Supporting Information for

Extraction of Lanthanide and Actinide Ions from Aqueous Mixtures Using a Carboxylic Acid-Functionalized Porous Aromatic Framework

Selvan Demir,[a,c,‡] Nicholas K. Brune,[a,c,‡] Jeffrey F. Van Humbeck,[a,1] Jarad A. Mason,[a] Tatiana V. Plakhova,[c,f] Shuao Wang,[a,c,2] Guoxin Tian,[c,h] Stefan G. Minasian,[c] Tolek Tyliszczak,[e] Tsuyoshi Yaita,[g] Tohru Kobayashi,[g] Stepan N. Kalmykov,[f] Hideaki Shiwaku,[g] David K. Shuh,[c] Jeffrey R. Long[a,b,d]*

[a]Departments of Chemistry and [b]Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA

[c]Chemical Sciences Division, [d]Materials Sciences Division, and [e]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA

[f]Chemistry Department, Lomonosov Moscow State University, Leninskie Gory, Moscow 11991, Russia

[g]Actinide Chemistry Group, Energy and Environment Science Division, Quantum Beam Science Center, Japan Atomic Energy Agency,1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

[h]Radiochemistry Department, China Institute of Atomic Energy, Beijing 102413, China.

ACS Central Science

Table of Contents

Figure S1. IAST: Amounts Adsorbed from 0.1 and 1 mM Nd^{3+}/Fe^{3+} mixture 3

Figure S2. IAST: Amounts Adsorbed from 0.1 and 1 mM Sr^{2+}/Fe^{3+} mixture 4

Figure S3. IAST: Amounts Adsorbed from 0.1 and 1 mM Nd^{3+}/Sr^{2+} mixture 5

Figure S4. a) K-edge XANES spectra
b) Schematic of possible Nd interactions with BPP-7. 6

Figure S5. XAFS Fitting Details 7

Figure S6. Carbon K-edge for Nd-BPP-7 8

Figure S7. Oxygen K-edge for Nd-BPP-7 8

Figure S8. Nd $M_{5,4}$-edge for Nd-BPP-7 8

Figure S9. Infrared spectrum of the unloaded BPP-7 and the neodymium-loaded combustion product. 9

