Supporting information

Gd-Al co-doped mesoporous silica nanoparticles loaded with $Ru(bpy)_3^{2+}$ as a dual-modality probe for fluorescence and magnetic resonance imaging

Dan Zhang [a], Ai Gao [a], Yang Xu [a], Xue-Bo Yin [*,a], Xi-Wen He [a], and Yu-Kui Zhang [a,b]

[a] State Key Laboratory of Medicinal Chemical Biology, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), and Research Center for Analytical Sciences, College of Chemistry, Nankai University, Tianjin, 300071, China.

[b] National Chromatographic R. & A. Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116011, China.

[*]Corresponding author, Fax: (+) (86) 22 23503034, E-mail: xbyin@nankai.edu.cn

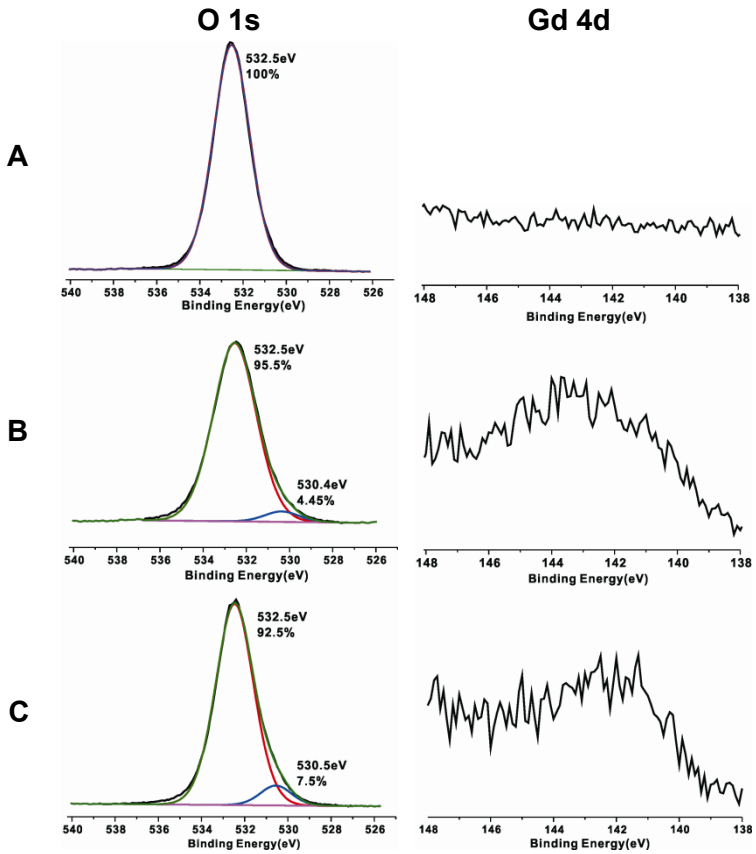

Fig. S1. XPS spectra of A: MSNs, B: 3.4% Gd @MSNs, C: 4.4% Gd-Al@MSNs.

X-ray photoelectron spectroscopy (XPS) analyses were performed with MSNs, 3.4 wt% Gd@MSNs and 4.4 wt% Gd-Al@MSNs samples to evidence that Gd^{3+} are incorporated in the framework by the O 1s peaks and Gd 4d peaks (Figure S1). As compared to the pristine MSNs which showed only O1s (532.5 EV), the O 1s of Gd@MSNs and Gd-Al@MSNs became broadened and the shoulder at lower energy was observed. For the O1s, the peaks at 532.5 eV and 530.5-530.3eV could be responsible for Si-O-Si and Si-O-Gd links, respectively. The binding energies 142.3 eV for Gd 4d of Gd-Al@MSNs are lower than 143.3 eV of Gd@MSNs. These observed chemical shifts for O 1s peaks and Gd 4d peaks of different Gd silica-containing nanoparticles shows Gd^{3+} exist in silica matrix and the Al doping has a positive effect on that.

Table S1. The zeta-potential of different samples.

Sample	Gd@MSNs	4.4% Gd-Al@MSNs	Ru/Gd-Al@MSNs
ζ-potential (mV)	-39.9±4.5	-31.2±3.7	-10.3±3.6

Zeta potential of different particles was tested to validate the success of doping $Ru(bpy)_3^{2+}$. The Gd@MSNs have a zeta potential of -39.9±4.5 mV and that for 4.4% Gd-Al@MSNs is -31.2±3.7 mV. However, after the adsorption of $Ru(bpy)_3^{2+}$, the surface negative charge changed to -10.3±3.6 mV. The sharp decline in charge was attributed to the ion-exchange interaction between hydroxyls on the surface in the pore of nanoparticles and $Ru(bpy)_3^{2+}$. In addition, a lower ζ-potential of Gd-Al@MSNs than Gd@MSNs was observed. This result reveals that Al co-doping has a direct influence on the the formation of silica host matrix.

