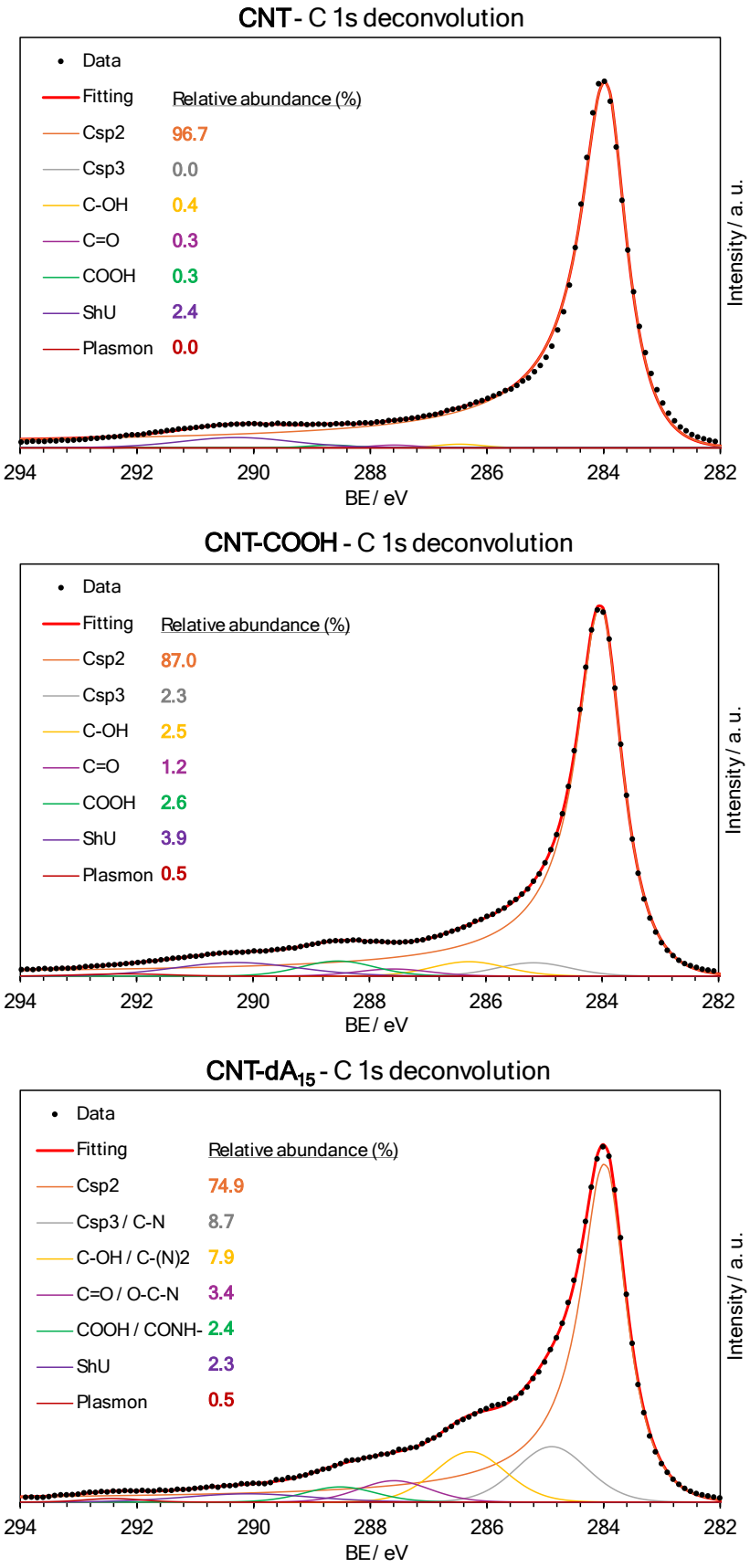


Figure S4 Deconvolution of XPS high-resolution C 1s spectra of the CNT, **CNT-COOH** and **CNT-dA$_{15}$** samples.