References 10

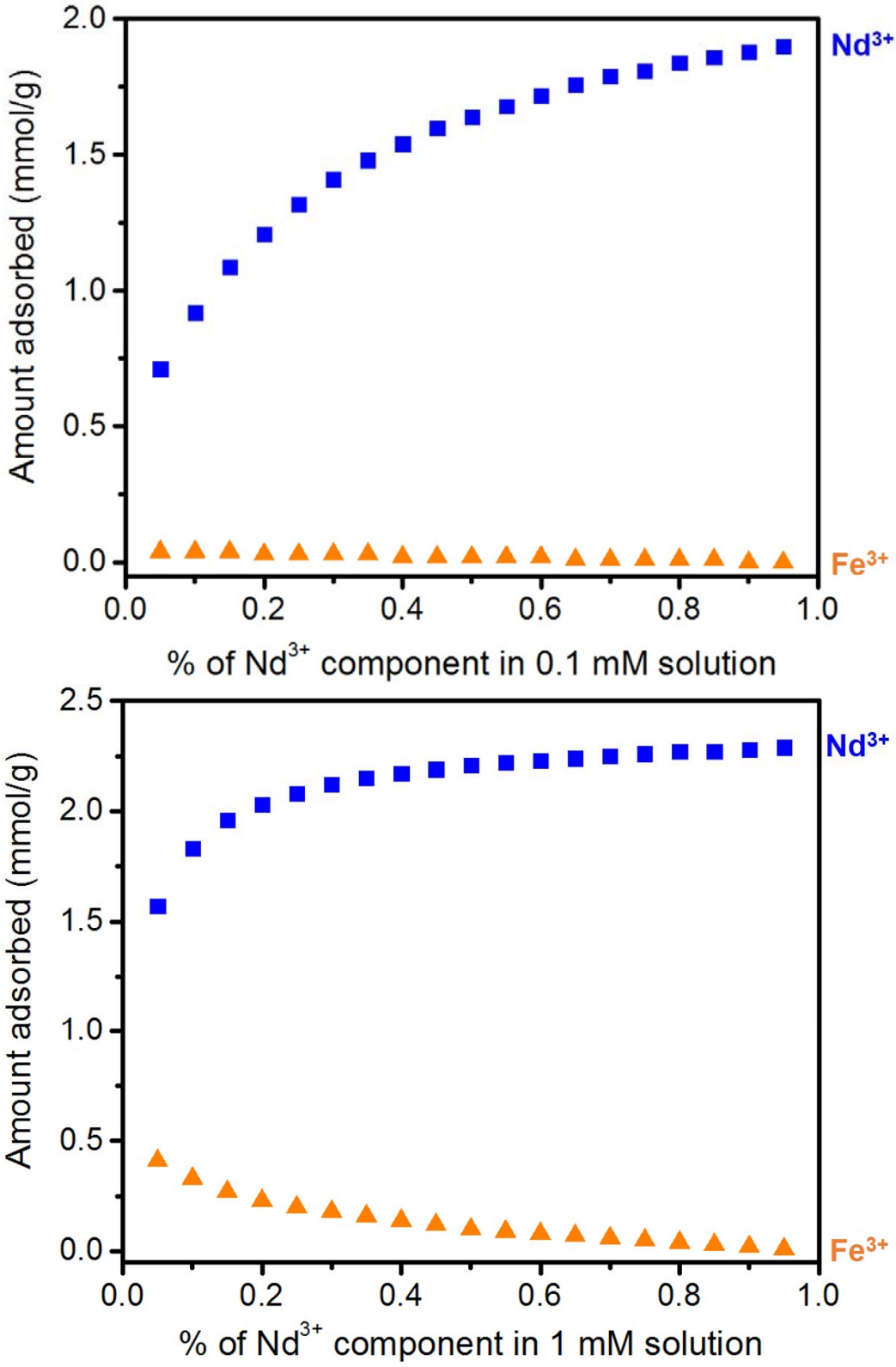


Figure S1. Ideal adsorbed solution theory (IAST): Amounts adsorbed from 0.1 mM (top) and 1 mM (bottom) Nd^{3+}/Fe^{3+} mixtures (Nd^{3+} = blue squares; Fe^{3+} = orange triangles).

