Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Supporting Information to:

The Gadonanotubes: Structural Origin of their High-Performance MRI Contrast Agent Behavior

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Line Shape Analyses of the Gd L_3 edge

The edge structure (-20 eV to 20 eV) is deconvoluted by an arctangent function for the edge step (continuum) and a Lorentzian function for the whiteline (see Fig. S1). Not shown is the result for $GdCl_3 \cdot 6H_2O$ whose whiteline is smaller by 12% than and has a peak characteristic identical to, that of 10-mM $GdCl_3$ The whiteline of 10-mM $GdCl_3$ is described best of Lorentzian, a transition to the bound state in nature due likely to the ionic nature of the Gd-O bonds in the solution. Using it as a bench mark, the Lorentzian characteristic diminishes for the others in the order of dry-GNTs, GdAc, $Gd(OH)_3$, aged-GNT solution, and as-prepared GNT solution. For dry-GNTs, its whiteline closely resemble that of 10-mM $GdCl_3$ in terms of the peak height, the edge position, and the peak shape, but with the high energy side of the whiteline extending somewhat more into the continuum. In contrast, the peak shape of 31.2-μM GNT solution is skewed with the whiteline leaning towards low energies. The peak width is narrower as well (by 0.3 eV), suggesting a long lifetime of the final state. The others are skewed in a similar way, but to a less extent, and their peak heights are lower as well (by 11-to-21 %). The peak width of aged 31.2-μM GNT solution is wider by ~0.6 eV.

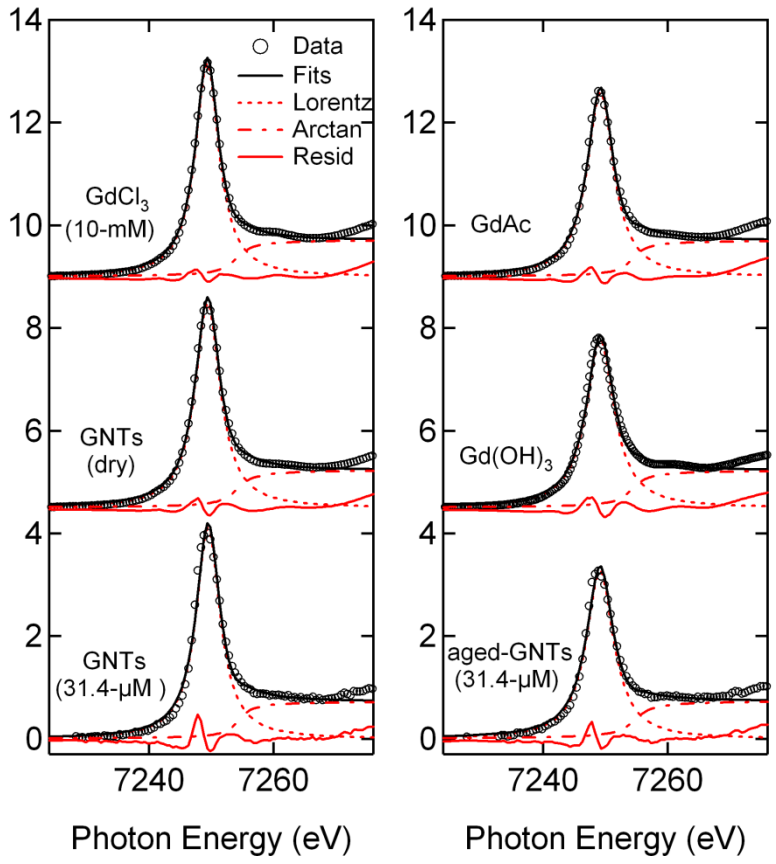


Figure S1

First Coordination Shell Fitting Results

The results from the EXAFS data fittings are presented in R-space in Fig. S2. They are the equivalents of those presented in k-space in Fig. 5 in the main text. As is seen, unlike 10-mM $GdCl_3$ whose EXAFS is reproduced nicely by assuming a single Gd-O distance, the single Gd-O bond distance does not reproduce well the EXAFS of dry-GNTs (curve a). The fit is improved when a third cumulant is included (curve b). However, the best fit is shown by the curve c where two Gd-O bond distances are assumed. Their separation is as large as 0.17 Å (see the discussion in the main text on Table 1). The lower-R shoulder is also well reproduced.