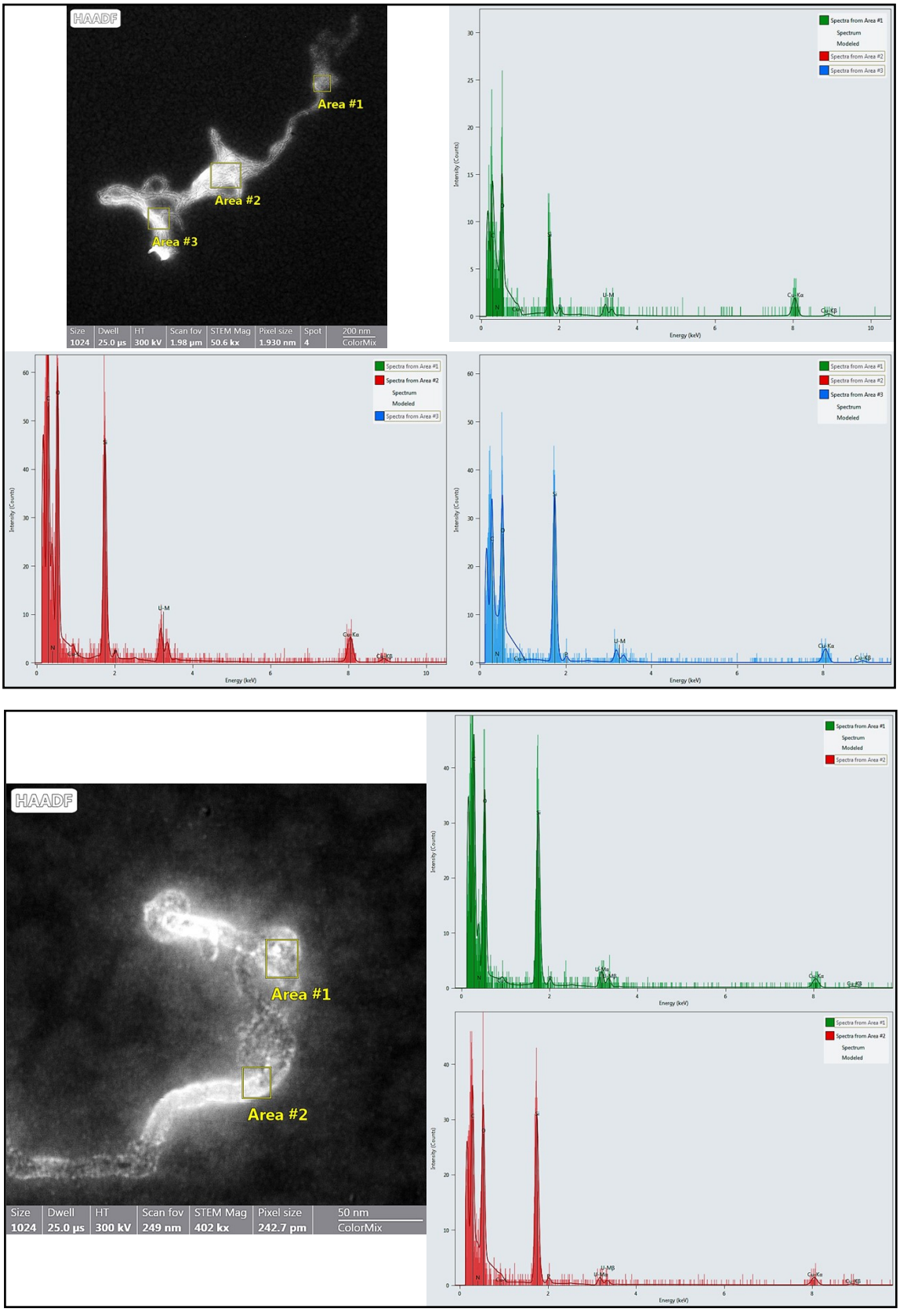


Figure S5 Two different HRTEM images and their corresponding EDS spectra of the **CNT-dA$_{15}$** hybrid. Note the P peaks at 2 keV in EDS spectra.

