Supplementary Information

Mechanisms underlying the nucleation processes of mesoporous ceria nanoparticles

Jian He, Ling Zou, Lu Yang, Guangyou Shi, Jinbao Li, Run Huang, Xiaoling Liu, Shiwu Dong* and Xiaochao Yang*

School of Biomedical Engineering and Medical Imaging, Army Medical University, Chongqing 400038, China

*E-mail: dongshiwu@tmmu.edu.cn; xcyang@tmmu.edu.cn

Experimental Procedures

Procedures for the synthesis of I-MCNs

The I-MCNs were synthesized by our previous method. In brief, $Ce(NO_3)_3 \cdot 6H_2O$ (Acros, 99.5%) (1 mmol) and TOPO (Sigma-Aldrich, 99%) (1.2 mmol) were dissolved in ethanol (2 mL) and heated to 80 ºC. The mixture was added 1-octadecene (ODE) (Acros, 90%) (5 mL) and heated to 180 ºC for 30 min. After cooling to room temperature, the product was washed by ethanol and acetone for several times until the supernatant was clear. Finally, the synthesized I-MCNs were dispersed in toluene (10 mL) and stored at 4 ºC. The conditions for the syntheses using other ligands including oleylamine (OAm), oleic acid (OAc) and oleyl alcohol (OAl) and solvents including octadecane (OAd), OAm, OAc and OAl were the same as that of TOPO and ODE respectively.

Transmission electron microscopy (TEM) analysis

The I-MCNs dispersed in toluene was dripped onto ultrathin carbon copper grid. The morphologies of the nanoparticles were observed on a Hitachi HT7700 TEM operated at 100 kV. The high-resolution images were observed on a FEI tecnai G2 F20 TEM operated at 200 kV. The selected area electron diffraction (SAED) analyses were performed using Gatan DigitalMicrograph 3.9 software.

N_2 adsorption/desorption analysis

The ceria nanoparticles were calcinated in air at 500 ºC for 2 h. The samples were degassed at 300 ºC for 2 h before testing. Then, they were backfilled with N_2 and weighted to get N_2 adsorption/desorption isotherms. Surface areas and pore diameters of the samples were analyzed by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method respectively.

X-ray diffraction (XRD) analysis

The XRD spectra of the samples were obtained on a Bruker D8 X-ray diffractometer equipped with a Cu Ka radiation source operated at 40 kV and 40 mA using a scanning step of 0.02º. Averaged grain size was analyzed based on Scherrer Equation using Jade 6 software.

Thermogravimetric (TG) analysis

The TG samples were prepared by stirring $Ce(NO_3)_3\cdot 6H_2O$ (1 mmol), TOPO (0-3.0 mmol) and ethanol (2 mL) at 80 ºC until the solution was clear. The samples were dyed at 80 ºC for 30 min under vacuum condition until white solid or yellow oil products were formed. The TG curves were determined on a TA Q50 analyzer using a heating rate of 20 ºC min^{-1}. The results were analyzed on a TA Universal Analysis software and the graphs were transferred into derivative thermogravimetric (DTG) data.

Electrospray ionization mass spectrometry (ESI-MS) analysis

The ESI-MS samples were prepared by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ (1 mmol) and TOPO (0-3.0 mmol) in ethanol (2 mL) at room temperature. The samples were diluted 500 times by ethanol before running the tests. The mass to charge ratios were determined by a Bruker Impact Ⅱquadrupole time-of-flight (QTOF) mass spectrometer operated at 2 kV. The signals with intensity lower than 5% were excluded from the results.

^{31}P nuclear magnetic resonance (^{31}P NMR) analysis

The ligands in the solvent and adsorbed at the I-MCNs surfaces after the synthetic reaction were collected and analyzed by ^{31}P NMR. The ligands in the solvent were collected by extraction. After the synthesis, the reaction solution was added ethanol (20 mL) and the mixture was centrifuged to separate the supernatant. The ethanol in the supernatant was removed by rotary evaporation and extracted by methanol (5 mL) for three times to separate the ligands from ODE. The ethanol solvent was removed by rotary evaporation and the ligands were dispersed in $CDCl_3$ (800 μL). The ligands adsorbed at the I-MCNs surface were collected by a ligand-exchange method. The I-MCNs dispersed in toluene were precipitated out by adding acetone and re-dispersed in THF (5 mL). The THF solution of I-MCNs was mixed with alendronate (100 mg) dissolved in H_2O (5 mL), and the mixture was stirred at 80 ºC for 12 h. After cooling to room temperature, the upper organic layer was separated by centrifugation. The solvent was removed by rotary evaporation and the ligands were dissolved in $CDCl_3$ (800 μL). One dimensional (1D) ^{31}P NMR spectra of the samples were recorded on an

Agilent Direct Drive 2 NMR spectrometer operated at frequency of 243 MHz.

