

## Supporting Information for

# Introduction of Amino Groups into Acid-resistant MOFs for Enhanced U(VI) Sorption

Zhi-Qiang Bai<sup>a,b</sup>, Li-Yong Yuan<sup>b</sup>, Lin Zhu<sup>b</sup>, Zhi-Rong Liu<sup>a\*</sup>, Sheng-Qi Chu<sup>c</sup>,  
Li-Rong Zheng<sup>c</sup>, Jing Zhang<sup>c</sup>, Zhi-Fang Chai<sup>d</sup>, Wei-Qun Shi<sup>b\*</sup>

<sup>a</sup> School of Nuclear Engineering and Geophysics, East China Institute of Technology, Nanchang 330013, China

<sup>b</sup> Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

<sup>d</sup> School of Radiological & Interdisciplinary Sciences, Soochow University, Suzhou 215123, China

Corresponding information:

Prof. Dr. Wei-Qun Shi

Tel: 86-10-88233968; E-mail: [shiwq@ihep.ac.cn](mailto:shiwq@ihep.ac.cn);

And Prof. Dr. Zhi-Rong Liu

E-mail: [zhrliu@ecit.cn](mailto:zhrliu@ecit.cn)

### SI-1 U(VI) sorption experiments

In a typical experiment, 4 mg of sorbent was added into either 10 mL U(VI) solution or 10 ml multi-ion test solution in a flask (the solid-liquid ratio is thus 0.4 g/L). The flasks were stirred for specified time ( $t$ , min) at room temperature, and then the solid phase was separated from the solution by using a 0.22  $\mu\text{m}$  nylon membrane filter. Before the determination, the initial solution and the supernatants, before and after the sorption, was diluted appropriate times for the concentration analysis. The concentrations of metal ions in the supernatant were determined by UV-Visible spectrometry for U(VI) and inductively coupled plasma optical emission spectrometer (ICP-OES) for the multi-ion solution. All values were measured in duplicate with the uncertainty within 5%.

### SI-2 The sorption data fitting by kinetic models

In order to clarify the sorption process of U(VI) in the prepared MOFs, the pseudo-first-order kinetic model and the pseudo-second-order kinetic model were applied to analyze the experimentally observed kinetic data. The linear forms of the two models are expressed as follows, respectively.

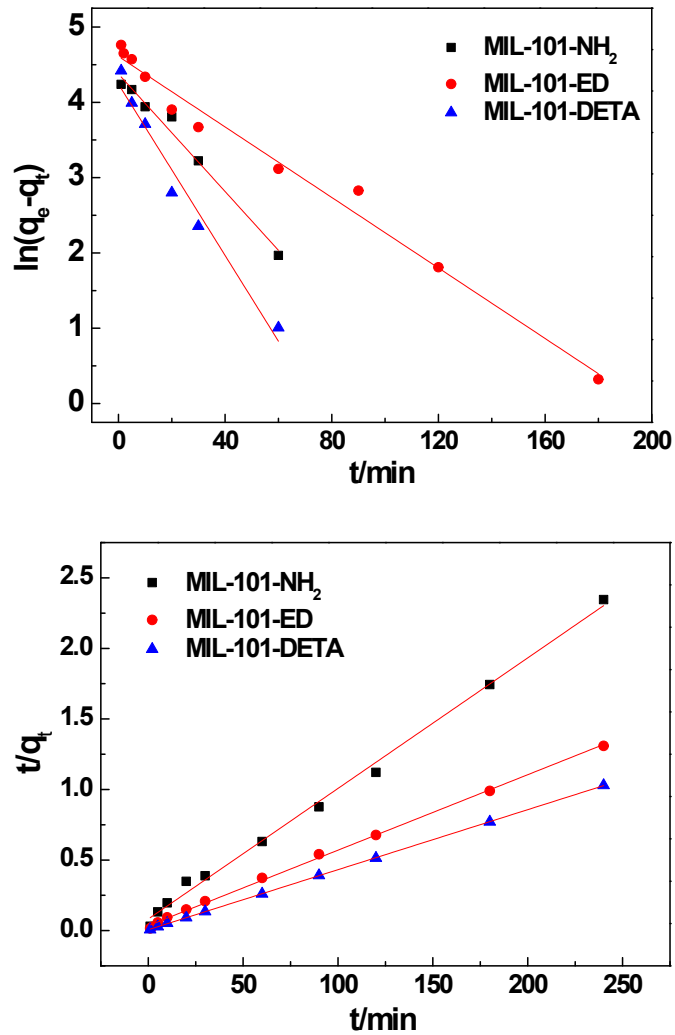
The pseudo-first-order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (\text{S1})$$

The pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (\text{S2})$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the quantities of the sorbed U(VI) at equilibrium and at time  $t$  respectively,  $k_1$  (1/min) and  $k_2$  (g/(mg·min)) are the pseudo-first-order and pseudo-second-order sorption rate constants. The plot of  $\log(q_e - q_t)$  versus  $t$  and  $t/q_t$  versus  $t$  give straight line (Fig. S1), and  $k_1$  and  $k_2$  can be calculated from the slope. The model parameters and the correlation coefficient obtained by both the models are shown in Table S1.



**Fig. S1** The pseudo-first-order kinetic model (top) and pseudo-second-order kinetic model (bottom) linearized plots for U(VI) sorption on MIL-101-NH<sub>2</sub>, MIL-101-ED, and MIL-101-DETA.

**Table S1** The kinetic parameters for the U(VI) sorption on MIL-101-NH<sub>2</sub>, MIL-101-ED, and MIL-101-DETA.

	pseudo-first-order kinetic model			pseudo-second-order kinetic model		
	$q_e(\text{mg g}^{-1})$	$K_1(\text{min}^{-1})$	$R^2$	$q_e(\text{mg g}^{-1})$	$K_2(\text{g mg}^{-1} \text{min}^{-1})$	$R^2$
MIL-101-NH <sub>2</sub>	80	0.039	0.979	101	0.001	0.996
MIL-101-ED	101	0.023	0.983	187	0.0008	0.999
MIL-101-DETA	70	0.057	0.966	235	0.0029	0.9999

### SI-3 The sorption data fitting by Isotherm models

The Langmuir model assumes that the sorption of metal ions occurs on a homogenous surface by monolayer sorption and there no interaction between adsorbed ions, with homogeneous binding sites and equivalent sorption energies. The linear equation of the Langmuir isotherm model is expressed as followed:

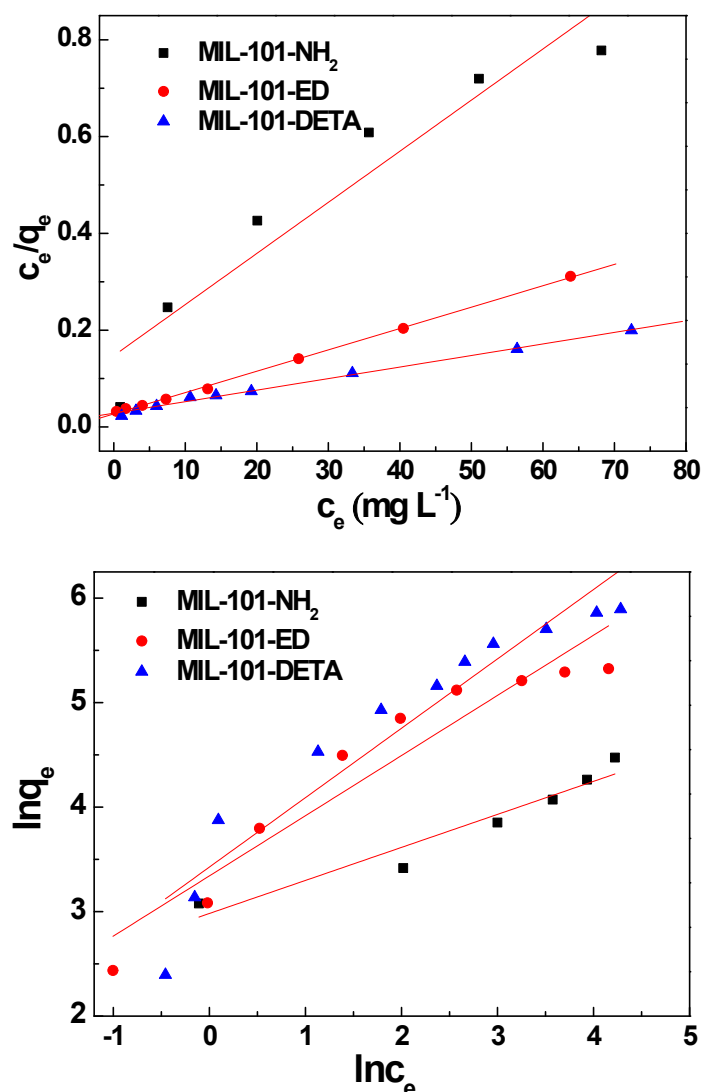
$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \quad (\text{S3})$$