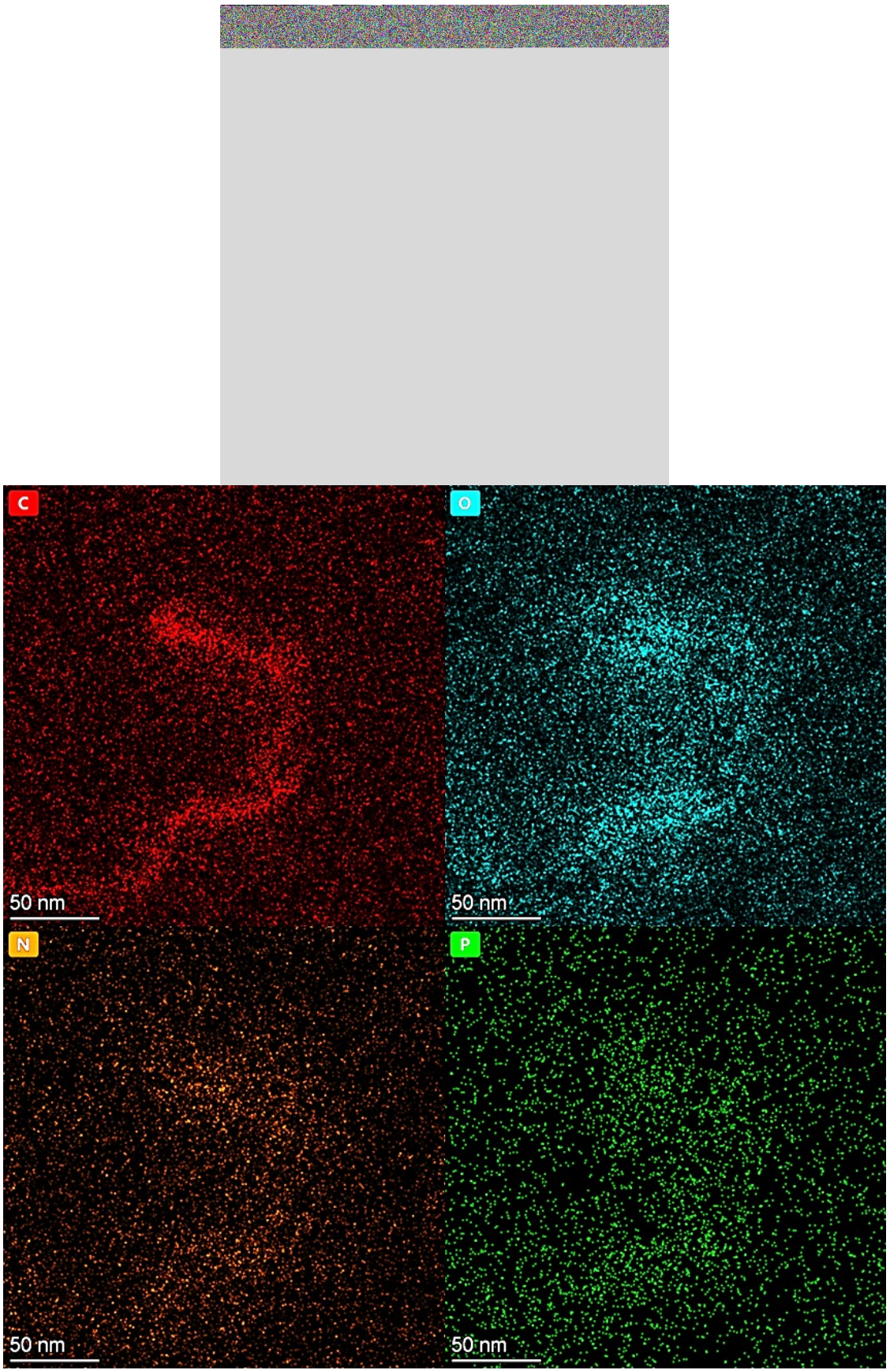


Figure S6 HRTEM image and EDS elemental distribution maps of C, O, N and P for the **CNT-dA$_{15}$** hybrid.

