Electronic Supplementary Information
for

Lattice distortion of CaF_2 nanocrystals for shortening their ^{19}F longitude relaxation time

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1. Experimental Section

Materials

Calcium oxide (CaO, 98%) was purchased from Adamas Reagent Co., Ltd. Trifluoroacetic acid (TFA, 99.50%), oleic acid (OA, 90%), oleylamine (OM, 90%) and 1-octadecene (1-ODE) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Ethanol (C_2H_5OH, 99.70%), n-hexane (99.70%) and cyclohexane (99.70%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Deuterated chloroform (99.80%) was purchased from Sigma-Aldrich Co., Ltd.

The Synthesis

The precursor, $Ca(CF_3COO)_2$, was prepared by dissolving calcium oxide (20mmol) in CF_3COOH/water (vol. 1:1) solutions in a 50 ml single-necked flask. The reaction system was stirred at 110℃ under vacuum for about 1h until the mixture became clear.

A typical procedure of the synthesis of CaF_2 nanocrystals was conducted as follows: $Ca(CF_3COO)_2$ (4mmol) was added into 80 ml of OA/OM/1-ODE mixture in a three-necked flask (150 mL) at room temperature. Then, the system was heated to 100 °C to remove water and oxygen with vigorous magnetic stirring under vacuum for 1h to form an optically transparent solution. The solution was then heated to 310 °C at a heating rate of 10 °C/min and kept for 1 h under an inert N_2 atmosphere. Once cooling to room temperature, the nanocrystals were washed with anhydrous ethanol and cyclohexane for three times. The collected nanoparticles were finally dispersed in cyclohexane for further use. The ratio between OA, OM and ODE, and the reaction time were specified in the manuscript.

Characterization

The size and morphology of the nanocrystals were observed with a Tecnai G2 Spirit Biotwin biology transmission electron microscope (Bio-TEM), and a TALOS F200X transmission electron microscope (HR-TEM) operated at 200 kV. Polydispersity index (PDI) of nanoparticles was conducted using dynamic light scattering (DLS) (Malvern Zetasizer Nano S) using a 4 mW He–Ne laser operating at 633 nm.

The impurities of the samples were determined by inductively coupled plasma (Thermo iCAP 6300). The transition elements contained in the nanoparticles were

qualitatively and semi-quantitatively characterized.

Nuclear magnetic resonance (NMR) experiments were performed on a Avance III 400MHz Nuclear Magnetic Resonance Spectrometer. The samples (1mM, 1ml) were sonicated for 3 min and then transferred into the NMR tube to detect the relaxation time of ^{19}F. The longitudinal (T1) and transverse (T2) relaxation times were calculated using inversion recovery (IR) and rotation inversion method experiments, respectively.

^{19}F magic angle spinning (MAS) NMR spectra were collected a Larmor frequency of 600.13 MHz (14.09 T) using a Bruker Avance NEO 600 MHz WB Solid-State Nuclear Magnetic Resonance Spectrometer. The freeze-dried samples was rotated at 33kHz at ambient temperature.1

The samples with 1mM concentration (or the concentration specified in the manuscript) were added into 5 ml bottles and sonicated for 3 min to ensure the solution well dispersed. ^{19}F-Magnetic Resonance Imaging (MRI) were performed on a Bruker Clinscan 7T MRI. A dual 1H/19F, 25 mm RF coil was used to acquire the ^{19}F-MR images with FLASH sequence. Parameters were used as follows: TR/TE=500/1.26 ms, FOV=80×50 mm^2, matrix size=32×32, scan time of 17.06 min. All ^{19}F spectra were acquired for 1024s for each sample, 8 times.

Figure S1.

