

Supporting information

A high-performance hybrid bismuth/carbon nanotube-based contrast agent for X-ray CT imaging

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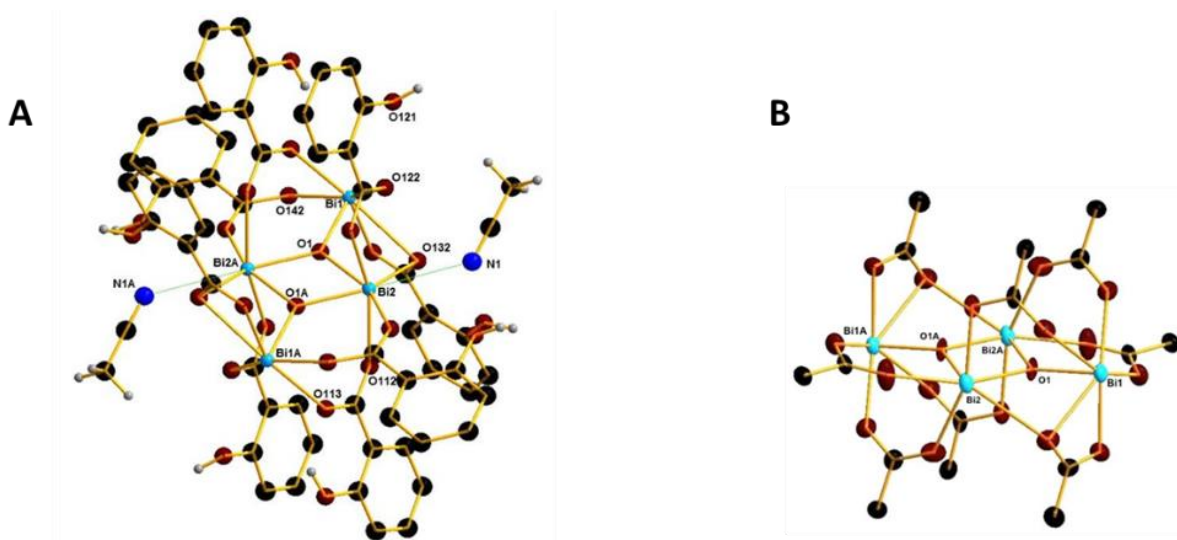


Figure S1: (A) Crystal structure of $[\text{Bi}_4(\mu_3\text{-O})_2(\text{HO-2-C}_6\text{H}_4\text{CO}_2)_8] \cdot 2\text{MeCN}$ (MW: 2046.91) and (B) the structure of the Bi_4 core. Reproduced from Ref ¹ with permission from The Royal Society of Chemistry.

Cutting of the SWCNTs ($> 1 \mu\text{m}$, Carbon Solutions, Inc.) was performed as described elsewhere.² The resulted ultra-short carbon nanotubes (20-80 nm long; US-tubes) were characterized using atomic force microscopy (AFM) to confirm the size of the US-tubes. AFM samples were prepared by suspending a small amount of US-tubes in EtOH followed by bath sonication for 10 min. Several drops were then placed on a mica sheet while spinning at high speed. Figure S2 shows the AFM image of the US-tubes and the analysis performed.