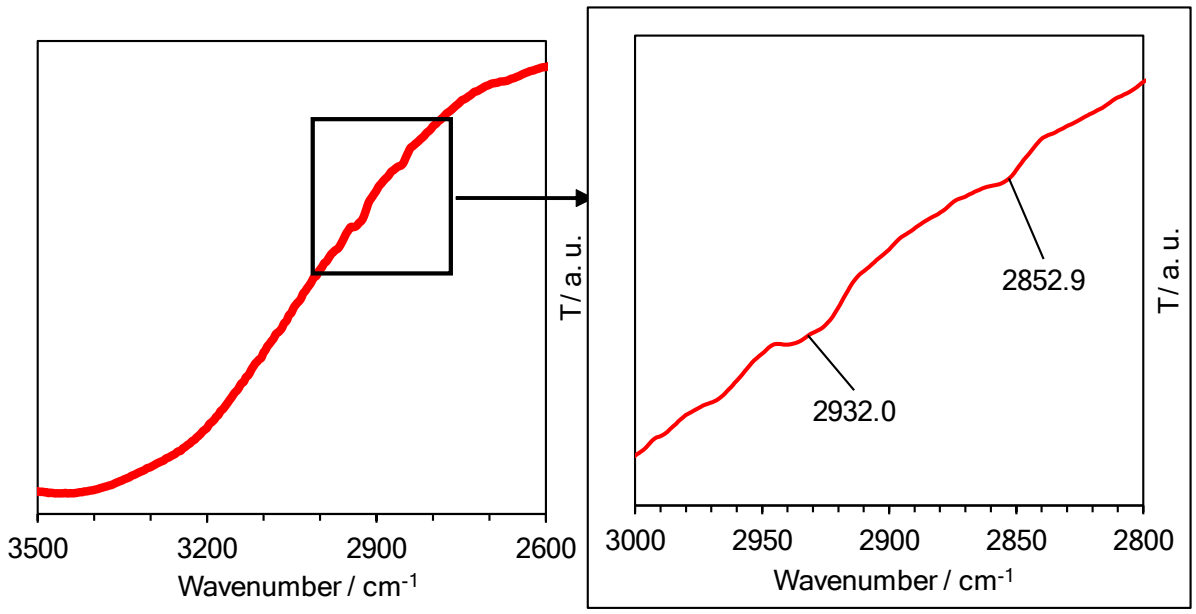


Figure S7 FTIR spectrum of the **CNT-dA$_{15}$** hybrid (high wavenumbers region). Measured in pressed KBr tablets with 0.01 wt.% **CNT-dA$_{15}$** content.