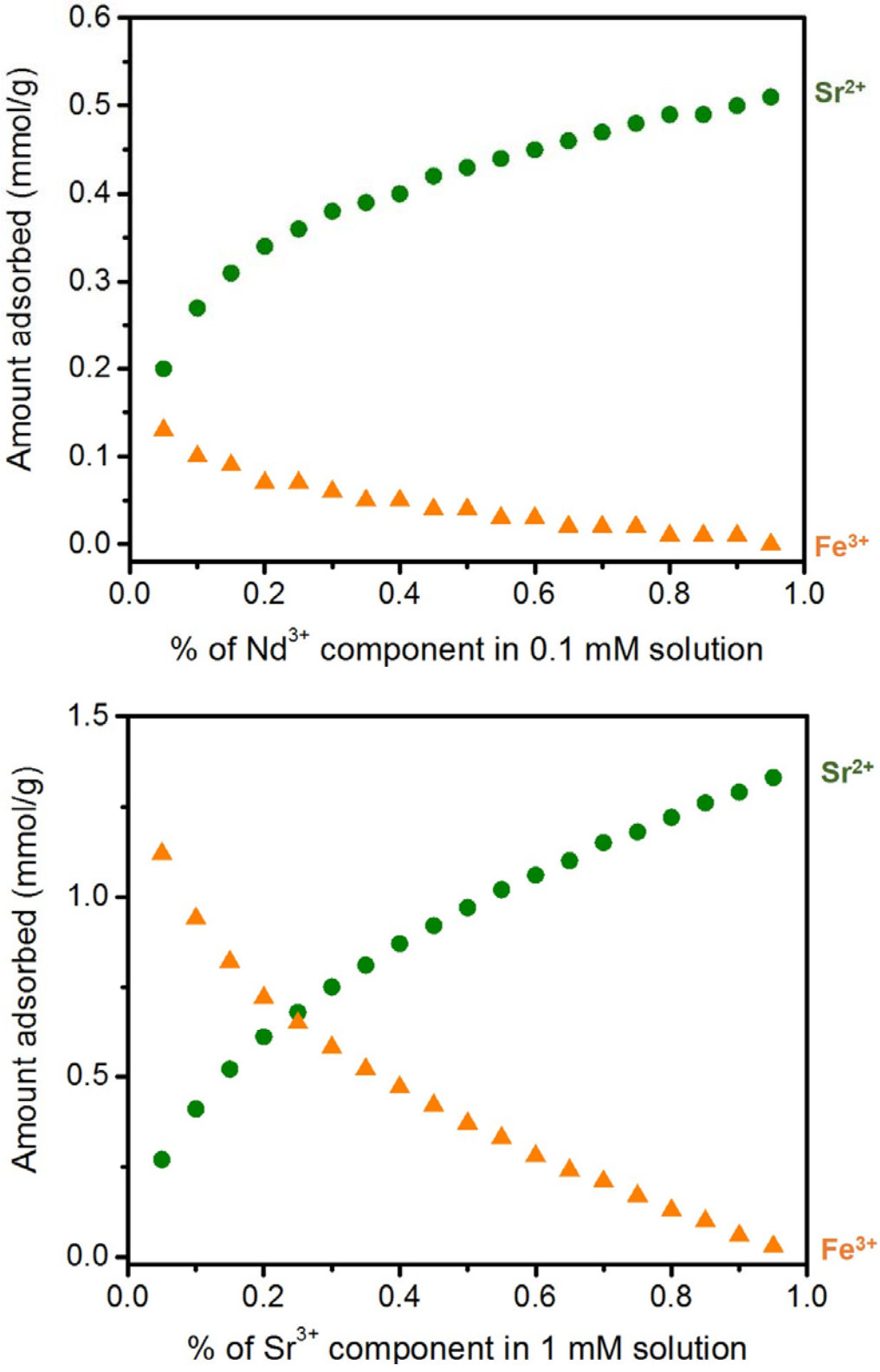


Figure S2. Ideal adsorbed solution theory (IAST): Amounts Adsorbed from 0.1 mM (top) and 1 mM (bottom) Sr^{2+}/Fe^{3+} mixtures (Sr^{2+} = green circles; Fe^{3+} = orange triangles).

