Supporting Information

A Smart $T_1$-weighted MRI Contrast Agent for Uranyl Cation based on a DNAzyme-Gadolinium Conjugate

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Experimental Details

Materials, equipment and DNA sequences

All DNA molecules with biotin or amine modifications were purchased from Integrated DNA Technologies, Inc. (Coralville, IA). The DNA was standard desalted by the vendor and used without further purification. NHS-activated DOTA was purchased from Macrocyclics, Inc. (Dallas, TX). Streptavidin and other chemicals were purchased from Sigma-Aldrich, Inc. or Fisher Scientific, Inc.

$T_1$ was measured on a Bruker Minispec mq 60 MRI contrast agent analyzer (1.5 T, Bruker), Varian NMR spectrometer (300 MHz), and 60 MHz - Varian EM360L NMR Spectrometer with Anasazi FT Upgrade. MRI measurements were acquired on a 1.5T GE Signa Horizon Echo Speed (1.5 T, GE) using the version 9.0 software package.

The sequences of the DNA strands used in this work are listed in Table S1.
**Table S1. DNA sequences used**

<table>
<thead>
<tr>
<th>39E</th>
<th>5’-CCATCTCTTTCAGGGGTAGTTAAACCGACCTCAGACATAGTGAGT-biotin-3’</th>
</tr>
</thead>
<tbody>
<tr>
<td>39S</td>
<td>5’-amine-ACTCACTATrAGGAAGAGATGG-3’</td>
</tr>
</tbody>
</table>

**T1 measurement**

39E-based contrast agent was prepared by dissolving the DOTA-Gd-coupled 39S and biotinylated 39E in 50 mM MES-Na (pH 5.5) buffer at a concentration of 30 µM. The solution was heated to 90 °C and cooled to ambient temperature over one hour. Streptavidin was then added into the solution at a concentration of 30 µM. Uranyl acetate (UO₂OAc₂) was added into the solution to reach different concentrations. EDTA (100 µM) was used to stop the reaction after 30 minutes. The sample was then subjected to $T_1$ measurement.

A Bruker Minispec mq 60 MRI contrast agent analyzer (1.5 T, Bruker) was used to measure the longitudinal relaxation time of water protons. The temperature was kept constant at 37 °C during all $T_1$ measurements. The parameters of the measurement are summarized in Table S2.

**Table S2. Parameters for T1 measurements**

<table>
<thead>
<tr>
<th>First Duration</th>
<th>Last Duration</th>
<th>Data points</th>
<th>Duration Factor</th>
<th>Total Analysis</th>
<th>Del. Sam. Win.</th>
<th>Sam. Win.</th>
<th>Expon. Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 ms</td>
<td>15 s</td>
<td>10</td>
<td>1.668</td>
<td>12.58 min</td>
<td>0.03 ms</td>
<td>0.03 s</td>
<td>1</td>
</tr>
</tbody>
</table>