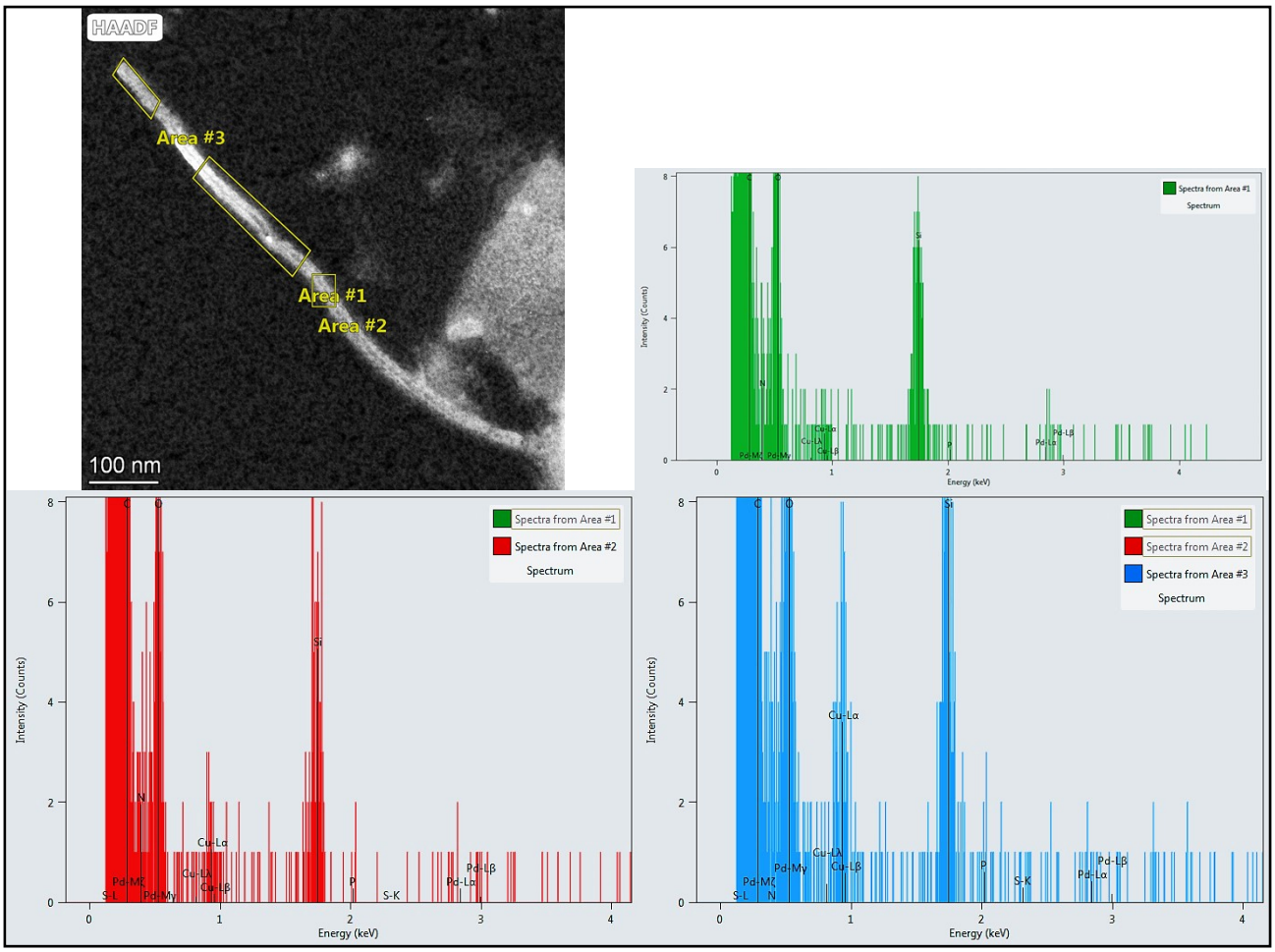


Figure S8 HRTEM image and the corresponding EDS spectra of the **CNT-dA$_{15}$-1Pd** hybrid.

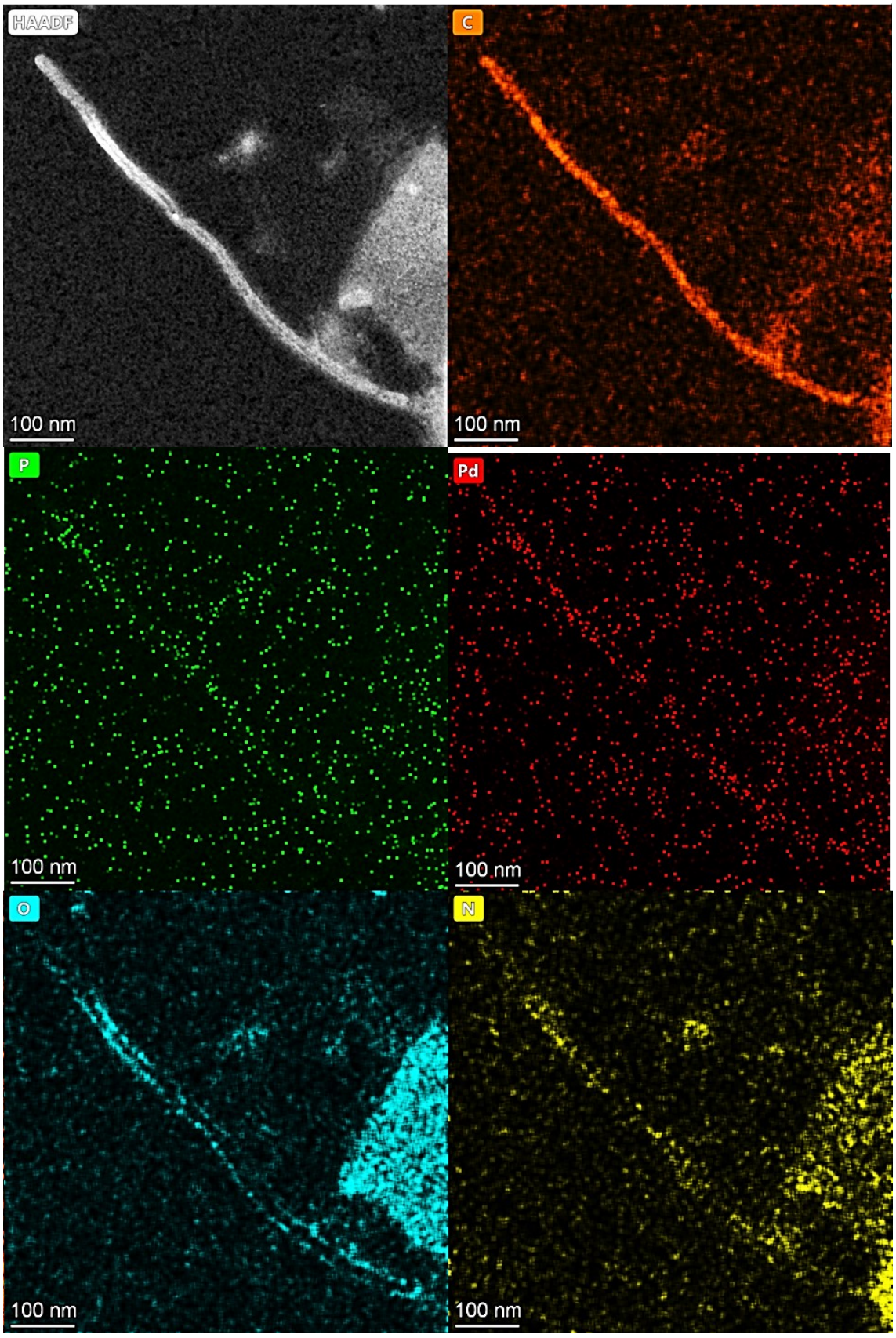


Figure S9 HRTEM image and EDS elemental distribution maps of C, O, H, N, P, and Pd for the **CNT-dA$_{15}$-1Pd** hybrid.