where  $q_m$  is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g) and  $k_L$  is a constant indirectly related to sorption capacity and energy of sorption (L/mg), which characterizes the affinity of the adsorbate with the adsorbent. The linearized plot (Fig. S2) was obtained when we plotted  $c_e/q_e$  against  $c_e$  and  $q_m$  and  $k_L$  (Table S2) could be calculated from the slope and intercept.

The Freundlich equation is an empirical equation with the assumption of sorption on a heterogeneous surface. The linear equation can be expressed by:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \quad (\text{S4})$$

where  $k_F$  and  $n$  are the Freundlich constants related to the sorption capacity and the sorption intensity, respectively. The linear plot was obtained by plotting  $\ln q_e$  against  $\ln c_e$ , and the values of  $k_F$  and  $n$  were calculated from the slope and intercept of the straight line.

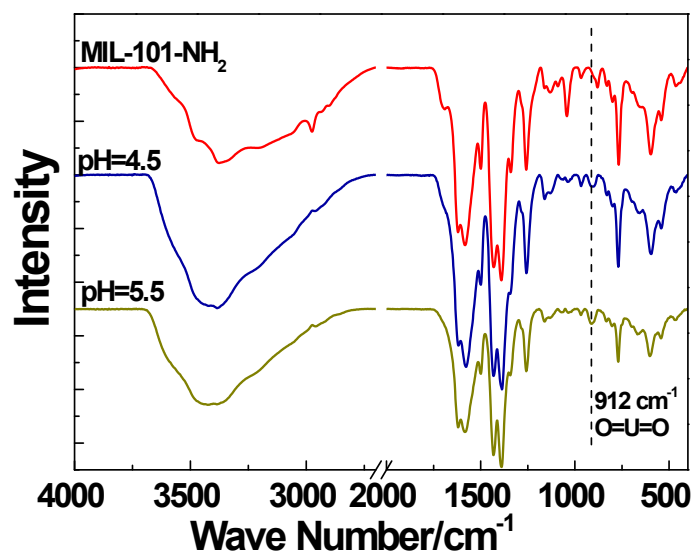


**Fig. S2** Langmuir isotherm (top) and Freundlich isotherm (bottom) models linearized plots for U(VI) sorption on MIL-101-NH<sub>2</sub>, MIL-101-ED, and MIL-101-DETA.

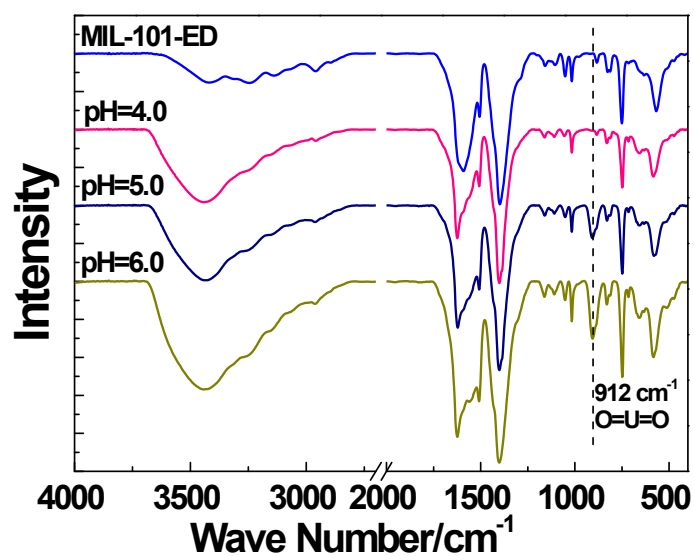
**Table S2** The sorption isotherm parameters for the U(VI) sorption on MIL-101-NH<sub>2</sub>, MIL-101-ED, and MIL-101-DETA.