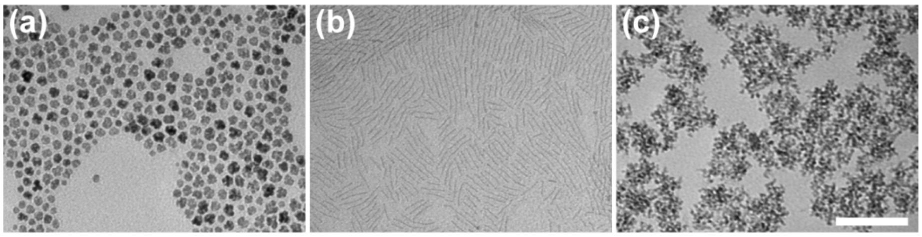

Fig. S1. TEM images of ceria synthesized using OAm, OAc and OAl as ligands respectively. All of the TEM images shared a same scale bar of 50 nm.

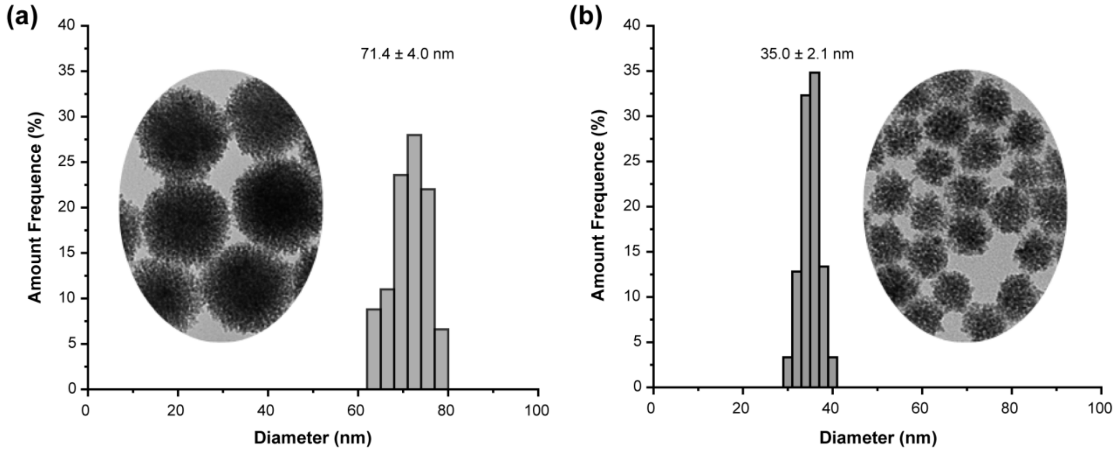

Fig. S2. The size distributions of I-MCNs synthesized with and without ethanol.

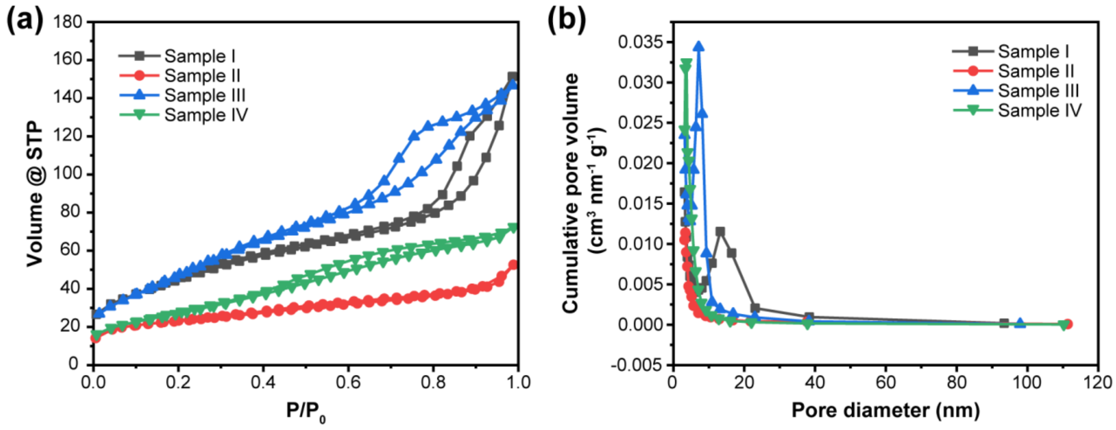

Fig. S3. The N_2 adsorption/desorption isotherms and pore diameter distribution of sample I, II, III and IV in Fig. 1.