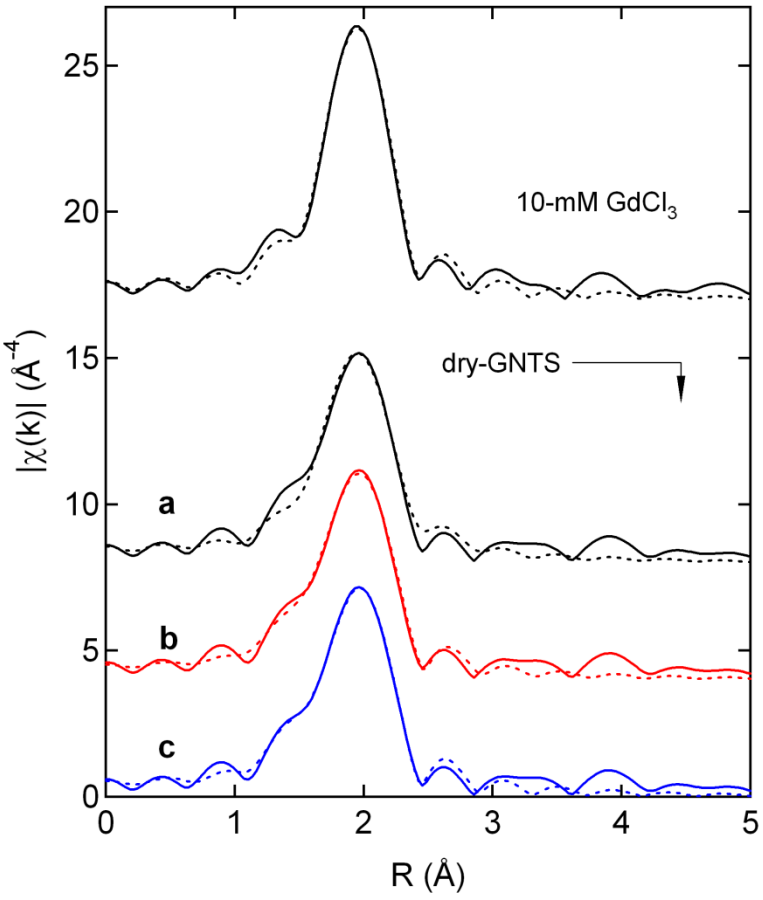


Figure S2

X-ray Absorption Measurements at 20 K

In order to remove possible thermal contribution to the EXAFS and thus the peak shapes, X-ray absorption measurements were carried out on the dry-GNTs sample at 20 K using a displex system (Advanced Research Systems Inc). The EXAFS data are compared to the EXAFS data measured at room temperature. Despite of noise, no enhancements of the EXAFS amplidues are seen by lowering the temperature, which occurs typically at low temperature.

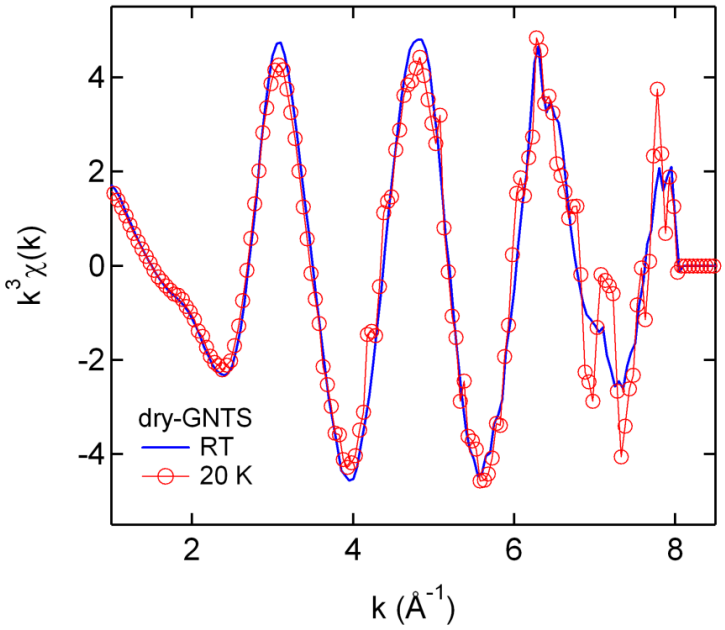
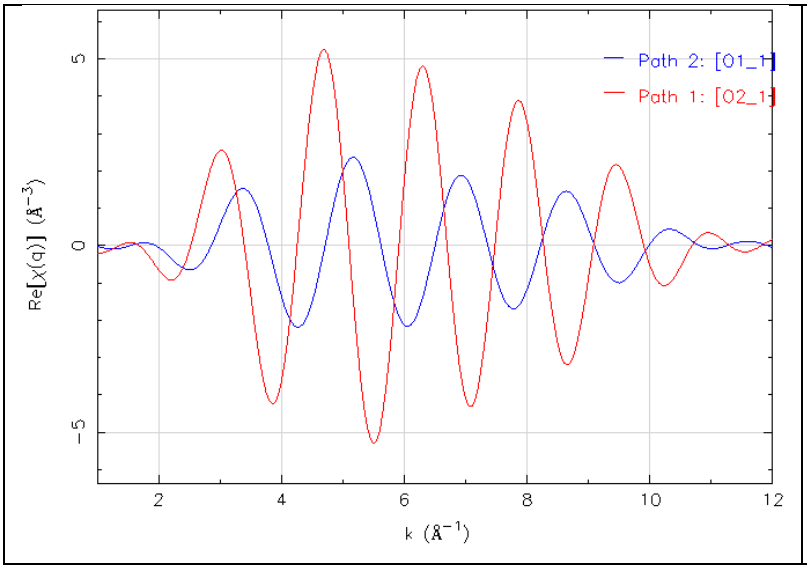