	Langmuir			Freundlich		
	$q_m(\text{mg g}^{-1})$	$K_L(\text{L mg}^{-1})$	$R^2$	$k_F(\text{mg g}^{-1})$	$n$	$R^2$
MIL-101-NH <sub>2</sub>	95	0.0717	0.896	20	3.164	0.918
MIL-101-ED	229	0.1483	0.996	28	1.737	0.906
MIL-101-DETA	410	0.0673	0.997	31	1.506	0.900

#### SI-4 Comparison of FTIR spectra of the sorbents before and after U(VI) sorption



**Fig. S3** FTIR spectra of MIL-101-NH<sub>2</sub> before and after U(VI) sorption at various pH



**Fig. S4** FTIR spectra of MIL-101-ED before and after U(VI) sorption at various pH.

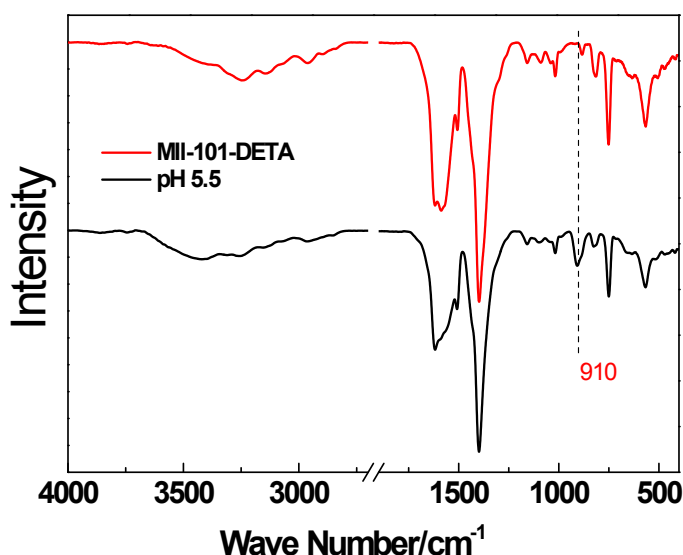


Fig. S5 FTIR spectra of MIL-101-DETA before and after U(VI) sorption

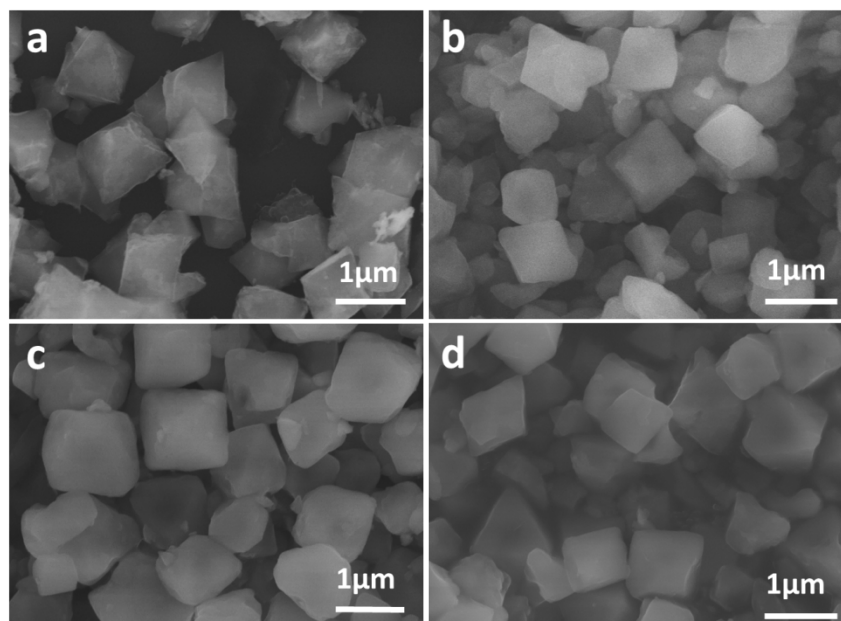
### SI-5 Extended X-ray absorption fine structure (EXAFS) measurements