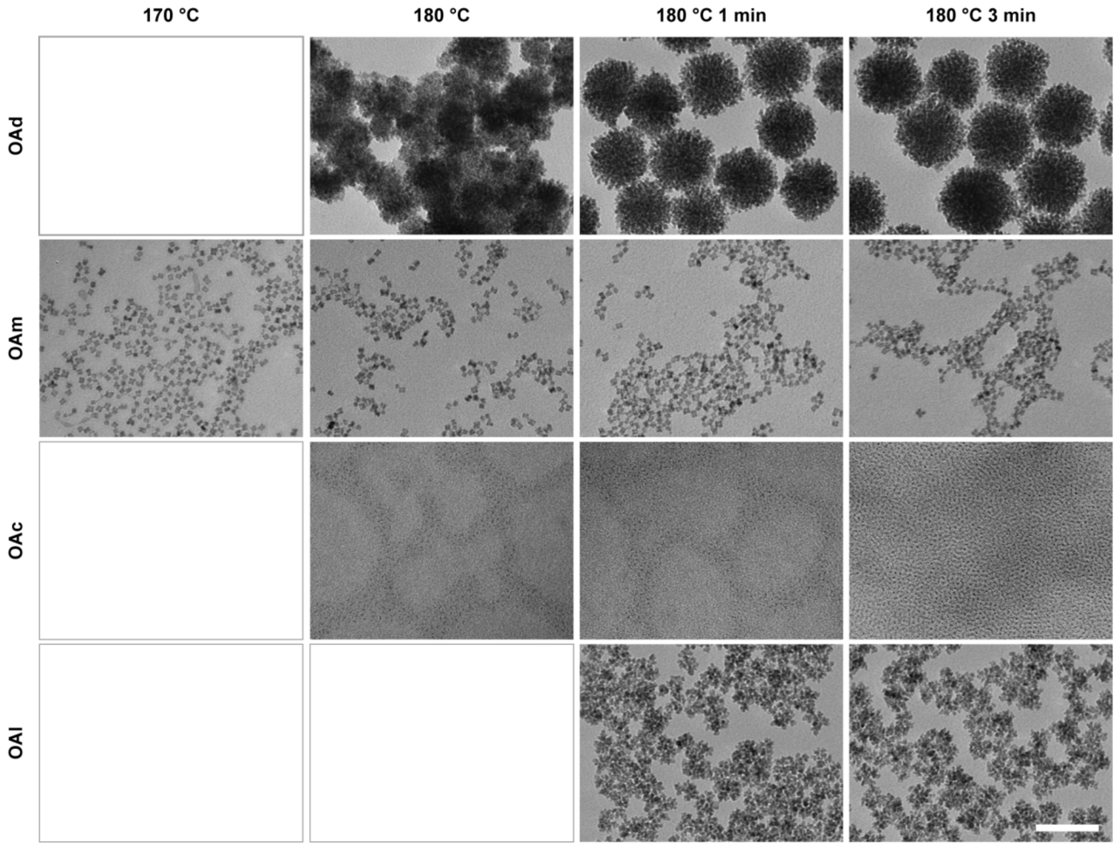

Fig. S4. TEM images of samples in the nucleation process with other solvents including OAd, OAm, OAc and OAl. All blank images represented that no samples were collected under this condition. All of the TEM images shared a same scale bar of 50 nm.

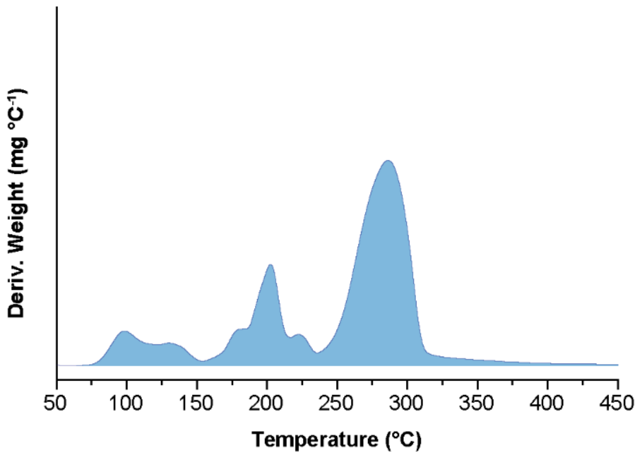

Fig. S5. The DTG graph of raw $Ce(NO_3)_3{\cdot}6H_2O$.

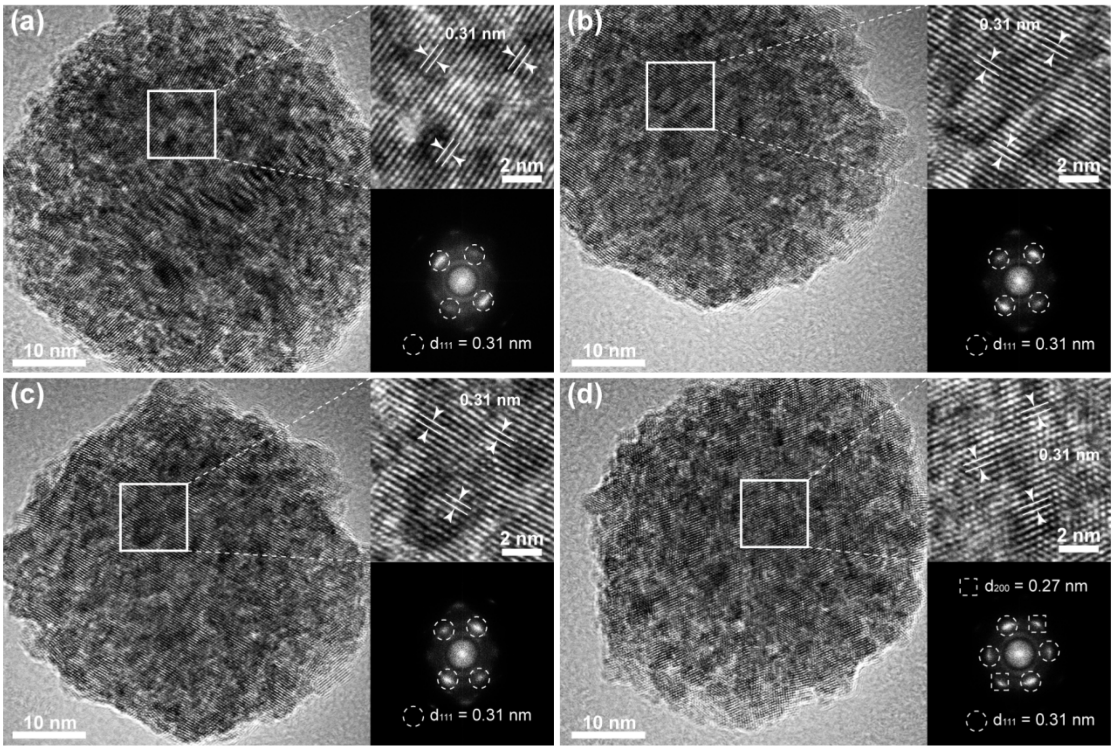

Fig. S6. HRTEM images of four I-MCNs showing the exposure of (111) plane at their surfaces.