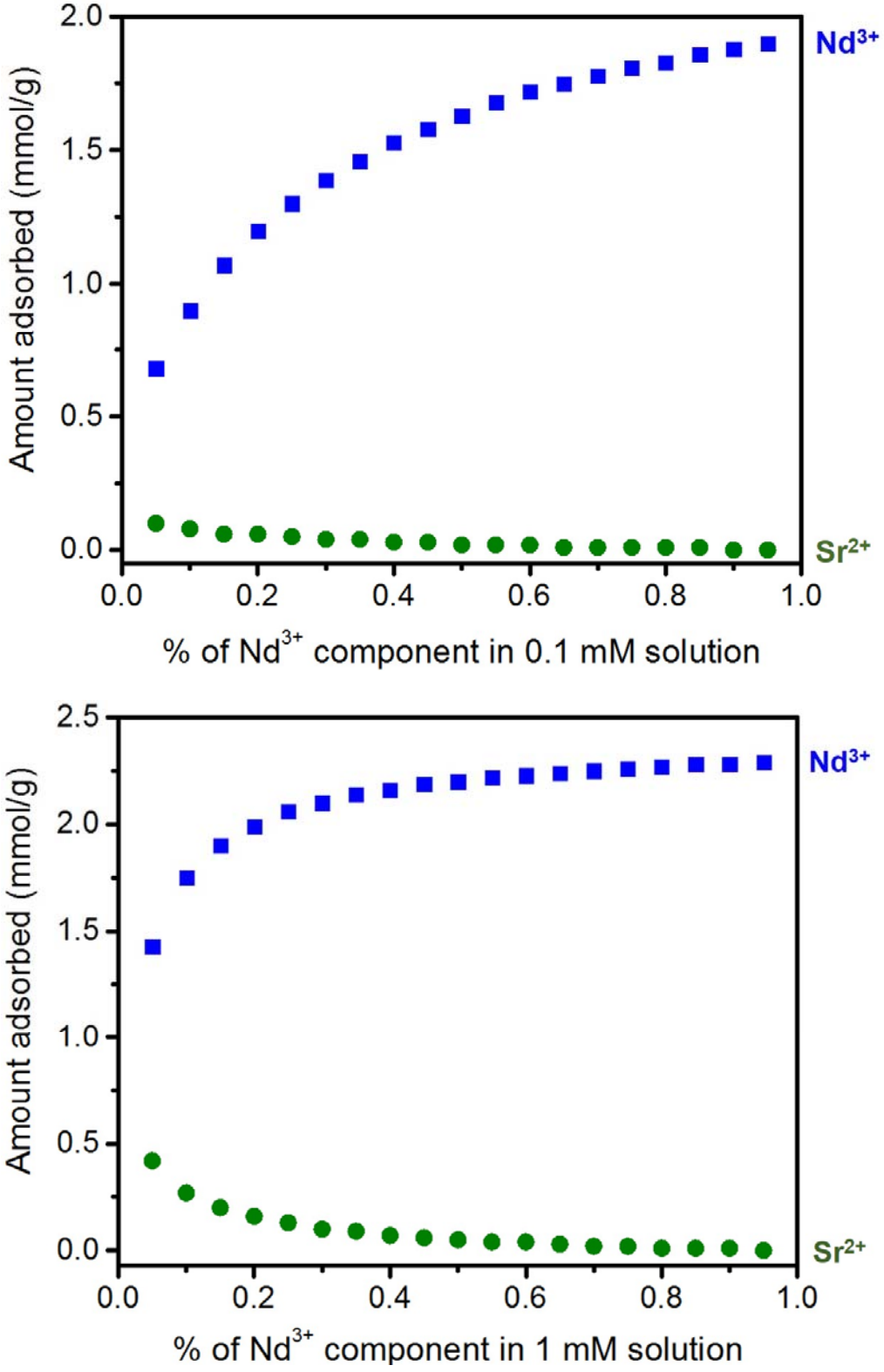
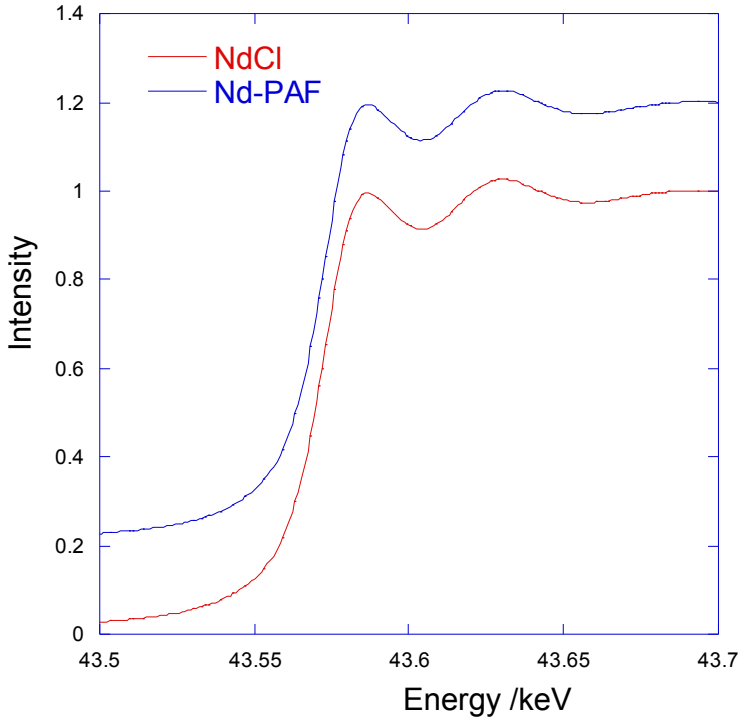
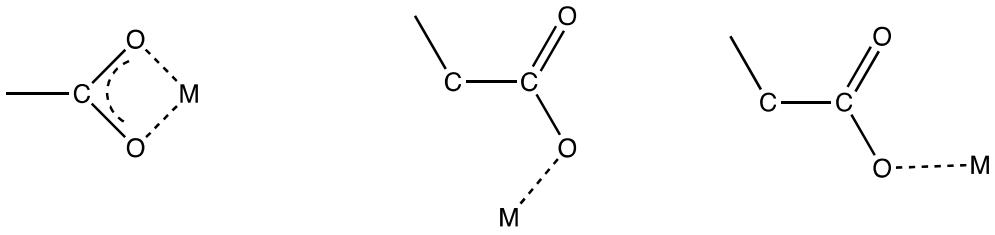