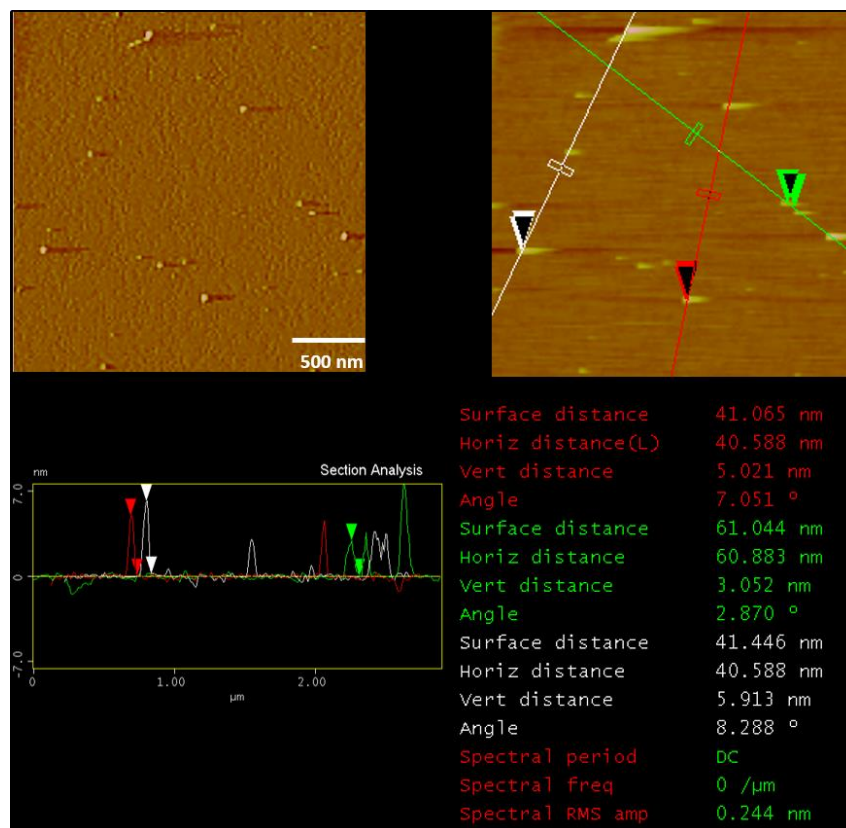


Figure S2: AMF image of the US-tubes (left) and image of the height-mode (right) with section analysis (three sections; white, red and green).

US-tubes, as well as the full-length SWCNT material, were analyzed by Raman spectroscopy. In Figure S3, (*) is attributed to the vibrational modes associate with the $\nu(-C-H)$ (sp^3 hybridization, which are present for the US-tubes but not in the full-length SWCNTs). The D4 small shoulder has been previously attributed to sp^2 - sp^3 bonds.^{3,4}

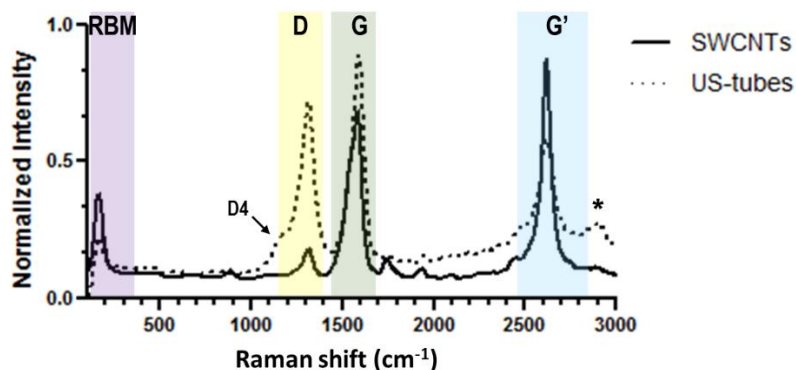


Figure S3: Raman spectra of the full-length SWCNTs and US-tubes.

To determine the quantity of Bi^{3+} present in the $\text{Bi}_4\text{C}@\text{US}$ -tube samples, inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used. For this technique, the material has to be first digested with a strong acid and an aqueous solution prepared. As a validation step, the recovery of Bi^{3+} was first obtained by placing 100 μL of a 1000 ppm Bi^{3+} plasma standard solution (Specpure[®]) in cantillation vials, followed by the addition of 1 mL of either 70% HNO_3 , 26% HClO_3 , or a combination of both acids. As shown in Figure S4, the best recovery % was obtained when using HClO_3 alone or when HNO_3 and HClO_3 were used in combination. Since better reproducibility was obtained when the combination of HNO_3 and HClO_3 was used, such acidic condition was used for all experiments described here.