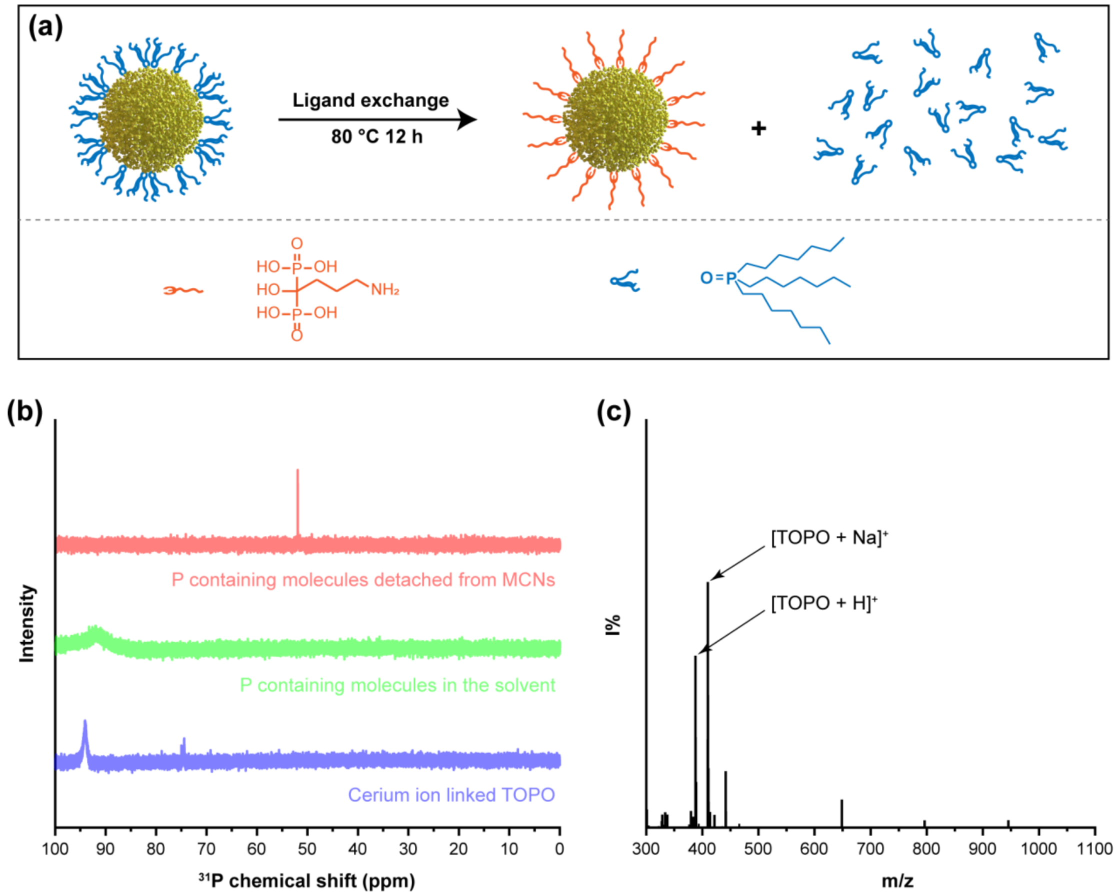

Fig. S7. (a) Schematic illustration of the ligand exchange between alendronate and TOPO. (b) The ^{31}P spectra of cerium ion linked TOPO, molecules in the solvent, and molecules detached from the surface of I-MCNs. (c) The MS spectrum of molecules detached from I-MCNs.