Figure S3



The contributions of two Gd-O bond distances obtained by the EXAFS data fitting shown by the curve c in Fig. 5 of the main text or shown by the curve c in R space in Fig. S2 in this document. The numbers are given in the row c in Table 1. This is to show the differences in their phases that may largely cancel the enhancement of the EXAFS amplitudes by lowering the temperature.

Figure S4

Gd L1 edge XANES

Figure S5 compares the first derivatives of the Gd L_1 edge XANES spectra measured on 10-mM $GdCl_3$, dry-GNTs, and GdAc, respectively. As mentioned in the main text, the Gd L_1 edge is due to the transition of the *2s* electrons to the empty states of the *p* character. The excited *2s* electrons may probe as well part of the empty *d* states that mixes with the ligand *2p* states under right conditions, meaning the available empty *d* states and suitable local geometries, which are found in many transition metal oxides. It is interesting that the XANES of dry-GNTs compares more favorably to that of GdAc in terms of lineshapes and peak positions, suggesting a similar local environment around Gd^{3+} ions. This may be due to the fact that a discrete Gd-O bond distribution exists in these two samples.

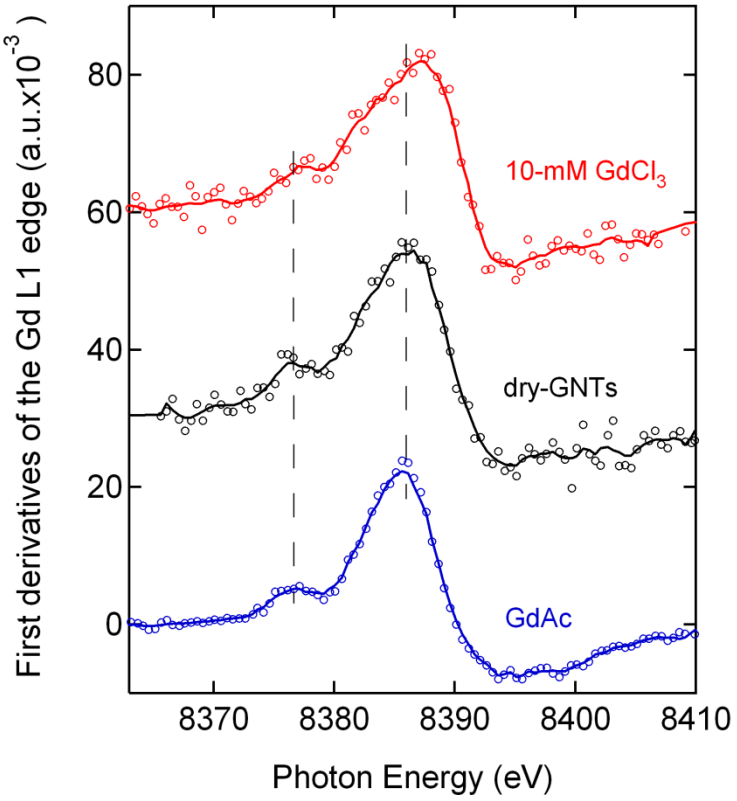


Figure S5.