The samples of U(VI)-loaded MOFs for EXAFS measurement were prepared at the same conditions used in a typical sorption experiments. After sorption processes, the samples were centrifuged at 10000 rpm for 1 hr to concentrate the solid phases. The sediments were then mounted in holes machined in Teflon sample holders, sealed with Kapton tape, and subjected to EXAFS measurements. The reference sample of U(VI) hydroxide precipitate was prepared in air by slow titration of a  $\text{UO}_2(\text{NO}_3)_2$  solution with  $\text{NH}_4\text{OH}$ .

The EXAFS spectra at the U-L<sub>III</sub> edge (17,166 eV) were recorded in fluorescence mode in the range of 17.0 ~17.9 keV, using synchrotron radiation at the beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF). A silicon (111) double-crystal monochromator was used to tune the incident X-ray beam to the desired energies. An yttrium foil (K-edge 17,038 eV) was simultaneously measured in transmission mode for energy calibration of the monochromator. At least four spectra of each sample were measured using a lytle-type ion chamber detector and then averaged. Raw EXAFS oscillations were pre-edge background subtracted, spline-fit, and normalized using the Athena software to obtain Fourier transform spectra. Rbkg 1.2 was used to optimize the atomic background function ( $\mu_0(E)$ ) using the autobk utility. To extract metric parameters (neighboring atomic distances (R), EXAFS Debye-Waller factors ( $\sigma^2$ ), coordination numbers (N)) from the EXAFS, the theoretical phase shift and amplitude functions for single and double scattering paths are calculated by the program FEFF6 and optimized as implemented in the FEFFIT code using the model structure of  $[\text{UO}_2][\text{NH}_2]_2\text{O}_2[\text{H}_2\text{O}]_3$ . Prior to analysis, the  $k^3$ -weighted EXAFS spectra are Fourier transformed

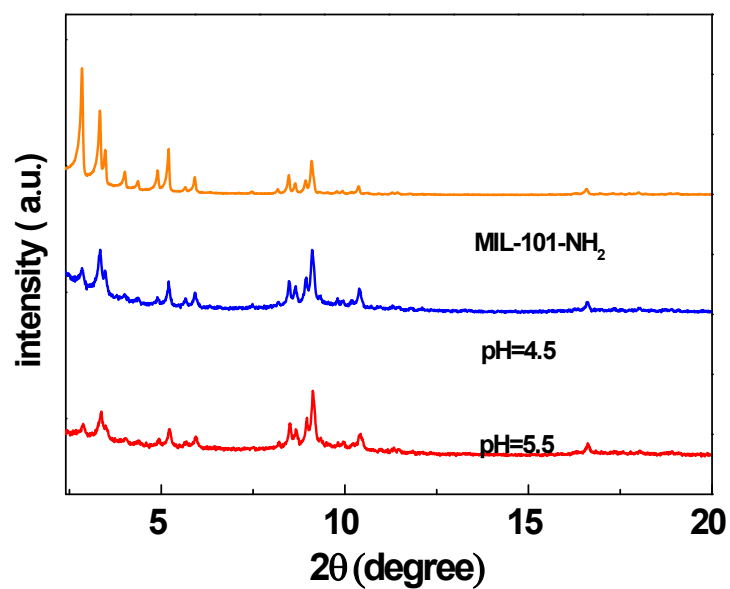
over a k-space range of  $\sim 3.7\text{-}14.3 \text{ \AA}^{-1}$ . All the fitting operations are performed in R-space of  $\sim 1.0 - 3.0 \text{ \AA}$ .