Figure S3. Ideal adsorbed solution theory (IAST): Amounts adsorbed from 0.1 mM (top) and 1 mM (bottom) Nd^{3+}/ Sr^{2+} mixtures (Nd^{3+} = blue squares; Sr^{2+} = green circles).



a



Bidentate
M-O_1: ~2.42 Å

Monodentate
M-O_1: ~2.48 Å (range 2.43-2.53 Å)

OH_2----M

Hydrated
M-O_1: ~2.48 Å

b

Figure S4. (a) Comparison of the K-edge XANES spectra collected from the Nd-BPP-7 and an aqueous neodymium(III) chloride solution (NdCl) that confirms the oxidation state of Nd in the Nd-BPP-7 as trivalent. (top) (b) Schematic of possible Nd interactions with BPP-7. Distances are from Ref.[1-4] (bottom)

XAFS Fitting Details

The parameters for the back scattering factors and phase shift were calculated Feff8.0 code.[5] The input file for the Feff calculation was prepared based on the model compound shown in Fig. S5: derived from SRef.[6] Since the coordination site for Nd is the carboxylate group, the nearest oxygen parameter calculated was utilized for the first shell fitting; and as a result, that the M-O bond distance as 2.48 Å was successfully obtained.

The residual second shell fitting was performed by the parameter of carbon or oxygen located around 3 Å, and then could obtain the bond distance about 3.3 Å and relatively large Debye-Waller factor of about 0.02. During all the fittings, the coordination number (N), Debye-Waller factor (DWF), and damping factor (S_0) were constrained from 6-12, 0.001-0.1 $Å^2$, and 0.8-1, respectively.

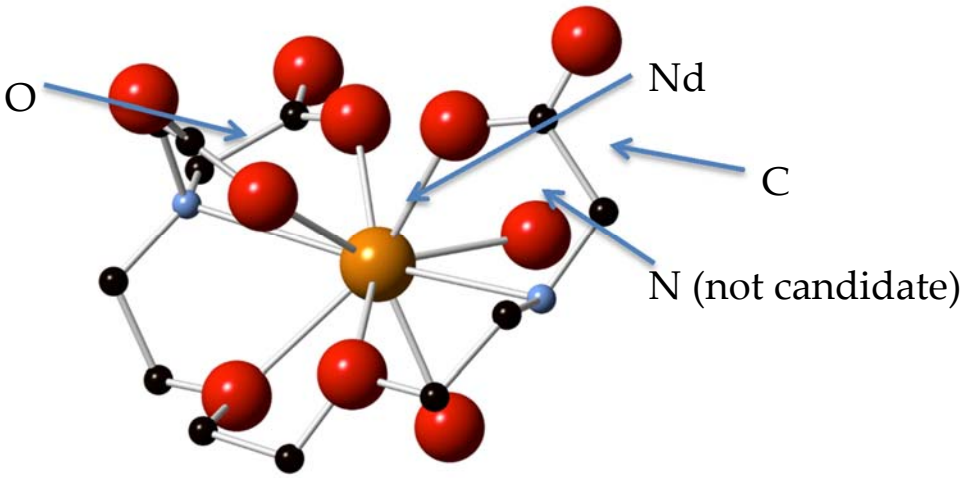


Figure S5. Model compound for calculation of the EXAFS fitting parameters.[6]