Analyses of the structure beyond the first coordination shell

Figure S6 shows the Fourier transforms of the EXAFS data for GdAc and GNT. Also shown are the fitting results (dash lines) of the data up to 4.5 Å. This is to detect possible Gd-Gd interactions in the GNTs. For GdAc, a full-path fit is presented. It is seen that one Gd-Gd interaction at 4.20 Å only contributes about one third of the apparent peak near 4 Å and that the rest of the peak is due mostly to the multi-scattering (MS) paths. Clearly, there are no direct,

referable models for the local structure around Gd^{3+} in a carbon nanotube, but GdAc from which the phases and amplitudes of all possible Gd-C, Gd-O, and Gd-Gd interactions can be produced. Fitting of the GNT data using the paths generated from GdAc produces a reasonably good fit, except for in the region from 2.5 to 3.5 Å where the MS's dominate. This should imply the differences in their structural geometries. Assuming that the MS's are at minimum in the GNT given the disorder and confined geometry, use of the single scattering paths up to 4.5 Å fits the GNT data reasonably well. Two fitting results presented in Fig. S6 for the GNT were so obtained. Fit 1 was obtained with the Gd-O interactions at 2.81Å, 3.54 Å, and 3.72 Å, respectively, and a Gd-Gd interaction existing at 4.13 Å with CN = 1.6 and σ^2 = 0.007 $Å^2$, in addition to the first coordination shell. Fit 2 was obtained with the Gd-C interactions near 2.81Å, 3.54 Å, and 3.72 Å and the Gd-Gd interaction at 4.14 Å. For the latter, CN = 2.7 and σ^2 = 0.012 $Å^2$. Clearly, correlation between CN and σ^2 is high (CN/σ^2 = *Constant*). However, due likely to the characteristics of the backscatters that contribute the peak around 4.0 Å, no convergences were achieved if the Gd-Gd interaction was replaced. Therefore, a Gd-Gd interaction is implied.

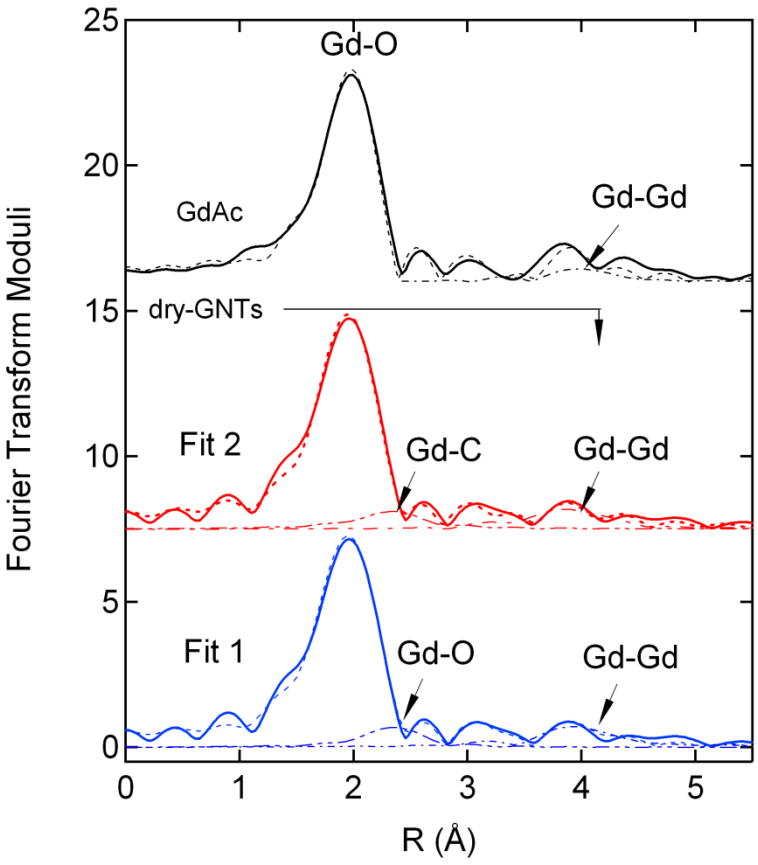


Figure S6