$aCe(NO_3)_3 \cdot 6H_2O + eEtOH$	$\longrightarrow$	$[Ce_a(OH)_b \cdot (NO_3)_c \cdot (H_2O)_d \cdot (EtOH)_e]^+$ Group I	+	$bH^+ + (3a\text{-}c)NO_3^- + (6a\text{-}b\text{-}d)H_2O$
$Ce(NO_3)_3 \cdot 6H_2O + dEtOH$	$\longrightarrow$	$[Ce(OH)_a \cdot (NO_3)_b \cdot (H_2O)_c \cdot (EtOH)_d]^+$ Group II	+	$aH^+ + (3\text{-}b)NO_3^- + (6\text{-}a\text{-}c)H_2O$
$Ce(NO_3)_3 \cdot 6H_2O + bEtOH$	$\longrightarrow$	$[Ce(NO_3)_2 \cdot (H_2O)_a \cdot (EtOH)_b]^+$ Group III	+	$NO_3^- + (6\text{-}a)H_2O$
$aCe(NO_3)_3 \cdot 6H_2O + dEtOH$	$\longrightarrow$	$[Ce_a(NO_3)_b \cdot (H_2O)_c \cdot (EtOH)_d]^{x+}$ Group IV	+	$(3a\text{-}b)NO_3^- + (6a\text{-}c)H_2O$
$Ce(NO_3)_3 \cdot 6H_2O + bEtOH + cTOPO$	$\longrightarrow$	$[Ce(NO_3)_2 \cdot (H_2O)_a \cdot (EtOH)_b \cdot (TOPO)_c]^+$ Group V	+	$NO_3^- + (6\text{-}a)H_2O$
$Ce(NO_3)_3 \cdot 6H_2O + cEtOH + dTOPO$	$\longrightarrow$	$[Ce(OH)_a \cdot (NO_3)_b \cdot (H_2O)_c \cdot (EtOH)_d \cdot (TOPO)_e]^{x+}$ Group VI	+	$aH^+ + (3\text{-}b)NO_3^- + (6\text{-}a\text{-}c)H_2O$

Fig. S8. Chemical reactions occurred ahead of ceria crystal nucleation.

Table S1. The specific surface areas of sample I, II, III and IV in Fig. 1

Sample	I	II	III	IV
Surface areas [m^2 g^{-1}]	164	77	182	100

Table S2. The grain sizes of samples shown in Fig. 2c-f

Sample	Fig. 2c	Fig. 2d	Fig. 2e	Fig. 2f
Grain sizes [nm]	4.7	6.4	6.1	6.8

Table S3. Detected m/z and proposed molecular structures (TOPO/Ce^{3+} = 0)

Categories	Molecular formula	Molecular structures	m/z
I	$[Ce_a(OH)_b{\cdot}(NO_3)_c{\cdot}(H_2O)_d{\cdot}(EtOH)_e]^+$	$[Ce_2(OH)_2{\cdot}(NO_3)_3{\cdot}(H_2O)_2{\cdot}(EtOH)_5]^+$	766
II	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^+$	$[Ce(OH)_2{\cdot}(H_2O)_3{\cdot}(EtOH)_3]^+$	366
		$[Ce(OH)_2{\cdot}(H_2O){\cdot}(EtOH)_4]^+$	376
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_2{\cdot}(EtOH)_3]^+$	393
		$[Ce(OH)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_4]^+$	394
III	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b]^+$	$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)]^+$	328
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)]^+$	346
		$[Ce(NO_3)_2{\cdot}(EtOH)_2]^+$	356
		$[Ce(NO_3)_2{\cdot}(H_2O)_3{\cdot}(EtOH)]^+$	364
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_2]^+$	374
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_2]^+$	392
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_3]^+$	420
IV	$[Ce_a(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^{x+}$	$[Ce_2(NO_3)_4{\cdot}(H_2O)_4{\cdot}(EtOH)_3]^{2+}$	369
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_6{\cdot}(EtOH)_3]^{2+}$	387
		$[Ce_2(NO_3)_5{\cdot}(H_2O)_2{\cdot}(EtOH)_2]^+$	718
		$[Ce_2(NO_3)_5{\cdot}(H_2O)_3{\cdot}(EtOH)_2]^+$	736
		$[Ce_2(NO_3)_5{\cdot}(H_2O){\cdot}(EtOH)_3]^+$	746
		$[Ce_2(NO_3)_5{\cdot}(H_2O)_2{\cdot}(EtOH)_3]^+$	764

Table S4. Detected m/z and proposed molecular structures (TOPO/Ce^{3+} = 0.4)

Categories	Molecular formula	Molecular structures	m/z
II	$[Ce(OH)_a·(NO_3)_b·(H_2O)_c·(EtOH)_d]^+$	$[Ce(OH)_2·(H_2O)·(EtOH)_4]^+$	376
		$[Ce(OH)_2·(H_2O)_2·(EtOH)_4]^+$	394
III	$[Ce(NO_3)_2·(H_2O)_a·(EtOH)_b]^+$	$[Ce(NO_3)_2·(EtOH)]^+$	310
		$[Ce(NO_3)_2·(H_2O)·(EtOH)]^+$	328
		$[Ce(NO_3)_2·(H_2O)_2·(EtOH)]^+$	346
		$[Ce(NO_3)_2·(EtOH)_2]^+$	356
		$[Ce(NO_3)_2·(H_2O)_3·(EtOH)]^+$	364
		$[Ce(NO_3)_2·(H_2O)·(EtOH)_2]^+$	374
		$[Ce(NO_3)_2·(H_2O)_2·(EtOH)_2]^+$	392
		$[Ce(NO_3)_2·(EtOH)_3]^+$	402
		$[Ce(NO_3)_2·(H_2O)·(EtOH)_3]^+$	420
IV	$[Ce_a(NO_3)_b·(H_2O)_c·(EtOH)_d]^{x+}$	$[Ce_2(NO_3)_4·(H_2O)_3·(EtOH)_3]^{2+}$	360
		$[Ce_2(NO_3)_4·(H_2O)_5·(EtOH)_3]^{2+}$	378
VI	$[Ce(OH)_a·(NO_3)_b·(H_2O)_c·(EtOH)_d·(TOPO)_e]^{x+}$	$[Ce(OH)·(H_2O)_3·(TOPO)_3]^{2+}$	686
		$[Ce(OH)·(NO_3)·(H_2O)_5·(TOPO)]^+$	696
		$[Ce(OH)·(NO_3)·(H_2O)_6·(TOPO)]^+$	714