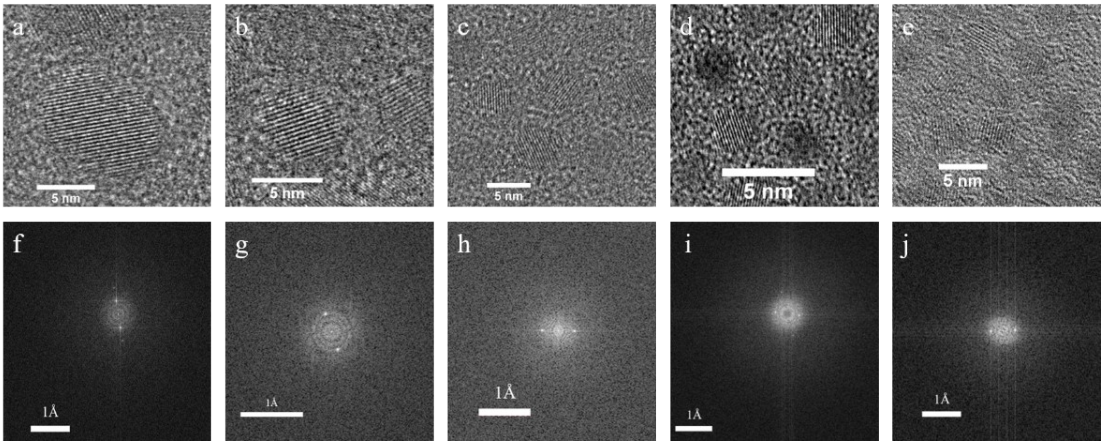
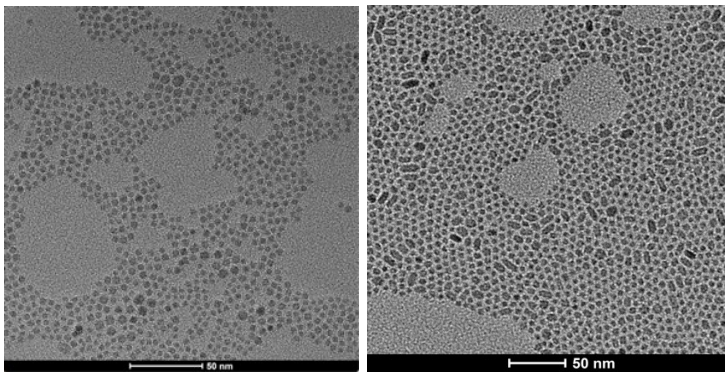


Figure S1. HR-TEM images (a-e) and their corresponding FFT diffraction points (f-j) for sample 1, 7, 6, 2, and 5, respectively.

Figure S2.



(a) (b)

Figure S2. TEM images of a) sample 2'and b) 5'

Figure S3.

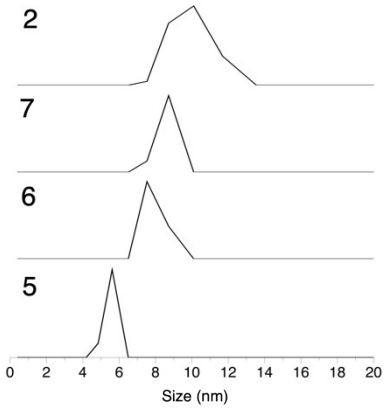


Figure S3. The size of nanocrystals measured by DLS.

Table S1. The synthesis conditions and the outcome of nanocrystals

No.	OA : OM : ODE	Size (nm)	DPI (%)	Lattice parameter (Å)	FWHM from NMR (Hz)
1#	0.5 : 0.125 : 0.375	14.2*8.6	24	5.57	360.8
2#	0.5 : 0.25 : 0.25	7.1	21	5.42	449.6
3#	0.75 : 0.25 : 0	6.1	46	/	/
4#	0.625 : 0.375 : 0	4.5	12	/	/
5#	0.5 : 0.5 : 0	3.9	8	5.30	1420.8
6#	0.375 : 0.625 : 0	4.2	7	5.51	274.8
7#	0.25 : 0.75 : 0	5.1	10	5.53	309.6
8#	0.375 : 0.5 : 0.125	4.2	8	5.52	244.4
9#	0.375 : 0.25 : 0.375	4.5	9	5.53	262.8
10#	0.25 : 0.25 : 0.5	12.6	42	/	/

Table S2. The correlation between sample Nos., lattice parameters, and their MRI imaging properties.

No.	Lattice parameter (Å)	T1(s)	T2(ms)	SNR
1#	5.57	20.9±1.24	2.0±0.20	77.19
2#	5.42	11.4±0.66	1.6±0.05	195.56
5#	5.30	2.1±0.20	1.3±0.03	220.64
6#	5.51	15.1±0.03	1.6±0.50	117.57
7#	5.53	16.3±0.29	1.8±0.16	112.85
8#	5.52	16.0±0.30	1.8±0.14	/
9#	5.53	14.6±0.36	1.7±0.31	/

Table S3. The detectable impurities of transition metals in Sample 5

Transition element	Average content (%)	Transition element	Average content (%)
Ti	0.0027	Co	0.0014
V	0.0006	Ni	0.0009
Cr	0.0003	Zr	0.0088
Mn	0.0017	Mo	0.0002
Fe	0.0080	W	0.0011

Table S4. The detectable impurities of transition metals in Sample 6.

Transition element	Average content (%)	Transition element	Average content (%)
Ti	0.0029	Co	0.0003
V	0.0004	Ni	0.0008
Cr	0.0005	Zr	0.0095
Mn	0.0002	Mo	0.0002
Fe	0.0028	W	0.0006
Nb	0.0001		