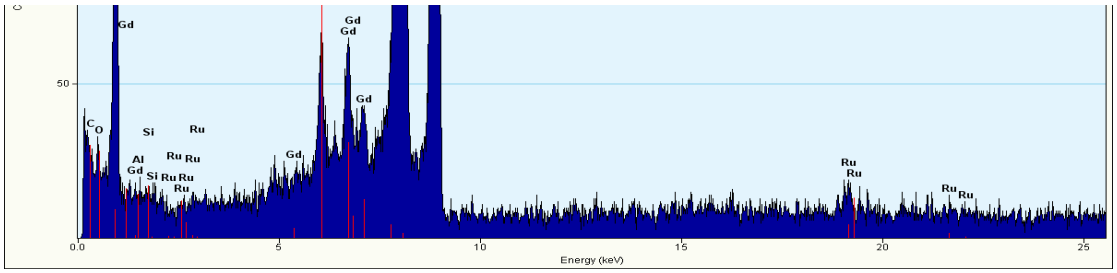

Fig. S2. EDX of Ru/Gd-Al@MSNs

The doped $Ru(bpy)_3^{2+}$ was also validated by the Energy dispersive X-ray spectroscopy (EDX) results, where Gd^{3+}, Al^{3+} or $Ru(bpy)_3^{2+}$ were found in the framework of mesoporous silica substrate.

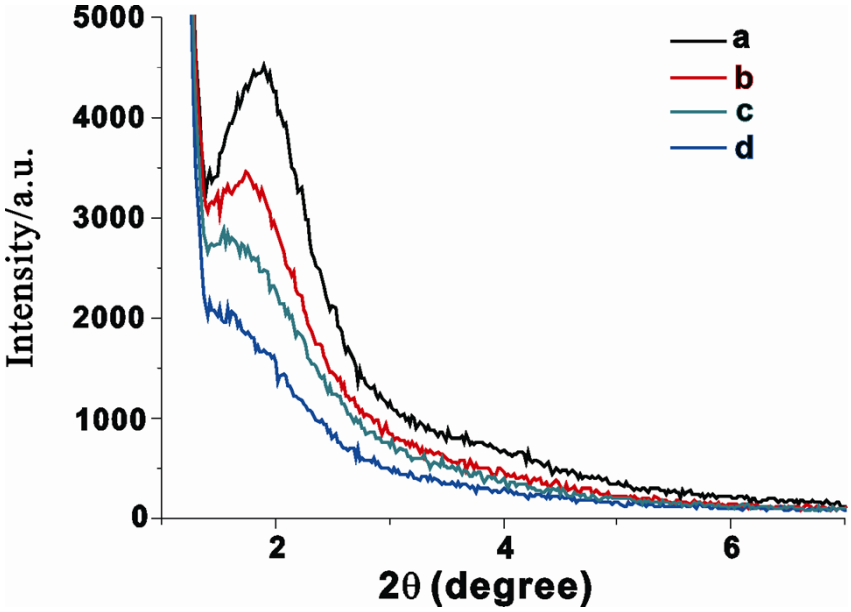

Fig. S3. XRD of (a) Gd@MSNs with a Gd mass fraction of 3.4 %, (b) Gd-Al@MSNs with Gd and Al mass fraction of 2.9 % Gd and 0.4 %, (c) Gd-Al@MSNs with Gd and Al mass fraction of 4.4 % and 0.8 %; and (d) Gd-Al@MSNs with Gd and Al mass fraction of 5.1 % and 2.3 %.

Table S2. Characterization of the various samples.

Sample	Gd wt%	Al wt%	Ru wt%	Gd μmol g^{-1}	Al μmol g^{-1}	Al/Gd m/m	Ru μmol g^{-1}	r_1 $mM^{-1}s^{-1}$	r_2/r_1
Ru/Gd-Al@MSNs	4.03	0.775	0.567	256.3	287.2	1.12	56.1	19.2	1.14
Gd-DTPA	--	--	--	--	--	--	--	4.19	1.12
Gd@MSNs	3.42	--	--	217.4	--	--	--	6.68	2.45
Gd-Al@MSNs	2.94	0.394	--	187.3	127.7	0.68	--	13.8	1.49
Gd-Al@MSNs	4.36	0.806	--	277.1	298.0	1.08	--	17.3	1.12
Gd-Al@MSNs	5.10	2.29	--	324.5	851.7	2.62	--	8.29	1.83
Ru/Gd-Al@NSNs	3.05	0.263	0.197	193.8	97.48	0.37	19.5	9.05	2.96

Table S3. Gd^{3+} and Al^{3+} amounts for the synthesis of various samples.

Sample	Added Gd^{3+}/mmol	Added Al^{3+}/mmol
Ru/Gd-Al@MSNs	0.10	0.05
Gd-DTPA	--	--
Gd@MSNs	0.10	--
Gd-Al@MSNs	0.10	0.025
Gd-Al@MSNs	0.10	0.05
Gd-Al@MSNs	0.10	0.20
Ru/Gd-Al@NSNs	0.10	0.05

To investigate the stability of the Ru/Gd-Al@MSNs, samples were dispersed into PBS (pH 7.4) with a concentration of Gd 2206 ppm, Al 246 ppm and Ru 284 ppm. No free Gd and Al ions were dissociated from the hybrid nanoparticles (The detection limit of Gd and Al was 0.0154 ppm and 0.0174 ppm, respectively) but 2.07 ppm, 2.53 ppm, and 2.53 ppm of Ru leakage was measured by ICP-AES after the storage for one day, one week, and one month, respectively.