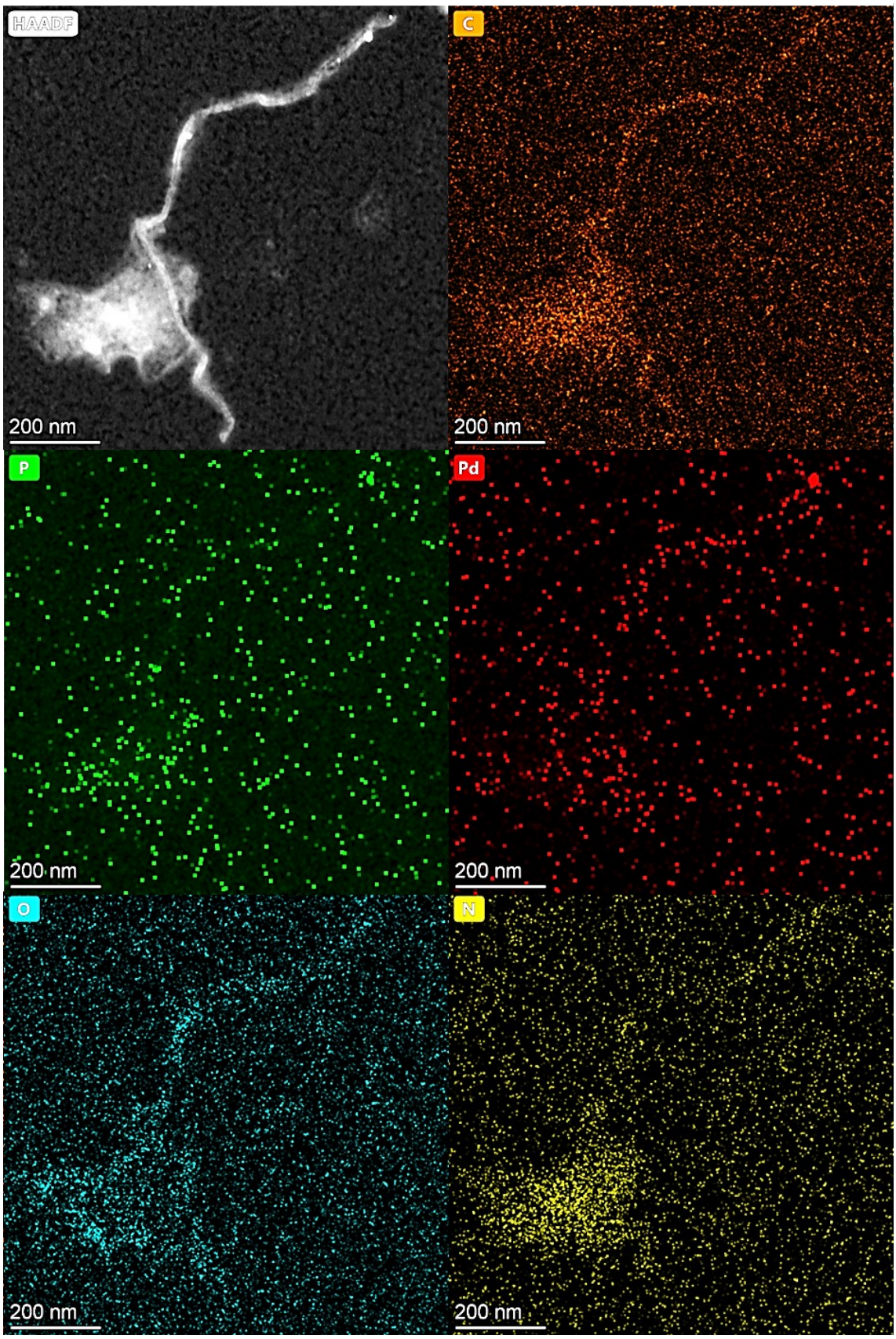


Figure S10 HRTEM image and EDS elemental distribution maps of C, O, N, P, and Pd for the **CNT-dA$_{15}$-1Pd** hybrid.

