Electronic Supplementary Information

Preparation of New Microporous Europium Silicate Molecular

Sieve by Selective Leaching of Alkali Metal Cations of Europium

Silicate Eu-AV-9

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Experimental Details

Analysis of the reagent EuCl₃·6H₂O

The XPS spectrum of EuCl₃·6H₂O (Fig. S7) shows that EuCl₃·6H₂O contains 22% of Eu²⁺, though Eu²⁺ may be locally distributed. The presence of Eu²⁺ in the starting reagent EuCl₃·6H₂O was previously reported.¹ On the other hand, the Cl/Eu ratio estimated by ICP analysis and ion chromatography was determined to be 3, and the value is consistent with the ratio calculated from the chemical formula of EuCl₃·6H₂O. This can be interpreted by assuming that one of the water molecules coordinated to Eu²⁺ is H₃O⁺,² suggesting that the reagent EuCl₃·6H₂O is composed of 78% EuCl₃·6H₂O and 22% EuCl₃·5H₂O(H₃O).

Data



Figure S1 N₂ adsorption-desorption isotherms of Eu-AV-9.



Figure S2 Powder XRD pattern and the Rietveld refinement of Eu-AV-9.



Figure S3 TG-DTA curves of Eu-AV-9 (top: TG curve, bottom: DTA curve).



Figure S4 SEM images of Eu-AV-9.



Figure S5 Eu 4d XPS profiles of a) Eu-AV-9, b) Ac1-Eu-AV-9, and c) Ac14-Eu-AV-9.



Figure S6 Eu 4d XPS spectrum of EuCl₃·6H₂O.



Figure S7 FT-IR spectra of a) Eu-AV-9, b) Ac1-Eu-AV-9 and c) Ac14-Eu-AV-9. The O– H stretching vibrations were observed around 3400–3700 cm⁻¹ and H–O–H deformation vibration was observed at 1640 cm⁻¹, which indicates the presence of hydrated water.³ The band around 1000 cm⁻¹ was assigned to Si–O–Si (possibly including Si–O–Eu) stretching vibration in Eu-AV-9, Ac1-Eu-AV-9, and Ac14-Eu-AV-9.⁴



Figure S8 STEM-EDS mapping images of Eu-AV-9. (a) STEM image, and (b) Eu, (c) K, (d) Na, (e) O, and (f) Si mapping images.



Figure S9 TEM image and ED pattern of the sample treated for 14 d of acid treatment at the higher acetic acid concentration (ED pattern was obtained from the area shown by the white dot circle in the TEM image).



Figure S10 PDF analysis of (a) Eu-AV-9 and (b) Ac14-Eu-AV-9.



Figure S11 SEM images of Ac1-Eu-AV-9.



Figure S12 SEM images of Ac14-Eu-AV-9.



Figure S13 STEM-EDS mapping images of Ac14-Eu-AV-9. (a) STEM image, and (b) Eu, (c) K, and (d) Na mapping images.



Figure S14 TG-DTA curves of Ac1-Eu-AV-9 (top: TG curve, bottom: DTA curve).



Figure S15 TG-DTA curves of Ac14-Eu-AV-9 (top: TG curve, bottom: DTA curve).



Figure S16 Powder XRD patterns of calcined Ac14-Eu-AV-9 ((a) 200 °C, (b) 300 °C).



Figure S17 Si 2p XPS profiles of a) Eu-AV-9, b) Ac1-Eu-AV-9, and c) Ac14-Eu-AV-9.



Figure S18 O 1s XPS profiles of a) Eu-AV-9, b) Ac1-Eu-AV-9, and c) Ac14-Eu-AV-9.



Figure S19 Ar adsorption-desorption isotherms of (a) Eu-AV-9 (black), (b) Ac1-Eu-AV-9 (red) and (c) Ac14-Eu-AV-9 (blue). Open circles indicate adsorption and closed circles indicate desorption.



Figure S20 Location of hydrated H₂O molecules in Eu-AV-9. Blue, Si; red, O; purple, Eu; green, Na; and yellow, K (Hydrogen atoms of H₂O molecules are omitted for clarity). The black rectangle in (c) represents the same area as in (a) and (b). Water molecules OW1 and OW2 are coordinated with Na⁺ and K⁺, respectively. OW3 are coordinated with OW1. The Crystal structure model of Eu-AV-9 was created using VESTA software.⁵

filtrate	Eu	Si
	/mass%	
Ac1	1.5	0.11
Ac14	6.7	0.43

Table S1 ICP analysis data of filtrate after acetic acid treatment of Eu-AV-9.

References

- 1 M. G. Silly, S. Blanchandin, F. Sirotti, F. Lux, S. Chevreux, G. Lemercier, and F. Charra, *J. Phys. Chem. C*, 2013, **117**, 9766.
- 2 J. W. Wen, W. T. Chen, Z. X. Zhang, W. J. Tao, C. Liu, *J. Solid State Chem.*, 2018, **263**, 30.
- 3 J. Rocha, P. Ferreira, Z. Lin, P. Brandão, A. Ferreira, and J. D. Pedrosa de Jesus, *J. Phys. Chem. B*, 1998, **102**, 4739.
- 4 D. Haranath, N. Gandhi, S. Sahai, M. Husain, V. Shanker., *Chem. Phys. Lett.*, 2010, **496**, 100.
- 5 K. Momma and F. Izumi, J. Appl. Crystallogr., 2011, 44, 1272.