Supporting Information

Sequential growth of CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles for efficient magnetic resonance angiography and tumor diagnosis

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Fig. S1. The detailed elemental compositions of the as-prepared CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles at different transmission electron microscopy (TEM) image area (a, b were at nanoparticles area 1 and c, d were at blank area 2).
Fig. S2. The X-ray photoelectron spectra (XPS) of the as-prepared CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles: (a) Survey spectrum, (b) Ca 2p spectrum, (c) Gd 4d spectrum, (d) F 1s spectrum.
Fig. S3. FT-IR spectra of the CaF$_2$:Yb,Er@CaF$_2$:Gd-OA (black line), the hydrophilic CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles (red line) and the PEG-PAA di-block copolymer (blue line).
Fig. S4. TEM images of (a) the as-prepared CaF$_2$:Yb,Er@CaF$_2$:Gd-OA nanoparticles dispersed in cyclohexane and (b) the hydrophilic CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles dissolved in water.

Fig. S5 Absorption spectra of arsenazo III at different filtrates time points obtained after dialysis of 1 mg Gd/mL (a) GdCl$_3$ aqueous solution and (b) the hydrophilic CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles aqueous solution to study the leaching of Gd ions from the original aqueous solution. Water and GdCl$_3$ aqueous solution (1 μg Gd/mL, 10 μg Gd/mL and 100 μg Gd/mL) were used as negative and positive controls, respectively.
**Fig. S6.** Hydrodynamic size of the hydrophilic CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles aqueous solution at different storage time points measured by dynamic light scattering (DLS).

**Fig. S7.** Zeta potential of the hydrophilic CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles aqueous solutions at different storage time points.
Scheme S1. Schematic illustration of the detail structure difference between as-prepared CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles and CaF$_2$:Gd nanoparticles.
Fig. S8. (a) $T_1$ maps of the hydrophilic CaF$_2$:Gd nanoparticles; (b) Comparison of longitudinal relaxivity $r_1$ of the hydrophilic CaF$_2$:Gd nanoparticles under 3.0 T.

Fig. S9 The other variations of indices of hepatic function, renal function and blood routine tests (n=3), including aspartate transaminase / alanine transaminase ratio (AST/ALT), albumin (ALB), blood urea
nitrogen / creatinine ratio (BUN/CREA), uric acid (UA), lactate dehydrogenase (LDH), white blood cells (WBC), red blood cells (RBC), hemoglobin (HGB), hematocrit (HCT), plateletcrit (PCT), mean corpuscular volume (MCV), mean corpuscular hemoglobin (MCH), red blood cell distribution width measured by standard deviation (RDW-SD), red blood cell distribution width measured by variation coefficient (RDW-CV), mean corpuscular hemoglobin concentration (MCHC), platelet distribution width (PDW), lymphocyte (LYM-PH), mean platelet volume (MPV), platelet-large contrast ratio (PLCR), platelets (PLT).

Table S1. The detailed elements composition of the hydrophilic CaF$_2$:Yb,Er@CaF$_2$:Gd nanoparticles measured by means of ICP-AES.

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP-AES data (µg/mL)</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tr>
<td>Ca</td>
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<td>Yb</td>
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