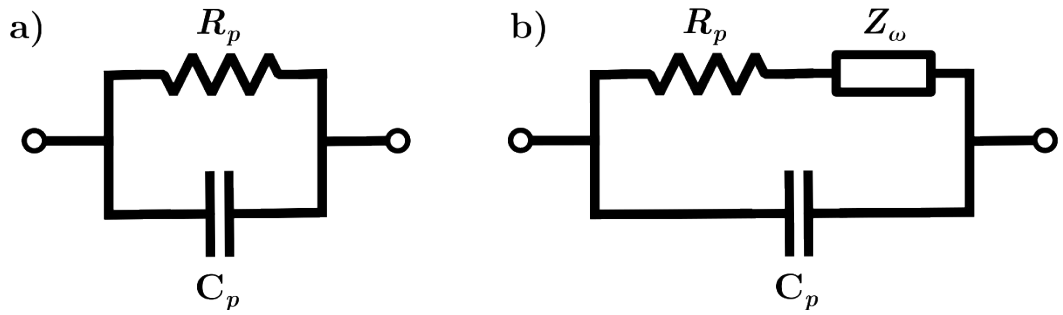
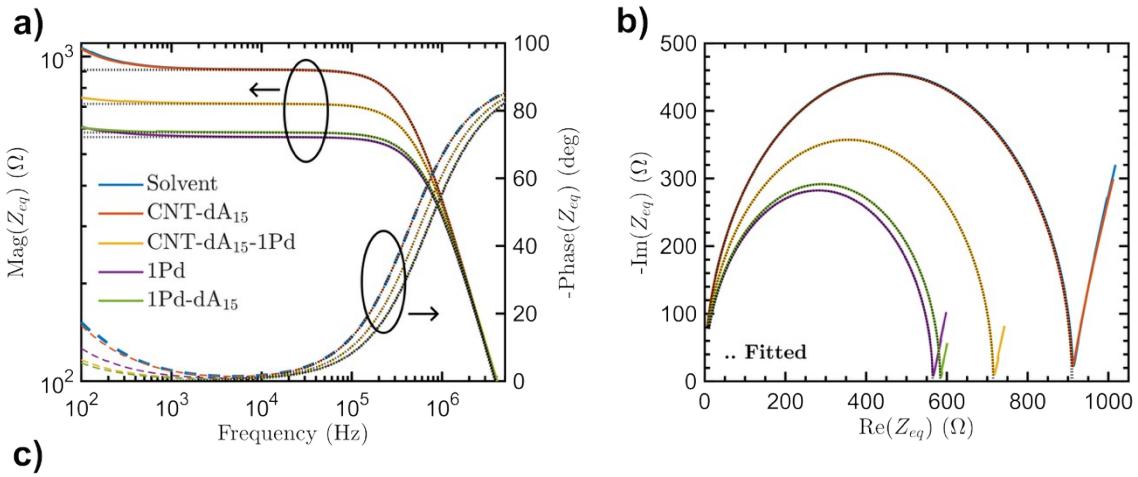


Figure S11 a) Parallel capacitance-resistance circuit corresponding to the equivalent electrical model of the SUT. b) Parallel capacitance-resistance circuit including Warburg impedance (Zω).



	Solvent	CNT-dA$_{15}$	CNT-dA$_{15}$-1Pd	1Pd	1Pd-dA$_{15}$
Rp (Ω)	910.7	908.7	714.3	564.8	583.1
Cp (pF)	406.1	406.2	400.8	406.6	401.3

Figure S12 a) Real and imaginary components of the measured impedances in the frequency range between 100 Hz and 5 MHz. Dotted lines represent the RpCp model fits. b) Nyquist plot from 100 Hz to 5 MHz. Dotted lines represent the R_pC_p model fits. Note that the solvent and the CNT-dA$_{15}$ curves are almost fully overlapping in both figures. c) Fitted parameters for the R_pC_p model for the studied solutions.

