Supporting Information Gadolinium-doped carbon nanoparticles: coordination, spectroscopic characterization and magnetic resonance relaxivity

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Figure S1. TEM images of samples Gd_4 (a) and Gd_8 (b). Insert - particle size distribution for sample Gd_4.

The average size of CNPs in Gd_0 sample is estimated to be about 16 nm. With increasing Gdconcentration the particle size decreases to 4 and 3 nm for samples Gd_4 and Gd_8, respectively. This fact can be explained by the particle growth limitation due to the coordination of larger amount of Gd ions at the NP' surfaces.



Figure S2. Percentage of gadolinium loss during dialysis. Gadolinium was quantified by spectrophotometric analysis of dialysis solutions.

The percentage of gadolinium washed out during dialysis was determined by spectrophotometric method of analysis. For all the solutions studied, gadolinium leaching during dialysis reaches saturation within 150–200 minutes. That indicates both the completion of the dialysis process and the fact that the remaining gadolinium is chemically bound to carbon nanoparticles by strong coordination bonds.

The spectrophotometric data on Gd concentration correlates with results of the XRF analysis of dried Gd-CNPs (see Table S1).

Some discrepancies between the XRF results and spectrophotometric data are observed for the samples prepared at lower Gd concentrations. This fact can be explained by the limited sensitivity of the latter method.

Table S1. XRF data on Gd-concentration in Gd-CNPs prepared with different precursor concentrations.

Concentration of Gd precursor, mg/ml	0.2	2	4	8
Concentration of Gd in dialyzed Gd- CNPs solutions, mg/ml	0.8±0.1	2.1 ± 0.2	5.5 ± 0.8	8.0 ± 1.0



Figure S3. Zeta potential for Gd-CNPs upon increasing concentration of Gd precursor (GdCl₃:6H₂O).

Figure S3 shows that both pure CNPs and Gd_02 samples have negative surface charges, which can be associated with the presence of carboxyl groups on the CNPs' surfaces. The absolute values of the zeta potential of Gd-CNPs decrease gradually upon increasing Gd concentration in precursors. This fact indicates that Gd impurities approach the limit of coordinating ability on the CNPs' surface, since almost all positively charged Gd ions are coordinated by negatively charged oxygen and nitrogen groups. Despite the near-zero surface potential of Gd-CNPs with large Gd concentrations their colloidal solutions did not lose stability and did not precipitate for several days.



Figure S4. IR absorption bands of Gd-CNPs and their fitting with Gaussian components in the following regions: (a)1320-1500 cm⁻¹, and (b) 1500-1770 cm⁻¹.

To calculate the obtained fractions of Gaussian components, we integrated the obtained peaks, the total area of the spectrum of the selected IR absorption band, and then divided the peak area by the total area of the spectrum. This operation was performed for samples of each of the presented concentrations and we obtained the dependence of decreasing contribution to the IR absorption band of carboxyl groups with increasing concentration of gadolinium in the obtained particles.

	Peak	E _b ,	FWHM,	1 %	
	Peak		eV	1, 70	
C_1s	C-C/C=C	285.2	1.9	66.3	
	C-N/C=N	286.9	1.1	5.6	
	С-0/С=0/0=С-ОН	288.7	2.1	28.1	
N_1s	Atomic N	398.2	1.5	5.1	
	Pyridine N	400	1.9	88.9	
	Graphitized	401.6	1.5	6.0	
0_1s	O=C-OH	530.4	1.8	5.1	
	C=0	531.7	1.6	56.9	
	C-OH	532.4	2.2	38.0	

Table S2. Summary table of the XPS spectra of Gd_8 sample. The position of the peaks, their width at half-height, and the relative contribution of area to each of the analyzed atomic spectra.

Based on the data of Table S2, namely the contribution of Gaussian components in the coordination environment of carbon, the following chemical formula of the particle of composition Gd_8 - $CO_{0,2}N_{0,04}$ was obtained. The calculation was carried out as follows: each functional group contains a certain number of nitrogen, oxygen or carbon atoms. Thus, the C=C/C-C group, corresponding to the peak of the same name, contains 1.5 carbon atoms (C=C - 2, C-C - 1, since the hybridization ratio is uncertain, we consider it in the ratio 1:1, which corresponds to the aromatic ring), the C-N/C=N group - 1 carbon atom and 1 nitrogen atom, the C-O/C=O/O=C-OH group - 1 carbon atom and 1 nitrogen atom. Then we multiply the obtained number of atoms of each peak by its relative area. We obtain the coefficients that correspond to the chemical composition of the particle without taking gadolinium into account.



Figure S5. Diagrams with normalized contributions of the absorption bands by area relative to the sample Gd_0, for the UV region (a) and visible spectral range (b).

These plots were obtained by baseline subtraction and further peak area calculation. Then the obtained values were normalized to the area of the initial sample Gd_0 and the change of nanoparticle absorption with increasing gadolinium concentration was evaluated. As can be seen from the figures, the absorption intensity decreases with increasing gadolinium concentration. As suggested earlier from the IR spectra, this is due to the surface coordination of gadolinium and the replacement of functional groups by its ions. This leads to a stronger decrease in the visible absorption band with increasing the Gd concentration (see Fig. S5).



Figure S6. Fluorescence intensity of Gd-CNPs relative to the sample Gd 0.



Figure S7. Spectra of optical density and fluorescence of diluted samples of CNPs and Gd-CNPs **Table S3.** The estimated values of the QY values of the CNPs and Gd-CNPs

Sample	QY, %
Gd_0	14.9±0.9
Gd_2	14.8±0.9
Gd_4	14.6±0.9
Gd_8	14.1±0.8

The luminescence diagram obtained by analogy with absorption indicates a decrease in luminescence intensity with increasing gadolinium concentration. These data are in good agreement with the decrease in particle absorption in the UV region.



Figure S8. Q-band EPR spectra of dried CNPs and Gd-CNPs. Normalized by mass (a) and by maximal intensity (b).



Figure S9. MRI maps for (a) T1 and (b) T2 relaxation times in phantoms with aqueous solutions of Gd-CNPs (1 mg/ml).

Table S4. Gd-concentrations from XFA analysis and Gd-related MR relaxivities in aqueous solutions of Gd-CNPs prepared with different precursor concentrations.

Samples	Concentration of GdCl ₃ 6H ₂ O,	Gd concentration in diluted dialyzed Gd CNP 1 mg/mL	r ₁ , s ⁻¹ ,mM ⁻¹	r ₂ , s ⁻¹ ,mM ⁻¹
•	mg/ml	solutions, mM	1, ,	27 7
Gd_0.2	0.2	0.6 ± 0.1	4.9 ± 1.8	11.2 ± 3.8
Gd_2	2.0	2.0 ± 0.1	6.4 ± 1.6	8.6 ± 1.9
Gd_4	4.0	1.8 ± 0.1	8.3 ± 2.1	11.4 ± 2.0
Gd_8	8.0	2.5 ± 0.1	0.5 ± 0.2	1.0 ± 0.2