Table S5. Detected m/z and proposed molecular structures ($TOPO/Ce^{3+}$ = 0.8)

Categories	Molecular formula	Molecular structures	m/z
II	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^+$	$[Ce(OH)_2{\cdot}(H_2O){\cdot}(EtOH)_4]^+$	376
		$[Ce(OH)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_4]^+$	394
III	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b]^+$	$[Ce(NO_3)_2{\cdot}(EtOH)]^+$	310
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)]^+$	328
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)]^+$	346
		$[Ce(NO_3)_2{\cdot}(EtOH)_2]^+$	356
		$[Ce(NO_3)_2{\cdot}(H_2O)_3{\cdot}(EtOH)]^+$	364
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_2]^+$	374
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_2]^+$	392
		$[Ce(NO_3)_2{\cdot}(EtOH)_3]^+$	402
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_3]^+$	420
IV	$[Ce_a(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^{x+}$	$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)_3]^{2+}$	360
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_5{\cdot}(EtOH)_3]^{2+}$	378
		$[Ce_2(NO_3)_4{\cdot}(H_2O){\cdot}(EtOH)_5]^{2+}$	388
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)_5]^{2+}$	406
V	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b{\cdot}(TOPO)_c]^+$	$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH){\cdot}(TOPO)]^+$	715
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_8{\cdot}(TOPO)]^+$	1037
VI	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d{\cdot}(TOPO)_e]^{x+}$	$[Ce(OH){\cdot}(H_2O){\cdot}(TOPO)_3]^{2+}$	668
		$[Ce(OH){\cdot}(H_2O)_3{\cdot}(TOPO)_3]^{2+}$	686
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_5{\cdot}(TOPO)]^+$	696
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_6{\cdot}(TOPO)]^+$	714
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O){\cdot}(EtOH)_2{\cdot}(TOPO)]^+$	716
		$[Ce(OH){\cdot}(EtOH)_3{\cdot}(TOPO)_3]^{2+}$	728

Table S6. Detected m/z and proposed molecular structures (TOPO/Ce^{3+} = 1.2)

Categories	Molecular formula	Molecular structures	m/z
I	$[Ce_a(OH)_b{\cdot}(NO_3)_c{\cdot}(H_2O)_d{\cdot}(EtOH)_e]^+$	$[Ce_2(OH){\cdot}(NO_3)_4{\cdot}(EtOH)_4]^+$	729
II	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^+$	$[Ce(OH)_2{\cdot}(H_2O){\cdot}(EtOH)_4]^+$	376
		$[Ce(OH)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_4]^+$	394
III	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b]^+$	$[Ce(NO_3)_2{\cdot}(EtOH)]^+$	310
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)]^+$	328
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)]^+$	346
		$[Ce(NO_3)_2{\cdot}(EtOH)_2]^+$	356
		$[Ce(NO_3)_2{\cdot}(H_2O)_3{\cdot}(EtOH)]^+$	364
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_2]^+$	374
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_2]^+$	392
		$[Ce(NO_3)_2{\cdot}(EtOH)_3]^+$	402
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_3]^+$	420
IV	$[Ce_a(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^{x+}$	$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)_3]^{2+}$	360
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_5{\cdot}(EtOH)_3]^{2+}$	378
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)_5]^{2+}$	406
V	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b{\cdot}(TOPO)_c]^+$	$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(TOPO)]^+$	687
		$[Ce(NO_3)_2{\cdot}(EtOH){\cdot}(TOPO)]^+$	697
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH){\cdot}(TOPO)]^+$	715
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_8{\cdot}(TOPO)]^+$	1037
		$[Ce(NO_3)_2{\cdot}(TOPO)_2]^+$	1038
VI	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d{\cdot}(TOPO)_e]^{x+}$	$[Ce(OH){\cdot}(H_2O){\cdot}(TOPO)_3]^{2+}$	668
		$[Ce(OH){\cdot}(H_2O)_3{\cdot}(TOPO)_3]^{2+}$	686
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_2{\cdot}(EtOH){\cdot}(TOPO)]^+$	688
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_5{\cdot}(TOPO)]^+$	696
		$[Ce(OH){\cdot}(H_2O)_2{\cdot}(EtOH){\cdot}(TOPO)_3]^{2+}$	700
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_6{\cdot}(TOPO)]^+$	714
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O){\cdot}(EtOH)_2{\cdot}(TOPO)]^+$	716
		$[Ce(OH){\cdot}(EtOH)_3{\cdot}(TOPO)_3]^{2+}$	728
		$[Ce(OH){\cdot}(NO_3){\cdot}(EtOH){\cdot}(TOPO)_2]^+$	1039
		$[Ce(OH){\cdot}(EtOH)_3{\cdot}(TOPO)_5]^{2+}$	1115

Table S7. Detected m/z and proposed molecular structures (TOPO/Ce^{3+} = 1.6)