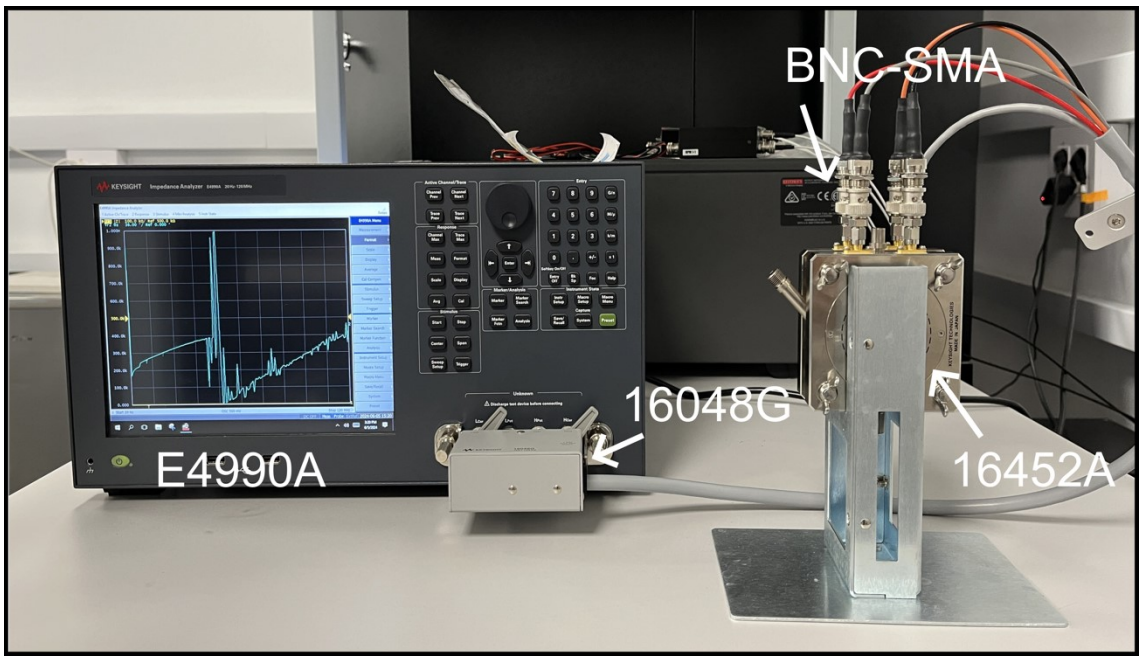


Figure S13 Illustration of the impedance measurement setup, comprising the impedance analyzer E4990A, the 16048G 1-meter 4-probe extension, BNC-SMA adapters, and the 16452A liquid measurement fixture.

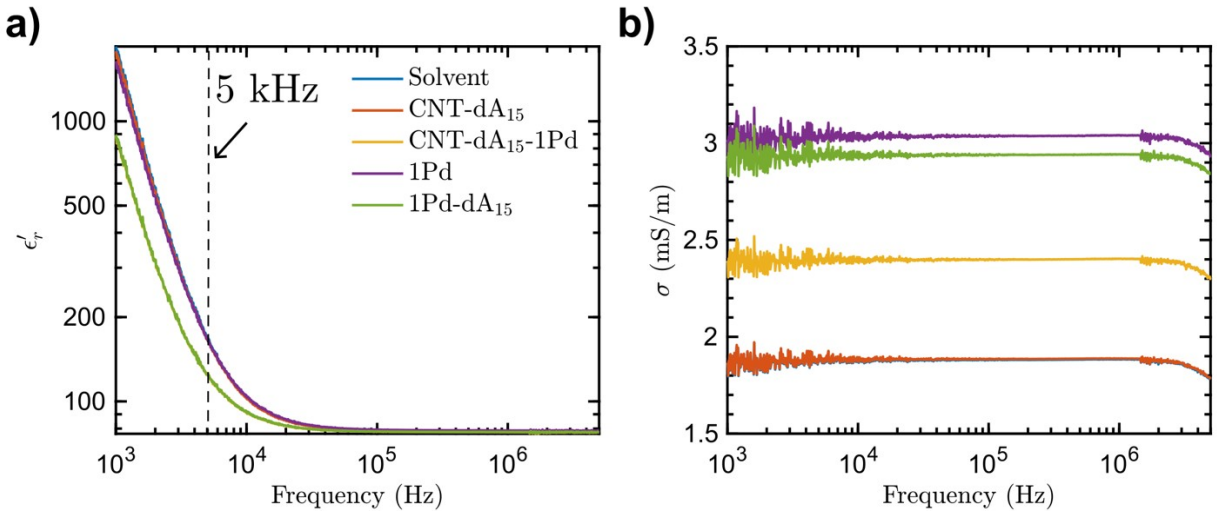


Figure S14 a) Relative dielectric constant (ϵ'r) and, b) conductivity in the frequency range 1 kHz - 5 MHz.

References

(1) Hiura, H.; Ebbesen, T. W.; Tanigaki, K. Opening and purification of carbon nanotubes in high yields. *Advanced Materials* **1995**, *7* (3), 275-276. DOI: 10.1002/adma.19950070304.