Electronic Supplementary Material (ESI) for RSC Advances

Supporting information

Fluorescein-polyethyleneimine coated gadolinium oxide nanoparticles as T_1 magnetic resonance imaging (MRI) – cell labeling (CL) dual agents

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(1) XRD patterns

We measured an XRD pattern of a powder sample of fluorescein-PEI coated gadolinium oxide n anoparticles. The additional peaks (*) other than (222) peak from cubic Gd_2O_3 also appeared (Fig. S1). These additional peaks are likely due to surface coated materials. The lattice constant (= 10.82 Å) estimated from the (222) peak is consistent with that (= 10.813 Å) reported in PCPDFWIN with card number of 43-1014. We also measured an XRD pattern of a TGA analyzed powder sample of fluorescein-PEI coated gadolinium oxide nanoparticles. The broadness of (222) peak of the TGA analyzed powder sample is likely due to surface contamination by reaction with surface coated fluorescein-PEI during TGA analysis, resulting in reduced core particle diameter of Gd_2O_3.

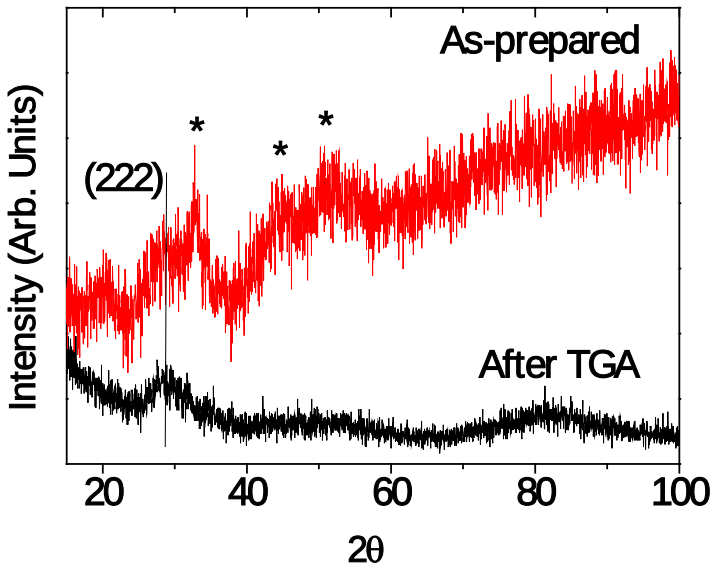

Fig. S1 XRD patterns of as-prepared and TGA analyzed power samples of fluorescein-PEI coated gadolinium oxide nanoparticles. Additional peaks (*) are likely due to fluorescein-PEI.

(2) A HRTEM image of a TGA analyzed powder sample of fluorescein-PEI coated gadolinium oxide nanoparticles.

As can be seen in a HRTEM image below, the particle diameter increased after a TGA analysis and ranges from 5 to 20 nm (Fig. S2).

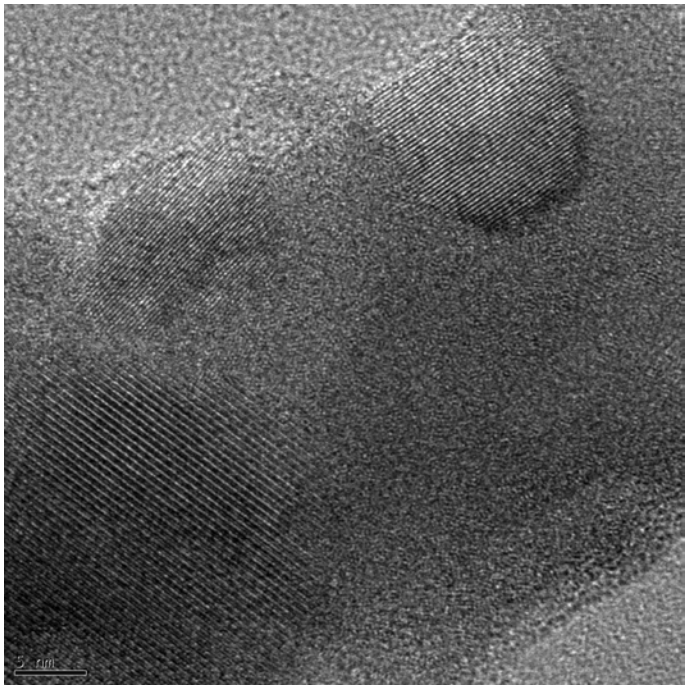

Fig. S2 A HRTEM image of a TGA analyzed powder sample of fluorescein-PEI coated gadolinium oxide nanoparticles. The scale bar is 5 nm.

(3) A NMR spectrum for fluorescein-PEI

400 MHz NMR spectrum of fluorescein-PEI as well as those of PEI, fluorescein, and a physical mixture of all reactants (i.e., PEI, fluorescein, EDC, NHS, and PBS solution) as comparison are provided in Fig. S3. Two solvents (DMSO-d_6 and D_2O) were used because of different solubilities of reactants in water. That is, fluorescein is only slightly soluble in water, whereas the other reactants are highly or completely soluble in water. Therefore, a NMR spectrum of fluorescein itself can be seen only in DMSO-d_6 but not in D_2O, whereas NMR spectra of other reactants (i.e., PEI, EDC, NHS) can be seen only in D_2O. A NMR spectrum of fluorescein is not seen even in a physical mixture of all reactants in D_2O due to the same reason. There are also only little NMR peaks of PEI in a physical mixture likely because of its aggregation with fluorescein so that aggregated PEI with fluorescein is not soluble in D_2O (i.e., the precipitation was in fact observed in a physical mixture). However, some peaks from EDC and NHS with low molecular weights can be seen in a physical mixture because most of them do not form aggregation due to fluorescein. However, after reaction

was completed, fluorescein-PEI is the main peaks. That is, fluorescein-PEI is highly soluble in D_2O and thus, peaks from both fluorescein and PEI can be seen in D_2O as shown in Fig. S3. Here, impurity peaks from those of EDC and NHS can be seen in a NMR spectrum of fluorescein-PEI because the fluorescein-PEI was not separated from other molecules in the final reaction solution. This is because nanoparticles were added to the final reaction solution to synthesize fluorescein-PEI coated nanoparticles in one-pot. However, the final product (i.e., fluorescein-PEI coated nanoparticles) was separated from other reactants through a thorough washing with a triply distilled water three times for further characterizations.