Categories	Molecular formula	Molecular structures	m/z
I	$[Ce_a(OH)_b{\cdot}(NO_3)_c{\cdot}(H_2O)_d{\cdot}(EtOH)_e]^+$	$[Ce_2(OH){\cdot}(NO_3)_4{\cdot}(EtOH)_4]^+$	729
		$[Ce_2(OH)_2{\cdot}(NO_3)_3{\cdot}(EtOH)_5]^+$	730
		$[Ce_3(OH){\cdot}(NO_3)_7{\cdot}(H_2O)_6{\cdot}(EtOH)_3]^+$	1117
II	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^+$	$[Ce(OH)_2{\cdot}(H_2O){\cdot}(EtOH)_4]^+$	376
III	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b]^+$	$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)]^+$	328
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)]^+$	346
		$[Ce(NO_3)_2{\cdot}(EtOH)_2]^+$	356
		$[Ce(NO_3)_2{\cdot}(H_2O)_3{\cdot}(EtOH)]^+$	364
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_2]^+$	374
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_2]^+$	392
		$[Ce(NO_3)_2{\cdot}(EtOH)_3]^+$	402
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_3]^+$	420
IV	$[Ce_a(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^{x+}$	$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)_5]^{2+}$	406
		$[Ce_3(NO_3)_8{\cdot}(H_2O)_6{\cdot}(EtOH)_2]^+$	1116
V	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b{\cdot}(TOPO)_c]^+$	$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(TOPO)]^+$	687
		$[Ce(NO_3)_2{\cdot}(EtOH){\cdot}(TOPO)]^+$	697
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH){\cdot}(TOPO)]^+$	715
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_8{\cdot}(TOPO)]^+$	1037
		$[Ce(NO_3)_2{\cdot}(TOPO)_2]^+$	1038
VI	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d{\cdot}(TOPO)_e]^{x+}$	$[Ce(OH){\cdot}(H_2O){\cdot}(TOPO)_3]^{2+}$	668
		$[Ce(OH){\cdot}(H_2O)_3{\cdot}(TOPO)_3]^{2+}$	686
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_5{\cdot}(TOPO)]^+$	696
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_6{\cdot}(TOPO)]^+$	714
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O){\cdot}(EtOH)_2{\cdot}(TOPO)]^+$	716
		$[Ce(OH){\cdot}(EtOH)_3{\cdot}(TOPO)_3]^{2+}$	728
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_5{\cdot}(EtOH){\cdot}(TOPO)]^+$	742
		$[Ce(OH){\cdot}(H_2O)_2{\cdot}(EtOH)_3{\cdot}(TOPO)_3]^{2+}$	746
		$[Ce(OH){\cdot}(H_2O){\cdot}(EtOH)_6{\cdot}(TOPO)_3]^{2+}$	806
		$[Ce(OH){\cdot}(NO_3){\cdot}(EtOH){\cdot}(TOPO)_2]^+$	1039
		$[Ce(OH){\cdot}(EtOH)_3{\cdot}(TOPO)_5]^{2+}$	1115

Table S8. Detected m/z and proposed molecular structures (TOPO/Ce^{3+} = 2.0)

Categories	Molecular formula	Molecular structures	m/z
I	$[Ce_a(OH)_b{\cdot}(NO_3)_c{\cdot}(H_2O)_d{\cdot}(EtOH)_e]^+$	$[Ce_2(OH){\cdot}(NO_3)_2{\cdot}(EtOH)_5]^{2+}$	334
		$[Ce_2(OH)_2{\cdot}(NO_3)_2{\cdot}(EtOH)_7]^{2+}$	380
		$[Ce_2(OH){\cdot}(NO_3)_4{\cdot}(EtOH)_3]^+$	683
		$[Ce_2(OH){\cdot}(NO_3)_4{\cdot}(H_2O){\cdot}(EtOH)_3]^+$	701
		$[Ce_2(OH)_2{\cdot}(NO_3)_3{\cdot}(H_2O){\cdot}(EtOH)_4]^+$	702
		$[Ce_2(OH){\cdot}(NO_3)_4{\cdot}(EtOH)_4]^+$	729
		$[Ce_2(OH)_2{\cdot}(NO_3)_3{\cdot}(EtOH)_5]^+$	730
		$[Ce_2(OH)_3{\cdot}(NO_3)_2{\cdot}(EtOH)_6]^+$	731
		$[Ce_2(OH){\cdot}(NO_3)_4{\cdot}(H_2O){\cdot}(EtOH)_4]^+$	747
		$[Ce_2(OH)_2{\cdot}(NO_3)_3{\cdot}(H_2O){\cdot}(EtOH)_5]^+$	748
		$[Ce_3(OH){\cdot}(NO_3)_7{\cdot}(H_2O)_6{\cdot}(EtOH)_3]^+$	1117
II	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^+$	$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_2{\cdot}(EtOH)]^+$	301
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O){\cdot}(EtOH)_2]^+$	329
		$[Ce(OH)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_3]^+$	348
		$[Ce(OH)_2{\cdot}(H_2O)_3{\cdot}(EtOH)_3]^+$	366
III	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b]^+$	$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)]^+$	328
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)]^+$	346
		$[Ce(NO_3)_2{\cdot}(H_2O)_3{\cdot}(EtOH)]^+$	364
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_2]^+$	374
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_2]^+$	392
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_3]^+$	420
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(EtOH)_3]^+$	438
IV	$[Ce_a(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d]^{x+}$	$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)]^{2+}$	314
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_5{\cdot}(EtOH)]^{2+}$	332
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_7{\cdot}(EtOH)]^{2+}$	350
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)_3]^{2+}$	360
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_5{\cdot}(EtOH)_3]^{2+}$	378
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_6{\cdot}(EtOH)_3]^{2+}$	387
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_7{\cdot}(EtOH)_3]^{2+}$	396
		$[Ce_2(NO_3)_4{\cdot}(H_2O)_3{\cdot}(EtOH)_5]^{2+}$	406
		$[Ce_3(NO_3)_8{\cdot}(H_2O)_6{\cdot}(EtOH)_2]^+$	1116
		$[Ce_3(NO_3)_8{\cdot}(H_2O){\cdot}(EtOH)_4]^+$	1118
V	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b{\cdot}(TOPO)_c]^+$	$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(TOPO)]^+$	669
		$[Ce(NO_3)_2{\cdot}(H_2O)_2{\cdot}(TOPO)]^+$	687
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH){\cdot}(TOPO)]^+$	715
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_3{\cdot}(TOPO)]^+$	807
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_8{\cdot}(TOPO)]^+$	1037
		$[Ce(NO_3)_2{\cdot}(TOPO)_2]^+$	1038
VI	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d{\cdot}(TOPO)_e]^{x+}$	$[Ce(OH){\cdot}(H_2O){\cdot}(TOPO)_3]^{2+}$	668
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O){\cdot}(EtOH){\cdot}(TOPO)]^+$	670
		$[Ce(OH){\cdot}(EtOH){\cdot}(TOPO)_3]^{2+}$	682
		$[Ce(OH){\cdot}(H_2O)_3{\cdot}(TOPO)_3]^{2+}$	686