### SI-6 SEM images of the sorbents after U(VI) sorption



**Fig. S6** SEM images of (a) MIL-101, (b) MIL-101-NH<sub>2</sub>, (c) MIL-101-ED, and (d) MIL-101-DETA after U(VI) sorption.

### SI-7 Comparison of XRD patterns of the sorbents before and after U(VI) sorption



**Fig. S7** XRD patterns of MIL-101-NH<sub>2</sub> before and after U(VI) sorption at various pH.

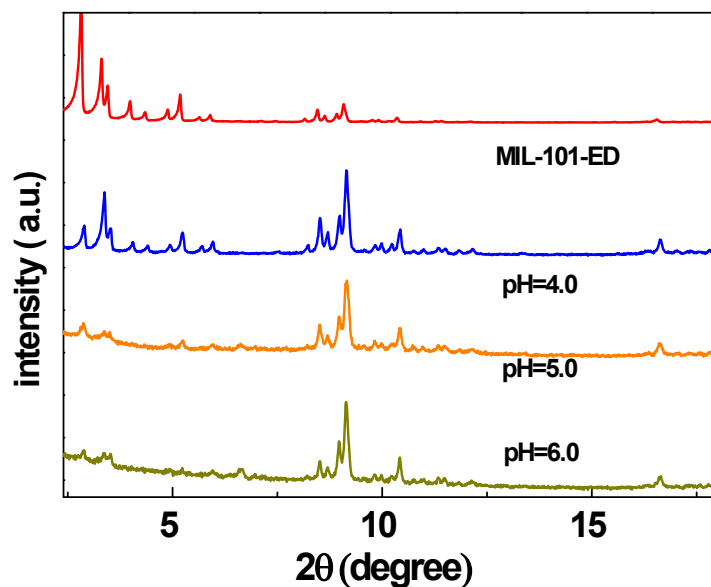


Fig. S8 XRD patterns of MIL-101-ED before and after U(VI) sorption at various pH.

### SI-8 Selectivity test

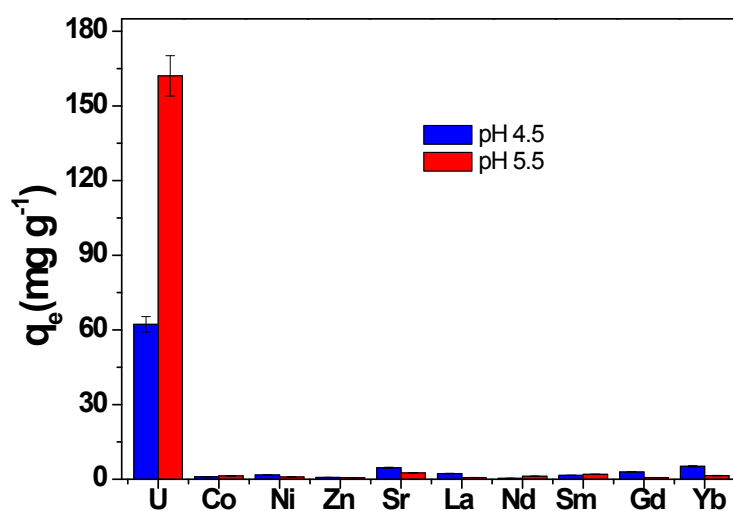


Fig. S9. Competitive sorption of coexistent ions on MIL-101-ED at pH 4.5 and 5.5. The initial concentration of all metal ions was 0.5 mmol L<sup>-1</sup>.

Table S3. Compositions of the coexistent ions solution

Coexistent ion	Reagent	Reagent purity
U	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Standard reagent
Co	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	AR
Ni	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	AR
Zn	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	AR
Sr	Sr(NO <sub>3</sub> ) <sub>2</sub>	AR
La	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	AR
Nd	Nd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	AR
Sm	Sm(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	99.9% metal basis
Gd	Gd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	AR
Yb	Yb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	99.9% metal basis