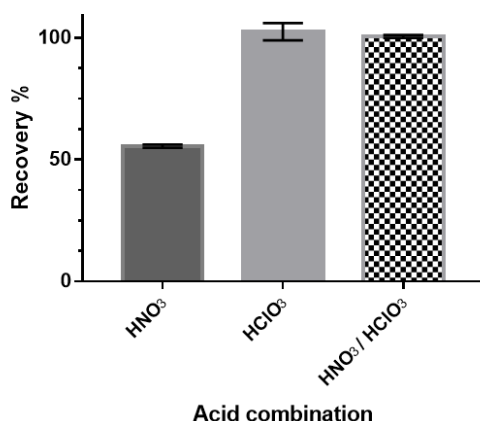


Figure S4: Percent of recovery for the digestion of a Bi^{3+} -ion standard solution (1000 ppm, Specpure[®]) with different acids. Analysis performed using ICP-OES. Values reported as mean \pm SEM.

NMR spectra of the Bi_4C cluster were obtained (400 MHz, d_6 -DMSO) after (1) dissolving the cluster in THF and (2) sonicating the cluster in THF for 1 h. The spectrum after sonication in THF was unchanged with the same observed signals and relative intensities as before sonication, with the exception of the loss of the methyl signal attribute to acetonitrile.

Table S1: ^1H NMR data for the $\text{Bi}(\text{III})$ oxo-salicylate cluster (Bi_4C) before and after sonication in THF.

Bi_4C dissolve in THF δ (ppm)	Bi_4C sonicated in THF δ (ppm)
11.9 (s, 1H, PhOH),	11.9 (s, 1H, PhOH),
7.67 (s, 1H, o-H),	7.67 (s, 1H, o-H),
7.31 (s, 1H, p-H),	7.31 (s, 1H, p-H),
6.80 (s, 2H, m-H)	6.80 (s, 2H, m-H)
2.07 (s, 1H, CH_3)	2.45 (s, 1H, DMSO)
2.45 (s, 1H, DMSO)	1.74 (m, 2H, THF)
1.74 (m, 2H, THF)	

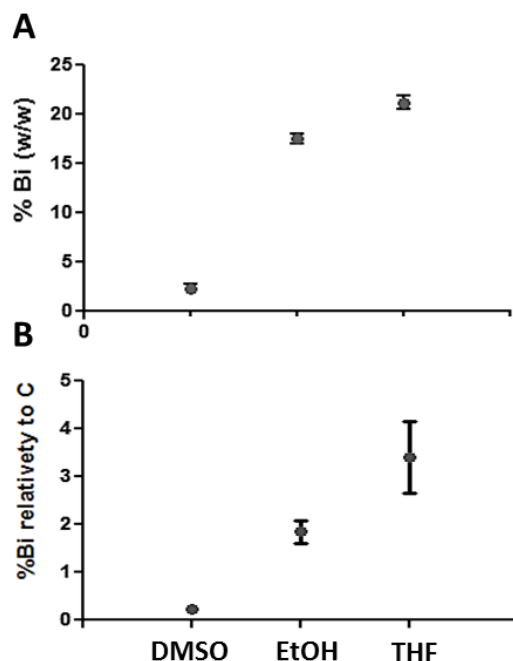


Figure S5: The concentration of Bi^{3+} in the $\text{Bi}_4\text{C}@$ US-tubes as obtained by (A) ICP-OES, and (B) XPS.

References

- (1) Boyd, T. D.; Kumar, I.; Wagner, E. E.; Whitmire, K. H. Synthesis and Structural Studies of the Simplest bismuth(III) Oxo-Salicylate Complex: $[\text{Bi}_4(\mu_3\text{-O})_2(\text{HO-2-C}_6\text{H}_4\text{CO}_2)_8] \cdot 2\text{Solv}$ (Solv = MeCN or MeNO₂). *Chem. Commun.* **2014**, 50 (27), 3556–3559.
- (2) Gu, Z.; Peng, H.; Hauge, R. H.; Smalley, R. E.; Margrave, J. L. Cutting Single-Wall Carbon Nanotubes through Fluorination. *Nano Lett.* **2002**, 2 (9), 1009–1013.
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