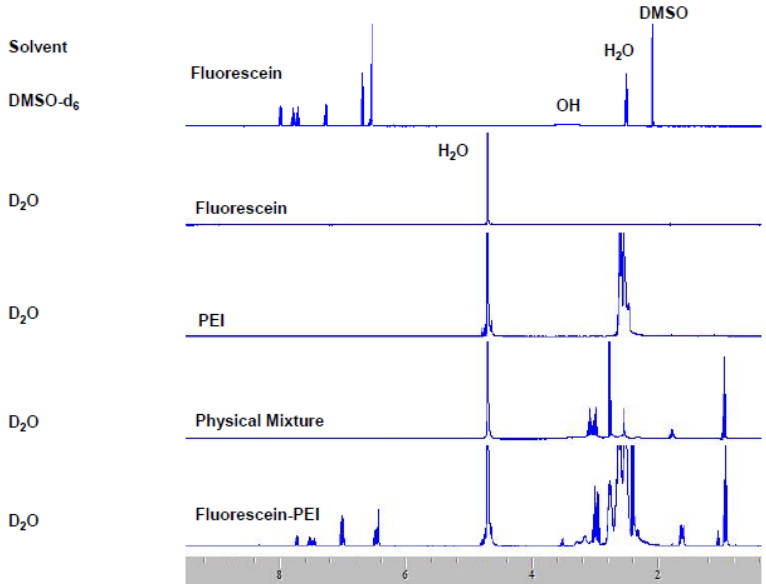

Fig. S3 A NMR spectrum of fluorescein in DMSO-d_6 and those of fluorescein, PEI, a physical mixture of all reactants (i.e., PEI, fluorescein, EDC, NHS, and PBS solution), and fluorescein-PEI in D_2O.

The synthesis of fluorescein-PEI is described in the text. After the reaction was completed, the solvent was removed under vacuum to dryness. The residue was washed by ethanol and then dissolved in D_2O for NMR characterization: ^{1}H NMR (400 MHz, D_2O) d 3.49-3.55 (m, 2H, -CH_2), 6.43-6.49 (4H, m), 6.98-7.01 (2H, m), 7.04 (1H, d, J = 7.2 Hz), 7.46 (1H, td, J = 1.0, 6.8 Hz), 7.53 (1H, td, J = 1.0, 6.8, Hz), 7.73 (1H, d, J = 7.6 Hz). Since there are many amine groups in PEI, many amide bonds between PEI and fluorescein are possible. Among them, one of possible amide bonds of fluorescein-PEI is shown in Fig. 1b in the text (also in Fig. S4). Therefore, the NMR spectrum of fluorescein-PEI in Fig. S4 corresponds to that of a mixture of all possible structures of fluorescein-PEI. There are some impurity peaks from EDC and NHS in Fig. S4 because they were not removed from the compound as mentioned above.

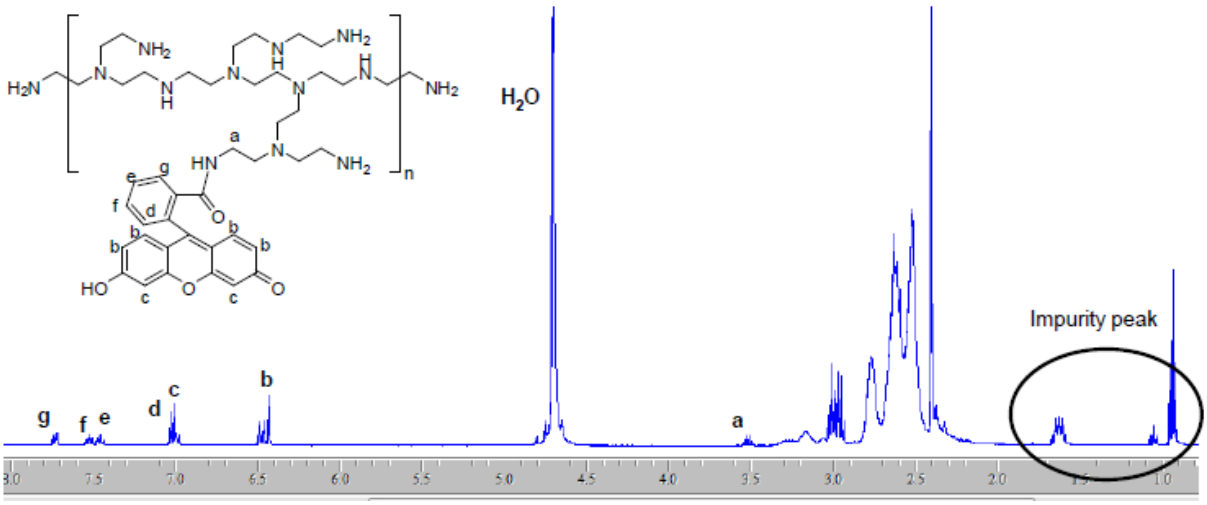

Fig. S4 One of possible structures of fluorescein-PEI and a NMR spectrum with contributions from all possible structures of fluorescein-PEI in D_2O.