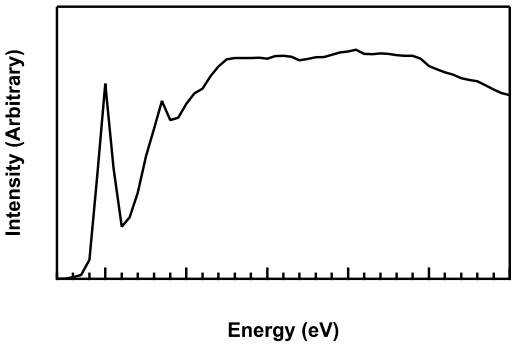


Figure S6. Carbon K-edge for Nd-BPP-7

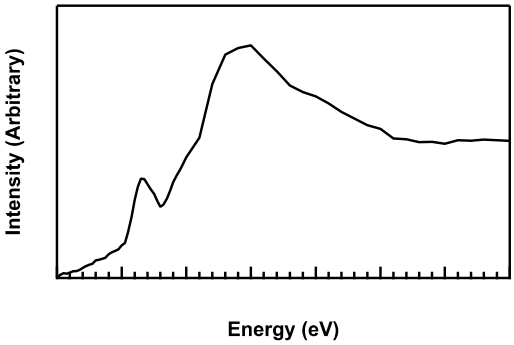


Figure S7. Oxygen K-edge for Nd-BPP-7

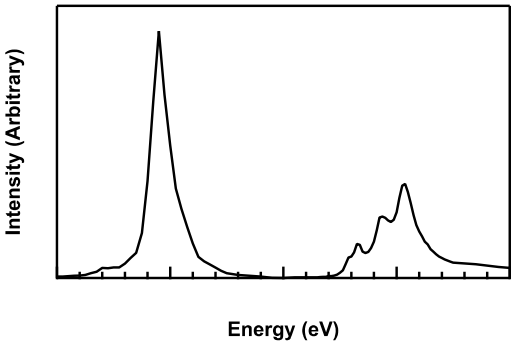


Figure S8. Nd $M_{5,4}$-edge for Nd-BPP-7

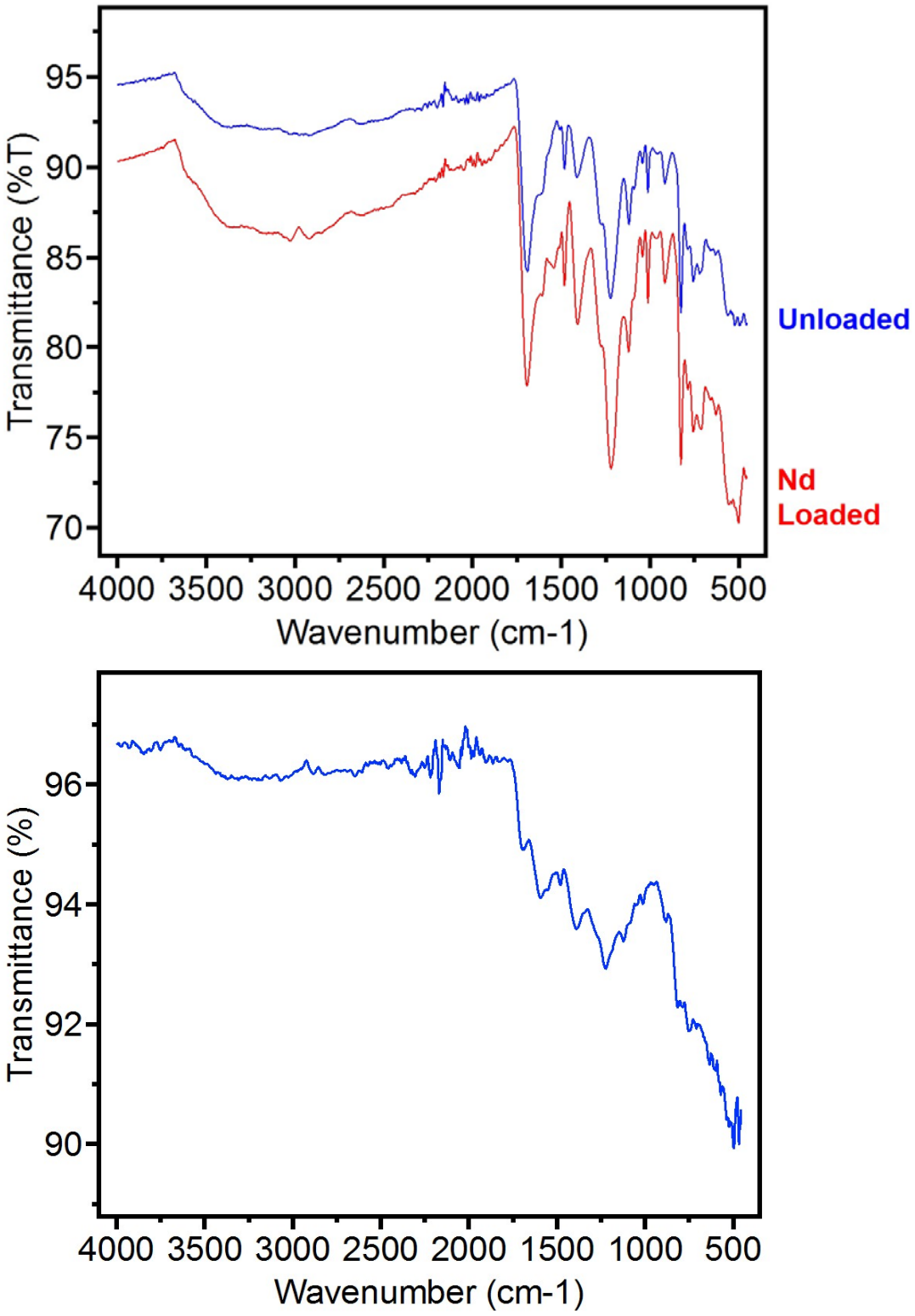


Figure S9. Top: Infrared spectrum of the unloaded BPP-7 (blue) and the neodymium-loaded BPP-7 (red). Bottom: Neodymium-loaded combustion product (blue).

References

1. Tang, X.; Yue, S.; Li, P.; Wang, N.; Liu, Y. Hydrothermal synthesis and crystal structure study of two novel 3-D mellitates $\{Nd_2[C_6(COO)_6](H_2O)_6\}$ and $\{Ho_2[C_6(COO)_6](H_2O)_6\}$. *J. Rare Earth* **2008**, *26*, 800-803.
2. Huskowska, E.; Legendziewicz, J.; Schleid, T.; Meyer, G. A Special Double Issue Devoted to the Workshop on the Basic and Applied Aspects of Rare Earths do the Lanthanides Form Inner Sphere Complexes with ClO_4^- Ions in Competition with H_2O Molecules? *Mater. Chem. Phys.* **1992**, *31*, 117-122.
3. Csoregh, I.; Huskowska, E.; Ertan, A.; Legendziewicz, J.; Kierkegaard, P. Crystal Structure of a Novel Neodymium Hydroxide Perchlorate Hydrate, $Nd_2(OH)_3(ClO_4)3.5H_2O$. *Acta Chem. Scand.* **1989**, 829-833.
4. Mondry, A.; Starynowicz, P. Crystal Structure and Absorption Spectroscopy of a Neodymium(III) Complex with Triethylenetetraaminehexaacetic Acid, $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$. *Inorg. Chem.* **1997**, *36*, 1176-1180.
5. Ankudinov, A. L.; Rehr, J. J. Theory of solid-state contributions to the X-ray elastic scattering amplitude. *Phys. Rev. B* **2000**, *62*, 2437-2445.
6. Schauer, C. K.; Anderson, O. P. Highly polydentate ligands. Part 4. Crystal structures of neodymium(III) and erbium(III) complexes of 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioate(4-). *J. Chem. Soc., Dalton Trans.* **1989**, 185-191.