	$[Ce(OH)\cdot(NO_3)\cdot(H_2O)_2\cdot(EtOH)\cdot(TOPO)]^+$	688
	$[Ce(OH)\cdot(NO_3)\cdot(H_2O)_5\cdot(TOPO)]^+$	696
	$[Ce(OH)\cdot(H_2O)_2\cdot(EtOH)\cdot(TOPO)_3]^{2+}$	700
	$[Ce(OH)\cdot(H_2O)_5\cdot(TOPO)_3]^{2+}$	704
	$[Ce(OH)\cdot(NO_3)\cdot(H_2O)_6\cdot(TOPO)]^+$	714
	$[Ce(OH)\cdot(EtOH)_3\cdot(TOPO)_3]^{2+}$	728
	$[Ce(OH)\cdot(H_2O)_2\cdot(EtOH)_3\cdot(TOPO)_3]^{2+}$	746
	$[Ce(OH)\cdot(H_2O)\cdot(EtOH)_6\cdot(TOPO)_3]^{2+}$	806
	$[Ce(OH)\cdot(NO_3)\cdot(H_2O)\cdot(EtOH)_4\cdot(TOPO)]^+$	808
	$[Ce(OH)\cdot(NO_3)\cdot(EtOH)\cdot(TOPO)_2]^+$	1039
	$[Ce(OH)_2\cdot(EtOH)_2\cdot(TOPO)_2]^+$	1040
	$[Ce(OH)\cdot(EtOH)_3\cdot(TOPO)_5]^{2+}$	1115

Table S9. Detected m/z and proposed molecular structures (TOPO/Ce^{3+} = 3.0)

Categories	Molecular formula	Molecular structures	m/z
III	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b]^+$	$[Ce(NO_3)_2{\cdot}(H_2O)_{10}{\cdot}(EtOH)_2]^+$	536
V	$[Ce(NO_3)_2{\cdot}(H_2O)_a{\cdot}(EtOH)_b{\cdot}(TOPO)_c]^+$	$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH){\cdot}(TOPO)]^+$	715
		$[Ce(NO_3)_2{\cdot}(H_2O){\cdot}(EtOH)_8{\cdot}(TOPO)]^+$	1037
		$[Ce(NO_3)_2{\cdot}(TOPO)_2]^+$	1038
VI	$[Ce(OH)_a{\cdot}(NO_3)_b{\cdot}(H_2O)_c{\cdot}(EtOH)_d{\cdot}(TOPO)_e]^{x+}$	$[Ce(OH){\cdot}(H_2O)_5{\cdot}(EtOH)_4{\cdot}(TOPO)]^{2+}$	409
		$[Ce(OH){\cdot}(H_2O)_3{\cdot}(TOPO)_3]^{2+}$	686
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_5{\cdot}(TOPO)]^+$	696
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O)_6{\cdot}(TOPO)]^+$	714
		$[Ce(OH){\cdot}(NO_3){\cdot}(H_2O){\cdot}(EtOH)_2{\cdot}(TOPO)]^+$	716
		$[Ce(OH){\cdot}(NO_3){\cdot}(EtOH){\cdot}(TOPO)_2]^+$	1039
		$[Ce(OH)_2{\cdot}(EtOH)_2{\cdot}(TOPO)_2]^+$	1040
		$[Ce(OH){\cdot}(EtOH)_3{\cdot}(TOPO)_5]^{2+}$	1115